

**Metal Doped Nanocomposites of Tin Dioxide ( $\text{SnO}_2$ ) and Zinc Oxide ( $\text{ZnO}$ )  
for Photocatalytic Removal of Organic Dye and  $\text{CuO-SnO}_2/\text{rGO}$  Hybrid  
Nanocomposite for Supercapacitor Applications**



**Zewdu Weldemichael Zena**

**A Dissertation Submitted to  
The Department of Applied Physics  
School of Applied Natural Sciences**

**Office of Graduate Studies  
Adama Science and Technology University**

**June, 2024  
Adama, Ethiopia**

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Nanocomposite for Supercapacitor Applications**

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**A Dissertation Submitted to  
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Physics (Materials Physics)**

**Office of Graduate Studies  
Adama Science and Technology University**

**June, 2024  
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## DECLARATION

I hereby declare that this PhD dissertation entitled “*Metal Doped Nanocomposites of Tin Dioxide (SnO<sub>2</sub>) and Zinc Oxide (ZnO) for Photocatalytic Removal of Organic Dye and CuO-SnO<sub>2</sub>/rGO Hybrid Nanocomposite for Supercapacitor Applications*” is my original work. That is, it has not been presented for the award of any academic degree, diploma or certificate in any other university. All sources of materials used for this thesis have been duly acknowledged through appropriate citations.

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This PhD dissertation has been submitted for examination with our approval as dissertation supervisor.

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## APPROVAL OF SUPERVISORS

**To: Department of Applied Physics**

**Subject: Dissertation Submission**

This is to certify that the dissertation titled “*Metal Doped Nanocomposites of Tin Dioxide ( $\text{SnO}_2$ ) and Zinc Oxide ( $\text{ZnO}$ ) for Photocatalytic Removal of Organic Dye, and CuO- $\text{SnO}_2$ /rGO Hybrid Nanocomposite for Supercapacitor Applications*” was submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics (Material Physics), the Graduate Program of the Department of Applied Physics, and has been carried out by Zewdu Weldemichael Zena, ID. No. PGR/18563/11, under our supervision. Therefore, we recommend that the student fulfill the requirements, and he can submit the dissertation to the department for further review and defense.

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## APPROVAL OF BOARD OF EXAMINERS

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## ABBREVIATIONS AND ACRONYMS

|                                |                                 |
|--------------------------------|---------------------------------|
| EDLC                           | Electric Double Layer Capacitor |
| eV                             | Electro-Volt                    |
| nm                             | Nanometer                       |
| $\alpha$                       | Alpha                           |
| Å                              | Angstrom                        |
| °C                             | Degree Celsius                  |
| V                              | Volt                            |
| m <sup>2</sup>                 | Meter Squared                   |
| Wh                             | Watts-Hour                      |
| KW                             | Killo-Watt                      |
| kJ                             | Killo-joule                     |
| g                              | Gram                            |
| F                              | Farad                           |
| PDF                            | Powder Diffraction File         |
| F/g                            | Farad per Gram                  |
| $\lambda$                      | Lambda                          |
| kHz                            | Killo Hertz                     |
| Rev/min                        | Revolution per Minute           |
| mM                             | Milli Molar                     |
| ml                             | Milli litre                     |
| MW                             | Molecular Weight                |
| g/mol                          | Gram per Mole                   |
| KOH                            | Potassium hydroxide             |
| Kg                             | Killo gram                      |
| $\gamma$                       | Gamma                           |
| Eg                             | Energy Bandgap                  |
| NaSO <sub>4</sub>              | Sodium Sulphate                 |
| H <sub>2</sub> SO <sub>4</sub> | Sulfuric Acid                   |
| UV                             | Ultraviolet                     |
| NM                             | Nanomaterial                    |
| MB                             | Methylene Blue                  |

|       |                                                |
|-------|------------------------------------------------|
| XRD   | X-ray Diffraction                              |
| SEM   | Scanning Electron Microscope                   |
| EDS   | Energy Dispersive X-Ray Spectroscopy           |
| TEM   | Transition Electron Microscope                 |
| HRTEM | High Resolution Transition Electron Microscope |
| DRS   | Diffusive Reflectance Spectroscopy             |
| FWHM  | Full Width Half Maxima                         |
| FTIR  | Fourier Transform Infrared Spectroscopy        |
| CV    | Cyclic Voltammetry                             |
| GCD   | Galvanostatic Charge-Discharge                 |
| EIS   | Electrical Impedance Spectroscopy              |
| PL    | photoluminescence Spectroscopy                 |
| PVA   | Polyvinyl Alcohol                              |
| CNT   | Carbon Nanotube                                |
| SWCNT | Single Wall Carbon Nanotube                    |
| DWCNT | Double Wall Carbon Nanotube                    |
| PPM   | Parts per Million                              |
| RhB   | Rhodamine B dye                                |
| BET   | Brunauer-Emmett-Teller                         |
| SAED  | Selected Area Electron Diffraction             |

## ABSTRACT

*In this dissertation work, Cu-SnO<sub>2</sub>/ZnO and Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite was synthesized using a simple sol-gel method for efficient photocatalytic removal of methylene blue dye in an aqueous basic medium, and hydrothermally synthesized CuO-SnO<sub>2</sub>/rGO hybrid composite for supercapacitor applications. The structural, optical, morphological, and compositional properties of both Cu-SnO<sub>2</sub>/ZnO and Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite were studied using different spectroscopic techniques. The XRD results of Cu-SnO<sub>2</sub>/ZnO nanocomposite show that SnO<sub>2</sub> was tetragonal rutile and ZnO was hexagonal wurtzite which is similar to the HRTEM and SAED. The crystallite sizes of Cu-SnO<sub>2</sub>, SnO<sub>2</sub>/ZnO and Cu-SnO<sub>2</sub>/ZnO were decreased compared to the pristine SnO<sub>2</sub>. The XRD result of Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite revealed hexagonal structured ZnO and cubic spinel structure of Co<sub>3</sub>O<sub>4</sub> were fused together to form it, and its crystallite size was greater than the constituent pristine oxides. In CuO-SnO<sub>2</sub>/rGO hybrid composite, the tetragonal rutile structure of SnO<sub>2</sub> amalgamated with monoclinic structure of CuO. The simultaneous incorporation of CuO and rGO restrained the crystal growth of SnO<sub>2</sub> host without changing its preferential growth directions. The UV-DRS analysis showed that the band gap energy of SnO<sub>2</sub> and ZnO hosts were reduced after modifications. PL analysis exhibited a higher defect density, strong quenching and lower swift of charge carriers in Cu-SnO<sub>2</sub>/ZnO, Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO and CuO-SnO<sub>2</sub>/rGO composites. The Fourier Transform Infrared (FTIR) spectroscopy identifies the functional groups attached to Cu-SnO<sub>2</sub>/ZnO and Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposites. The EDS results of Cu-SnO<sub>2</sub>/ZnO and Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposites revealed the presence of all its components. The morphology of both Cu-SnO<sub>2</sub>/ZnO and Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposites were investigated by SEM. The TEM, HRTEM and SAED analysis further confirmed the XRD result, and polycrystalline nature of the synthesized nanomaterials. The photocatalytic efficiencies of Cu-SnO<sub>2</sub>/ZnO and Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite photocatalysts were 78 % and 95.1% recorded for MB dye removal. The enhancement of their photocatalytic performance compared to the pristine oxides could be attributed to more absorption of visible light and reduction of charge carrier recombination rate. In Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO composite, the electrons and hydroxyl active radicals plays the major role in degrading the MB dye into CO<sub>2</sub> and H<sub>2</sub>O. We conclude that Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO composite Photocatalyst is a good photocatalytic material recommended for further investigation and practical applications. Moreover, CV and GCD analysis revealed that CuO-SnO<sub>2</sub>/rGO hybrid composite exhibited enhanced specific capacitance and energy density compared to pristine SnO<sub>2</sub>. Therefore, it can be recommended as alternative electrode materials for supercapacitor applications.*

**Keywords:** Nanocomposite, Photocatalyst, SnO<sub>2</sub>, ZnO, Supercapacitor, MB dye, Electrode Materials.

# 1. INTRODUCTION

## 1.1 Background of the Study

The issue of environment, pure water and energy crisis are among the top problems in the world. Pollution causes a serious environmental and water crises, whereas poor management of energy during storage and consumption results in energy crises. Pollution refers to the introduction of harmful or toxic substances into the environment, which could have detrimental effects on the natural ecosystem, human health, and the well-being of other living organisms. Pollution can take many forms, including air pollution, water pollution and soil contamination. Common sources of pollution include industrial activities, transportation emissions, agricultural practices, and improper waste disposal. Efforts to reduce pollution often involve regulatory measures, technological advancements, and public awareness campaigns aimed at promoting sustainable and environmentally friendly practices. Industrial wastewater contains many synthetic industrial dyes (Olusakin *et al.*, 2022). Improper disposal of these pollutant dyes discharged from industries causes environment and water pollutions. Thus, human beings and other living things are directly victimized with it. In developing countries, it is commonly observed that the management of wastes are very poor.

Industrial dyes are pollutant dyes discharged from industries that makes water unsafe to drink and pollute the environment. Among the toxic, poisonous, non-biodegradability and carcinogenic organic dyes, methylene blue (MB) causes a serious risk to both human health and the environment. This dye is discharged from textile, paper and leather industries. Besides, due to its low biodegradability, MB dye stays longer in the environment and causes severe problems to living things in general (Khan *et al.*, 2022). Human health is at a risk from multiple effects of MB dye, including respiratory discomfort, gastrointestinal diseases, eyesight, and digestive and mental issues. Together with these side effects, it also raises the heart rate, induces tissue necrosis, nausea, vomiting, cyanosis, shock, gastritis, jaundice, methemoglobinemia, premature cell death in tissues, and irritates the skin and eyes (Khan *et al.*, 2022). Methylene blue is a basic and cationic synthetic or model dye. It is a heterocyclic basic dye with a molecular weight of 373.9 g/mol and a maximum absorbance wavelength of 664 nm. The cationic MB dye is more poisonous than anionic dyes. Textile, rubber, plastics, leather, cosmetics, pharmaceuticals, and food sectors are just a few of the industries that employ MB dye (Modi *et al.*, 2023). Removal of the organic dyes from waste water is

obligatory. However, effective removal of dyes from aqueous wastes are remains a major challenge for many countries. It is typically discharged into untreated natural water sources, endangering the health of people and other living things. This toxic dye does not be treated using traditional methods of water treatment such as filtration, solar disinfection, sedimentation and boiling. A variety of other proposed chemical and biological methods have no longer be used because of their high cost, slow process, toxicity, high power consumption, and creation of harmful by-products. Therefore, the development of an efficient, effective and environmentally friendly method for eliminating MB from wastewater is mandatory. A popular advanced method for removing MB dye is photocatalysis. It is the process of breakdown of organic dyes into carbon dioxide and water using a photocatalyst upon irradiation of light. To date, the photocatalytic degradation method appears feasible to reduce (or remove) organic pollutants from aqueous medium. The fundamental benefit of photocatalytic degradation is that it eliminates the need for waste disposal because harmful contaminants are broken down into carbon dioxide, water, acid, and other simple salts (Modi *et al.*, 2023).

Moreover, the need for sustainable energy is growing faster and faster globally for human growth. Like pollution, energy wastage is also a serious problems in the world. As a result the sustainable energy sources such as tidal, solar, wind *etc* can help us to sustain the current energy crisis. Apart from energy production, transmission and conversion, energy storage devices are one of the essential component in the sustainable energy system. Among the energy storage devices such as conventional capacitors, batteries and fuel cells, supercapacitors also plays a great role everywhere in the areas where we need energy for our day today life together with commercialized batteries. Supercapacitors, also known as ultracapacitors, which have high-capacitance, lower energy density, high power density and fast charging-discharging capability compared to rechargeable batteries and fuel cells. Still it is difficult to use it alone for practical application areas where we need high energy for a longer period of time due to its low energy density. It fills the gap left by rechargeable batteries and electrolytic capacitors. It can take in and transfer charge more quickly than batteries, stores 10 to 100 times more energy per unit volume or mass than electrolytic capacitors, and can withstand many more charge-discharge cycles than rechargeable batteries (Vandeginste, 2022). Supercapacitors can be made of carbon materials, metal oxides and polymer materials, and mixed hybrid materials. In electric double-layer capacitors (EDLC) and pseudocapacitors, their electrodes are made up of carbon materials and transition metal

oxides or conducting polymers respectively whereas hybrid capacitors are a combinations of both. EDLCs have high power density and long cycle life but they usually have lower energy density compared to other types of capacitors. Pseudocapacitors store energy through fast and reversible faradaic redox reactions at or near the surface of the electrode material. These results in higher energy density compared to EDLC capacitors. Hybrid capacitors typically consist of an EDLC electrode and a pseudocapacitive electrode, allowing them to exhibit a combination of high power density from the EDLC component and high energy density from the pseudocapacitive component. This combination results in capacitors with improved overall performance characteristics, making them suitable for a wide range of applications. Generally, the performance of supercapacitors depends on the properties of the electrode materials, the type of electrolytes, the separators, current collectors, binders and the electrode preparation methodologies. To produce a quality energy storage device, investigating the noble electrode materials plays a key role.

Nowadays, nanomaterials with a large specific surface area to volume ratio, more number of surface atoms and a large number of surface defects, quantum confinement effects, better light absorption capacity, very high porosity, fine-tunable band gaps, and unique physicochemical properties compared with bulk materials could enhance the photocatalytic and supercapacitor performance. Semiconducting metal oxides such as  $\text{SnO}_2$ ,  $\text{TiO}_2$  and  $\text{ZnO}$  with their outstanding properties showed enhanced degradation of pollutant dyes than their counterparts. For instance, Phil *et al.*, 2016 and Pham Van Viet *et al.*, 2016 reported that  $\text{SnO}_2$  nanoparticles showed higher photocatalytic degradation efficiency of methylene blue dye than a bulk  $\text{SnO}_2$  (S. P. Kim *et al.*, 2016; Viet *et al.*, 2016a).  $\text{TiO}_2$  showed enhanced photocatalytic performance due to the dominant surface effects as the particle size reduced and the band gap blue-shifted (Y. Chen, 2021). Moreover, by doping strategy, Lamba *et al.*, 2015 reported that synthesized  $\text{ZnO}$  doped  $\text{SnO}_2$  nanoparticles showed better performance to remove MB dye under Uv-light illumination (Lamba, *et al.*, 2015). Simultaneous use of doping and making a composite, Olga Długosz & Marcin Banach, 2021 reported Sn-doped  $\text{ZnO-SnO}_2$  photocatalyst showed a higher visible light assisted photodegradation of rhodamine B (Długosz & Banach, 2021). Perveen and Akhyar 2017 reported that La metal doped  $\text{SnO}_2\text{-TiO}_2$  nanocomposites exhibited higher photocatalytic efficiency of MB dye under illumination of sun light (Perveen & Akhyar, 2017). Asaithambi *et al.*, 2021 also reported visible light assisted Mn-doped  $\text{SnO}_2@\text{ZnO}$  nanocomposite showed higher photocatalytic efficiency of 98% for methylene blue dye (Asaithambi *et al.*, 2021). The



photocatalytic performance improvement might be due to more visible light absorption and reduction of fast charge carrier recombination after modification of the pristine oxides.

Similarly, for supercapacitor application, the key required properties of NM's such as large specific surface area, high electrical conductivity, wide potential windows, electron mobility, chemical stability, porosity, compatibility with electrolytes, and synthesis scalability could be properly controlled. The large specific area, compatibility with electrolytes, and porosity provide active sites, and high electrical conductivity facilitates rapid electron transport for achieving increased specific capacitance, energy density, and high power density. The chemical stability of nanomaterials ensures long-term performance and prevents degradation of the electrode material during charge-discharge cycles. For instance, carbon materials such as graphene, carbon nanotubes, activated carbons, and mesoporous carbons have a high specific surface area, rapid ion diffusion, electrical conductivity, and high porosity or mesopores resulting in enhanced electric double-layer capacitor performance (S. Sharma & Chand, 2023; Vandeginste, 2022). Compared to carbon-based materials with electric double layer capacitance, all of the metal oxides nanomaterials used for pseudocapacitors electrode offer a significantly higher energy density but low power density, worsen cycle stability and rate capability might be occurred due to the slow ion transfer and relatively low conductivity (S. Kim *et al.*, 2022; J. Zhang *et al.*, 2018). Apart from achieving large surface area, shorten the diffusion paths of electrons and electrolyte ions, reduction of the size of the metal oxide nanoparticles provides an abundance of excess interspace to buffer the large volume expansion of active materials during charge-discharge processes (Asaithambi *et al.*, 2020). Moreover, to alleviate the limitations of both EDLC's and pseudocapacitors, hybrid nanostructures made of a combinations of carbon materials (carbon nanotubes, graphene, reduced graphene oxide, etc), and conducting polymers or metal oxides ( $\text{Fe}_2\text{O}_3$ ,  $\text{RuO}_2$ ,  $\text{ZnO}$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{SnO}_2$ ,  $\text{CuO}$ , etc) has been used as an alternative electrode materials. Thus, the better synergy results in better capacitance, rate capability, and longer cycling stability of supercapacitors that could be achieved due to increased surface area, boosting morphological stability and increased electrical conductivity. For instance, the combination of  $\text{SnO}_2/\text{rGO}$  nanocomposite showed an enhanced performance in the supercapacitor (Y. Zhang *et al.*, 2020). The intercalation of  $\gamma\text{-MnO}_2$  and  $\alpha\text{-Ni(OH)}_2$  into rGO exhibited a high specific capacitance and a remarkable degree of cyclic stability even after 10,000 cycles (Tarek *et al.*, 2022).

Lastly, this thesis is organized in five chapters. The first chapter includes the brief background introduction, general and specific objectives, and statement of the research problem, and significance of the study. The second chapter includes detailed review of related literatures. The third chapter includes the chemicals and solvents used, synthesis and characterization methods of the synthesized nanomaterials, and electrode preparation for supercapacitor tests, and photocatalytic experiment procedures. The fourth chapter includes results and discussion, and the fifth chapter wind up by conclusions, and future research recommendations.

## **1.2 Statement of the Problem**

The issue of environmental pollution, lack of pure water and sustainable energy supply to the society are serious problems all over the world in general and in developing countries in particular. To date, photocatalysis seems feasible to remove pollutants such as MB dye from aqueous medium using semiconducting metal oxide nanomaterials. It can be used to degrade or decompose MB dye into carbon dioxide and water using a combination of light and catalyst to facilitate the rate of photoreaction. The major challenges in photocatalysis are poor absorption of visible light and fast recombination of charge carriers during photocatalytic redox reaction. Semiconducting metal oxide nanomaterials with the desired properties could be chosen as a good photocatalyst in photocatalysis.

Among semiconducting metal oxides, tin oxide ( $\text{SnO}_2$ ) and zinc oxide ( $\text{ZnO}$ ) are n-type semiconductors that has been chosen as a host photocatalytic materials due to their outstanding properties such appropriate wide bandgap, good electrocatalyst, strong adsorption capacity, high carrier mobility, high photosensitivity, high thermal stability, low toxicity and low cost. They are also a good photocatalysts in the UV region. However, as literature reports confirmed that  $\text{SnO}_2$  and  $\text{ZnO}$  host exhibits poor photocatalytic efficiency in the visible light spectrum range between 400-700 nm which constitutes around 45 % of the entire incoming light spectrum (Perumal *et al.*, 2023). The major challenge is poor absorption of visible light due to their wide band gap. For overcoming the limitations and boost the photocatalytic efficiency of  $\text{SnO}_2$  and  $\text{ZnO}$ , the modification strategies like doping, making a composite and simultaneous use of both have been employed. For this purpose, metal dopants like copper ( $\text{Cu}^{2+}$ ), tin ( $\text{Sn}^{4+}$ ) and for coupling narrow band gap oxides such copper oxide

(CuO), cobalt oxide ( $\text{Co}_3\text{O}_4$ ) could be used. The transition metal dopant  $\text{Cu}^{2+}$  used as a grain growth inhibitor to simultaneously increase the surface area and reduce the band gap, and whereas the aforementioned oxides such as cupric oxide (CuO) is a narrow band gap (1.5 eV) and  $\text{Co}_3\text{O}_4$  is a dual bandgap coupled with the host effectively reduce the band gap to the visible spectrum region, the absorption of visible light increased and fast recombination of charge carriers reduced. Moreover, incorporation of  $\text{Cu}^{2+}$  ion dopant into  $\text{SnO}_2$  host and making a composite with ZnO enhances the photocatalytic performance. Similarly, doping of  $\text{Sn}^{4+}$  into ZnO host and coupled with  $\text{Co}_3\text{O}_4$  also enhances the photocatalytic efficiency for MB dye removal. Incorporation of p-type CuO into  $\text{SnO}_2$  host enhance the performance of a supercapacitor due to presence of copper vacancies defects, lower the bandgaps and facilitate the electrolytic ions flow rate. Moreover, the additions of reduced graphene oxide into the CuO- $\text{SnO}_2$  composite further enhances the supercapacitor performance due to large surface area or more active sites for adsorption of electrolytic ions, increased the electrical conductivity and reduce the crystallite size to shorten the path at the electrode-electrolyte interface for electrolytic ions. Modifications of  $\text{SnO}_2$  host for supercapacitor electrode materials by simultaneous addition of CuO and rGO alleviates the low power density, poor electrochemical stability, short life time and low charge-discharge cycles in pristine  $\text{SnO}_2$ . Specifically, reduced graphene oxide due to its narrow bandgap, large surface area, excellent electrical conductivity and chemical stability expected to further improve the limitations of  $\text{SnO}_2$  mentioned above. Therefore, CuO- $\text{SnO}_2$ /rGO hybrid composite are expected to be a good alternative electrode material for supercapacitors. For synthesis of the above nanomaterials sol-gel was chosen due to its simplicity, low cost and high yield whereas hydrothermal method was selected due to its simplicity, low cost, high quality, and suitability to synthesize hybrid composite.

### **1.3 Objectives of the Study**

#### **1.3.1 General Objectives**

The general objective of this dissertation is to study the metal doped nanocomposites of tin dioxide ( $\text{SnO}_2$  and) zinc oxide (ZnO) synthesized by sol-gel method for enhanced photocatalytic removal of organic dye and electrochemical investigation of hydrothermally synthesized CuO- $\text{SnO}_2$ /rGO hybrid nanocomposite for supercapacitor applications.

### 1.3.2 Specific Objectives

Based on the general objectives, the following specific objectives of the dissertation were accomplished:

- 1) Synthesize and characterize of  $\text{SnO}_2$ ,  $\text{ZnO}$ ,  $\text{SnO}_2/\text{ZnO}$  and  $\text{Cu-SnO}_2/\text{ZnO}$  nanocomposites for photocatalytic degradation of MB dye
- 2) Synthesize and characterize  $\text{Co}_3\text{O}_4$ ,  $\text{ZnO}$ ,  $\text{Sn-ZnO}$ ,  $\text{Co}_3\text{O}_4/\text{ZnO}$  and  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposites for photocatalytic degradation of MB dye.
- 3) Optimize the pH and catalyst dosage for  $\text{Cu-SnO}_2/\text{ZnO}$  and  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposites during photocatalytic degradation of MB dye.
- 4) Determine the electrochemical performance of  $\text{CuO-SnO}_2/\text{rGO}$  hybrid nanocomposite for supercapacitor applications.

### 1.4 Significance of the Study

Now a days, industrialization and population growth results in environmental and water pollutions, and high energy consumption. Therefore, this study has importance to know the science behind & take part in searching nontoxic, low cost and environmentally friendly  $\text{SnO}_2$  and  $\text{ZnO}$  based alternative materials for a photocatalytic and supercapacitor device. Moreover, this investigation can be used as a basis for industries to scale up or use it as an input to design an efficient and effective energy storage devices, and photocatalysts to use it in waste water treatment plant to commercialize for practical utilization.

### 1.5 Scope of the Study

The title of this dissertation is “to study the metal doped nanocomposites of tin dioxide ( $\text{SnO}_2$ ) and zinc oxide ( $\text{ZnO}$ ) for photocatalytic removal of organic dye, and  $\text{CuO-SnO}_2/\text{rGO}$  hybrid nanocomposite for supercapacitor applications". The primary goal of this work was to investigate the photocatalytic degradation performance of methylene blue dye using  $\text{Cu-SnO}_2/\text{ZnO}$  and  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite photocatalysts under visible light irradiation, and to study the hydrothermally synthesized  $\text{CuO-SnO}_2/\text{rGO}$  hybrid nanocomposite for supercapacitor electrode modification. The goal of doping and making composites based on  $\text{SnO}_2$  and  $\text{ZnO}$  host was to improve the photocatalytic efficiencies and supercapacitor

performance. The structural, optical, morphological, and composition of the synthesized nanomaterials were examined. The operational parameters (pH and catalyst dosage) of photocatalysis were optimized. The electrochemical characterization of the supercapacitor also studied using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS). To conclude, the extent of this study incorporates synthesizing, characterizing and performance testing of the above mentioned nanomaterials.

### **1.6 Limitation of the study**

Even though our major objectives were properly achieved, some limitations we faced were the lack of access to advanced characterization instruments like X-ray photoelectron spectroscopy (XPS) and Brunauer-Emmett-Teller (BET) during the dissertation work for further analysis of our work. These instruments are expensive and are not available in our country.

## 2. REVIEW OF LITERATURES

### 2.1 Introduction to Nanoscience and Nanotechnology

Nanoscience is the study of the behavior of objects at a very small scale, roughly between in the range 1 to 100 nanometers (nm). The word "nano" (or "nanus") comes from the Greek word "nanos," which means "dwarf," and the word "science," means "knowledge." Nanoscience is the investigation of phenomena on a nanoscale. It is an interdisciplinary field that focuses on the nanoscale interactions of fields like physics, biology, engineering, chemistry, and computer science in order to advance nanotechnology (Bayda *et al.*, 2020; M. Rafique *et al.*, 2020).

The history of nanoscience and nanotechnology can be traced back to ancient times when people were unknowingly manipulating materials at the nanoscale. However, the formal development and understanding of nanotechnology and nanoscience as a scientific field began in the 20th century.

Early observations and practices involving nanoscale materials date back centuries. For example, the vibrant colors seen in stained glass windows from medieval times were a result of nanoparticles embedded in the glass. Gold and silver nanoparticles created colors in the stained-glass windows of medieval churches hundreds of years ago. Although modern nanoscience and nanotechnology are relatively new, nanoscale materials have been used for centuries. The artists back then just didn't know that they were using nanotechnology to create these beautiful works of art!

The concept of nanotechnology was popularized by physicist Richard Feynman in his famous lecture titled "There's Plenty of Room at the Bottom" delivered in 1959. Feynman envisioned the possibility of manipulating and controlling matter at the atomic and molecular scale. The global enthusiasm on nanotechnology is inspired by his speech when he mentioned "to synthesize nanoscale building blocks with precisely controlled size and composition, and assemble them into larger structures with unique properties and functions" At this size, atoms and molecules work differently and provide a variety of surprising and interesting uses. Although the idea of nanoscience and technology was discovered by Feynman, the term nanotechnology was first coined by a Japanese Professor Norio Taniguchi at Tokyo

University of science in 1974. In the 1980's, the invention of scanning probe microscopes, such as the scanning tunneling microscope (STM) and atomic force microscope (AFM), revolutionized the field of nanoscience. These instruments allowed scientists to directly observe and manipulate individual atoms and molecules, opening up new avenues for nanoscale research and development. The National Nanotechnology Initiative was launched in 2000. This coordinated effort between multiple federal agencies aimed to advance nanotechnology research, development, and application across various sectors, such as electronics, medicine, energy, and materials. According to this initiative, nanotechnology is defined as “the understanding and control of matter at dimensions of roughly 1 to 100 nm, where unique phenomena enable novel applications”. It is the science of the small; the very small. It is also the use and manipulation of matter at a tiny scale. Nanotechnology is the term given to those areas of science and engineering where phenomena that take place at dimensions in the nanometer scale are utilized in the design, characterization, production and application of materials, structures, devices and systems. Nanotechnology encompasses nanoscale science, engineering, and technology in fields such as chemistry, biology, physics, materials science, and engineering. Nanoscience and nanotechnology have the potential to reshape the world around us. They could lead to revolutionary breakthroughs in fields ranging from manufacturing to health care. Scientists have developed various techniques for synthesizing and characterizing nanomaterials, including nanoparticles, nanowires, and nanocomposites. These materials have found applications in fields such as electronics, medicine, energy storage, environmental remediation, and more (Bayda *et al.*, 2020; Malik and Muhammad 2023; Yadav *et al.*, 2023).

Nanomaterials is defined as the material having a size of roughly 1 to 100 nm or at least one external dimension measuring approximately in the nanometer range. Nanomaterial is a material with one or more external dimensions, or an internal structure in the nanoscale, which could exhibit novel characteristics compared to the bulk counterparts (Rafique *et al.*, 2020; Yadav *et al.*, 2023) The comparison of nanoscale materials with the naturally occurring things and macro-sized objects is given in the figure 1. The reduction in size of the bulk matter to the nanoscale level results in an enormous increase of surface to volume ratio and quantum confinement effects (Lobnik *et al.* 2010; Rafique *et al.*, 2020). Now a day's most of the novel devices are based on properties of nanoscale materials. Matter can exhibit unusual physical, chemical, and biological properties at nanoscale, differing in important ways from the properties of bulk materials, single atoms and molecules. Some nanostructured materials

are stronger or have different magnetic properties compared to sizes of the same material, and others may have enhanced optical, chemical, electrical and thermal conductivities, catalytic and luminescent properties. They may become more chemically reactive, reflect or absorb light better, or change color as their size or structure or morphology is altered. Nanomaterials in general have gained prominence in technological advancements due to their tunable properties. The performance of nanoscale materials depends on the modulation of the desired properties depending on the application areas we are interested in.

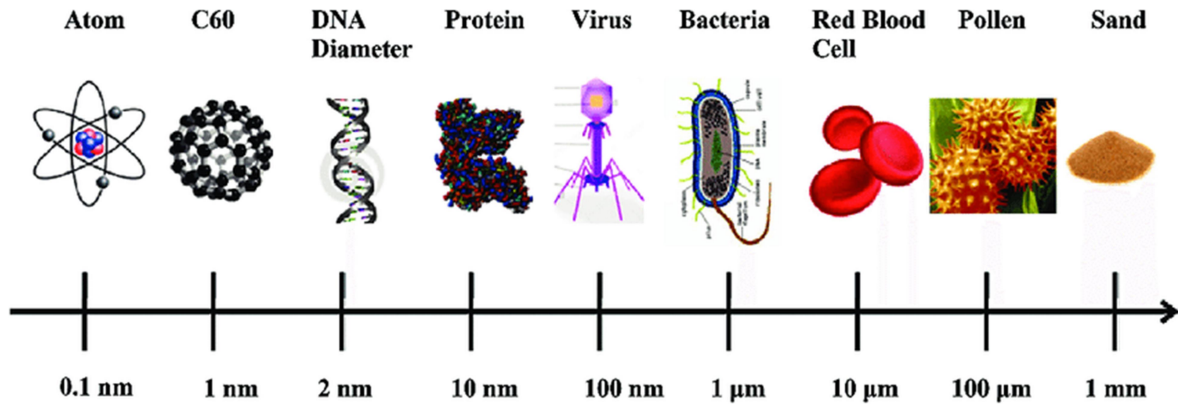


Figure 1: The relative size of nanomaterials in comparison to naturally occurring things (Ismail *et al.*, 2016).

Nanomaterials are categorized depending on their origin, size, composition and shape. Based on origin, nanomaterials are classified as natural and synthetic or engineered nanomaterials. Synthetic nanomaterials further classified based on compositions and dimensions as follows.

## 2.2 Classifications of Nanomaterials Based on Dimensions

According to Siegel based on dimensions, nanostructured materials are classified as zero dimensional, one dimensional, two dimensional, and three dimensional nanostructures.

### 2.2.1 Zero Dimensional Nanomaterials

Zero dimensional nanomaterials are materials having size between 1 to 100 nm in all the three dimensions. These nanomaterials are three dimensionally confined and their growth are restricted in all directions. Examples of 0D materials are fullerenes, quantum dots, nanoparticles, etc (Aziz *et al.*, 2013; Geng *et al.*, 2020; Sedira & Mendaci, 2020). The examples of 0D nanomaterials with structures are given in figure 2(a).



### **2.2.2 One Dimensional Nanomaterials**

One dimensional nanomaterials are nanostructures which have dimensions less than 100 nm in two of the three dimensions and grow only along one of the remaining dimension. These class of materials are two dimensionally confined and the length to thickness or width aspect ratio is larger. Examples of 1D nanomaterials are nanotubes, nanohorns, nanowires, nanorods, fibres and filaments, whiskers and belts, and spirals and springs etc (Ejsmont & Goscianska, 2023; Mandi *et al.*, 2022; Zhou *et al.*, 2017). The examples of 1D nanomaterials with structures are given in figure 2(b).

### **2.2.3 Two Dimensional Nanomaterials**

Two dimensional nanomaterials are materials having dimensions less than 100 nm in one of the three dimensions and grow along the remaining two dimensions. These materials are one dimensionally confined. Examples of 2D materials are nanosheets, nanodiscs, nanolayers, nano-coatings, nanofilms, graphene,(Han *et al.*, 2021; Navneet Kumar & Srivastava, 2018; Liu *et al.*, 2016; Sahu, Satpati, & Mohapatra, 2021) etc. The examples of 2D nanomaterials with corresponding structures are given in figure 2(c).

### **2.2.4 Three Dimensional Nanomaterials**

Three-dimensional nanomaterials often known as bulk materials, are nanomaterials that are not limited to the nanoscale in any dimension or range of dimensions. A 3D substance has three arbitrary dimensions that exceed 100 nm since all of its dimensions are outside of the nanoscale range or larger than 100 nm, however the bulk material is composed of discrete blocks that fall within the nanometer scale 1–100 nm. It consists of multi-nanolayers with interfaces formed by intimate contact between the 0D, 1D, and 2D structural elements as well as dispersion of nanoparticles and bundles of nanowires and nanotubes. Three dimensional nanomaterials include colloids, free nanoparticles with different morphologies, and thin films with atomic-scale porosity (Mekuye & Abera, 2023). The examples of 3D nanomaterials with corresponding structures are given in figure 2(d).

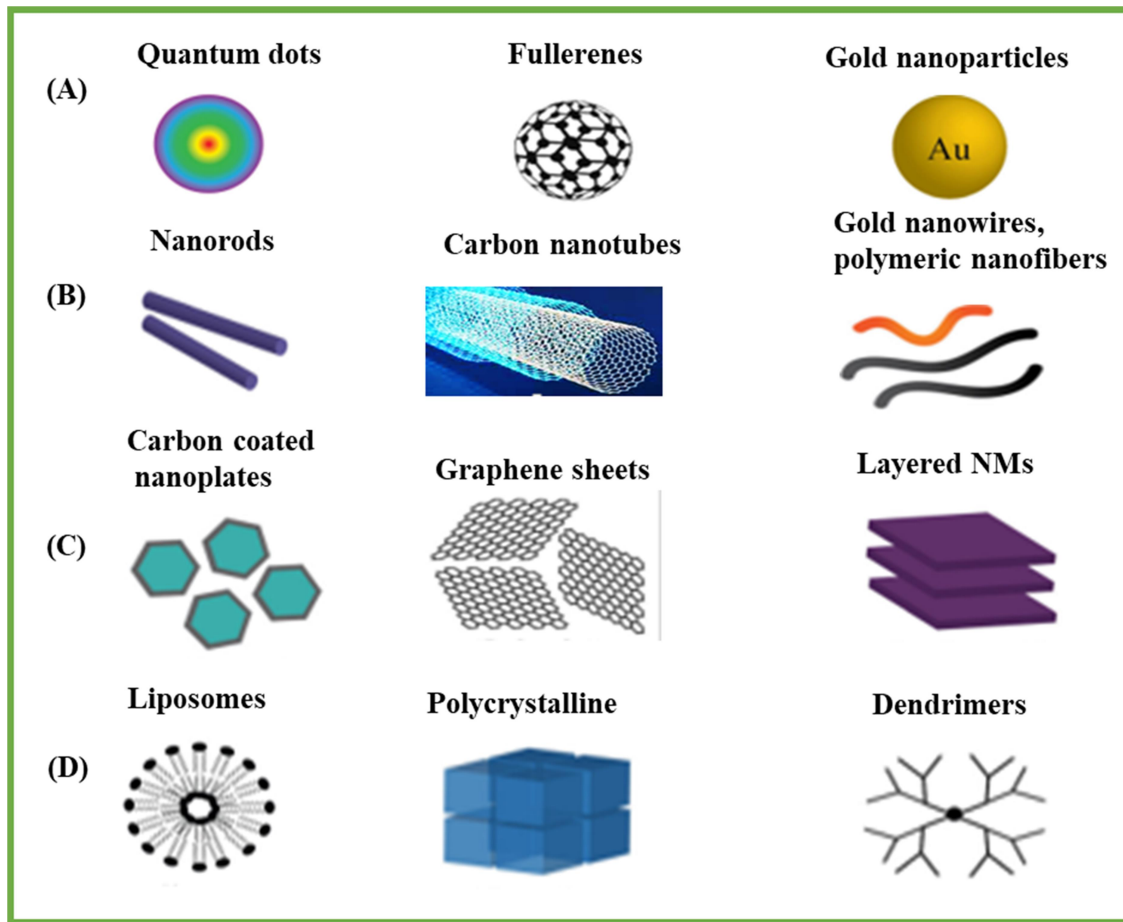


Figure 2: Summarized diagrammatic representation of classification of nanomaterials based on the number of dimensions as: (a) Zero dimensional NMs, (b) One dimensional NMs, (c) Two dimensional NMs and (d) Three dimensional NMs, modifications from (Poh *et al.*, 2018).

## 2.3 Nanomaterials Based on Compositions

Based on the compositions, nanomaterials are mainly classified as follows.

### 2.3.1 Carbon Based Nanomaterials

#### 2.3.1.1 Graphite

Graphite is a form of carbon with unique properties. It has a layered structure composed of stacked graphene sheets as shown in figure 3. Each graphene sheet consists of a two-dimensional hexagonal lattice of carbon atoms bonded together in a  $sp^2$  hybridized

arrangement. The layers are held together by weak van der Waals forces, allowing them to slide over each other easily (Albero *et al.*, 2019). Graphite is an excellent conductor of electricity. The delocalized  $\pi$  electrons within the graphene sheets enable the efficient movement of charge carriers, making graphite highly conductive. It is widely used in applications requiring good electrical conductivity, such as electrodes, electrical contacts, and conductive coatings.

Graphite also exhibits high thermal conductivity due to the strong covalent carbon-carbon bonds within the graphene sheets. Heat can be rapidly conducted through the lattice, making graphite a suitable material for thermal management applications, including heat sinks, crucibles, and thermal insulators. Graphite is chemically stable and unreactive under normal conditions. It is resistant to most acids, bases, and organic solvents. This stability makes graphite suitable for applications involving exposure to corrosive environments or high temperatures. It has a high melting point of approximately 3,600 degrees Celsius (6,500 degrees Fahrenheit). This high melting point, along with its thermal stability, makes graphite suitable for use in high-temperature applications such as crucibles, refractory materials, and nuclear reactors. Graphite exhibits anisotropy, meaning it has different properties in different directions within the crystal structure. Properties such as electrical conductivity, thermal conductivity, and mechanical strength can vary depending on the orientation of the layers. It is also a lightweight material due to its low atomic weight and the presence of void spaces between the graphene layers. This property makes graphite useful in applications where weight reduction is important, such as aerospace components and sporting goods.

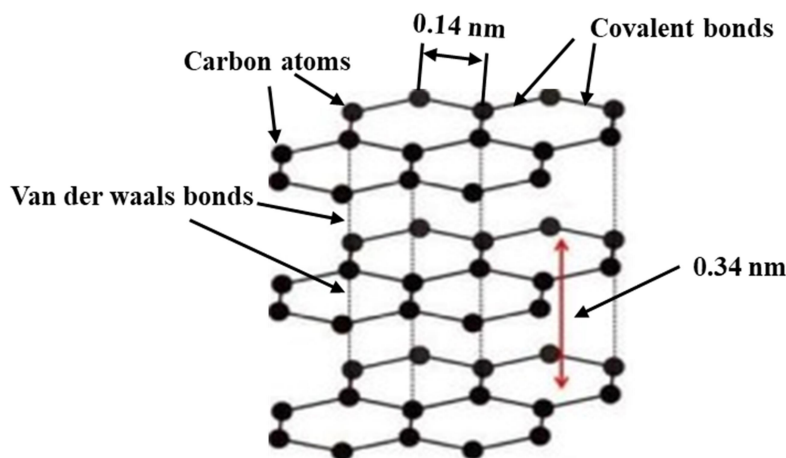


Figure 3: Structure of graphite modified based on the figure taken from (Albero *et al.*, 2019).

### 2.3.1.2 Graphene Oxide (GO)

Graphene oxide (GO) is a derivative of graphene, which is a single layer of carbon atoms arranged in a two-dimensional honeycomb lattice, containing hydrogen and oxygen molecules. It is created by the oxidation of graphite, and it contains a significant number of oxygen functional groups on its surface. It also consists of graphene sheets with various sizes and shapes, containing  $SP^2$  hybridized carbon atoms. It retains the two-dimensional structure of graphene but has oxygen-containing functional groups attached to the carbon lattice (Aliyev *et al.*, 2019) as referred from figure 4.

Graphene oxide has high water dispersibility. The presence of oxygen functional groups, such as hydroxyl (-OH), carboxyl (-COOH), and epoxy (-O-) groups, makes GO hydrophilic and easily dispersible in water and other polar solvents. It is an electrical insulator due to the presence of oxygen functional groups, which disrupt the electron delocalization in the carbon lattice. However, it can be reduced to reduced graphene oxide (rGO) by removing a portion of the oxygen groups, leading to the restoration of electrical conductivity to varying degrees. Graphene oxide is optically active and exhibits characteristic absorption in the ultraviolet (UV) and visible regions. The absorption properties can be tuned by controlling the size, shape, and functionalization of the graphene oxide sheets.

The oxygen functional groups in graphene oxide make it highly reactive, allowing for various chemical modifications and functionalization. These functional groups provide sites for chemical reactions, enabling the attachment of other molecules or materials to the GO surface (Adéla *et al.*, 2022). Graphene oxide films or coatings possess excellent barrier properties against gases and liquids. The densely packed, stacked layers of graphene oxide can hinder the permeation of molecules, making it suitable for applications such as gas separation, water purification, biomedical applications and corrosion protection (Ray, 2016). It's important to note that the properties of graphene oxide can vary depending on the synthesis methods, degree of oxidation, and the specific functional groups present. Every method has its own set of advantages and limitations concerning scalability, cost, and the quality of the resultant graphene oxide. Therefore, various graphene oxide samples may display differences in their characteristics. The selection of a method depends on the particular needs of the application and the desired features of the graphene oxide. The common methods for synthesizing graphene oxide (GO) are summarized below:

#### **2.3.1.2.1 Hummers' Method**

It is one of the most widely used approaches for the synthesis of graphene oxide. It involves the oxidation of graphite using a mixture of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ), potassium permanganate ( $\text{KMnO}_4$ ), and a strong oxidizing agent such as sodium nitrate ( $\text{NaNO}_3$ ). This method introduces oxygen-containing functional groups onto the graphene surface, resulting in the formation of graphene oxide. The advantage is that it can produce high-quality GO with a high degree of oxidation, and its disadvantages is that it is a complex and time-consuming process, which requires the use of hazardous chemicals, such as concentrated sulfuric acid and potassium permanganate. For example, Francisco and Gonz, 2022 synthesized graphene oxide by the modified Hummer's method involved adding concentrated  $\text{H}_2\text{SO}_4$  to a mixture of graphite flakes and  $\text{NaNO}_3$ . This reaction mixture was then cooled and  $\text{KMnO}_4$  was added slowly. After various steps of purification, the resulting solid product was obtained (M. Francisco, and Gonz 2022).

#### **2.3.1.2.2 Staudenmaier's Method**

It is another popular technique for synthesizing graphene oxide. It is similar to the Hummers' method but employs a mixture of concentrated sulfuric acid, potassium chlorate ( $\text{KClO}_3$ ) and nitric acid ( $\text{HNO}_3$ ) as the oxidizing agent. The reaction conditions are milder compared to the Hummers' method. It is relatively simple and fast method that produces GO with a high degree of oxidation. It also requires the use of hazardous chemicals, such as concentrated nitric acid, which can lead to the formation of nitrogen-containing impurities. For instance, graphene oxide (GO) prepared using the Staudenmaier method has a higher concentration of the more polar carbonyl group. This leads to increased hydrophilicity and porosity of the GO membrane compared to GO prepared using the Hummers' and Tour methods (Sali & Mackey, 2019).

#### **2.3.1.2.3 Improved Hummers' Method**

This modified version of the Hummers' method incorporates additional steps to enhance the oxidation efficiency and reduce the reaction time. It often involves the use of microwave-assisted or ultrasonication-assisted oxidation to improve the exfoliation of graphite and

increase the yield of graphene oxide. It is a modified version of the original Hummer's method that uses fewer hazardous chemicals and produces GO with a high degree of oxidation. But it is still a time-consuming process that requires multiple steps and careful control of reaction conditions. For instance, Marcano *et al.*, 2010 synthesized graphene oxide by improved Hummers' method using  $\text{KMnO}_4$  and  $\text{H}_2\text{SO}_4$  to  $\text{H}_3\text{PO}_4$  (9:1). The improved method offers advantages such as a simpler protocol, higher yield, no toxic gas evolution during preparation, and equivalent conductivity upon reduction (Marcano *et al.*, 2010).

#### **2.3.1.2.4 Electrochemical Oxidation Method**

It involves the anodic oxidation of graphite in an electrolyte solution, typically containing an acidic or alkaline medium. By applying a voltage, graphite electrodes are oxidized, and graphene oxide is formed on the anode surface. This method allows for better control over the oxidation process and can produce high-quality graphene oxide with good electrical conductivity. It is a simple and environmentally friendly approach that does not require the use of hazardous chemicals. The disadvantage of this method is that it requires expensive specialized equipment, such as a potentiostat or galvanostat, and it is time-consuming depending on the desired degree of reduction and the size of the electrode used. It also produces GO with a lower yield compared to other methods (Nishina & Eigler, 2020) (Gutiérrez-pineda *et al.*, 2023).

#### **2.3.1.2.5 Chemical Vapor Deposition (CVD) Method**

It can also be used to synthesize graphene oxide. In this method, a carbon precursor, such as methane ( $\text{CH}_4$ ), is decomposed in the presence of an oxidizing agent, such as oxygen ( $\text{O}_2$ ), to form graphene oxide. The produced graphene oxide can then be exfoliated and dispersed in a suitable solvent. The advantage is it can produce high-quality GO with a high degree of crystallinity in large quantities and good electrical conductivity. It can also be used to produce large-area graphene films and coatings with a controlled number of layers, making it suitable for various applications. It requires expensive high-temperature furnace and high degree of control over reaction conditions, such as temperature, pressure, and gas flow rate, which can be challenging. It can also produce graphene oxide with impurities, such as residual metals, which can affect its properties (Y. Liu & Chen, 2016).

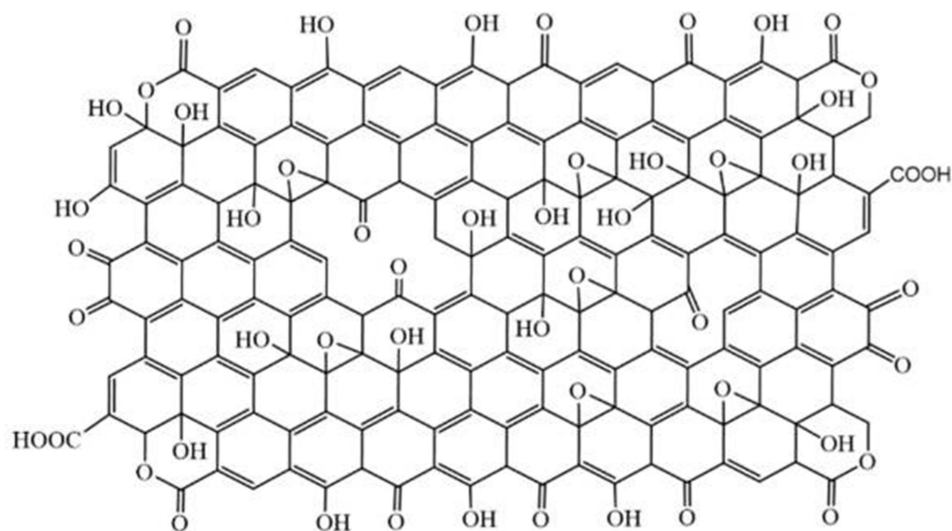


Figure 4: Structure of graphene oxide (GO) (Aliyev *et al.*, 2019).

### 2.3.1.3 Reduced Graphene Oxide (rGO)

It is a material derived from graphene oxide (GO) through a reduction process that removes a significant portion of the oxygen functional groups as indicated in figure 5. This reduction process restores the  $sp^2$  hybridization of carbon atoms, leading to improved electrical conductivity and other properties. Reduced graphene oxide has a better electrical conductivity compared to graphene oxide because the removal of oxygen functional groups restores the  $\pi$ -electron conjugation in the carbon lattice, allowing for the efficient movement of electrons. Reduced graphene oxide can exhibit electrical conductivity on the order of thousands to millions of Siemens per meter (S/m) (Jaafar *et al.* 2018). It demonstrates enhanced thermal conductivity compared to GO. The restoration of the  $sp^2$  carbon network facilitates efficient heat transfer through the material. It also can exhibit thermal conductivities ranging from hundreds to thousands of watts per meter-kelvin (W/m·K). Reduced graphene oxide exhibits improved chemical stability compared to GO due to the removal of oxygen functional groups, which are more susceptible to chemical reactions. Reduced graphene oxide is less prone to degradation under harsh chemical environments, making it suitable for various applications where chemical stability is important. Reduced graphene oxide has a greater specific surface area ( $90 \text{ m}^2/\text{g}$ ) three times greater than graphene oxide ( $29 \text{ m}^2/\text{g}$ ) due to the loss of its oxygen functional groups (Das *et al.*, 2024) that can be advantageous for applications such as energy storage, catalysis, and sensing (Ling *et al.*, 2020; Sivasubramanian & Vhanbatte, 2019). It tends to exhibit reduced light absorption in the ultraviolet (UV) and visible regions compared

to GO and therefore it has a poor photocatalytic efficiency (Ling *et al.*, 2020). The optical properties of rGO can be further tuned by controlling the reduction process and incorporating additional functional groups or dopants or coupling with other metal oxides enhances its performance in practical application (W. Chen *et al.*, 2018)(Ali *et al.*, 2022). It's important to note that the properties of rGO can vary depending on the degree of reduction, the specific reduction method used, and any additional treatments or modifications applied to the material. Some of the prominent reducing methods of graphene oxide (GO) to obtain reduced graphene oxide (rGO) are discussed below:

#### **2.3.1.3.1 Hydrothermal Reduction Method**

It is a method used to convert graphene oxide (GO) into reduced graphene oxide (rGO) using a hydrothermal reaction (Hu & Gao, 2023). The process involves subjecting GO to high-temperature and high-pressure conditions in an aqueous solution or solvent. First, a solution of GO is prepared by dispersing an appropriate amount of it in water or another suitable solvent. Next, the GO solution is transferred to a sealed reactor vessel capable of withstanding high pressure. The vessel is then sealed to maintain a controlled environment during the reaction. The reactor vessel is heated to a specific temperature, typically ranging from 150 °C to 250 °C, and the pressure is increased accordingly. The reaction conditions are maintained for a specific duration, typically several hours. Under high-temperature and high-pressure conditions, the oxygen-containing functional groups present on the surface of GO undergo reduction. This reduction process leads to the removal of oxygen atoms and the restoration of  $SP^2$  carbon bonds, resulting in the formation of rGO (Mei *et al.*, 2015). After the desired reaction time, the reactor is allowed to cool down naturally or through controlled cooling methods. The rGO suspension is then collected by filtration or centrifugation, followed by thorough washing and drying. The hydrothermal reduction method offers advantages such as simplicity, scalability, and the ability to control the degree of reduction by adjusting reaction parameters. The resulting rGO can exhibit improved large area, electrical conductivity and other desirable properties for various applications in electronics, energy storage, and catalysis (Hayes *et al.*, 2015; Neeraj Kumar *et al.*, 2022).



#### **2.3.1.3.2 Thermal Reduction Method**

It involves subjecting graphene oxide to high temperatures in an inert atmosphere, such as argon or hydrogen, to remove the oxygen functional groups. The heat treatment facilitates the restoration of  $SP^2$  carbon bonding and the reduction of GO to rGO. The temperature and duration of the thermal treatment can influence the degree of reduction and the resulting properties of rGO (Alam *et al.*, 2017)(N. Kumar *et al.*, 2022). For instance, Schmiedova *et al.* 2017 used thermal reduction process and UV reduction were used to synthesize rGO from GO (Schmiedova *et al.*, 2017).

#### **2.3.1.3.3 Chemical Reduction Method**

It utilizes reducing agents to remove the oxygen functional groups from graphene oxide. Commonly used chemical reducing agents include hydrazine, sodium borohydride, ascorbic acid, and hydrogen peroxide. These reducing agents react with the oxygen functional groups, leading to the restoration of  $sp^2$  carbon bonding and the reduction of GO to rGO. The reaction conditions, such as temperature and pH, can affect the efficiency and quality of the reduction process (Hu & Gao, 2023).

#### **2.3.1.3.4 Electrochemical Reduction**

It involves the application of an electrical potential to a GO electrode immersed in an electrolyte solution. The reduction process occurs at the electrode-electrolyte interface, where the oxygen functional groups are removed, and the GO is reduced to rGO. Electrochemical reduction allows for precise control over the reduction process by adjusting the applied potential and the electrolyte composition (Hu & Gao, 2023)

#### **2.3.1.3.5 Photoreduction Method**

It utilizes light energy to induce the reduction of GO to rGO (Tai *et al.*, 2019). Ultraviolet (UV) light or other light sources are used to irradiate a GO suspension or film, promoting the removal of oxygen functional groups and the restoration of  $SP^2$  carbon bonding. Photoreduction can be performed in the presence of specific sensitizers or catalysts to enhance the efficiency of the reduction process (Hu & Gao, 2023; Lee *et al.*, 2018).

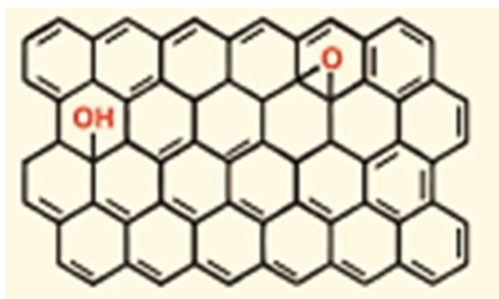


Figure 5: Representative structure of reduced graphene oxide (rGO) synthesized by reduction of graphene oxide (GO) (Tadyszak and Wychowaniec, 2018).

#### 2.3.1.4 Graphene

Graphene is a single layer graphite sheet shown in figure 6. It is a two-dimensional (2D) carbon-based material, which has recently attracted particular attention due to specific electronic structure, which gives it unusual electronic properties and startling high carrier mobility at relatively high charge carrier concentrations (Tadyszak and Wychowaniec 2018). Recently, it was shown that graphene also provides extraordinary optical properties. It transmits 97.7% of the incident light. However, graphene sheets have limited practical application due to the fact that graphene is insoluble and infusible. Graphene alone is not a good photocatalyst due to its zero band gap and fast recombination of charge carriers but it has emerged as a promising material in photocatalysis for enhancing the performance of semiconductor photocatalysts.

By combining graphene with semiconductors, benefits such as enhanced structure stability, increased adsorption and active sites, and used as an electron acceptor. This combination addresses limitations of traditional photocatalysts, improving efficiency in pollutant degradation and hydrogen production. Graphene-based photocatalysts have demonstrated enhanced activity and stability in degrading pollutants. Future prospects include optimizing photocatalyst design, exploring new graphene-based materials, and developing scalable synthesis methods. Challenges remain in cost-effective large-scale production and understanding photocatalytic activity mechanisms. Overall, graphene-based materials hold great potential in photocatalysis and further research is needed to fully exploit their capabilities (M. A. Ahmed & Adel, 2023; Mondal *et al.*, 2021). Graphene-based nanomaterials is used as an efficient photocatalyst for water splitting (Albero *et al.*, 2019).

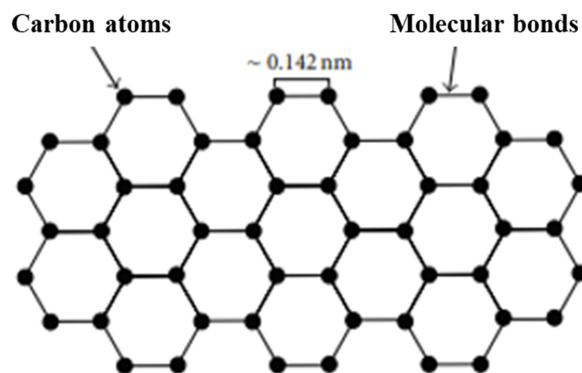


Figure 6: Structure of graphene (Roberts *et al.*, 2014).

### 2.3.2 Inorganic-Based Nanomaterials

It refers to nanoscale materials composed primarily of inorganic elements. They do not contain carbon. These nanomaterials include metal and metal oxide nanoparticles. These nanomaterials can be synthesized into metal nanoparticles such as Au, Ag, Al, Cu, Fe, etc, and metal oxides such as  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{SnO}_2$ , CuO and ZnO nanoparticles etc, and semiconductors such as silicon and ceramics. Basic properties of some metal oxide inorganic based nanomaterials are discussed below.

#### 2.3.2.1 Tin dioxide ( $\text{SnO}_2$ )

There are two types of tin oxide namely tin dioxide or stannic oxide ( $\text{SnO}_2$ ) and tin monoxide or stannous oxide ( $\text{SnO}$ ). Tin (Sn) has 4 and 2 oxidation states in  $\text{SnO}_2$  and  $\text{SnO}$  respectively. Stannic oxide is thermodynamically stable whereas stannous oxide is not stable. Stannic oxide is an n-type and stannous oxide is p-type semiconductor. The stannous oxide ( $\text{SnO}$ ) formed with tetragonal structure at a calcination temperature of  $300^\circ\text{C}$  undergone a phase change to orthorhombic stannic oxide by oxidation at calcination temperature of  $500^\circ\text{C}$  in air environment (Campo, Rodríguez, & Ramírez, 2016; Kai *et al.*, 2023; Nikiforov *et al.*, 2020). At room temperature and pressure, the most stable crystal structure of  $\text{SnO}_2$  is known as cassiterite, which is related to the tetragonal rutile structure ( $a = b = 0.473 \text{ nm}$ ,  $c = 0.318 \text{ nm}$ ) and its unit cell is shown in figure 7 (Pinto *et al.*, 2022). For instance, according to Dhinakar and Meenakshi, 2016 report that the annealed  $\text{SnO}_2$  samples exhibited tetragonal crystalline structure with crystallite size ranging from 13 to 25 nm (Dhinakar & Meenakshi, 2016).

Tin dioxide ( $\text{SnO}_2$ ) is an *n*-type direct band gap semiconductor with a rutile tetragonal structure and outstanding properties such as large exciton binding energy, electrocatalyst (Jiang *et al.*, 2005), strong adsorption capacity (Abdelkader *et al.*, 2016), high carrier mobility (Mun *et al.*, 2020), high thermal stability, high photosensitivity (Bahishti & Majid, 2017), high abundance, inexpensive and low toxicity. It is a transparent material with a refractive index of around 2.0 to 2.2. It exhibits low reflectivity in the visible range and minimal absorption, making it suitable for transparent applications. The band gap of  $\text{SnO}_2$  is approximately 3.6 eV at room temperature, determining its optical absorption and emission properties. It is used in various applications such as low-emission window coatings, solar cells, lithium-ion batteries, and gas sensors.  $\text{SnO}_2$  serves as a catalyst and catalyst support for oxidation reactions (Karmaoui *et al.*, 2018). Furthermore, the highly thermal stable  $\text{SnO}_2$  nanocrystals exhibited high sensor response to hydrogen due to their small crystalline size and changes in surface properties compared to the bulk via hydrothermal treatment (Yuasa *et al.*, 2016). The dielectric constant of  $\text{SnO}_2$  decreases with increasing frequency of applied signals but increases with higher calcination temperature. The direct energy bandgaps of  $\text{SnO}_2$  thin films were measured as 4.85 eV, 4.80 eV, 4.75 eV, and 4.10 eV for different calcination temperatures, indicating that calcination temperature affects the material's properties (Al. *et al.*, 2020).

According to Koshy *et al.* (2015), there is a blue shift in the absorption edge of  $\text{SnO}_2$  nanoparticles at UV region ( $\lambda = 278$  nm,  $E_g = 4.47$  eV) when compared to the bulk (3.60 eV). Oxygen vacancies and impurities cause visible emission in the photoluminescence spectra of  $\text{SnO}_2$  nanoparticles (Koshy *et al.*, 2014). Sarmah and Kumar (2014) state that the lattice parameters *a* increase from 2.78 to 3.17 Å and *c* decrease from 5.09 to 4.68 Å when the reaction temperature rises. Photoluminescence intensity of  $\text{SnO}_2$  nanoparticle increases with the rise of reaction temperature. PL intensity also rises with increasing particle size and decreasing microstrains (Sarmah & Kumar, 2010).

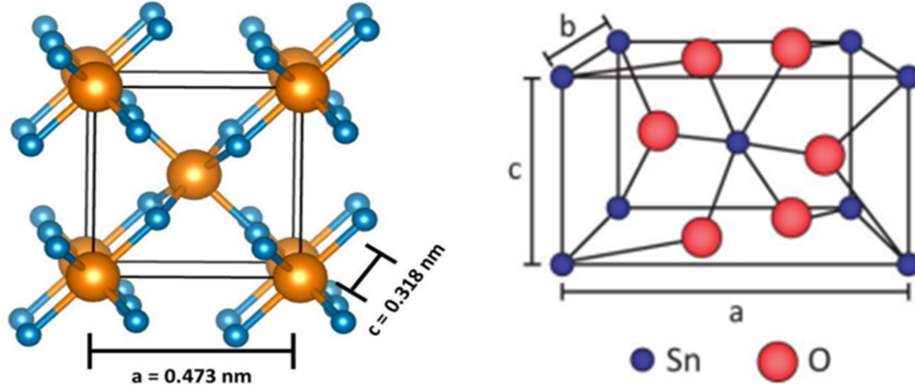


Figure 7: A unit cell consists of the tetragonal cassiterite structure of  $\text{SnO}_2$ . In this structure, the Sn atoms are represented by orange spheres, while the O atoms are represented by blue spheres (Pinto *et al.*, 2022).

### 2.3.2.2 Zinc Oxide (ZnO)

ZnO has three different types of crystal structures such as rock salt, cubic zinc blend and hexagonal wurtzite structure as indicated in figure 8. The wurtzite structure is more common at room temperature, while the zinc blende structure is observed at high temperatures or under certain growth conditions. The lattice parameters of the hexagonal unit cell are  $a = b = 3.2495 \text{ \AA}$ ,  $c = 5.2069 \text{ \AA}$  and the density is  $5.605 \text{ g/cm}^3$ . As a result of the positive charge of zinc atoms and the negative charge of oxygen atoms during the formation of zinc oxide (ZnO), strong electrostatic bonds are created between them.

Zinc oxide (ZnO) is a highly promising semiconductor material that has been extensively studied in recent years. It possesses several advantageous properties, including technological feasibility, abundance, high carrier mobility (Jayah *et al.*, 2015), chemical stability, high catalytic properties (Gomathi *et al.*, 2021), high photosensitivity (Bahishti & Majid, 2017), ease of synthesis of its crystal (Boon, Yong, & Wahab, 2018; Hong *et al.*, 2021) and non-toxicity. It has a wide bandgap of 3.37 eV at room temperature, making it suitable for applications involving ultraviolet (UV) light (Kadinskaya *et al.*, 2023). Additionally, ZnO exhibits a large exciton binding energy of 60 meV (C. Klingshirn, 2007), which is significantly higher than the thermal energy at room temperature. These characteristics make ZnO a favorable choice for the development of UV light sources. It is transparent to visible light while increasingly absorbing in the UV range (Janotti & Walle, 2014). ZnO is also thermally stable (Jones *et al.*, 2013) and has the significant benefit of being inexpensively and

easily grown (Look *et al.*, 2004). Moreover, ZnO demonstrates strong photoluminescence in Uv light region in the range 370-420 nm, and in the visible light region 420-650 nm due to singly ionized oxygen vacancies (or surface defects) which means it can emit light when excited by photons or other energy sources (Jangir *et al.*, 2017). ZnO nanoparticles can be used for photo-degradation, agriculture, concrete and rubber industry, optoelectronic industry, immunotherapy, anti-inflammatory activity, anticancer activity, drug delivery, antibacterial activity, textile industry and cosmetic industry (Raha & Ahmaruzzaman, 2022). The ability of ZnO to emit light also has significant implications in various optoelectronic devices, including light-emitting diodes (LEDs).

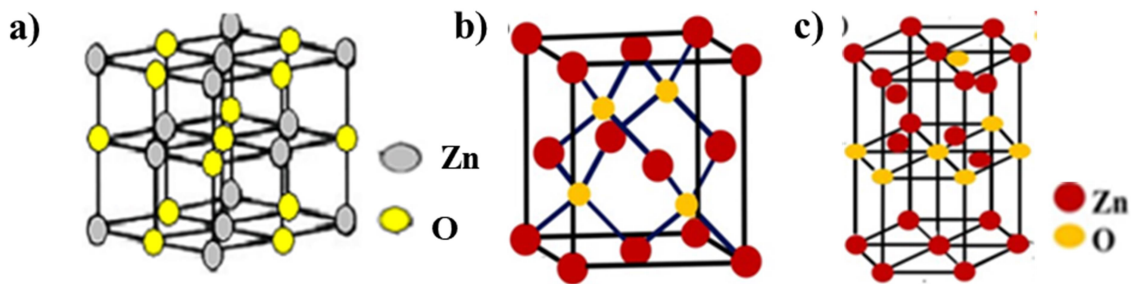


Figure 8: (a) The cubic rock salt (Mustapha *et al.*, 2020), (b) zinc blende crystal structure of ZnO, and (c) The hexagonal wurtzite crystal structure of ZnO (Srivastava *et al.*, 2022).

### 2.3.2.3 Cobalt oxide ( $\text{Co}_3\text{O}_4$ )

Cobalt oxide ( $\text{Co}_3\text{O}_4$ ) nanoparticles are a p-type dual band gap and magnetic semiconductor. They appear as a white powder with cubic spinel crystal structure.  $\text{Co}_3\text{O}_4$  nanoparticles typically exhibit a cubic crystal structure, with a spinel arrangement of cobalt and oxygen ions. This structure influences their physical and chemical properties. Cobalt ions in two distinct oxidation states,  $\text{Co}^{3+}$  ions occupying octahedral sites, and  $\text{Co}^{2+}$  ions occupying tetrahedral sites crystallize in a spinel structure with oxygen ions forming a closely packed face-centered cubic lattice (Mbongo & Mata, 2019). Cobalt oxide is indeed known for its high surface-to-volume ratio, affordability, eco-friendliness, ease of preparation, and strong chemical and physical stability. Among cobalt oxides  $\text{Co}_2\text{O}_3$  and  $\text{CoO}$ ,  $\text{Co}_3\text{O}_4$  is the most stable, and its phase changed to  $\text{CoO}$  at  $800\text{ }^{\circ}\text{C}$ - $900\text{ }^{\circ}\text{C}$  (F. Kong *et al.*, 2019; Mandi *et al.*, 2022). These unique properties of  $\text{Co}_3\text{O}_4$  nanoparticles have led to its extensive exploration for various applications, including solar absorption (Gardey *et al.*, 2015), lithium-ion batteries (Liang *et al.*, 2018; Sennu *et al.*, 2020; Tao *et al.* 2015), supercapacitors (Lu *et*

*al.*, 2020; Priyadharsini *et al.*, 2021; Sharma *et al.* 2021; Umar *et al.* 2021), gas sensors (Choi *et al.*, 2010; Vetter *et al.*, 2015; Z. Zhang, Wen, & Zhu, 2015; T. Zhou *et al.*, 2017; Zhu & Wang, 2017), good catalysis and fuel additives (Ramzan & Ashraf, 2019), and efficient antioxidant and antibacterial behavior (D. Das & Jyoti, 2023).  $\text{Co}_3\text{O}_4$  is a good photocatalyst in the visible light region. For instance, Vennela *et al.* 2019 synthesized  $\text{Co}_3\text{O}_4$  nanoparticles using cobalt acetate precursor by sol-gel method showed a high degradation efficiency of 93.8 % of methylene blue dye under visible light irradiation (Vennela *et al.*, 2019).

#### 2.3.2.4 Copper Oxide (CuO)

Copper oxide is a p-type, narrow band gap semiconductor, and the band gap can be tuned roughly in the range of 1.2-2.1 eV through quantum confinement effect. Cu–O bond length is found to be 1.96 Å. The crystal structure of CuO and  $\text{Cu}_2\text{O}$  are given in figure 9 (a & b). The lattice constants of copper oxide nanoparticles, are  $a = 4.67 \text{ Å}$ ,  $b = 3.42 \text{ Å}$ ,  $c = 5.13 \text{ Å}$ ,  $\alpha = 90^\circ$ ,  $\beta = 99^\circ$ ,  $\gamma = 90^\circ$ , monoclinic  $C_2/c$  space group tenorite as a mineral (S. A. J. M. Devi, 2023). Phase changes could be occurred depending on the calcination temperature. As reported in literatures, pure CuO phase can synthesized at 350 °C whereas  $\text{Cu}_2\text{O}$  formed at 200 °C in cubic structure, and both tenorite (CuO) and cuprite ( $\text{Cu}_2\text{O}$ ) phase are observed at 300 °C (Balık, Bulut, & Erdogan, 2018; Raship *et al.*, 2017). Copper oxide is an inexpensive, abundantly available, environmentally benign, non-toxic, magnetic semiconductor. It has a high thermal stability up to 830 °C and excellent conductivity (Wang *et al.*, 2020).

Copper oxide (CuO) nanoparticles due to the outstanding properties could be used in many areas of applications. For instance, the electrical conductivity of CuO NPs leads high-performance symmetric flexible supercapacitor (Amirtharaj & Mariappan, 2021; Bhise *et al.*, 2017; Moosavifard *et al.*, 2015; Sayyed *et al.*, 2023). Sonochemically synthesized spherical CuO nanoparticles were used in solar cell (Dhineshababu & Vetumperumal, 2016; Raizada *et al.*, 2020) and textile production (Dhineshababu & Vetumperumal, 2016). It also used in optoelectronic device application due to its good optical characteristics (Saleem *et al.*, 2022). Copper oxide is a good candidate for removing dyes by photocatalytic process from waste water (Aroob *et al.*, 2023; Pavithra *et al.*, 2021; Raizada *et al.*, 2020). Moreover, it could be used as antioxidant, antibacterial, and photocatalytic activity for the removal of methylene blue (Dulta *et al.*, 2022; Fuku, Thovhogi, & Maaza, 2018; Peddi *et al.*, 2021; Martha

Ramesh, 2021), antimicrobial activity (Chauhan *et al.*, 2021), as the cathode material for thermal battery (Wang *et al.*, 2020), rechargeable alkaline zinc batteries (Meng *et al.*, 2020; Schorr *et al.*, 2021), superior sensitivity towards toxic and flammable gases (Su *et al.*, 2014), and as anode material for the Li-ion battery (Deng *et al.*, 2018; Pavithra *et al.*, 2021).

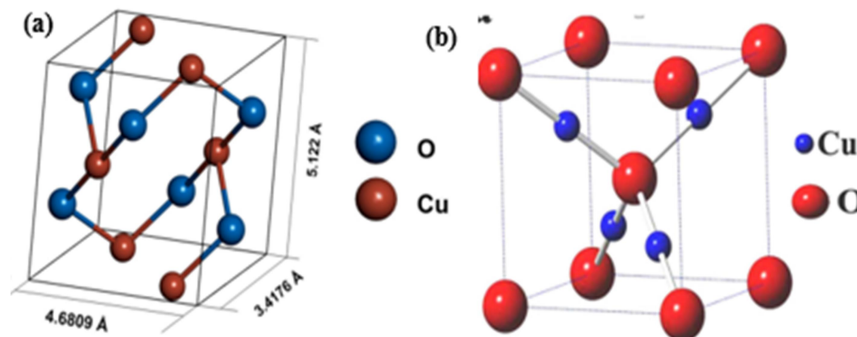


Figure 9: The diagram of (a) monoclinic structure of CuO (Ungeheuer *et al.*, 2022), and (b) Cubic structure Cu<sub>2</sub>O ( $a = 4.2696 \text{ \AA}$ ) (Gao *et al.*, 2015).

### 2.3.3 Organic-Based Nanomaterials

Organic-based nanomaterials are materials at the nanoscale that are primarily composed of organic compounds or have organic molecules incorporated into their structure excluding carbon. These materials often exhibit unique properties due to their small size and organic composition, making them suitable for various applications such as drug delivery, electronics, energy, medicine, and environmental science, sensors, and electronic devices (Alshammari *et al.*, 2023). Organic nanoparticles are small particles made of aggregated molecules or polymers. Some of the examples of organic nanoparticles are micelles, dendrimers, liposomes, nanogels, polymeric nanoparticles, polymeric nanocapsule, and layered biopolymer. Dendrimers are nano-sized polymers built from branched units. The surface of a dendrimer has numerous chain ends, which can be tailored to perform specific chemical functions like catalysis and also three-dimensional dendrimers contain interior cavities into which other molecules could be placed, they may be useful for drug delivery (Alshammari *et al.*, 2023; Dong & Hu, 2013).



### 2.3.4 Composite Based Nanomaterials

Composite nanoparticles are nanomaterials with a composite structure made up of two or more components at the nanoscale, each with unique physical and chemical properties and mutual contact interfaces. They are engineered to combine the distinct characteristics of each component, leading to tailored functionalities for various applications. When two or more components with differing properties are combined, the resulting composite material exhibits enhanced strength and tailored characteristics suitable for specific applications. Composite nanomaterials are multiphase nanoparticles and/or nanomaterials with one phase on the nanoscale dimension that can either combine nanoparticle with other nanoparticles or nanoparticles combined with larger or with bulk-type materials (e.g., hybrid nanofibers) or more complicated structures, such as a metalorganic frameworks. The composites may be any combinations of carbon-based, metal-based, or organic-based nanomaterials with any form of metal, ceramic, or polymer bulk materials. For instance, metal oxide composites such as CuO/ZnO (Sakib *et al.*, 2019), Fe-SnO<sub>2</sub>/CeO<sub>2</sub> (Asaithambi *et al.*, 2021), ZnO–TiO<sub>2</sub> (M. M. Ali *et al.*, 2021), Ni doped ZnO-TiO<sub>2</sub> (Zou *et al.*, 2014), CuO/TiO<sub>2</sub>/ZnO (Taufik *et al.*, 2017), CuO-ZnO (Nagarjuna *et al.*, 2017), ZnO/CuO (Mubeen *et al.*, 2023), and metal oxide–reduced graphene oxide (rGO) based composites like Ag-SnO<sub>2</sub>/rGO (S. Zhang *et al.*, 2019), Cu-ZnO/rGO (Shewale & Yun, 2020), ZnCo<sub>2</sub>O<sub>4</sub>/rGO (Mary *et al.*, 2017), Bi-SnO<sub>2</sub>/rGO (Guo *et al.*, 2019), Pd-doped rGO/ZnO-SnO<sub>2</sub> (X. Zhang *et al.*, 2022), CeO<sub>2</sub>–SnO<sub>2</sub>/rGO (G. S. Kumar *et al.*, 2020), SnO<sub>2</sub>/rGO (Khan *et al.*, 2019), SnO<sub>2</sub>-rGO (ZabnAllah M. Alaizeri, Hisham A. Alhadlaq, Saad Aldawood, 2022), SnO<sub>2</sub>/rGO (Zhang, H., Xu, P., Ni, Y., Geng, H., Zheng, G., Dong, B., & Jiao, 2014), SnO<sub>2</sub>/rGO (Viet *et al.*, 2016b), Cu/ZnO/rGO (He *et al.*, 2018), ZnO-GO (Jin *et al.*, 2022) and Ce-SnO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> (Asaithambi *et al.*, 2021). As a conclusion, based on the reported literatures, improving performance of a pristine host was confirmed by altering the desired properties through the use of various methods for different applications.

### 2.4 Synthesis Methods of Nanomaterials

In general there are two types of approaches for the synthesis of nanomaterials as shown in figure 10. These are top-down and bottom-up approaches. Top-down approach is the breakdown of bulk materials to form a fine powder then from the fine powder, nanoparticles are produced. Bottom-up approach refers to the building up of a material from the bottom

atom-by-atom or molecule-by-molecule. This method also promises a better chance to obtain nanostructures with less defects, more homogeneous chemical composition and nearly uniform size distribution. Some of the bottom up methods used to produce nanostructures as well as nanoparticles and composites are discussed below.

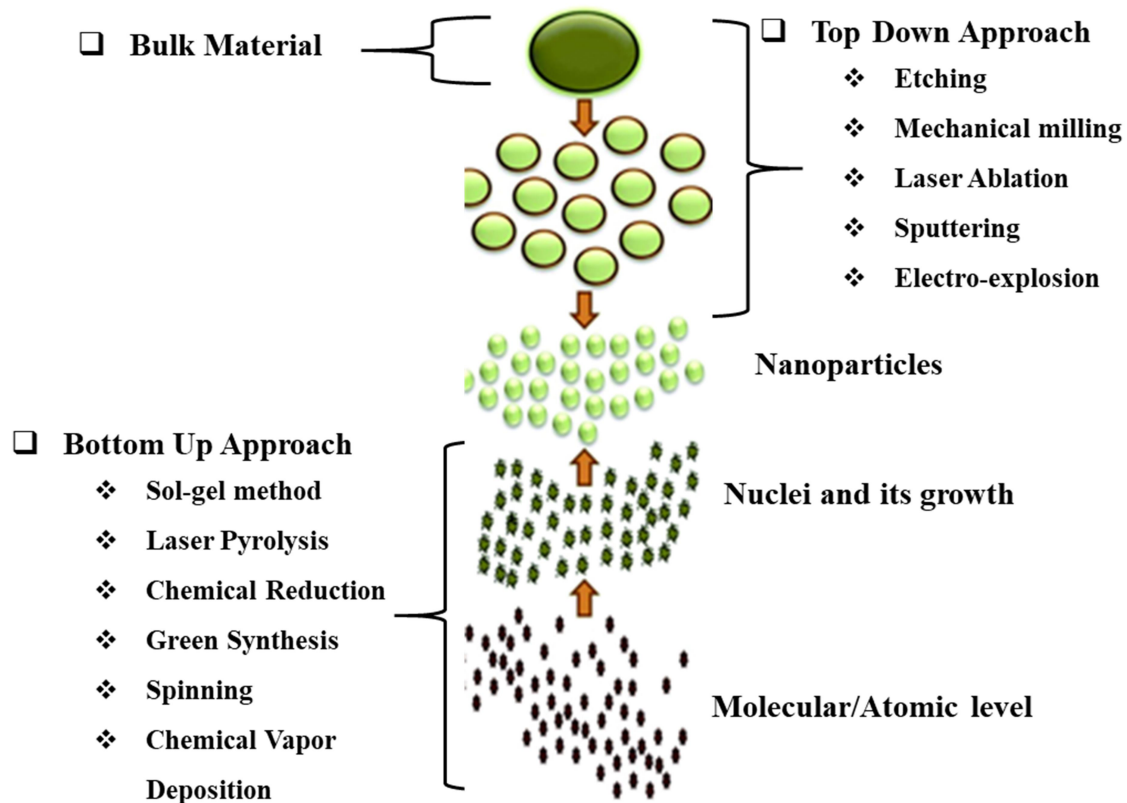


Figure 10: Classifications of top down and bottom up nanomaterials synthesis methods re-drawn based on (Kammakakam, 2021).

#### 2.4.1 Sol-gel Method

Sol-gel synthesis is an effective and economical substitute for traditional methods for producing nanocrystalline elemental, alloy, and composite powders. The general procedures for nanomaterials synthesis using sol-gel method is given in figure 11. Using a chemical solution (sol, short for solution) as the starting point, this method is primarily used to fabricate nanomaterials, such as metal oxide nanoparticles, which results in an integrated network (or gel) of discrete particles or network polymers. This low-cost, low-temperature method regulates the chemical makeup of the final product. Rare Earth metals and other dopants can be added to the sol in small amounts, and the final product end up uniformly

dispersed in the final product. An effective and economical substitute for traditional methods for producing nanocrystalline elemental, alloy, and composite powders. It can be also used in ceramics processing and manufacturing as an investment casting material, or as a means of producing very thin films of metal oxides for various purposes. Sol-gel derived materials have various applications in optics, electronics, energy, biosensors, medicine and separation technology. Sol-gel synthesis of SnO<sub>2</sub> nanoparticles exhibited particle size of 12 nm with absorption peak at 278 nm, and shows a blue shift when compared to the bulk due to quantum confinement (Koshy *et al.*, 2014). The crystalline size of SnO<sub>2</sub> nanoparticles depends on the molar concentration of the precursor used. SnO<sub>2</sub> Nanoparticles prepared by the sol-gel method with increasing the molar concentration of the precursor increases the crystalline size and shifts to the short wavelength. The crystalline size of 0.1 M, 0.3 M and 0.5 M are 11.7 nm, 18.8 nm, and 74.8 nm respectively. This means that the band gap decreased as a result of increasing of particle size (Reza *et al.*, 2018). Zhang *et al.* 2023 synthesized porous Si/ZnO Nanorod composites using sol-gel method (Liqiang Zhang *et al.*, 2023). The Factors affecting the quality of a synthesized nanomaterials in the sol-gel method are discussed below:

#### 2.4.1.1 pH

The synthesis pH has a great impact on the properties of the synthesized nanomaterials. For instance, silica gel obtained at a pH of 2 exhibits microporous characteristics, with an average pore size of 2 nm. On the other hand, in an alkaline medium with a pH of 10, mesoporous SiO<sub>2</sub> with a narrow pore size distribution of 18 nm and a specific surface area of 110 m<sup>2</sup>/g were reported (Faustova & Slizhov, 2017). The pH of the solution used in the sol-gel synthesis of ZnO also affects its band gap. When the pH value increases, the band gap decreases. This is because the nanocrystallites tend to agglomerate into larger crystallites, leading to an increase in crystallite size with pH. As a result, there is a significant red shift in the optical spectra due to the reduction in bandgap (Dar & Zubair, 2022). Moreover, the crystallization property of La<sub>2</sub>CuO<sub>4</sub> crystallites follows a trend of initially increasing and then decreasing as the solution pH value vary from 1.0 to 2.5. However, all of the samples maintain a single sphere-like morphology. Notably, when the solution pH value is precisely controlled at 2.0, the grains exhibit a uniform size distribution ranging from 100 nm to 120 nm after undergoing a 2-hour sintering process at 600°C (Yi-feng *et al.*, 2012). The Pr<sup>3+</sup> doped YPO<sub>4</sub> nanophosphors prepared using a simple sol-gel method at pH 4 exhibited the highest luminescent intensity (Kahouadji *et al.*, 2017).

#### **2.4.1.2 Effect of Reaction Time**

The reaction time in the sol-gel method can have several effects on the final product. Longer reaction times can promote better crystallinity in the synthesized nanoparticles. This can result in improved material properties such as higher surface area and enhanced electrical or optical properties. It can also influence the particle size of the synthesized nanoparticles. Longer reaction times may lead to larger particle sizes, while shorter reaction times can result in smaller particles. The particle size can affect the material's surface area, reactivity and other physical properties. Adequate reaction time allows for sufficient mixing and homogenization of the precursor solution, leading to a more uniform distribution of metal ions. This can contribute to the formation of uniform and well-defined nanoparticles. Prolonged reaction times may increase the likelihood of impurity incorporation or contamination in the synthesized nanoparticles. It is essential to optimize the reaction time to minimize impurity formation and ensure high purity of the final product (Sayyed *et al.*, 2023).

#### **2.4.1.3 Effect of the Precursor**

The precursor can also influence the particle size of the synthesized nanoparticles. Different precursors may result in variations in the nucleation and growth processes during synthesis, leading to differences in particle size distribution, and variations in the electronic structure, which can affect the energy levels and band structure of the resulting nanoparticles. This, in turn, can alter the band gap of the material, influencing its optical and electronic properties. For example, successful synthesis of zinc oxide nanoparticles was achieved using zinc nitrate and zinc acetate as precursors via the sol-gel method. The properties, structure, and morphology of the nanoparticles depends on the choice of zinc oxide precursor. The type of precursor used had a significant impact on various characteristics, including bandgap, crystallite size, surface area, total pore volume, and pore diameter (Lim *et al.*, 2022).

#### **2.4.1.4 Stirring Rate**

The stirring rate in the sol-gel method can have an impact on the synthesis process and the resulting properties of the material. The stirring rate affects the mixing and dispersion of the precursors, which in turn can influence factors such as particle size, morphology,

crystallinity, and homogeneity of the product. A higher stirring rate can promote better mixing and dispersion, leading to smaller particle sizes, improved crystallinity, and enhanced homogeneity. This can be beneficial for achieving desired material properties such as increased surface area, improved reactivity, and uniformity in the final product. On the other hand, a lower stirring rate may result in slower mixing and less efficient dispersion. This can lead to larger particle sizes, lower crystallinity, and potential inhomogeneity in the synthesized material. It is important to optimize the stirring rate to achieve the desired properties for a specific application. The optimal stirring rate may vary depending on the specific system and precursor used. Experimental investigation and optimization are necessary to determine the ideal stirring rate for a particular sol-gel synthesis.

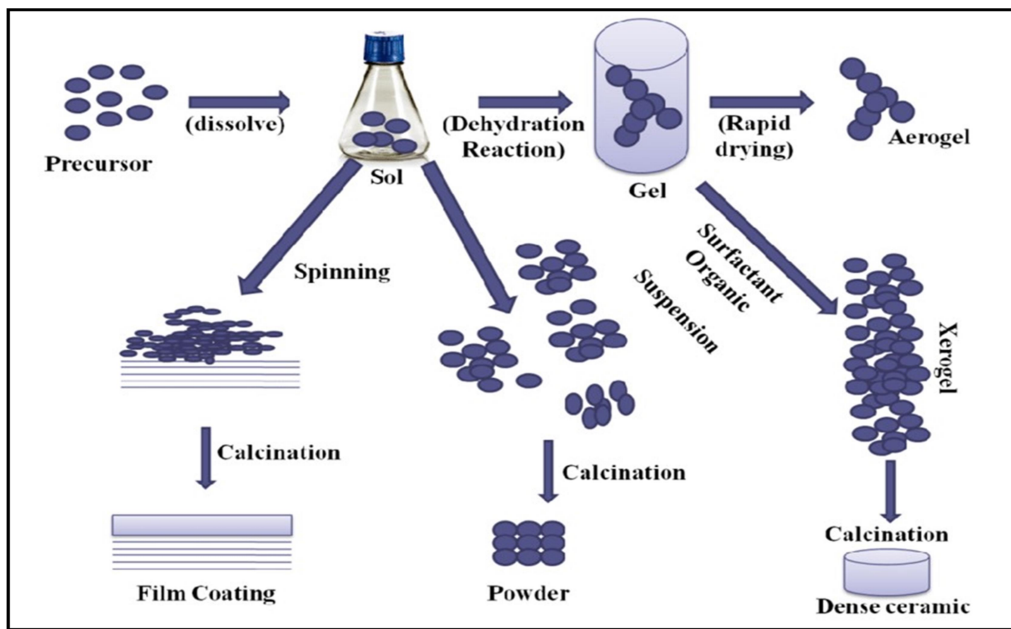


Figure 11: General procedures for nanomaterials synthesis using sol-gel method (Tripathi *et al.*, 2015).

#### 2.4.2 Hydrothermal Route

Hydrothermal synthesis is one of the most commonly used methods for preparation of nanomaterials using the procedures given in figure 12. It is basically a solution reaction-based approach. In hydrothermal synthesis, the formation of nanomaterials can happen in a wide temperature range from room temperature to very high temperatures (Gan *et al.*, 2020). In this method water is used as a solvent due to environmentally friendly and cheaper than other solvents, and it can act as a catalyst for the formation of desired materials by tuning the

temperature and the pressure. It is nontoxic, nonflammable, non-carcinogenic, non-mutagenic and thermodynamically stable. Another advantage is that water is very volatile, so it can be removed from the product very easily. Varieties of morphologies and particle sizes could be produced with hydrothermal processing. By using this method powders with controlled size and morphology for a wide range applications can be synthesized. This facile method does not need any seed, catalyst, harmful and expensive surfactant or template thus it is promising for large scale and low-cost production with high-quality crystals. Disadvantages of the method include the need of expensive autoclaves, and the impossibility of observing the crystal as it grows if a steel tube is used.

The crystalline size, nanostructure morphology, porosity, optimal crystallinity, pore size, lattice spacing and band gap can be properly controlled in hydrothermal synthesis method by synthesis parameters such as reaction time, hydrothermal temperature and pressure, and drying temperature. For instance, in a simple hydrothermal synthesis route, the crystalline size and its distribution in the synthesized SnO<sub>2</sub> nanoparticles are dependent on the hydrothermal synthesis temperature (Pazouki & Memarian, 2021). The variation of synthesis hydrothermal temperature changes the morphology of nanomaterials. For example, at the reaction temperature of 120 °C irregular shaped particles, at 140 °C nanorods, and 230 °C bended foils and plates of SnO<sub>2</sub> formed (Khuc *et al.*, 2011). The sample that was prepared with a 20-hour reaction time had the most uniform particle size, optimum BET pore volume, and excellent crystallinity (Khajuee & Memarian, 2021).

The effect of pH on the properties of SnO<sub>2</sub> nanoparticles synthesized hydrothermally has been studied in various research papers. For instance, Kumar *et al.* 2022 investigated the effect of pH levels on the photocatalytic activity, dielectric and supercapacitor properties of SnO<sub>2</sub> nanoparticles at the values 8, 10 and 12 with respect to particle size/shape variation (S. Kumarl., 2022). Song *et al.* 2015 also found that SnO<sub>2</sub> nanocrystalline shows the strong absorption in the ultraviolet light range, and the highest absorbance value obtained at pH = 11 (Song *et al.*, 2015).

In the modified hydrothermal synthesis of ZnO nanoparticles, it was observed that the average crystallite size slightly increased, while the bandgap value decreased with longer reaction times and higher synthesis temperatures. The fluorescence spectra analysis further revealed that the emission characteristics of the ZnO nanoparticles were influenced by both the reaction time and temperature (Wasly, El-sadek, and Henini, 2018). Hydrothermal synthesis method has been used to synthesize nanomaterials with different morphologies such

as nanorods, spherical nanoparticles, nanosheets, flowers and nanowires. For instance, Sedira and Mendaci, 2019 synthesized stable colloidal suspension of spherical carbon nanoparticles with good crystalline structure, uniformity of size and shape using synthesis conditions at a heating temperature of 120 °C for 12 hour (Sedira & Mendaci, 2020). Zhang *et al.* 2019 synthesized SnO<sub>2</sub> nanorods using template free hydrothermal method under synthesis temperature of 150 and 180 °C for 24 hour without surfactant after calcination at 700 °C for 7 h in air atmosphere with an aspect ratio of 4.9 and 3.5 respectively as anode materials for lithium-ion battery (Zhang *et al.*, 2019). Small sized nanocrystalline SnO<sub>2</sub> particles with a size of around 3 nm have been fabricated using a hydrothermal process. The thermally treated SnO<sub>2</sub> was as an effective gas sensor for alcohol and the detection limit can be as low as 1.7 ppm (Chiu & Yeh, 2007).

Hydrothermal method also used to synthesize nanocomposites. Sardarali Khan *et al* 2019 synthesized SnO<sub>2</sub>/GO nanocomposite with small grain size, large number of grain boundaries and high defect density contributed to increased dielectric constant and conductivity at large frequencies (Khan *et al.*, 2019). This method also is used to synthesize hetrostructured nanomaterials. For example, Lamba *et al* 2015 synthesized ZnO doped SnO<sub>2</sub> nanoparticles heterojunction photocatalyst for photocatalytic application (Lamba *et al.*, 2015). The SnO<sub>2</sub>-MoS<sub>2</sub> hetrostructure synthesized for visible light photocatalytic performance by hydrothermal route (Ni *et al.*, 2019).

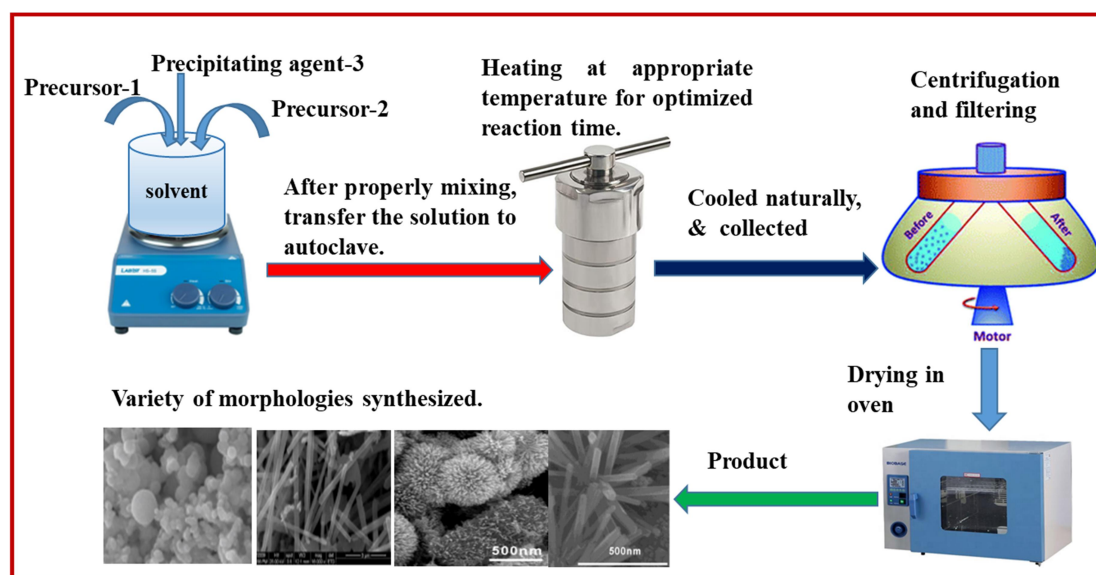


Figure 12: General synthesis procedures of nanomaterials using hydrothermal method. The SEM images morphologies used in this figure are taken from (Khajuee & Memarian, 2021; Khuc *et al.*, 2010; Y. Liang & Fang, 2013).

## 2.5 Modification Strategies of Nanomaterials

### 2.5.1 Addition of Dopant

The process of addition of suitable dopants into the host oxide is known as doping, and the purpose of doping is to enhance the properties of the host material to improve its performance in the desired application area. For instance, the optimum 4% Sn-doped ZnO nanoparticle showed highest photocatalytic activity when compared to the host synthesized by simple co-precipitation assisted method (Venkatesh *et al.*, 2021). The maximum MB dye degradation (93%) was achieved with Ni-Th-ZnO (0.375 g/L) synthesized by co-precipitation method shows an excellent photocatalytic activity for the degradation of MB dye (1.5 mM) at pH of 10 under light irradiation time of 180 minutes (Vignesh *et al.*, 2014).

Selvinsimpson *et al.* 2021 reported that the 5% Sn doped ZnO photocatalyst improve the transfer rate of photo-excited carrier and decrease the rate of recombination which greatly influence on the photocatalytic and antibacterial performance via ultrasonic aided co-precipitation technique UV lamp of 8 Watt (Selvinsimpson *et al.*, 2021). Toloman *et al.* 2020 reported that Co-SnO<sub>2</sub> nanoparticles were synthesized by chemical precipitation method exhibited enhanced crystallinity, red shift, lower recombination rate of photogenerated electron-hole pairs due to the intermediate energy levels introduced in the band gap of SnO<sub>2</sub> and increased optical absorption of visible light. Among the synthesized samples, the best photocatalytic activity against RhB synthetic solution was obtained using 1% Co-SnO<sub>2</sub> under visible light irradiation (Toloman *et al.*, 2020). Yu *et al.* 2013 synthesized Er-ZnO nanoparticles by homogeneous precipitation method, exhibited significantly higher light absorption in the ultraviolet region compared to ZnO, due to redshift, and due to the formation of defect energy levels between the valence and conduction band in the ZnO band structure, resulting in enhancing the catalytic activity of ZnO. However, the introduction of Er into ZnO enhanced the intensity of fluorescence emission which is in contradiction with the reports that best photocatalytic efficiency has been archived when intensity was quenched (Yu *et al.*, 2013). The QDs with 0.03 mol % Cu-SnO<sub>2</sub> NPs showed the highest photocatalytic performance with 99% degradation of the dye under visible light within 180 minutes, which means they could be used to treat polluted water xenon lamp (Babu *et al.*, 2017). Recently, at pH = 9, ZnO-Sb nanophotocatalyst exhibited 91% of the MB dye removing using 300 mg/L, and an initial MB dye dose of 10 ppm on exposure to solar and UV irradiation (Modi *et al.*,



2023). The intensity of visible emission also reduces as the content of Co dopant increases. The photocatalytic activity to degrade methylene blue (MB) dye under visible light irradiation (Goswami, 2020). The 1wt % of Ag/SnO<sub>2</sub> has a better photocatalytic performance of 97.63% for methylene blue (MB) dye when compared to undoped SnO<sub>2</sub> under solar light irradiation 120 minutes (Shittu *et al.*, 2023). Due to high oxygen vacancy concentration in 3% Sr-doped SnO<sub>2</sub>, Sr-doped SnO<sub>2</sub> with 5% doping content exhibits the outstanding photocatalytic performance and can degrade 94% MB in 60 min under UV light illumination might be due to facilitate the separation of charge carriers through trapping sites created by Sr ions as well as by the creation of oxygen vacancy (Ahmed *et al.*, 2018).

### 2.5.2 Making of Composites

Reported research results confirmed that making different composites such as metal oxide-metal oxide coupling, coupling of metal oxide with carbon based materials and formation of ternary composites of metal oxides or combining with carbon materials enhanced the photocatalytic performance. For instance, metal oxide composites such as CuO/ZnO synthesized by simple mechanochemical combustion method exhibited enhanced photodegradation of toxic textile dye like methylene blue under direct sun light irradiation for 2 hours (Sakib *et al.*, 2019), sol-gel synthesized 65ZnO-35TiO<sub>2</sub> composites demonstrated better photocatalytic activity under Uv light irradiation for 100 minutes (M. M. Ali *et al.*, 2021), chemical synthesis of 10% CuO/ZnO nanocomposite for enhanced photocatalysis for degradation of methylene blue under visible light irradiation compared to pure ZnO nanoparticles (Mubeen *et al.*, 2023). Simultaneous use of doping metals into metal oxide semiconductor and coupling it with another metal oxide semiconductor also improved the photocatalysis performance for removal of a synthetic organic dye. For instance, Ni doped ZnO-TiO<sub>2</sub> nanocomposite synthesized by sol-gel route for enhanced photocatalytic activity (Zou *et al.*, 2014), and sol-gel route synthesized CuO/TiO<sub>2</sub>/ZnO (0.5:1:1) ternary nanocomposites shows enhanced photocatalytic efficiency of 100 % and 98 % methylene blue removal recorded under Uv and visible light irradiation respectively within 2 hours (Taufik *et al.*, 2017).

The coupling of semiconductor metal oxides with carbon materials such as reduced graphene oxide (rGO), graphite nitride etc as a support also enhances the photocatalytic performance. Hydrothermally synthesized SnO<sub>2</sub>-rGO nanocomposite shows enhanced photocatalytic efficiency of methylene blue (MB) dye by SnO<sub>2</sub>-rGO NCs (93%) was almost 2-fold higher

than for pure SnO<sub>2</sub> NPs (54%) (ZabnAllah M. Alaizeri, Hisham A. Alhadlaq, Saad Aldawood, 2022), single -step hydrothermal synthesis of SnO<sub>2</sub>/rGO nanocomposite exhibited better photocatalytic efficiency of 90 % after visible light irradiation for 90 minutes (Viet *et al.*, 2016b), ZnO/GO nanocomposite synthesized by simple and efficient hydrothermal method exhibited improved optical properties make it suitable for photocatalytic applications (Kachere *et al.*, 2022). hydrothermal synthesis of ZnO-GO nanocomposites for degradation of Rhodamine B improved greater than two folds by addition of appropriate amount of GO into ZnO (Jin *et al.*, 2022). Moreover, the combination of metal doped semiconductor oxides with carbon based materials also degrades organic dyes effectively and efficiently. Hydrothermally synthesized Cu-ZnO/rGO composite in the presence of solar light can be a promising photocatalyst in the field of wastewater treatment (He *et al.*, 2018), hydrothermal synthesis of Ce doped SnO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> composites shows visible light photocatalytic performance of 98 % compared with individual components (Asaithambi *et al.*, 2021). In conclusion, the main reasons for enhancement of photocatalytic efficiency in this strategy reviewed above were due to the higher specific surface area and narrowing the band gap for improving light absorption capability, and suppressing of the photogenerated charge carrier's recombination rates as PL analysis confirmed.

## **2.6 Characterization Methods of Nanomaterials**

Different characterization techniques have been used to investigate different properties of the material. The major techniques used to characterize nanomaterials are presented below.

### **2.6.1 Structural Characterization Tools**

#### **2.6.1.1 X-ray Diffraction (XRD)**

X-ray diffraction is a versatile, non-destructive analytical method for identification and quantitative determination of various crystalline forms, known as 'phases' of compound present in powder and solid samples. It also used to know the detailed information of a crystal structures such as the lattice spacing, lattice parameters, full width at half-maximum, crystallinity, crystallite size, volume of unit cell, specific surface area of crystals, dislocation density and micro-strain of a material. XRD uses x-rays. X-rays are electromagnetic radiation

of wavelength about  $1 \text{ \AA}$  ( $10^{-10} \text{ m}$ ), which is about the same size as an atom. They occur in that portion of the electromagnetic spectrum between gamma-rays and the ultraviolet. The discovery of x-rays in 1895 enabled scientists to probe crystalline structure at the atomic level. Diffraction occurs as x-ray waves interact with a regular structure. That means x-rays can be diffracted from minerals which, by definition, are crystalline and have regularly repeating atomic structures. When certain geometric requirements are met, x-rays scattered from a crystalline solid can constructively interfere and producing a diffracted beam. If an X-ray beam with wavelength  $\lambda$  strikes the object sample with  $\theta$  incident angle then the scattered ray is determined by Bragg's law:

$$n\lambda = 2d \sin\theta \quad (2.1)$$

Where  $n$  is the order of diffraction,  $\lambda$  is the wavelength of the beam,  $d$  is the spacing between diffracting planes and  $\theta$  is the incident angle.

### **2.6.1.2 Transmission Electron Microscope (TEM)**

Transmission electron microscopes (TEM) utilize a particle beam of electrons to visualize specimens and produce highly-magnified images. It indeed involves transmitting a beam of energetic electrons through a sample to form an image based on the interaction of electrons with the specimen. Transmission Electron Microscope is known for its high lateral spatial resolution and its capability to provide both imaging and diffraction of the sample, making it a valuable tool for detailed analysis at the nanoscale. It uses a series of electromagnetic lenses to manipulate the electron beam generated at high potential in an electrically heated filament. Depending on imaging conditions either the particle or wave properties of the emitted electrons have to be considered. The wavelength of electrons depends on the acceleration voltages. As an electron wave penetrates the sample, the resulting diffraction pattern reveals the structure of the observed sample. In the transmission electron microscope, one can simultaneously obtain the image and the corresponding diffraction pattern from the same part of the sample, and the concentration of elements in the sample, as well as the mapping elements in the same region of the sample. This includes the determination of the crystal structure and lattice parameter of individual nanomaterials and the measurement of mechanical properties of individual nanotubes and nanowires.

### **2.6.1.3 High Resolution Transmission Electron Microscope (HRTEM)**

It is a sophisticated tool that generates detailed images of a material's atomic structure, due to its high lateral resolution down to 0.050 nm, yielding valuable insights into its properties and behavior at the nanoscale. In electron microscopy, an electron beam is transmitted through an ultra-thin specimen, interacting with the material as it passes through. This technique is used for obtaining comprehensive information including morphological, crystallographic, atomic, structural, chemical composition, bonding, electronic structure, and coordination number from samples. It also confirms the crystal structure obtained in the XRD result.

## **2.6.2 Optical Characterization Tools**

### **2.6.2.1 Ultraviolet-Visible Absorption Spectroscopy**

UV-Vis absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Absorption measurements can be at a single wavelength or over an extended spectral range. Ultraviolet and visible light are energetic enough to promote outer electrons to higher energy levels, and UV-Vis spectroscopy is usually applied to molecules or inorganic complexes in solution. The UV-Vis spectra have broad features that are of limited use for sample identification but are very useful for quantitative measurements. The concentration of an analyte in solution can be determined by measuring the absorbance at some wavelength.

### **2.6.2.2 UV-Visible Diffusive Reflectance Spectroscopy (Uv-Vis DRS)**

It is a more convenient characterization method for solid samples. It uses the measurement of reflectance or transmittance data to determine the band gap ( $E_g$ ) of solid materials such as films and powders. Based on these data using the Tauc plot or Kubelka-Munk (K-M) method, the band gap of a material could be calculated.

### **2.6.2.3 Fourier Transform Infrared Spectroscopy (FTIR)**

FTIR technique mainly used to identify the functional groups attached on the surface of the synthesized nanomaterials. The FTIR analysis method uses infrared light to scan test samples and observe chemical properties. It is used for quality control when evaluating industrially manufactured material, and can often serve as the first step in the material analysis process. A change in the characteristic pattern of absorption bands clearly indicates a change in the composition of the material or the presence of contamination. If problems with the product are identified by visual inspection, the origin is typically determined by FTIR microanalysis. This technique is useful for analyzing the chemical composition of smaller particles, typically 10 -50 microns, as well as larger areas on the surface.

### **2.6.2.4 Photoluminescence Spectroscopy (PL)**

PL spectroscopy is one of the non-contact and non-destructive optical characterization technique used to measure the emission intensity as a function of the emission wavelength when the excited electron returns back to the ground state or its initial state after excitation by absorbing appropriate energy. The fluorescent or quenching of light emission intensity of the synthesized samples can be determined using PL spectroscopy. Apart from the detection of light emission patterns, PL spectroscopy is of great significance in other fields, especially semiconductors to determine band gap, impurity levels and defect detection, recombination mechanisms, and surface structure and excited states. The main scientific limitation of photoluminescence is that many optical centers may have multiple excited states, which are not populated at low temperature. The disappearance of luminescence signal is another limitation of photoluminescence spectroscopy. For example, in the characterization of photoluminescence centers of silicon no sharp-line photoluminescence from 969 MeV centers was observed when they had captured self-interstitials. PL is not applicable for metals since the band gap overlaps or no radiative transition of electron occurred around the Fermi level and therefore no significant emission occurred.

## **2.6.3 Morphological and Compositional Characterization Tools**

### **2.6.3.1 Scanning Electron Microscope (SEM)**

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons. These electrons interact with the atoms to make the sample producing signals that contain information about the sample's surface topography or surface morphology. This method also usually is applied to get information about the particle size, surface roughness, porosity, particle size distributions, material homogeneity, and inter-metallic distribution and diffusion.

### **2.6.3.2 Energy Dispersive X-Ray Spectroscopy (EDS)**

Energy dispersive X-ray spectroscopy (EDS) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is one of the variants of x-ray spectroscopy. As a type of spectroscopy, it focuses on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing rays emitted by the matter in response to being hit with charged particles. The fundamental idea that every element has a distinct atomic structure, which makes it possible to distinguish rays that are indicative of an element's atomic structure from one another, is largely responsible for its characterization capabilities.

## **2.7 Photocatalytic Applications of Nanomaterials**

Photocatalysis is a combination of "photo" and "catalysis." The term "photo" is related to photons and light, while "catalysis" refers to the acceleration or alteration of reaction rates in the presence of photocatalyst. The photocatalysis process uses a photocatalyst to decompose toxic organic pollutants into carbon dioxide and water. The catalyst that absorbs light and catalyzes chemical reactions by reducing the activation energy without being consumed or altered in the process, is called a photocatalyst. Photocatalysis involves generating an electron-hole pair when a semiconducting material is exposed to light. In this process, an oxidation and reduction reaction plays a great role in photocatalysis process in the presence of light. It is an important phenomenon with applications in various fields, including environmental remediation, water purification, and energy conversion. The major limitations

in photocatalysis are the low absorption capability of visible light due to wide band gap and fast recombination of electron-hole pairs. To alleviate these challenges for enhancing the performance of the photocatalysts, the common strategies were used.

## **2.7.1 The Synthesis Parameters that Affects the Photocatalytic Activity**

### **2.7.1.1 Variation of Dopant Concentration**

The primary purpose of optimization of dopant amount during synthesis was to get the best photocatalyst that has high capacity to absorb visible light for efficient and effective degradation of organic pollutants such as methylene blue dye. Literature reports show that variation of dopant concentration results in variation of the photocatalysis performance. For instance, Anil, Vinod, and Shrivastava, 2019 reported that 2% Fe-ZnO NPs synthesized by sol-gel method showed a more promising and superior photocatalytic efficiency for MB dye (92%) than pure ZnO (86 %) when exposed to UV light under optimized operational parameters (Isai & Shrivastava, 2019). Moreover, according to Goswami, 2020 reports 8 mol % Co-doped ZnO catalysts showing better degradation efficiency (98%) compared to pure ZnO in 180 minutes by irradiation of visible light (Goswami, 2020). Zhu *et al.* 2021 synthesized that 1% Ag-ZnO nanoparticles using sol-gel method and the photocatalytic activity tested at optimized amount of 100mg catalyst and 10 ppm MB dye 97.1% by UV light irradiation for 15 minutes (Zhu *et al.*, 2021). Venkatesh *et al.* 2021 also reported 4% Sn-ZnO synthesized by co-precipitation method exhibited an efficiency of 94.5 % at optimized values of 25 mg and 20 mg/L MB dye under sunlight exposure for 180 minutes (Venkatesh *et al.*, 2021). In conclusion, the photocatalytic improvement due to variation of dopant concentration may be attributed to the introduction of impurity levels, which are introduced closer to the conduction band, resulting in band gap narrowing, and improvement of visible light absorption ability of ZnO.

### **2.7.1.2 Synthesis Temperature**

The photocatalytic activity strongly influenced by the reaction temperature, and therefore should be optimized. Cui *et al.* 2015 optimized the synthesis temperature during the synthesis of Ag<sub>3</sub>PO<sub>4</sub> microcrystal using precipitation and hydrothermal methods. They obtained highest photocatalytic activities for Ag<sub>3</sub>PO<sub>4</sub> at 120°C with the degradation efficiency of RhB 97.83%

in 6 min, might be due to high separation efficiency of electron and hole pairs (Cui *et al.*, 2015). In facile hydrothermal synthesis of  $V_2O_5$  as the hydrothermal reaction temperature increases the particles' size became larger, the band gap slightly increased so that lower band gap obtained at lower reaction temperature exhibited an enhanced photocatalytic efficiency (Jalil *et al.*, 2023). The effect of reaction temperature is different for different catalysts. For instance, Chen, 2021 reported that the activity of  $TiO_2$  and  $Pd/TiO_2$  increased with an increase of reaction temperature up to 70 °C, and decreases beyond, however for the case of  $Cu/TiO_2$  nanoparticles more effective at room temperature, recombination rate of carriers increased as reaction temperature increases. The reaction temperature mainly influences quantum effect, *i.e.*, electron-hole separation and recombination, and therefore it affects the methylene blue degradation under UV light irradiation (Y. Chen, 2021). Moreover, Bárdos *et al.* 2019 proved, that low synthesis temperature (120 °C) and time (3 h) resulted a highly active catalyst, both under UV and visible light (Bárdos *et al.*, 2019).

#### **2.7.1.3 Synthesis Reaction Time**

According to the findings of Kong, Hu, and Pan, 2017, suggest that the reaction time during synthesis plays a crucial role in determining the morphology of ZnO nanoparticles, and the elliptical-shaped ZnO nanoparticles obtained after 4 h of reaction time exhibited the most efficient photodegradation (about 98.2%) of MB in aqueous solution under UV light within 20 minutes. The reason could be the change of morphology from flower-like at a reaction time of 1 hour to elliptical-shaped ZnO nanoparticles at a reaction time of 4 hours (X. Kong et al., 2017). Bárdos *et al.* 2019 also reported that in solvothermal crystallization route, the low crystallization temperature and duration shows the highest photocatalytic efficiency, both under UV and visible light (Bárdos *et al.*, 2019).

#### **2.7.1.4 Surfactant and Capping Agent**

The use of surfactants and capping agents during synthesis of a catalyst affects the surface characteristics which might influence the photocatalytic performance. For instance, Fakhri-Mirzanagh *et.al*, 2020 reports that MgO synthesized by ultrasound-assisted method using Oleic acid (OA) as a capping agent for avoiding MB organic pollutant under visible light irradiation. This result shows that the degradation efficiency of MB was 99 % at 25 minutes, there was no significant difference MgO-OA compared to the pure MgO (S.Fakhri-



Mirzanagh *et al.*, 2020). A high methylene blue removal efficiency of 96.3% was achieved using the BiOCl-ZnO-PEG photocatalyst at a methylene blue concentration of 20 ppm, a catalyst dosage of 1 g/L, and a solution pH of 9.5 when exposed to visible light within a short period of irradiation time. Additionally, it demonstrated good stability and recyclability characteristics (Halvaeifard & Sharifnia, 2018). Li *et al.* 2013 prepared a highly active ZnO photocatalyst using the sol-gel method with the assistance of cetyltrimethylammonium bromide (CTAB). CTAB modifies the surface and morphology of ZnO, leading to improved photoinduced charge separation rates, and the photocatalytic activity of ZnO-CTAB was three times higher than the reference ZnO without CTAB for degrading methyl orange dye (Li *et al.*, 2013). Mbuyazi and Ajibade, 2023 reported that the synthesis of Fe<sub>3</sub>O<sub>4</sub>-Octylamine (OTA) using the co-precipitation method demonstrates high degradation efficiency for the removal of methylene blue (MB) and methyl orange (MO) dyes. They concludes at optimum values of pH of 10 for methylene blue and a pH of 2 for methyl orange using the iron oxide nanophotocatalyst shows a good recyclability, that means, reused three times without a significant loss of photocatalytic activity (Mbuyazi & Ajibade, 2023).

According to Rana, 2023, increasing the concentration of CTAB leads to an increase in the crystallite size of CdO, and the morphology changes from flat sheets to thin needle-like structures, and causes a slight decrease in the optical band gap of CdO. This experiment showed that CdO nanoparticles were capable of degrading methylene blue (MB) by up to 83% under UV light and Rose Bengal (RB) dye by up to 85% under sunlight within an 80-minute exposure period (Rana, 2023). However, Akhil *et al.* 2016 reported that ZnO-PVA, ZnO-EG and ZnO-PVP synthesized by co-precipitation method exhibited reduced photocatalytic activity of MB under visible radiation compared to pure ZnO nanoparticles (Akhil *et al.*, 2016).

#### **2.7.1.5 Synthesis pH**

In general, the photocatalytic activity of a material can be influenced differently by the synthesis pH, depending on the specific photocatalyst being studied. The pH level can affect several properties that are crucial for photocatalysis, such as the surface charge, crystallinity and crystal phase, morphology, and band structure of the photocatalyst. The pH of the synthesis solution can influence the surface charge of the photocatalyst particles. This can affect the adsorption of reactants and the interaction between the catalyst and the target

pollutants. The optimal pH range for maximum photocatalytic activity may vary depending on the specific photocatalyst and the nature of the pollutants. Different crystal phases (e.g., anatase, rutile) most commonly in case of  $\text{TiO}_2$  may exhibit different photocatalytic activities (Tryba *et al.*, 2016). In addition, different morphologies (e.g., nanoparticles, nanowires, thin films) may have different surface areas and exposed facets, leading to variations in photocatalytic activity. By adjusting the synthesis pH, it is possible to control the morphological features and enhance the photocatalytic performance. The synthesis pH can influence the energy levels and band structure of the photocatalyst, affecting its ability to generate electron-hole pairs upon light absorption. This, in turn, can impact the efficiency of pollutant degradation or other photocatalytic reactions. To sum up, it is important to note that the optimal synthesis pH for maximum photocatalytic activity can vary depending on the specific photocatalyst and target pollutants. Therefore, systematic studies and optimization are often required to determine the ideal synthesis pH for a given photocatalytic application.

#### **2.7.1.6 Effect of Synthesis Precursors**

The quality and nature of the precursor used in the synthesis of the catalysts affects the required desirable properties and affects its performance in different application areas. For example, Rocha *et al.* 2022 synthesizing zinc oxide (ZnO) nanoparticles using zinc nitrate and zinc acetate precursors through the sol-gel method. The choice of precursor influenced various properties such as bandgap, crystallite size, morphology, surface area, total pore volume, and pore diameter. In terms of photocatalytic activity, ZnO synthesized using both zinc nitrate and zinc acetate precursors demonstrated effective degradation of Dichlorophenoxyacetic acid (2, 4-D) and Dichlorophenol (2, 4-DCP). ZnO synthesized using zinc acetate precursor showed better performance, achieving degradation efficiencies of 90.9% for 2,4-D and 86.7% for 2,4-DCP, while ZnON achieved lower efficiencies of 74.7% for 2,4-D and 78.4% for 2,4-DCP under UV-light irradiation (Rocha *et al.*, 2022).

#### **2.7.1.7 Calcination Temperature**

The calcination temperature has a significant impact on the performance of the synthesized catalyst for different applications because it directly affects the desired properties of the catalyst. For instance, Sharma *et al.* 2023 synthesized ZnO nanoparticles produced by chemical precipitation route. The decrease in energy band gap was ascribed to an increase in

crystallite size produced at the calcination temperature from 400 to 600 °C photocatalytic degradation of leather dye in the presence of sunlight. It has been demonstrated that ZnO nanoparticles calcined at 400 °C removed 90 % of the leather dye in 30 min (V. Sharma *et al.*, 2023). The hydrothermally synthesized SnO<sub>2</sub> photocatalyst annealed at 600 °C showed excellent photocatalytic efficiency in degrading methylene blue dye. This enhanced performance can be attributed to its unique morphology, high crystalline nature, and efficient charge separation. It exhibited moderate activity and remained stable up to its fifth usage (Prakash *et al.*, 2016).

According to Velardi *et al.*, 2020, the photocatalytic activity of the TiO<sub>2</sub> nanoparticles synthesized using the sol-gel method treated at 100°C and 450°C exhibited superior photocatalytic performance compared to those treated at 800°C evaluated for the case of MB dye for a duration of 4 hours. This difference in performance was attributed to the higher recombination rate of photogenerated electrons and holes in rutile compared to anatase, indicating that the rutile phase present in the TiO<sub>2</sub> nanoparticles due to the presence of rutile and its effects on recombination rates (Velardi *et al.*, 2020). However, the Bi<sub>0.65</sub>K<sub>0.2</sub>Ba<sub>0.15</sub>FeO<sub>3</sub> perovskite material was synthesized using the sol-gel method via citric acid route in the presence of sodium dodecyl sulfate annealed at the temperature range between 400-800 °C, and photocatalysis efficiency was better at 800 °C after 2 hour of visible light irradiation to degrade MB dye. This enhancement was due to high crystallinity and photoabsorption of visible light (Haruna *et al.*, 2020). We notice that calcination temperature has different impact on different host nanocatalysts for photocatalytic activity. That means, the variation of this parameter changes the properties of the host materials such as the particle size, bandgap and surface states in some materials and even it changes crystal phase in other materials.

## **2.7.2 The Operational Parameters that Affects Photocatalytic Activity**

### **2.7.2.1 Effect of pH**

Methylene blue is a cationic (or positively charged) dye having pH level of 6 at a concentration of 10 g/L and at an ideal temperature of 25 °C interacts strongly with negative charged surface. Methyl orange exists in the anionic (or negatively charged) form at acidic pH. The lower pH favors the adsorption of the anionic methyl orange dye and the higher pH favors methylene blue adsorption on the surface of the photocatalysts due to electrostatic

interaction between oppositely charged surfaces resulting in an enhanced photocatalytic activity but at lower and higher pH the photocatalytic efficiency reduced due to excess charged positive  $H^+$  ions and negative  $OH^-$  radicals in acidic and basic medium respectively (Prabakaran & Pillay, 2019; Zou *et al.*, 2014). For instance, Abbasi and Hasanpour, 2017 reported that the ZnO-SnO<sub>2</sub> (1-0.5) hybrid composite tested for methyl orange photocatalytic degradation. The variation of pH shows that the maximum removal efficiency of methyl orange observed at pH of 7 and 4 respectively, whereas lower removal efficiency at 10 (Abbasi & Hasanpour, 2017). Adeel *et al.* 2021 reported that the degradation efficiency of methyl orange dye using Co-ZnO nanoparticles was greater at pH of 7 and 4 compared to 10. However, the strongly acidic solution less than pH of 4 causes the dissolution of ZnO (Adeel *et al.*, 2021). Khalid *et al.* 2022 reports that hydrothermally synthesized Cu-ZnO nanoparticles (70 mg) at different pH of 4,6,8 and 10 shows degradation efficiency of 65 %, 80 %, 85 % and 90 % respectively, keeping constant MB dye concentration (5ppm) and Uv light irradiated for 120 minutes at room temperature (Khalid *et al.*, 2022). As a conclusion the pH is the major factor that affects the performance of the catalyst and therefore depending on the nature of the organic pollutants, the surface of the active material used as a catalyst must be adjusted as positive or negative by varying the pH values to obtain the optimum efficiency.

### **2.7.2.2 Effect of Initial Dye Concentration**

The amount of dye concentration should be optimized to find out a good catalyst that could be effectively and efficiently degrade large amount of dye concentration. Now a days most of the photocatalysts reported were exhibited high efficiency at very low dye concentration and falls to degrade it as the amount of dye concentration increases. To verify this, Adeel *et al.* 2021 reported that for high concentration of methyl orange dye tested using 10% Co-ZnO nanoparticles photocatalyst exhibited a decrease of photocatalytic efficiency because as the concentration of dye increases the photons cannot penetrate to the surface of the catalyst as the dye molecules are absorbed (Adeel *et al.*, 2021). Goswami, 2020 also reported that degradation efficiency decreases with increasing dye concentration, falling from 98.4% to 72.4% due to inhibition of photon-catalyst interaction when dye molecules are adsorbed (Goswami, 2020). Khalid *et al.* 2022 also reported that as the content of MB increases the photocatalytic efficiency of Cu-ZnO nanoparticle photocatalyst decreases due to blocking of UV light from interaction with the active sites of catalyst (Khalid *et al.*, 2022). Moreover, It

was confirmed that the increase of dye concentration diminished the photodegradation efficiency of the photocatalyst used (Halvaeifard & Sharifnia, 2018; Shubha *et al.*, 2021; Zou *et al.*, 2014).

#### **2.7.2.3 Effect of Catalyst Dosage**

The amount of photocatalyst used in the photocatalytic process is a vital parameter that affects the efficiency of the organic dye removal. Khalid *et al.* 2022 reported that increases of hydrothermally synthesized Cu-doped ZnO catalyst dosage increases the photocatalytic performance to degrade MB dye (Khalid *et al.*, 2022). Adeel *et al.* 2021 reported that the increase of catalyst dosage from 0.01 to 0.05 g the efficiency linearly increases but at higher amount of dosage the degradation efficiency of MO dye decreases due to preventing of light from penetrating the interior parts of the solution during photocatalytic process (Adeel *et al.*, 2021). Moreover, Goswami, 2020 report shows that as the catalyst concentration increases, there is a corresponding rise in particle-particle interactions, or agglomeration and reduces light penetration due to screening effect which lowers the catalyst's surface area for both light absorption and pollutant adsorption (Goswami, 2020). It has been reported that the photocatalytic efficiency increases with increasing the catalyst dosage up to the optimum amount, and beyond it the photocatalytic reaction is hindered due to nanoparticles become more opaque and scatters light reduces amount of light absorbed by the sample (Halvaeifard & Sharifnia, 2018; Shubha *et al.*, 2021; Zou *et al.*, 2014).

#### **2.7.2.4 Intensity of Light and String Rate**

Pirgholi-givi *et al.*, 2019 reported that TiO<sub>2</sub> synthesized by microwave assisted method calcined at 700 °C for 2 hours with high crystallinity investigated for photocatalytic decomposition MB dye under different irradiation intensity and stirring rate. The results shows increasing the irradiation intensity and stirring rate increases the degradation value of methylene blue (Pirgholi-givi *et al.*, 2019).

#### **2.7.2.5 Light Source**

In a photocatalytic experiment performed by Shubha *et al.* 2021 using ZnO/Eu<sub>2</sub>O<sub>3</sub>/NiO nanoparticles under sunlight, UV ray irradiation (wavelength 254 nm), and in the dark for the

case of MB dye, reported that its degradation occurred under irradiation of UV and visible light, however, negligible in dark (Shubha *et al.*, 2021).

#### **2.7.2.6 Temperature of the Heater**

According to Adeel *et al.* 2021, thermal activation plays a crucial role in facilitating the diffusion of methyl orange to the Co-ZnO catalyst, and the results indicate a positive correlation between photocatalytic activity and temperature (Adeel *et al.*, 2021).

#### **2.7.3 Photocatalytic Degradation Mechanism**

In general when a composite catalyst absorbs light energy on its surface, electrons could be excited to the conduction band and holes are produced in the valance band as shown in figure 13. The electrons combined with the oxygen molecule ( $O_2$ ) in air producing oxygen superoxide anion ( $O_2^{*-}$ ), and the holes react with water and produces hydroxyl active radicals ( $OH^*$ ). The process in which the electron reacts with oxygen molecule to produce superoxide anion is called reduction reaction whereas the process of producing hydroxyl radicals due to reaction of holes and water is called oxidation reaction. In coupled semiconductor photocatalyst, based on the band edge potentials, the motion of electrons and holes are along different direction and showing an extended lifetime of carriers for the redox reaction to takes place. That means, when the electrons gain enough energy greater than the band gap of the semiconductor they excited to the conduction band, the electrons in the conduction band of the lower band gap might be transferred to the conduction band of semiconductor-1, whereas the holes generated in the semiconductor-1 transferred from its valance band to the valance band of semiconductor-2. The active radicals produced due to electrons and holes are responsible in degrading the MB dye in the redox reaction. Finally, the methylene blue dye could be decomposed into water and  $CO_2$  as a byproduct.

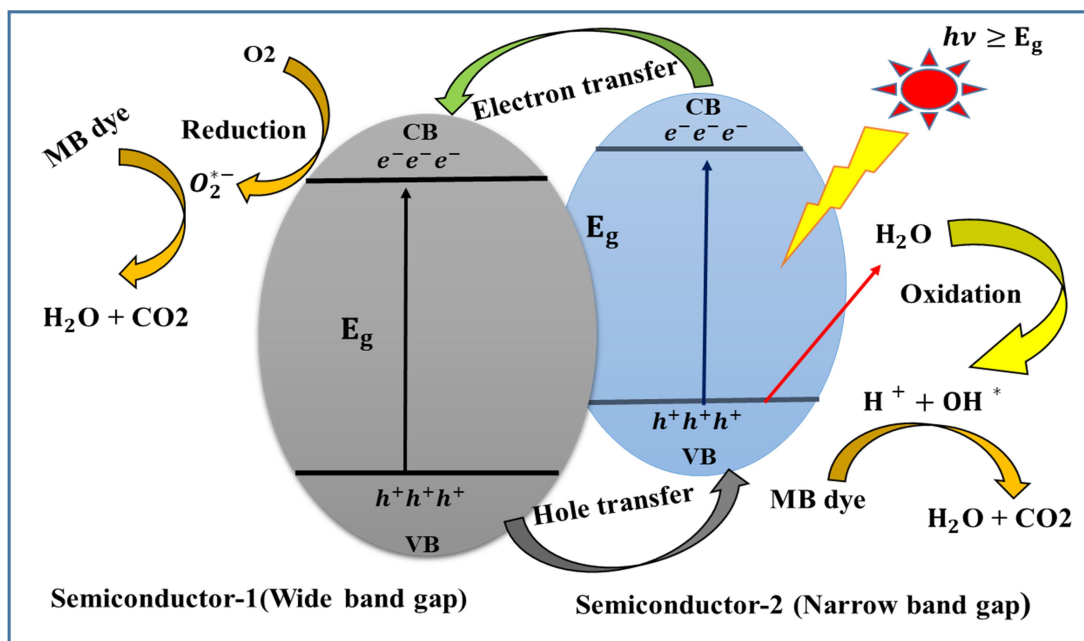


Figure 13: General Photocatalytic mechanism for the degradation of methylene blue dye by coupling of two semiconductor oxides.

## 2.8 Supercapacitor

A supercapacitor also known as ultra-capacitor or electrochemical capacitor is a type of energy storage device that can store and release energy much faster than a traditional battery. It has a high capacitance compared to regular capacitors, allowing it to store a large amount of electrical charge electrostatically, by separating positive and negative charges across an electrolyte whereas batteries store energy chemically through reversible chemical reactions. Supercapacitors have lower energy density and higher power density but batteries have high energy density and lower power density. Supercapacitor can be operated at low voltages and withstand more charging-discharging cycles compared to batteries which could be degraded when operated at high voltage depending on the chemical reactions taking place within it. The capacitance of the supercapacitor can be increased by using high applied voltage, large surface area electrode materials and thin dielectrics. In this regard, nanomaterials having a large surface area can be used as an electrode material to enhance its storage capacity compared to the bulk counterparts. Supercapacitors are often used in applications where rapid energy storage and release are required, such as in regenerative braking systems in vehicles or to provide short bursts of power in electronic devices and batteries can be used in application areas where sustainable energy supply is needed. Nanomaterial-based

supercapacitors are used to increase the electrode surface area so as to achieve high performance and enhanced capacitance. Summarizing, supercapacitors have long cycling time with a high cycle efficiency, a low energy density, the longer charge-discharge time, longer service life and higher capacitance with lower voltage limits, and therefore they are preferred over batteries and conventional capacitors. Supercapacitors have different components that determine their performance in practical applications. These are electrode materials, electrolytes, current collectors, binders and separators. Electrodes and electrolyte are considered as active components, and others such as binders, separators and current collectors are passive components. The detailed descriptions of the components of a supercapacitor are discussed as follows:

### **2.8.1 Electrode Materials of Supercapacitors**

Electrode materials are substances used to conduct electricity in various devices like batteries, capacitors, sensors, and more. Based on electrode materials and their energy storage mechanisms, supercapacitor can be categorized into three groups and discussed as follows:

#### **2.8.1.1 Electrochemical Double-Layer Capacitors (EDLC)**

In electrochemical double-layer capacitance, a large-area material separates the actual positive charges resulting from an electron shortage on one plate and the negative charges resulting from an excess of electrons on the other plate, providing a very high capacitance with extended life cycles. In double-layer capacitors charges were stored electrostatically on carbon based nanomaterials activated carbons, carbon aerogels, carbon nanotubes (CNT), graphene and carbide-derived carbon. Utilizing these carbon electrodes or their derivatives with significantly higher electrostatic double-layer capacitance than electrochemical pseudocapacitance. In electrostatic double-layer capacitors (EDLCs) achieve charge separation in a Helmholtz double layer at the interface between the surface of a conductive electrode and an electrolyte as shown in figure 14. The charge separation is significantly less than in a traditional capacitor, on the order of a few angstroms (0.3–0.8 nm). A two-dimensional interphase or surface between an ionic conductor (electrolyte solution) and an electronic conductor (carbon particles, for example) is where the electric charge in EDLCs is kept. Carbon-based electrodes predominantly exhibit static double-layer capacitance, while, depending on the pore size distribution, a tiny degree of pseudocapacitance may also be



present. Only microspores (less than 2 nm) contribute to pseudocapacitance whereas mesopores (2–50 nm) are the typical range of pore sizes in carbon materials. Carbon materials are the best EDLC materials because of their better electrical conductivity and high surface area. For instance, the specific surface area of activated carbon, graphene and multi-wall carbon nanotube are 3000 m<sup>2</sup>/g, 2630 m<sup>2</sup>/g and 1315 m<sup>2</sup>/g respectively. Activated carbons due to it's a theoretical capacitance of 100 F/g, low cost, good electric conductivity and chemical resistivity towards various electrolytes and extremely high specific surface area been used for commercial supercapacitor. However, graphene has theoretical capacitance of 550 F/g and carbon nanotubes 180 F/g for SWNT's and 102 F/g for MWNT's. The reason for graphene exhibits an excellent capacitance than activated carbons and carbon nanotubes were due to its high surface area and electrical conductivity. But agglomeration during synthesis, and low yield remains a serious challenge that bottle-necked graphene from practical application (Hakim *et al.*, 2021). Double-layer capacitors has low energy density but high power density with longer life time of million charge-discharge cycles (Jalal *et al.*, 2021). Researchers reported that for graphene and CNTs-based supercapacitor the energy density were 81 Wh/Kg and 91 Wh/ Kg, and power density were 12 kW/Kg and 13.6 kW/Kg respectively using a mixture of PVA and H<sub>3</sub>PO<sub>4</sub> gel electrolyte with a good cyclic stability after 2000 charge/discharge cycles (Aval *et al.*, 2018).

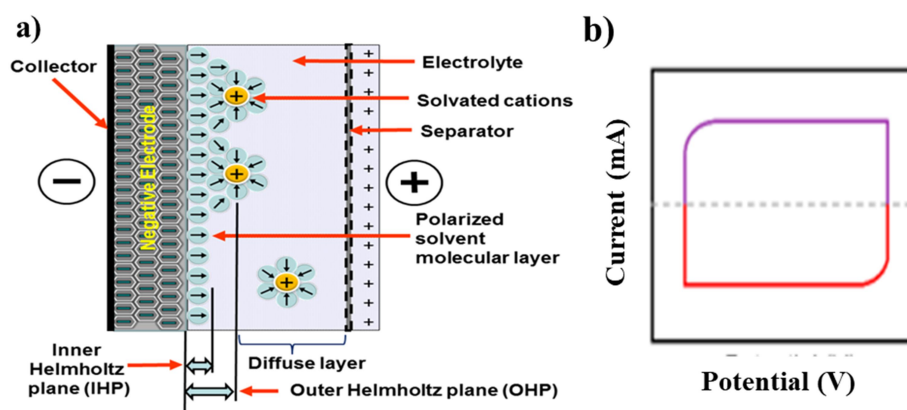


Figure 14: The charge storage mechanisms in ideal double-layer capacitors (Huang *et al.*, 2015).

### 2.8.1.2 Pseudocapacitors

A pseudo-capacitor is an energy storage device that combines features of both a capacitor and a battery. Pseudo-capacitor incorporates mixed metal oxides, metal sulfides, metal

hydroxides, metal nitrides and conducting polymers. Metal oxides such as  $\text{RuO}_2$ ,  $\text{ZnO}$ ,  $\text{SnO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{NiO}$  etc., conducting polymers like polypyrrole and polyaniline, and metal sulfides like molybdenum sulfide, nickel sulfide, zinc sulfide, iron disulfide etc are examples of pseudocapacitor. The mechanism for storing charge is Faradaic mechanism, like oxidation-reduction reactions and/or intercalation, involve charge's transfer between electrolyte and electrode (Sharma & Chand, 2023) as indicated in figure 15. The pseudo-capacitors mentioned above shows a high specific capacitance and energy density but low power density compared to EDLC. Ruthenium oxide ( $\text{RuO}_2$ ) used as an ideal pseudo-capacitive material due to their high specific capacitance and excellent reversibility but its high cost and toxic nature significantly limit its commercial application. The conducting polymers are also a good choice as a pseudo-capacitor but still the electrochemical stability is poor. For instance, Ruthenium dioxide in combination with  $\text{H}_2\text{SO}_4$  electrolyte provides specific capacitance of 720 F/g and a high specific energy of (96.12 kJ/kg) (Zheng *et al.*, 1995). The specific capacitance of pure  $\text{MnO}_2$  was enhanced by addition of  $\text{NiO}$  (Jiang *et al.*, 2020).

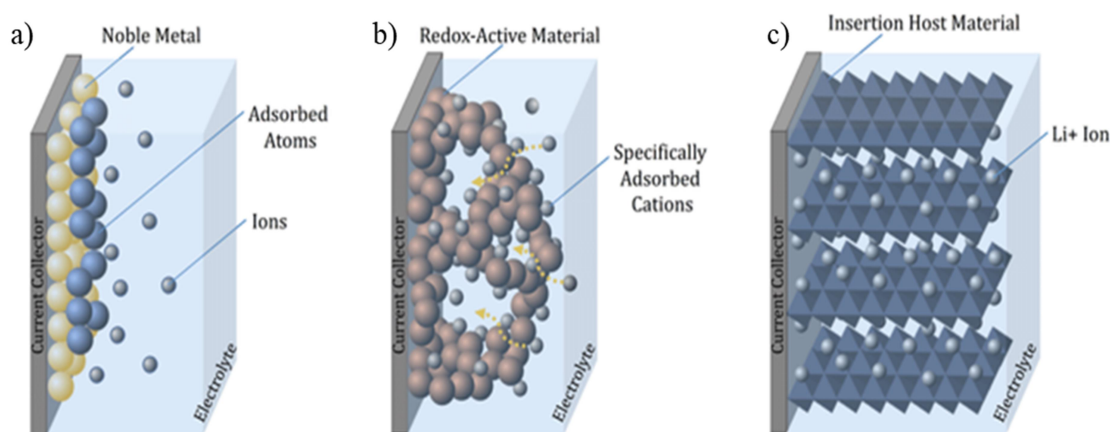


Figure 15: a) Underpotential deposition b) Redox pseudocapacitance c) Intercalation pseudocapacitance (Giannakou, 2020).

### 2.8.1.3 Hybrid Supercapacitor

Hybrid supercapacitors (HSCs) are made by the combination of electric double-layer capacitor (EDLC) materials, various types of pseudocapacitive, and battery-type materials as indicated in figure 16. This integration of electrodes from both capacitor and battery types to combine the benefits of both types of capacitors in order to achieve energy storage device with high energy and power densities, long cycle life, and safety. In HSCs, the advancements gained in energy density increase without compromising power density are what drew

researchers to focus on it. These capacitors use both the EDLC and pseudo-capacitor storage mechanisms. That means, electrostatic capacitance is displayed by one electrode, while electrochemical capacitance is provided by the other (Han *et al.*, 2021). The overall benefit is greater energy density, capacitance, and maximum operating voltage of up to 3.8 V.

In battery-type materials, the electrostatic electrode stores energy by separating charges with without chemical reaction. This feature prolongs the life of the battery by enabling quick cycles of charging and discharging with a lower risk of damage, resulting in a longer life span. But in the battery-like electrode higher energy is stored by the slower electrochemical reaction that could compensate the lower energy density of capacitors. In this process, balancing the rapid charge transfer in electrostatic electrode with the high energy storage of the battery type electrode, we can achieve a hybrid supercapacitor of intermediate performance with a balanced power and energy densities that surpasses the capacitor and batteries.

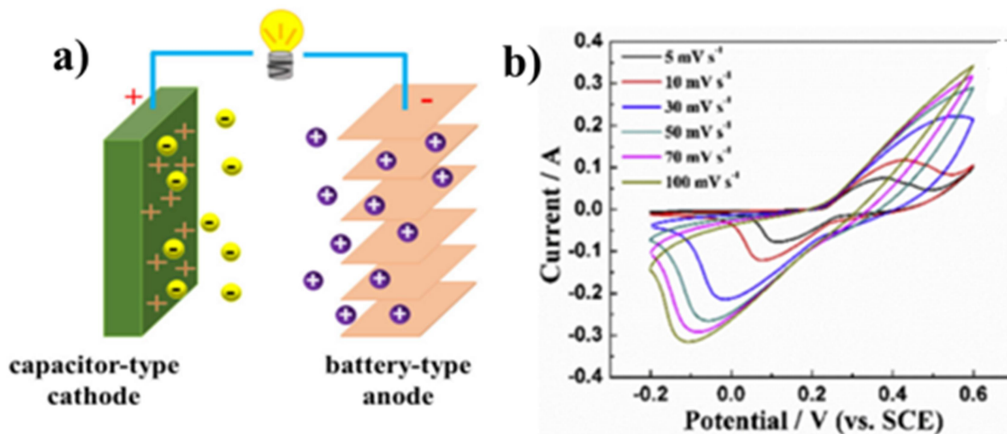


Figure 16: Shows (a) hybrid Supercapacitor and (b) its cyclic voltammetry curves (Luojiang Zhang *et al.*, 2016).

### 2.8.2 Electrolytes in Supercapacitor

Electrolytes are substances that can give ions (cations or anions) when dissolved in water. Electrolyte is one of the constituents of a supercapacitor that can affect the performance of a supercapacitor, such as the energy density, power density, cycle stability and safety. Different electrolytes have different impact on the performance of a supercapacitor. The selection of the suitable electrolyte and working electrode materials are a challenge to enhance the energy density and the working potential window of the device. The energy density of a supercapacitor can be enhanced in two ways either by increasing the working potentials (or

voltage) or by increasing the capacitance of the capacitor. In order to increase the capacitance of the capacitor we must control the pore size, surface area, and electrical conductivity which is not easy task. Alternatively, the voltage can be increased by selecting appropriate electrolytes among the known aqueous electrolytes, organic electrolyte and semi-solid electrolytes. Optimization of the electrolyte for the corresponding electrode materials could increase the cell voltage that would be more effective way to increase the energy density of the supercapacitor than increasing the capacitance of the capacitor. Therefore, the selection of the suitable electrolyte is mandatory and it could be based on the chemical stability, ionic conductivity, thermal stability, diffusion coefficients, ionic size, viscosity, and dispersion interaction. The choice of suitable electrolyte would enhance not only the energy density but also the lifespan, reduce the internal resistance, operating temperature and control the self-discharging rate (Iqbal, Zakar, & Haider, 2020; Pal, Yang, & Ramesh, 2019; Panda, 2023; Pathak *et al.*, 2024; Ullah *et al.*, 2023).

Based on the cell voltage window, electrolytes can be categorized as aqueous electrolytes, organic electrolytes and semi-solid electrolytes. Aqueous electrolytes in general have strong ionic conductivity, low internal resistance, environmentally friendly, non-volatile and non-flammable, thermally and chemically stable, however, shows low electrochemical stability, and narrow voltage window (1.0-1.30 V) (Ji & Kim, 2024). Based on the pH value aqueous electrolytes are further classified as acidic ( $\text{H}_2\text{SO}_4$ ), basic (KOH, NaOH, LiOH, etc) and neutral electrolytes ( $\text{Na}_2\text{SO}_4$ ,  $\text{NaNO}_3$ , KCl,  $\text{K}_2\text{SO}_4$ ,  $\text{Li}_2\text{SO}_4$  etc). Among the basic electrolytes, KOH due to its high ionic conductivity, smaller ionic size, and low viscosity still considered as better electrolyte in EDLC and pseudo capacitive type electrode, however, it exhibits low energy density due to its narrow potential window compared to organic electrolytes. Neutral electrolytes have wide potential window and low ionic conductivity so that gives low specific capacitance, and overall electrochemical performance is the lowest of all however the lowest corrosive and the safest than acidic and basic electrolytes.  $\text{NaSO}_4$  is the most studied neutral electrolytes next to  $\text{H}_2\text{SO}_4$  and KOH (Panda, 2023). Neutral aqueous electrolytes like  $\text{Li}_2\text{SO}_4$  are capable to attain a wide potential window of 4.0 V and exhibits minimal internal resistances than organic electrolytes.

### **2.8.3 Binders in Supercapacitor**

Together with active electrode materials, binders serve as the ideal catalyst for good adherence between the active material and the current collector and preserve the structural excellence of the materials. Binder type and quantity have a significant impact on supercapacitor performance. Optimal quantities of binders mixed with the electrode materials to increase wettability and electrolyte absorption. Because binder-free electrodes have fewer drawbacks, including low conductivity, limited active surface area and low stability. Therefore, to alleviate these drawbacks, binders such as polyvinylidene fluoride, polytetrafluoroethylene, cellulose, nafion, polyvinyl pyrrolidone and polyvinyl alcohol can be used.

### **2.8.4 Separators in Supercapacitor**

Like current collectors and binders, separators in electrochemical supercapacitors are thought of as passive parts that do not affect capacitive performance but instead allow charge transfer by preventing physical contact between the electrodes. Properties that affect a supercapacitor's performance and stability include (i) electrical insulator; (ii) ion transfer ability; (iii) chemical/electrochemical inertness; (iv) high mechanical strength; (v) optimal thickness; (vi) porosity; and (vii) surface morphology. Polypropylene, polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), and cellulose polymer membrane are a few examples.

### **2.8.5 Current Collectors in Supercapacitors**

Appropriate current collectors, which function as a passive part of supercapacitors, improve the device's durability and cell potential. The selection of the current collector is contingent upon the electrolyte type and the fabrication technique employed in the supercapacitor device. Corrosion-resistant metal plate current collectors like gold (Au) are utilized in strong acid-based electrolytes. Furthermore, materials including carbon-based materials and indium tin oxide (ITO) plates have been developed to lower the cost of supercapacitor devices. Low-cost materials based on nickel (Ni) are chosen as suitable current collectors for supercapacitors based on alkaline electrolyte. Ni foam, for instance, has established itself as the best current collector due to its higher surface area compared to traditional metal plates

and its ability to increase the electrochemical activity of the material used as the active electrode. Particularly when the electrode material is small in size, the Ni foam current collector adds a tiny pseudo-capacitance value to the total capacitance of the supercapacitors. Additionally, certain metals including alloys, carbon-based materials like graphite foam, carbon fiber paper, and carbon cloth, and stainless steel sheets and foams are thought to be appropriate current collectors in alkaline electrolytes. The majority of non-aqueous electrolytes (ionic liquids and organic electrolytes) based on supercapacitors use aluminum-based current collectors.

## **2.8.6 Electrochemical Characterization of Supercapacitor**

The Potentiostat is used to characterize the electrochemical performance which includes cyclic voltammetry, Galvano-static charge-discharge (GCD) and electrochemical impedance spectroscopy.

### **2.8.6.1 Cyclic Voltammetry (CV)**

It is a potentiodynamic electrochemical measurement technique used to analyze the redox characteristics of samples. The CV measurement is done by linearly sweeping the potential of the working electrode at a certain scan rate within the desired potential window, then it is swept in the opposite direction back to the initial potential. CV curves are used to identify the nature and type of the electrode materials whether it is a supercapacitor such as asymmetric, symmetric, EDLC or hybrid supercapacitor type, and battery behavior also. Typically, the CV curve of ideal supercapacitor is a perfect rectangle shape, but most CV curves always deviate from the ideal shape because of the existing of redox reactions on the interface. In this case, it is easy to judge the capacitor behavior of supercapacitors based on the shape of CV curve. Moreover, the shape of the CV curve, especially the peaks and peak locations, provides key insight into the characteristic of the material's redox property such as oxidation and/or reduction. CV also uses to optimize the potential window of the working electrode which is different for different working electrodes. In CV analysis, the relation between scan rate and the current sensitivity of the working electrode could be recorded between an optimized potential window ranges. In addition, CV can also be used to evaluate the cycle life of supercapacitors and calculate the specific capacitance. The relation between specific capacitance versus scan rate could be drawn based on CV data. For a given working

electrode, the behavior of the anodic and cathodic current with the scan rate could be determined. Based on the calculated specific capacitance, the energy and power density could be evaluated.

#### **2.8.6.2 Galvanostatic Charge-Discharge (GCD)**

Galvanostatic charge-discharge technique, in a mixed mode gives charge-discharge current and voltage versus charge-discharge time. The specific capacitance, the energy density, power density, coulombic efficiency and the number of charge-discharge cycles of a supercapacitor were investigated using GCD. This technique also helps us to determine the stability of the electrode materials based on the number of charge-discharge cycles. The more the number of GCD cycles the more stable the material is for supercapacitor applications.

#### **2.8.6.3 Electrochemical Impedance Spectroscopy (EIS)**

It is another useful technique that uses small amplitude alternating current signals to detect the impedance characteristics of working electrode. The alternating current signal is scanned over a wide frequency range to generate an impedance spectrum for the electrochemical cell under test. Here, the amplitude of the excitation signal is very small so that the system is almost in the equilibrium state. In this case, EIS technique is employed to evaluate the electrochemical system (e.g., supercapacitors, batteries, fuel cells, photovoltaics, corrosions and coatings) without being significantly affected. Many important parameters including the equivalent series resistance, charge transfer kinetics and ion diffusion process as well as frequency response could be explained by Nyquist plot and Bode plot.

#### **2.8.7 Applications of Supercapacitors**

Supercapacitors are applicable in portable and flexible electronic such as watches, sensors, mobile phones, headphones, laptops and cameras. They are applicable in hybrid electric vehicles such as electric vehicle, boat, and bus systems. In wind and solar powering, the energy produced by solar cells and wind turbines are stored in a supercapacitor device, which can be used as a backup when needed. In addition to being utilized in implantable medical systems that require power in the microwatt to milliwatt range, piezoelectric supercapacitors are also found in insulin pumps, pacemakers, and other medical equipment. Since they have a

high power, a long life cycle, and can withstand low temperatures, supercapacitors are among the best devices for a variety of military and aerospace applications. These include armored vehicles, GPS-guided missiles and projectiles, black boxes on helicopters, fire control systems in tanks, emergency handheld radios, power backup electronic equipment, etc. In aerospace applications, they are also utilized for spacecraft and satellite on-board systems, as well as power backup.



### 3. MATERIALS AND METHODS

#### 3.1 Chemicals and Solvents

The chemicals and solvents used for synthesis were: potassium permanganate ( $\text{KMnO}_4$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), hydrochloric acid ( $\text{HCl}$ , 37%), sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98%), phosphoric acid, graphite black powder, tin tetrachloride pentahydrate ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , MW-350.6 g/mol, purity >98 %, Merck, India), zinc acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , MW-219.5 g/mol, purity >99, Merck Life Science Private Ltd, India), ammonium hydroxide ( $\text{NH}_4\text{OH}$ , MW-35.046 g/mol, 30 %), cobalt chloride (MW-237.93 g/mol), copper chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , MW-170.48 g/mol, purity >99%), sodium hydroxide pellets (Blulux laboratories Ltd, MW-40 g/mol), ethanol, Silver nitrate ( $\text{AgNO}_3$ ), polyvinyl alcohol (PVA), isopropyl alcohol (IPA), ethylenediaminetetraacetic acid ( $\text{EDTA-2Na}$ ), Barium sulphate ( $\text{BaSO}_4$ ), acetone, dimethylsulphoxide (DMSO) and distilled water.

#### 3.2 Synthesis Methods

##### 3.2.1 Synthesis of $\text{SnO}_2$ , $\text{Cu-SnO}_2$ , $\text{SnO}_2/\text{ZnO}$ and $\text{Cu-SnO}_2/\text{ZnO}$ Nanocomposites

To synthesize  $\text{Cu-SnO}_2/\text{ZnO}$  nanocomposite by using the sol-gel method, 0.2058 M tin tetrachloride pentahydrate ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ), 0.09 M zinc acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) and 4.2 mM copper chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) were each dissolved in distilled water and stirred for 30 minutes until the solution became transparent. The solution was stirred by using a magnetic stirrer for 2 hours at a speed of 360 rev/min at a temperature of 70 °C. During stirring, ammonia solution was added drop wise until the pH reached 8. A white gel precipitate was formed. The gel precipitate was aged for 15 hours. Next, the washing process was done by filtration with distilled water repeatedly using cellulose filter paper. The obtained gel precipitate was dried for 24 hours at 80 °C in an air oven. The dried solid crystal was milled using a mortar and pestle until a uniform powder was produced. The powder was then calcined at 500 °C for 2 hours. Finally,  $\text{Cu-SnO}_2/\text{ZnO}$  nanocomposite was obtained for characterization.

Similarly, to synthesize  $\text{SnO}_2/\text{ZnO}$  nanocomposite, first, 0.21M of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  was dissolved in distilled water and stirred for 30 minutes until the solution became transparent. Second, 0.09 M zinc acetate dehydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) was dissolved in distilled water.

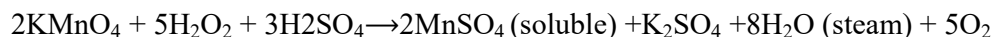
Thirdly, a zinc acetate pentahydrate solution was added dropwise and slowly into the first solution. The mixed solution was stirred by using a magnetic stirrer for 2 hours at a speed of 360 rev/min at a temperature of 70 °C. During stirring, ammonia solution was added dropwise until the pH reached 8. A white gel precipitate was formed. The gel precipitate was aged for 15 hours. Next, the washing process was done by filtration with distilled water repeatedly using cellulose filter paper. The obtained gel precipitate was dried for 24 hours at 80 °C in an air oven. The dried solid crystal was milled using a mortar and pestle until a uniform powder was produced. The powder was then calcined at 500 °C for 2 hours. Using similar procedures Cu-SnO<sub>2</sub> nanoparticles were synthesized using 4.2 mM copper chloride dihydrate (CuCl<sub>2</sub>·2H<sub>2</sub>O) and 0.296 M SnCl<sub>4</sub>·5H<sub>2</sub>O. The pristine SnO<sub>2</sub> and ZnO Nanoparticles were also synthesized by similar procedures using 0.30 M of tin tetrachloride pentahydrate (SnCl<sub>4</sub>·5H<sub>2</sub>O) and 0.30 M of zinc acetate pentahydrate (Zn (CH<sub>3</sub>COO)<sub>2</sub>·5H<sub>2</sub>O) respectively.

### **3.2.2 Synthesis of ZnO, Sn-ZnO, ZnO/Co<sub>3</sub>O<sub>4</sub> and Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO Nanocomposite**

To synthesize Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite by sol-gel route, 0.015 M solution SnCl<sub>4</sub>·5H<sub>2</sub>O was added dropwise to 0.185 M Zn (CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O solution. Subsequently, a 0.10 M cobalt chloride solution was added drop wise into the previous solution, i.e., a solution having a mixture of Sn and Zn precursors. The mixed solution, having the three precursors, was stirred using a magnetic stirrer for 2 hours at 360 rev/min at a temperature of 70 °C. Then, ammonia solution was added drop wise to the solution while stirring until the pH value reached 8.0 and a gel precipitate was formed. The precipitated gel was aged for 15 hours; after aging, it was filtered and washed with ethanol and distilled water repeatedly using Whatman cellulose filter paper. The filtered gel-like precipitate dried for 24 hours in an ambient oven. The dried solid crystal was crushed to powder using a mortar and pestle until a uniform powder was obtained. The powder was calcined at 500 °C for 2 hours. Moreover, Sn-ZnO nanoparticles were synthesized similarly using the precursors 0.015 M solution of SnCl<sub>4</sub>·5H<sub>2</sub>O and 0.285 M of Zn (CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O. The Co<sub>3</sub>O<sub>4</sub>/ZnO nanocomposite was synthesized using 0.20 M zinc acetate dihydrate and 0.10 M cobalt chloride precursors. The individual metal oxides ZnO and Co<sub>3</sub>O<sub>4</sub> were synthesized following the same procedures using 0.30 M zinc acetate dihydrate and 0.30 M cobalt chloride as a precursors, respectively.

### 3.2.3 Synthesis of Graphene Oxide (GO)

Graphene oxide was synthesized using modified Hummer's method (Zaaba et al., 2017)(Benzait et al., 2021) as shown in figure 17. The precursors used for the synthesis of GO are graphite black powder, potassium permanganate (KMnO<sub>4</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), and orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>). To synthesize graphene oxide from graphite black powder, first, 90 ml of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and 10 ml of concentrated orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>) in a 9:1 (v/v) ratio were mixed in a 1000-ml bottle-necked volumetric flask. This mixture was allowed to freeze up to 4 °C in an ice bath and then stirred for 30 minutes. Next, 1 g of graphite powder was added to the above solution once and stirred for 30 minutes again, and here the solution became black. The weight ratio of graphite to potassium permanganate was considered to be 1:6, and 6 g of potassium permanganate (KMnO<sub>4</sub>) was slowly (2 g/min) added to the above solution, but still the solution was black. The addition of KMnO<sub>4</sub> resulted in a temperature change of 40–50 °C in the solution. Still, there was no external heat applied, which means the heater was kept off. Next, the temperature of the water bath was raised slowly, starting at 4 °C, until it became stable at a temperature of 50 °C, but the increase in temperature was measured using a thermometer and controlled by the addition of ice or cold water. After the temperature became stable, the solution was stirred for 14 hours. Here, an exothermic reaction was occurring. After a few hours of stirring, the color of the solution changed to pink due to excess potassium permanganate. After extended reaction time, the mixture turned out to be a paste or slurry. After 14 hours, when off the heater and stopping the reaction, quenching the temperature of the solution to room temperature was done by adding 400 ml or 400 g of ice prepared from distilled water. The color of the solution immediately changed to a dark brown. This indicates that oxidation was properly taking place. Next, 3 ml of hydrogen peroxide H<sub>2</sub>O<sub>2</sub> (30%) was added to completely stop the oxidation reaction and to reduce residual KMnO<sub>4</sub> to soluble manganese sulfate (MnSO<sub>4</sub>) in an acidic medium, and bubbling and a bright yellow color were observed, indicating a high level of oxidation. The balanced chemical reaction is given as follows (Habte & Ayele, 2019):



After oxidation completely stopped, the solution was settled overnight, and the supernatant was decanted away. Next, the washing process was done repeatedly using diluted hydrochloride acid (HCl) (2 M) (3x), ethanol (3x), and distilled water (3x) by centrifugation at 5000 rev/min for 1 hour each using a centrifuge. The removal of the metal sulfate ions was

confirmed using a barium chloride ( $\text{BaCl}_2$ ) solution. When an aqueous barium chloride solution was added to the supernatant solution, a white precipitate of barium sulfate could appear. This confirms the presence of sulfate ions. If properly washed and sulfates were removed, the white precipitates were not observed when  $\text{BaCl}_2$  solution was added. The cake-like paste of graphite oxide was obtained. This cake-like paste was dispersed in distilled water, stirred for 2 hours, and ultrasonicated for 30 minutes to exfoliate graphite oxide into a single graphene oxide (GO) sheet. The color of the solution was changed to a light brown. This is the suspension of GO. Finally, it was dried at room temperature, milled, and then characterized.

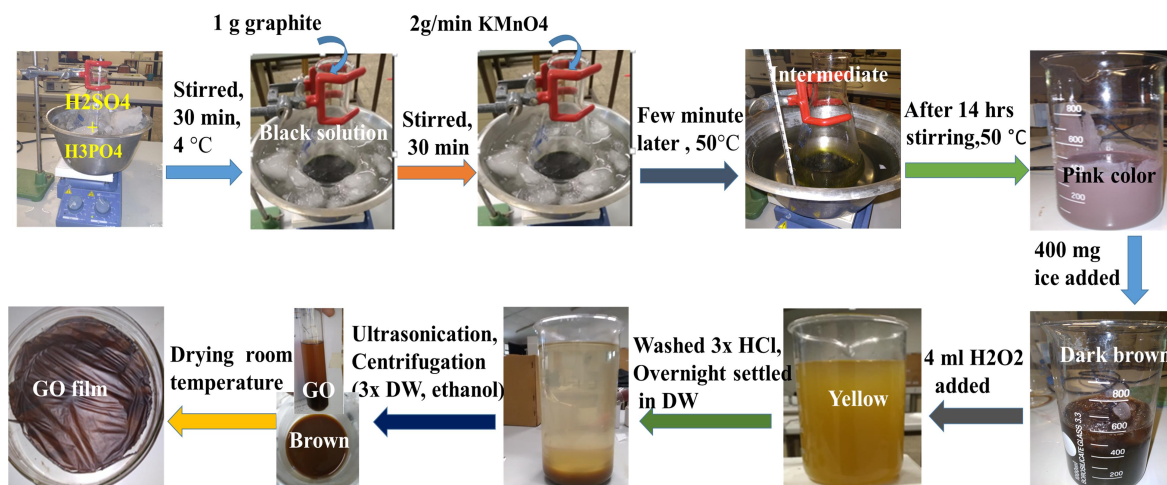


Figure 17: Diagrammatic representation for synthesis of GO using improved Hummer's method.

### 3.2.4 Synthesis of rGO, $\text{SnO}_2$ , $\text{CuO-SnO}_2$ and $\text{CuO-SnO}_2/\text{rGO}$ Nanocomposites

The  $\text{CuO-SnO}_2/\text{rGO}$  nanocomposite was synthesized by the hydrothermal method using the main precursors, such as tin tetrachloride pentahydrate ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ), graphene oxide (GO), and copper chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ). Sodium hydroxide ( $\text{NaOH}$ ) was used as a precipitating agent. A mixture of distilled water and ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) as a solvent in 2:1 ratio. First, 1% (12.5 mg) and 2% (25 mg) of GO was dispersed in a mixed solution of 10 ml of distilled water and 5 ml of ethanol and ultrasonicated for 30 min. Next, 0.12 M of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  and 12 mM of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  were dissolved in a mixed solution of 10 ml of distilled water and 5 ml of ethanol and stirred for 30 min. Then, the mixed solution of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  was added dropwise into the GO dispersion and stirred for 30 min. Moreover, 12 ml of 2 M  $\text{NaOH}$  was added dropwise until the pH of the above-mixed

solution reached 10. Finally, the mixed solution was poured into a 50-ml autoclave and heated at 180 °C for 14 hours. After heating, the autoclave was allowed to cool down to room temperature. The resulting precipitate was taken out and washed several times with deionized water and ethanol by centrifugation. Finally, the product was dried at 90 °C in an air oven. Similarly, to synthesize CuO-SnO<sub>2</sub> nanoparticles, 6 mM, 12 mM and 18 mM of CuCl<sub>2</sub>·2H<sub>2</sub>O was added into 0.12 M of SnCl<sub>4</sub>·5H<sub>2</sub>O solution following the same procedures. The pristine SnO<sub>2</sub> nanoparticle was synthesized using 0.12 M of SnCl<sub>4</sub>·5H<sub>2</sub>O under the same condition followed above. Reduced graphene oxide also synthesized hydrothermally using the same procedures as shown in figure 3.2 (a).

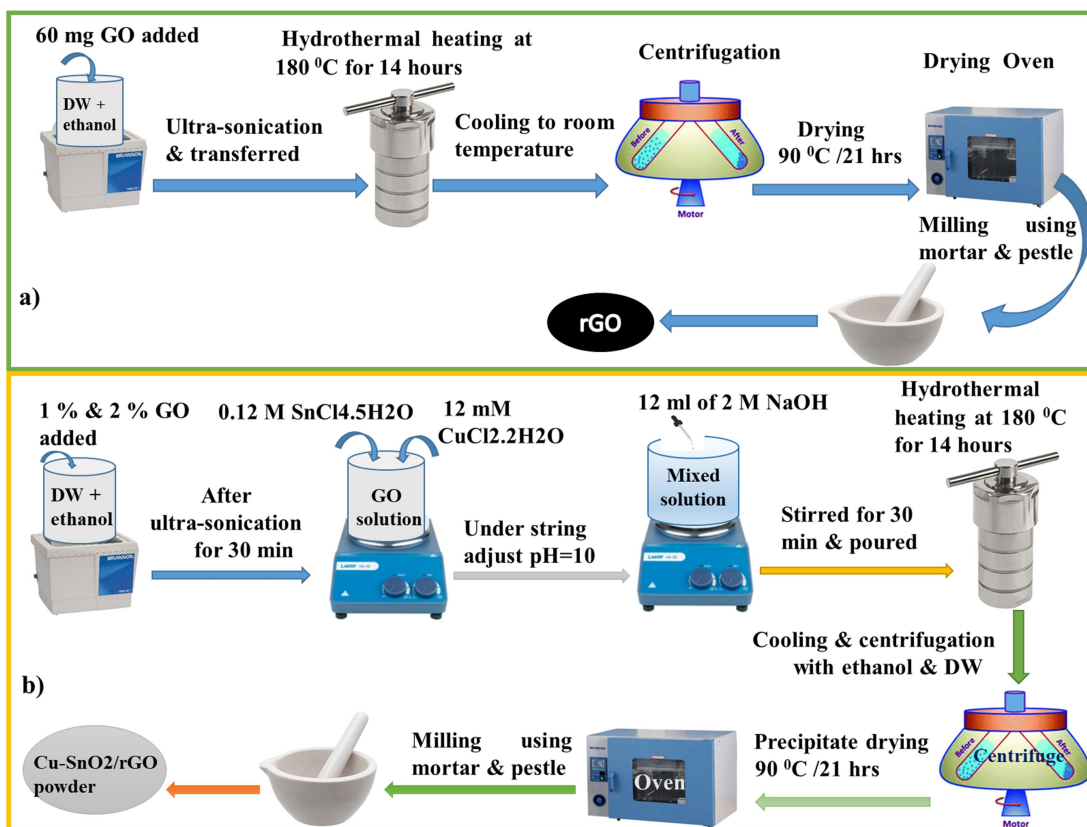


Figure 18: Shows hydrothermal synthesis procedures for (a) reduced graphene oxide (rGO) and (b) CuO-SnO<sub>2</sub>/rGO hybrid nanocomposite.

### 3.3 Characterization Techniques

The structural properties of the prepared powder was analyzed using x-ray diffraction (Shimadzu Maxima-7000 x-ray diffractometer, Tokyo, Japan) by generating CuK $\alpha$  monochromatic radiation or wavelength of x-ray ( $\lambda = 1.5406 \text{ \AA}$ ). The technique is used to determine the crystallite phase, crystallite size, lattice spacing, dislocation density and the

volume of a unit cell of crystals of the synthesized materials. The operation of the x-ray generator was performed at a voltage of 40 kV and current of 30 mA at room temperature. XRD intensities were measured in scan steps of  $0.0020^\circ$  in  $2\theta$  per second, at a scan speed of 3 degrees per minute for  $2\theta$  over the range of  $10^\circ \leq 2\theta \leq 80^\circ$  in a continuous scan mode. Using the XRD data, the crystallite size of the synthesized samples was calculated using Debye-Scherrer formula (Eq.3.1):

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (3.1)$$

Where D is the crystallite size,  $\beta$  is full width at half maximum in radians,  $\lambda$  is the wavelength of incident x-rays beam (0.1540 nm) for Cu target  $K\alpha$  radiation;  $\theta$  represents angle of diffraction and K represents the shape factor (0.94) for spherical nanoparticles. The lattice parameters for the rutile tetragonal structure of synthesized materials were calculated from 110 and 101 peaks using the Bragg's equation (Eq.3.2):

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (3.2)$$

The lattice parameters for the hexagonal wurtzite structure of ZnO nanoparticles were calculated using Bragg's equation (Eq.3.3):

$$\frac{1}{d^2} = \frac{4}{3} \frac{(h^2 + hk + k^2)}{a^2} + \frac{l^2}{c^2} \quad (3.3)$$

For tetragonal structure, to determine  $a$  using 110 plane, equation (3.2) becomes:

$$a = d \times \sqrt{h^2 + k^2} = \sqrt{2} \times d \quad (3.4)$$

For tetragonal structure, to determine  $c$  using 101 plane, equation (3.2) becomes:

$$c = \frac{ad}{\sqrt{a^2 - d^2}} \quad (3.5)$$

For hexagonal wurtzite structure, using lattice plane (100) equation (3.3) becomes:

$$a = b = \frac{2}{3} \sqrt{3} d_{100} \quad (3.6)$$

For hexagonal wurtzite structure, using lattice plane (002) equation (3.3) becomes:

$$c = 2 d_{002} \quad (3.7)$$

The lattice parameters for cubically structured  $\text{Co}_3\text{O}_4$  can be determined using lattice plane (220) based on the following eq.(3.8):

$$a = d_{220} \sqrt{h^2 + k^2 + l^2} \quad (3.8)$$

The volume of unit cell for tetragonal lattice structure of synthesized nanoparticles were calculated

Using (Eq.3.9):

$$V = a^2 \cdot c \quad (3.9)$$

The lattice distortion was calculated using the relation given below (Eq.3.10):

$$U = \frac{a}{c} \quad (3.10)$$

Dislocation density ( $\rho$ ) measures the number of dislocations or defects in a unit volume of nanocrystalline materials. It was calculated from the values of the crystallite size (Eq.3.11):

$$\delta = \frac{1}{D^2} \quad (3.11)$$

For further confirmation, the crystalline sizes of the SnO<sub>2</sub>, 5%, 10% and 15% CuO-SnO<sub>2</sub>, and CuO-SnO<sub>2</sub>/rGO (1%, 2 %) composites were determined from the Williamson-Hall method using the following equation:

$$\beta \cos \theta = \varepsilon (4 \sin \theta) + \frac{K\lambda}{D} \quad (3.12)$$

In Williamson-Hall plot of  $\beta \cos \theta$  versus  $4 \sin \theta$  using equation (3.12),  $\varepsilon$  is the microstrain obtained from the slope and  $\frac{K\lambda}{D}$  is the y-intercept,  $\theta$  is a diffraction angle,  $\lambda$  is the wavelength of incident x-rays beam (0.1540 nm) for Cu target K $\alpha$  radiation, and  $K$  represents the shape factor (0.94). Moreover, the crystal structure of the synthesized powder was determined using FEI Tecnai F20 transmission electron microscope (Thermo Fischer, USA). High resolution transmission electron microscopy (FEI Tecnai F20 microscope) with a beam energy of 300 kV (Thermo Fischer, USA) was used to get a high resolution images that shows the lattice planes of the synthesized samples. The particle size was calculated from imagej image processing software and the lattice spacing was determined using Gatan digital micrograph software.

The optical properties of the synthesized samples were investigated by Uv-visible diffusive reflectance spectroscopy (PerkinElmer Lambda 950 UV-Vis spectrophotometer) in the wavelengths range 250-800 nm, and the band gap was obtained using the Kubelka-Munk equation (eq.3.15). The Kubelka-Munk function is given (eq.4.13):

$$F(R) = \frac{k}{s} = \frac{(1 - R)^2}{2R} \quad (3.13)$$

Where  $F(R)$  a Kubelka-Munk function which is the ratio of absorption coefficient ( $k$ ) to the scattering coefficient ( $s$ ) in  $m^{-1}$ ,  $k$  is the absorption coefficient  $((1 - R)^2)$ ,  $s$  is the scattering coefficient ( $2R$ ), and  $R$  is the percent reflectance obtained in the DRS data. The band gap

energies of the synthesized samples were estimated from Kubelka-Munk equation of direct band gap semiconductor:

$$F(R) * hv = A(hv - E_g)^n \quad (3.14)$$

Where  $A$  is the proportionality constant depends on the nature of the material,  $E_g$  is the band gap that is the gap between the bottom of the conduction band and the top of the valence band,  $h$  is Planck's constant ( $6.63 \times 10^{-34} \text{Js}^{-1}$ ),  $\nu$  is the frequency of photon,  $n$  in the power index represent the nature of transition of electrons in the semiconductor, that is,  $n = 0.5$  for direct allowed transitions and  $n = 2$  for indirect transitions. ZnO and SnO<sub>2</sub> are direct band gap semiconductors, and therefore, equation (3.14) becomes:

$$(F(R) * hv)^2 = A(hv - E_g) \quad (3.15)$$

The band gap can be obtained from extrapolation of the straight line portions to  $(F(R) * hv)^2 = 0$  in the plot of  $(F(R) * hv)^2$  versus photon energy ( $h\nu$ ) for direct band gap semiconductor.

The functional groups attached to the synthesized samples were measured with Attenuated Total Reflection FTIR spectroscopy (model IS50 ABX Germany) in wave number ranges of 4000-400  $\text{cm}^{-1}$ . It also utilized to determine the chemical bonds of the samples. Before the sample measurement background spectrum was recorded with the ATR cell. Finally, subtraction of the background of the sample was carried. The photoluminescence property was studied by fluorescence spectrophotometer (Agilent Cary Eclipse Fluorescence Spectrophotometer) using a 150 W xenon lamp as the excitation source. To do the PL measurement, the synthesized powder samples were dispersed in dimethylsulphoxide (DMSO). Then, each sample was loaded into a rectangular sample holder using a cuvette. The grating slits were set at 10 nm for the excitation and 10 nm for the emission while photomultiplier voltage was maintained at medium. Emission spectra was obtained by setting the desired scanning wavelength range and excited at a wavelength of 325 nm and 265 nm. Scanning electron microscopy (Hitachi S4800) fitted with an EDS detector (Hitachi, Japan) was used to investigate the morphological features of the synthesized samples. SEM combined with EDX apparatus was also used to identify the elemental or chemical composition of the synthesized powder. The concentration and distribution of the elements in the synthesized samples were determined by the elemental mapping analysis.



### 3.4 Photocatalytic Degradation Experiment

The photocatalytic performance of the synthesized samples was evaluated through the photocatalytic degradation of methylene blue dye under visible light irradiation. In photocatalytic experiment, the solution containing 10 mg/L (10 ppm) of model pollutant methylene blue dye was prepared. The pH of the solution for all samples was adjusted at the desired pH value by 0.01M NaOH and HCl. Then, 100 mL of dye solution has been taken and the blank experiment (photolysis) was done without catalyst. Next, the desired amount of nanocatalyst was added. This mixed solution was magnetically stirred constantly at room temperature for 30 minutes in dark to reach at its adsorption-desorption equilibrium state. Next, immediately 3 ml of the solution prepared in dark was taken and the absorbance was measured. Again, after the mixed solution was exposed to visible light, 3 ml of the supernatant from the solution during the photocatalytic experiment was taken in 20 minute interval for the required irradiation time. The supernatant was centrifuged for 5 minutes to remove the photocatalyst. After centrifugation and filtering, the absorbance versus wavelength of the filtrates was measured for each samples by using UV-Visible spectroscopy. Based on these spectroscopic data, the photocatalytic efficiency of the methylene blue dye for the photocatalysts was calculated using (eq. (3.16)):

$$\text{Degradation efficiency(\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (3.16)$$

Where  $C_0$  is the absorbance at time  $t = 0$  min before light exposure, and  $C_t$  is the absorbance measured during the exposure of light in a 20 min intervals.

The photocatalytic rate constant values of the photocatalysts were determined by the Langmuir-Hinshelwood model at low MB concentrations using eq. (3.17):

$$\ln\left(\frac{C_0}{C_t}\right) = Kt \quad (3.17)$$

Where  $K$  is the first order rate constant that was determined from slope of graph  $\ln\left(\frac{C_0}{C_t}\right)$  versus illumination time, and  $t$  is the light illumination time.

The band edge position values of Cu-SnO<sub>2</sub> and ZnO can be calculated using equations (3.18 & 3.19) (Asaithambi, Sakthivel, Karuppaiah, Balaji, Yuvakkumar, *et al.*, 2021):

$$E_{VB} = X - E_e + 0.5E_g \quad (3.18)$$

$$E_{CB} = E_{VB} - E_g \quad (3.19)$$

In equations (3.18) & (3.19),  $E_{VB}$  and  $E_{CB}$  are valance and conduction band edge potentials, respectively. Whereas  $E_g$  represents the band gap energy.  $X$  is a symbol for the electronegativity of  $\text{SnO}_2$  (6.25eV) and  $\text{ZnO}$  (5.79 eV) and  $E_e$  is the free electron energy (4.50 eV) on the normal hydrogen electrode (NHE) scale. Moreover, to identify the more active degrading species in the photocatalytic process, 0.10 mM of isopropyl alcohol (IPA), ethylenediaminetetra acetic acid (EDTA-2Na) and silver nitrate ( $\text{AgNO}_3$ ) were added prior to the catalyst to scavenge hydroxyl ( $\text{OH}^*$ ), holes ( $e^+$ ) and electron ( $e^-$ ) respectively. The trapping or quenching experiment were carried out using the same procedures and conditions as photocatalytic degradation experiments.

### 3.5 Electrode Preparation and Performance Testing for Supercapacitor Application

The electrochemical performance of the synthesized electrode materials for supercapacitor application was determined based on operating voltage window, specific capacitance ( $C_s$ ), cycle stability, equivalent series resistance, energy density and power density. The characterization and performance were done using the cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) method and electrochemical impedance spectroscopy (EIS). To do this, the working electrode was prepared using a drop casting method. Cyclic voltammetry was done by linearly sweeping the potential of the working electrode at a certain scan rate within the desired potential window and then swept in opposite direction. Using CV analysis, the current versus scanned potential window curve was obtained. Then, from CV data, the specific capacitance was calculated using the following equation (3.20) (Shameem *et al.*, 2024):

$$C_s = \frac{A}{2mv\Delta V} \quad (3.20)$$

Where  $C_s$  the specific capacitance in (F/g),  $m$  is the mass of the active material loaded on the nickel substrate,  $v$  is the scanning rate (V/s),  $A$  is the area of the CV curve (AV), and  $\Delta V$  is the potential window of the electrode material in KOH electrolyte. Furthermore, the specific capacitance, cycle stability, energy density, power density and capacitive retention were determined from galvanostatic charge-discharge (GCD) analysis. The specific capacitance ( $C_s$ ) of the working electrode using the GCD technique was calculated using the following equation (3.21):

$$C_s = \frac{I\Delta t_d}{m\Delta V} \quad (3.21)$$

Where specific capacitance ( $C_s$ ) in F/g,  $I$  is the current (in mA),  $\Delta t_d$  discharge time (in sec),  $m$  is the mass of the catalyst deposited or casted on the nickel foam (in mg) and  $\Delta V$  is the voltage window (in volts).

The specific energy density ( $E_D$ ) of the working electrode was determined from the following formula (3.22):

$$E_D (\text{Wh kg}^{-1}) = \frac{1}{7.2} C_s (\Delta V)^2 \quad (3.22)$$

The specific power density ( $P_D$ ) of the working electrode was determined using the following equation (3.23):

$$P_D (\text{Wkg}^{-1}) = \frac{E_D * 3600}{\Delta t_d} \quad (3.23)$$

Where  $\Delta t_d$  is discharge time.

## 4. RESULTS AND DISCUSSION

### 4.1 XRD Analysis of Cu-SnO<sub>2</sub>/ZnO, Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO and CuO-SnO<sub>2</sub>/rGO Nanocomposites

The XRD spectra of Cu-SnO<sub>2</sub>/ZnO composite in figure 19 demonstrated that the samples' diffraction peaks at angles ( $2\theta$ ) of 26.7940°, 34.0762° and 51.9853° from the diffractions of 110, 101, and 211 crystallographic lattice planes respectively confirmed the formation of tetragonal rutile SnO<sub>2</sub> structure and in excellent agreement with the benchmark values (JCPDS Card No. 41-1445). The diffraction peaks for hexagonal wurtzite structure (with space group of P6<sub>3</sub>mc and mineral name-zincite) of ZnO were observed at angles ( $2\theta$ ) of 31.8393°, 34.4935°, 36.3215°, 47.6046°, 56.6624°, 62.9233°, 68.0129° and 69.1512° are respectively attributed to the diffraction from 100, 002, 101, 102, 110, 103, 112 and 201 crystallographic planes matching with standard values (JCPDS No: 36-1451). The XRD spectra of SnO<sub>2</sub>, Cu-SnO<sub>2</sub>, SnO<sub>2</sub>/ZnO, and Cu-SnO<sub>2</sub>/ZnO nanocomposite are polycrystalline. No secondary phase was observed in the SnO<sub>2</sub> though Cu atoms incorporated in the lattice position of the Sn atom. The SnO<sub>2</sub>/ZnO nanocomposite XRD spectra show almost all the peaks of SnO<sub>2</sub> and ZnO in the formation of ZnO and SnO<sub>2</sub>. Moreover, the peak width and intensity of the composite changed compared with the individual materials, and the physical properties change may alter the electronic and catalytic properties of the composite (D. K. Sharma *et al.*, 2020). The SnO<sub>2</sub> in Cu-SnO<sub>2</sub>, SnO<sub>2</sub>/ZnO, and Cu-SnO<sub>2</sub>/ZnO have a slightly greater full-width half-maximum (FWHM) that indicates the crystallite size was smaller than pristine SnO<sub>2</sub>. The crystallite size of SnO<sub>2</sub> in Cu-SnO<sub>2</sub>, SnO<sub>2</sub>/ZnO, and Cu-SnO<sub>2</sub>/ZnO, estimated from the three most intense peaks using Debye-Scherrer formula (Eq.3.1) and the pristine SnO<sub>2</sub> shows larger crystallite size than other samples as indicated in Table 1. The smaller crystallite size in the doped composite sample might be due to the Cu and ZnO inhibiting of the growth of grains. The lattice constants and unit cell volume of samples are estimated and summarized in Table 1. The lattice constant and unit cell volume of prepared SnO<sub>2</sub> and ZnO are almost similar to the standard values. However, the unit cell volume, lattice constant, and distortion of Cu-SnO<sub>2</sub>, SnO<sub>2</sub>/ZnO, and Cu-SnO<sub>2</sub>/ZnO were higher than SnO<sub>2</sub> nanoparticles might be the result of substituting Cu and Zn ions with greater ionic radii in the Sn lattice.

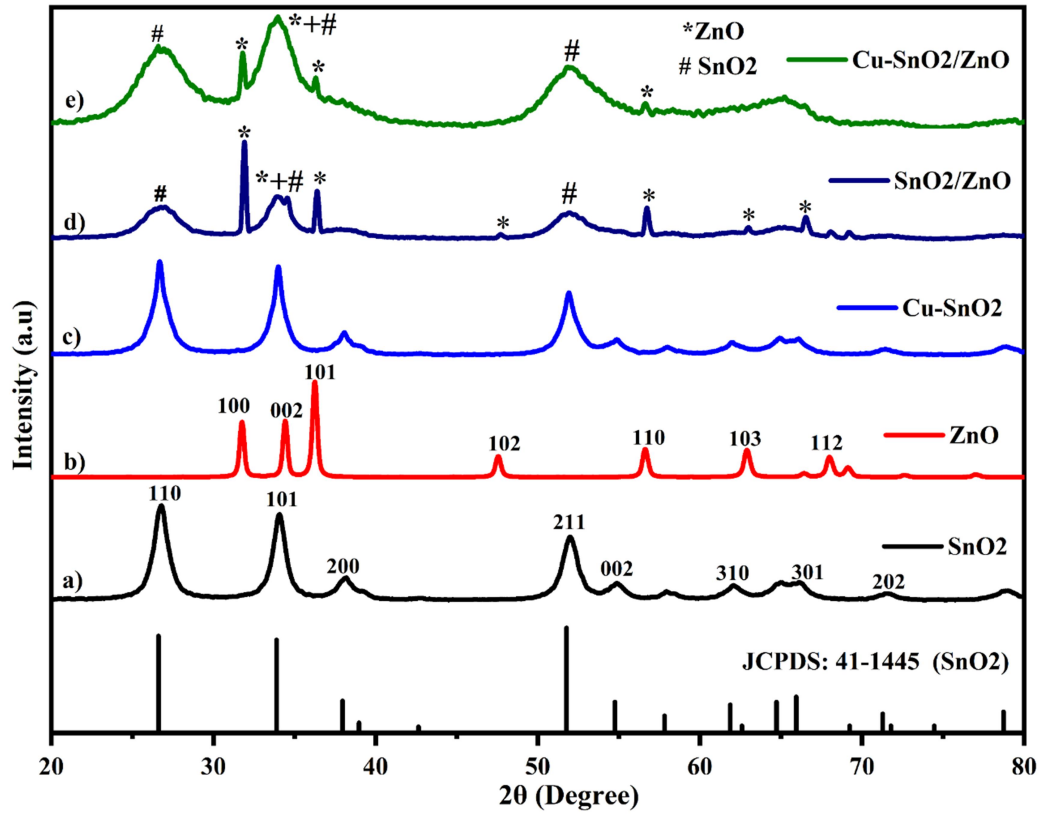


Figure 19: XRD patterns of a) Pure SnO<sub>2</sub> nanoparticles b) pure ZnO nanoparticles c) Cu-SnO<sub>2</sub> nanoparticles d) SnO<sub>2</sub>-ZnO nanocomposite e) Cu-SnO<sub>2</sub>/ZnO nanocomposite and all samples were calcined at 500 °C. The vertical lines indicated by JCPDS No: 41-1445 represents the standard for rutile tetragonal structured cassiterite phase of SnO<sub>2</sub>

Table 1: The average crystallite size, lattice parameters, unit cell volume and lattice distortion of SnO<sub>2</sub>, ZnO and Cu-SnO<sub>2</sub> nanoparticles, SnO<sub>2</sub>/ZnO and Cu-SnO<sub>2</sub>/ZnO nanocomposites calculated from intense peaks using equations (3.1-3.6).

| Samples                  | Crystallite size (nm) | $a = b$ | $c$     | unit cell Volume, Å <sup>3</sup> | Lattice distortion, U | Defect density |
|--------------------------|-----------------------|---------|---------|----------------------------------|-----------------------|----------------|
| SnO <sub>2</sub>         | 8.50                  | 4.7017  | 3.1709  | 70.0959                          | 1.48277               | 0.01384        |
| ZnO                      | 29.19                 | 3.24925 | 5.20466 | 54.9489                          | 0.62430               | 0.001174       |
| Cu-SnO <sub>2</sub>      | 6.42                  | 4.7133  | 3.1762  | 70.5612                          | 1.48394               | 0.02426        |
| SnO <sub>2</sub> /ZnO    | 7.10                  | 4.7687  | 3.1774  | 72.2557                          | 1.50082               | 0.01984        |
| Cu-SnO <sub>2</sub> /ZnO | 3.45                  | 4.7033  | 3.1819  | 70.3883                          | 1.47811               | 0.08402        |

The XRD spectra of Co<sub>3</sub>O<sub>4</sub>, ZnO, Sn-ZnO, Co<sub>3</sub>O<sub>4</sub>/ZnO and Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposites are shown in figure 20 (a). The hexagonal wurtzite structure of ZnO, which is in an excellent

agreement with the standard JCPDS No. 36-1451, is confirmed (Jangir *et al.*, 2017). The peak intensity of ZnO decreases with the addition of  $\text{Sn}^{4+}$  and  $\text{Co}_3\text{O}_4$ . The intense XRD peaks of  $\text{Co}_3\text{O}_4$  represent a cubic spinel phase, as confirmed by PDF: 74-2120 (Moradpoor *et al.*, 2019). No intermediate-phase peaks were observed in the XRD spectra of all the synthesized samples. In the composite sample  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$ , peaks representing ZnO and  $\text{Co}_3\text{O}_4$  were observed. The presence of the peaks that represent ZnO and  $\text{Co}_3\text{O}_4$  in the spectra suggests the existence and formation of composites. However, peaks of Sn do not appear in the XRD spectra, which might be due to its small amount, i.e., below the detection limit. When  $\text{Zn}^{2+}$  is substituted by  $\text{Sn}^{4+}$  in the ZnO host, a small shift towards a higher angle is observed (Naqvi & Badshah, 2013) but when it is coupled with  $\text{Co}_3\text{O}_4$ , there is no shift observed, as shown in figure 20 (b). The lattice spacings of ZnO,  $\text{Co}_3\text{O}_4$ , Sn-ZnO,  $\text{Co}_3\text{O}_4/\text{ZnO}$ , and  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposites obtained from the most intense peak are 2.47554 Å, 2.47672 Å, 2.47411 Å, 2.47460 Å, and 2.47534 Å, respectively.

The average crystalline size of ZnO,  $\text{Co}_3\text{O}_4$ , and Sn-ZnO particles,  $\text{Co}_3\text{O}_4/\text{ZnO}$ , and  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite were estimated from the three most intense peaks using the Debye-Scherrer formula (Eq.3.1) (Venkatesh *et al.*, 2021) and are given in Table 4.2. This XRD analysis showed that crystalline size increased as the FWHM of  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  decreased when  $\text{Sn}^{4+}$  and  $\text{Co}_3\text{O}_4$  were incorporated. The lattice parameters  $a$ ,  $b$  and  $c$  for hexagonally structured ZnO could be determined using lattice planes (100) and (002) using equation 3.6 and 3.7 respectively. The density of dislocations for the synthesized samples were calculated using (eq.3.11) and given in Table 2. The calculated values of lattice parameters ( $a$ ,  $b$ ,  $c$ ) decrease for Sn-ZnO and  $\text{Co}_3\text{O}_4/\text{ZnO}$ , but for the  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  composite,  $a$  and  $b$  increase and  $c$  decrease.

The density of dislocations decreases as the crystalline size increases for Sn-ZnO,  $\text{Co}_3\text{O}_4/\text{ZnO}$ , and  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  composites compared to bare ZnO and  $\text{Co}_3\text{O}_4$ , as given in Table 2. Moreover, the XRD result verified that  $\text{Sn}^{4+}$  was doped into ZnO and formed a composite with  $\text{Co}_3\text{O}_4$  to produce a high-performance  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite catalyst.

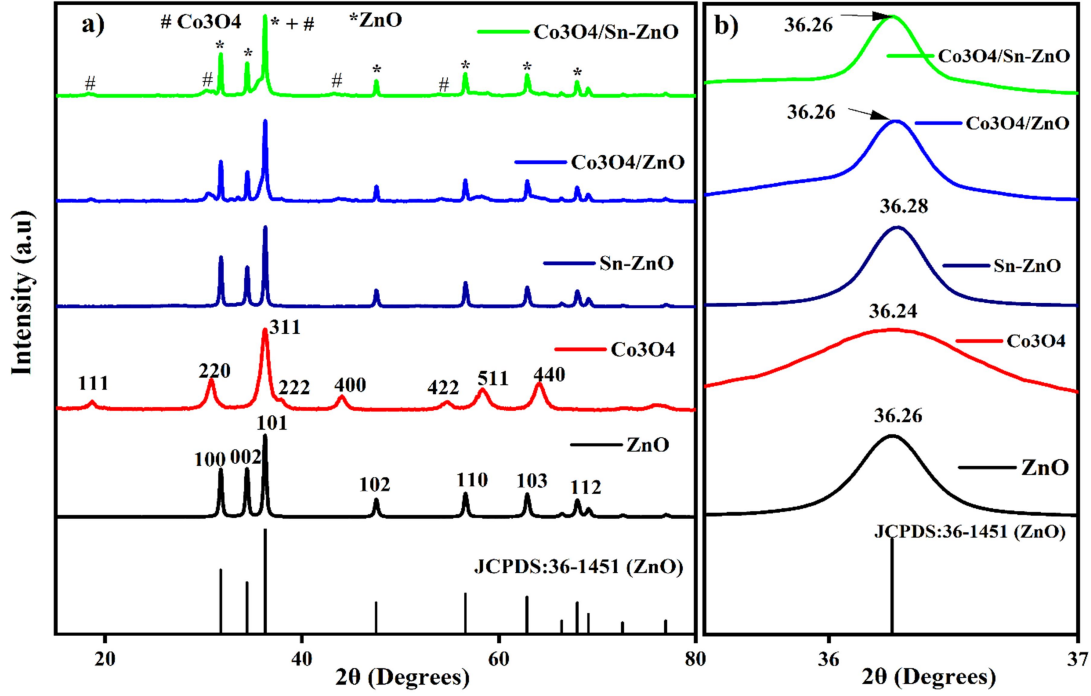


Figure 20: (a) XRD spectra of ZnO, Co<sub>3</sub>O<sub>4</sub>, Sn-ZnO, Co<sub>3</sub>O<sub>4</sub>/ZnO and Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO composite calcined at 500 °C, & (b) magnified spectra of the intense peak of the synthesized samples. The vertical line represents ZnO spectra of the standard (JCPDS: 36-1451).

Table 2: The average crystalline size (D), calculated lattice parameters, density of dislocations, and band gap of the synthesized samples are given below.

| Samples                                | D (nm) | $a=b$   | $c$     | Density of dislocations<br>$\times 10^{-3}$ |
|----------------------------------------|--------|---------|---------|---------------------------------------------|
| ZnO                                    | 29.19  | 3.24925 | 5.20466 | 1.1736                                      |
| Co <sub>3</sub> O <sub>4</sub>         | 9.51   | 8.20668 | 8.20668 | 11.057                                      |
| Sn-ZnO                                 | 39.20  | 3.24716 | 5.20224 | 0.651                                       |
| Co <sub>3</sub> O <sub>4</sub> /ZnO    | 39.28  | 3.24850 | 5.19988 | 0.648                                       |
| Co <sub>3</sub> O <sub>4</sub> /Sn-ZnO | 44.62  | 3.24971 | 5.20290 | 0.502                                       |

Figure 22 (c) shows the XRD results of graphene oxide (GO) and reduced graphene oxide (rGO). The thickness of the GO sheet is 4.83 nm calculated from the most intense peak 001 lattice plane at  $2\theta = 10.17$  degree and lattice spacing of 8.6879 Å. XRD analysis confirmed that the graphite powder was properly oxidized and exfoliated into graphene oxide. Again,

the graphene oxide is transformed into reduced graphene oxide as indicated by the wide peak with a lattice plane 002.

The XRD patterns of 5% Cu-SnO<sub>2</sub>, 10 % Cu-SnO<sub>2</sub> and 15% CuO-SnO<sub>2</sub> are depicted in figure 21. In the synthesized sample (15 % CuO-SnO<sub>2</sub>), XRD peaks for both crystal phases of SnO<sub>2</sub> and CuO were appeared. Based on the crystal information the tetragonal cassiterite SnO<sub>2</sub> (JCPDS: 41-1445) and monoclinic (Tenorite) CuO (PDF: 48-1548  $a = 4.688$  Å,  $b = 3.422$ ,  $c = 5.131$ ) were confirmed. In 5% Cu-SnO<sub>2</sub>, no visible peaks detected for CuO because Cu<sup>2+</sup> might be introduced into the interstitial sites as a dopant in SnO<sub>2</sub> host. In 5% Cu-SnO<sub>2</sub>, 10 % Cu-SnO<sub>2</sub> and 15% CuO-SnO<sub>2</sub> samples, the addition of varying molarity of copper enhanced the XRD peaks of the SnO<sub>2</sub> host that means the periodicity and crystallinity also improved. Furthermore, the most intense peaks along the 110 and 101 indicate that there was a competing preferential crystal growth along this direction. That means, the addition of Cu ion at varying concentration facilitates the crystal growth without changing the growth direction of the host. In 15% CuO-SnO<sub>2</sub> binary composite, peaks of both components are observed, and therefore the crystal phase of CuO is fused together with crystal phase of SnO<sub>2</sub> to form the composite. In addition, when 15% CuO-SnO<sub>2</sub> is coupled with reduced graphene oxide its preferential growth direction is not changed. The peaks for reduced graphene oxide is not observed in the XRD spectra of 10% CuO-SnO<sub>2</sub>/rGO hybrid composite which might be due to the addition of small amount of rGO sheet or overlapping with high intensity 110 (SnO<sub>2</sub>) peak (Pham Van Tuan *et al.*, 2019). The average crystalline sizes of the synthesized samples calculated from the Debye-Scherrer formula eqs. (3.1) were given in Table 3.

The lattice parameters, density of dislocations and volume of the unit cell for the synthesized samples were calculated using equations (3.4, 3.5, 3.9 & 3.11) were calculated based on the Bragg's equation for lattice spacing using (eq.3.2) are given in Table 3. The crystalline sizes calculated from Debye-Scherrer formula are consistent with Williamson-Hall method using equation (3.12) as indicated in Table 3.

Generally, the addition of varying concentration of copper ion and copper oxide results an increase of FWHM and the crystalline sizes decreased compared to the pristine oxide. Specifically, for samples 5 % CuO-SnO<sub>2</sub> and 10 % CuO-SnO<sub>2</sub> the FWHM increases with increasing copper concentration so that the average crystalline size decreases (Aragón *et al.*, 2023; Sagadevan *et al.*, 2019) but for sample 15 % CuO-SnO<sub>2</sub> the FWHM decreased results



the crystalline size to be increased a bit as indicated in figure 22 (a). This slight increment of crystalline size might be due to the formation of new crystal phase of CuO. Similarly, the density of dislocations exhibited an increment for samples 5% CuO-SnO<sub>2</sub> and 10% CuO-SnO<sub>2</sub> but a slight decrease in sample 15 % CuO-SnO<sub>2</sub> as shown in Table 3 and figure 22 (a). The slight variation in lattice parameters and volume of unit cell were also observed in 5% CuO-SnO<sub>2</sub>, 10% CuO-SnO<sub>2</sub> and 15 % CuO-SnO<sub>2</sub> nanomaterials as shown in Table 3 and figure 22 (b). Moreover, it was vivid that the coupling of reduced graphene oxide with 10% CuO-SnO<sub>2</sub> binary composite further reduces the grain size and acts as a grain growth inhibitor. The crystallite size calculated using Scherrer's formula are smaller than obtained by the W-H approach because it only predicts crystallite size based on an average crystallite distribution from distinct peaks and ignores the impacts of peak broadening due to strain (Munguti & Dejene, 2021). In the Williamson-Hall (W-H) plots shown in figure 23, the positive slope indicates a tensile strain in all synthesized samples.

According to the XRD study, in general, the greater the distortion and production of defect states, the smaller the crystallite size, and the higher the light harvesting and charge carrier trapping, which promotes electron-hole separation and increases the photocatalytic effectiveness of the photocatalyst. Moreover, the smaller the size of the crystallite the greater the surface area and the more the active sites on the electrode materials results improvement in the performance of the supercapacitor. The lower crystallite size electrode materials exhibited good supercapacitor stability because of lower volume expansion during charging and discharging. Therefore, Cu-SnO<sub>2</sub>/ZnO nanocomposites exhibited enhanced photocatalytic performance, and 10% CuO-SnO<sub>2</sub>/rGO (1% & 2 %) hybrid composite can be a good supercapacitor electrode material with a greater stability, and longer life time

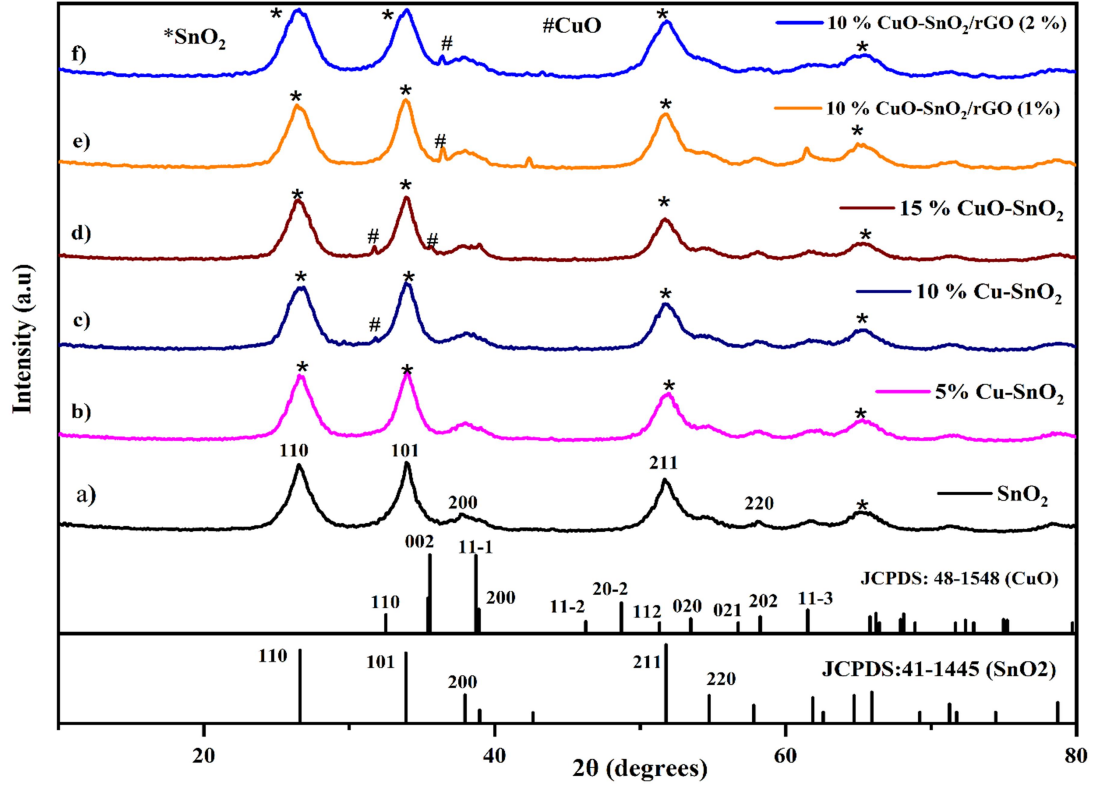


Figure 21: XRD spectra of samples (a-f). The vertical lines represent standards of SnO<sub>2</sub> and CuO.

Table 3: The structural parameters for pristine SnO<sub>2</sub>, and CuO-SnO<sub>2</sub> and CuO-SnO<sub>2</sub>/rGO composites.

| Sample                             | Debye-Scherer formula |                                       | W-H method | Lattice constants |               | Volume of unit cell (Å <sup>3</sup> ) |
|------------------------------------|-----------------------|---------------------------------------|------------|-------------------|---------------|---------------------------------------|
|                                    | D (nm)                | Dislocations (lines/nm <sup>2</sup> ) | D (nm)     | $a=b(\text{Å})$   | $c(\text{Å})$ |                                       |
| SnO <sub>2</sub>                   | 5.94                  | 0.028342                              | 10.07      | 4.72739           | 3.17823       | 71.0279                               |
| 5% Cu-SnO <sub>2</sub>             | 5.26                  | 0.036144                              | 6.52       | 4.71940           | 3.17421       | 70.6984                               |
| 10% Cu-SnO <sub>2</sub>            | 4.94                  | 0.040978                              | 6.41       | 4.72637           | 3.17571       | 70.9409                               |
| 15% CuO-SnO <sub>2</sub>           | 5.32                  | 0.035333                              | 7.03       | 4.73711           | 3.18575       | 71.4889                               |
| 10%CuO-SnO <sub>2</sub> /rGO (1%)  | 5.24                  | 0.036373                              | 5.26       | 4.74091           | 3.18634       | 71.6169                               |
| 10% CuO-SnO <sub>2</sub> /rGO (2%) | 4.20                  | 0.056779                              | 3.36       | 4.74850           | 3.18570       | 71.8321                               |

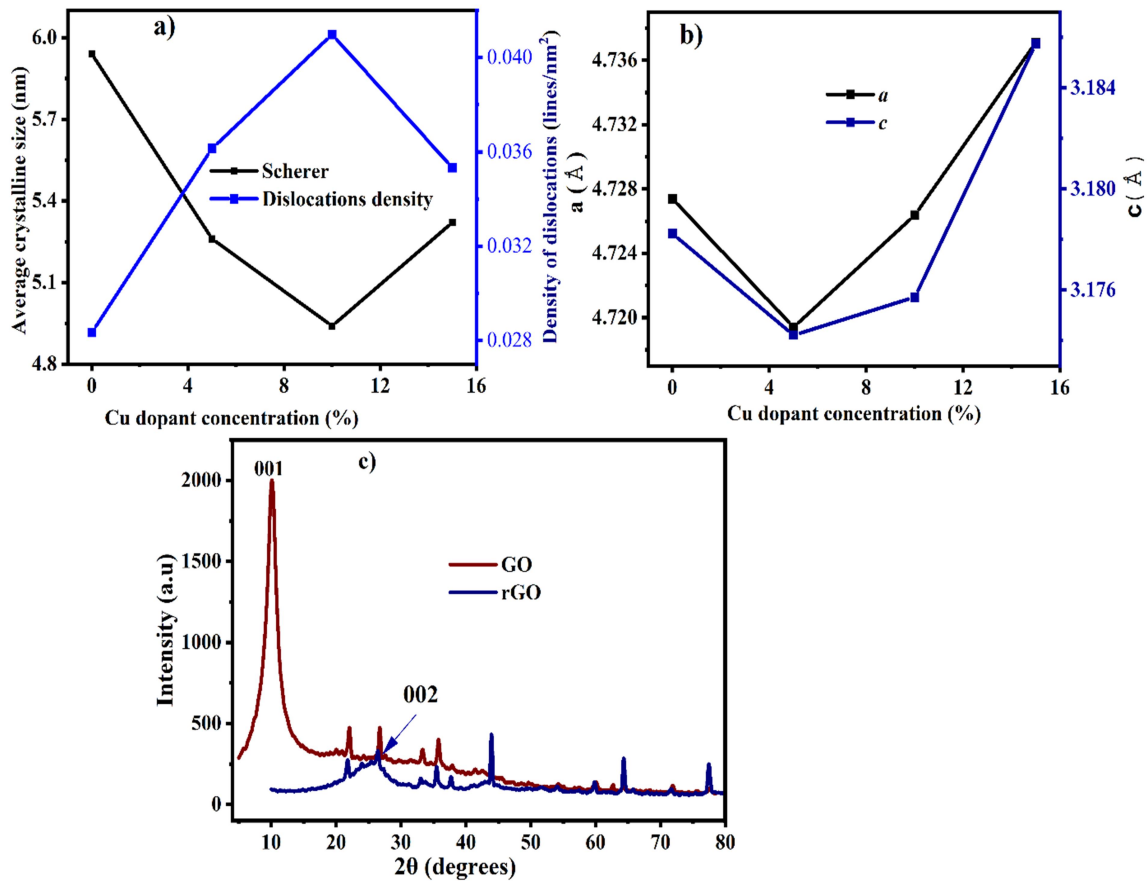


Figure 22:(a) Shows the average crystalline size and dislocation density of SnO<sub>2</sub> nanoparticles as a function of CuO concentration, and (b) lattice parameters of SnO<sub>2</sub> host as a function of the variation of CuO, & (c) the XRD spectra of graphene oxide (GO) & reduced graphene oxide (rGO).

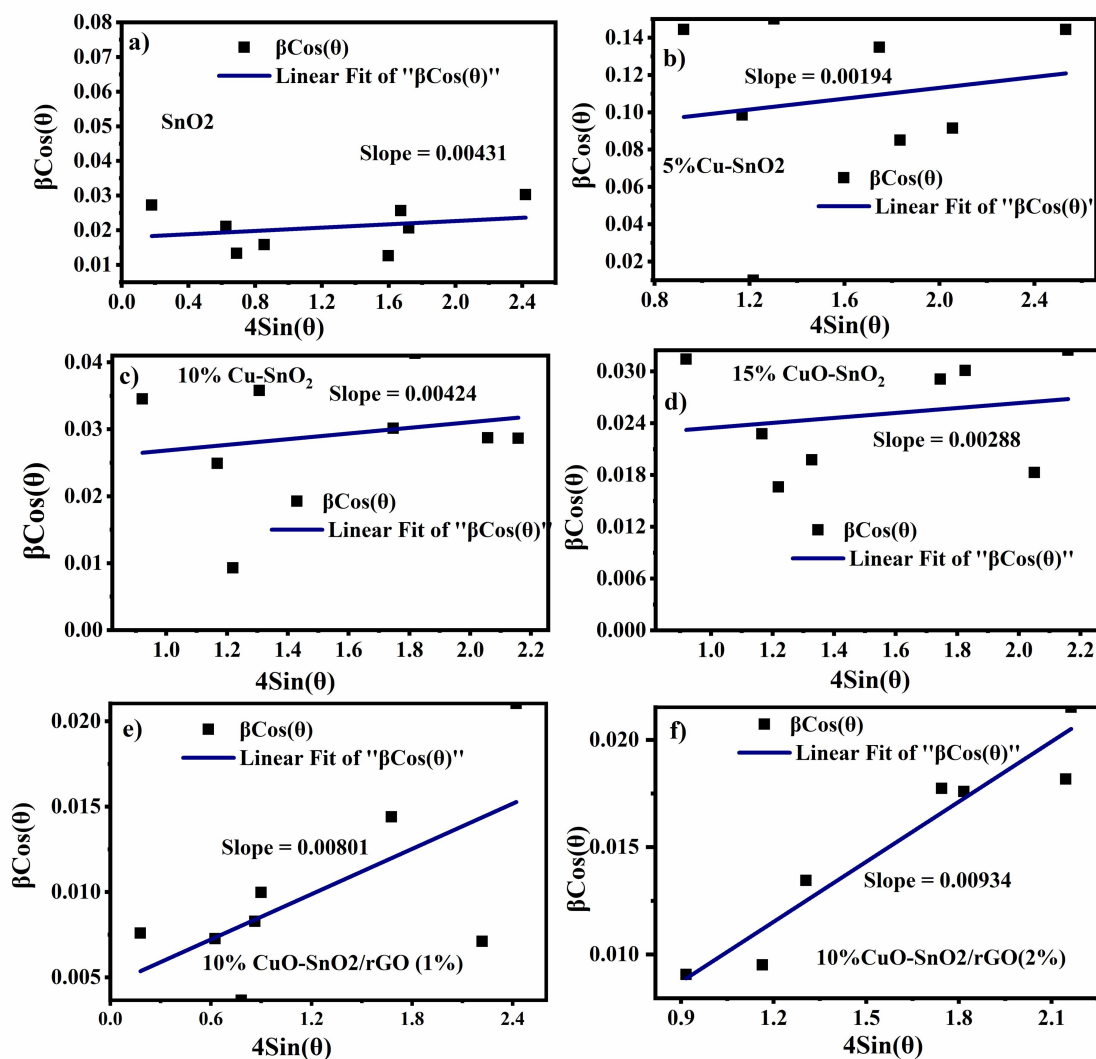


Figure 23: Linear fits of Williamson-Hall plots for samples (a-f).

#### 4.2 Uv-Vis DRS Analysis of Cu-SnO<sub>2</sub>/ZnO, Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO and CuO-SnO<sub>2</sub>/rGO Nanocomposites

The optical band gap of SnO<sub>2</sub>, ZnO, and Cu-SnO<sub>2</sub> nanoparticles, and SnO<sub>2</sub>/ZnO and Cu-SnO<sub>2</sub>/ZnO nanocomposites obtained from Uv-vis diffusive reflectance spectroscopy data measured at a wavelength range of 200-800 nm using the Kubelka-Munk equation (eq.3.15) and shown in figure 24. The calculated optical bandgap energy of SnO<sub>2</sub>, ZnO, and Cu-SnO<sub>2</sub> nanoparticles and SnO<sub>2</sub>/ZnO and Cu-SnO<sub>2</sub>/ZnO nanocomposites were 3.60, 3.20, 3.34, 3.48, and 3.09 eV, respectively as indicated in figure 24. Figure 24 shows the red shift on the light absorption peak was observed after modification by doping of metal or construction of the

composite with ZnO, which is similar to the previous report (Hamrouni *et al.*, 2014; Palai *et al.*, 2021). The redshift in Cu-SnO<sub>2</sub> nanoparticles is due to the addition of Cu ions into SnO<sub>2</sub> that create delocalized or defect energy levels between the valance and conduction band of SnO<sub>2</sub> (Asaithambi *et al.*, 2021; Babu *et al.*, 2017). In SnO<sub>2</sub>/ZnO the insertion of Zn ions into the Sn lattice might result in oxygen vacancies or defects between bands (Uddin *et al.*, 2020). Similarly, the Cu-SnO<sub>2</sub>/ZnO nanocomposite band gap decreases due to Cu and Zn ions incorporation into the Sn lattice sites (Asaithambi *et al.*, 2021).

The optical band gap of ZnO, Co<sub>3</sub>O<sub>4</sub>, and Sn-ZnO, Co<sub>3</sub>O<sub>4</sub>/ZnO, and Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO composites were calculated using (eq.4.14) and indicated in figure 25. The reflectance spectra of ZnO and Sn-ZnO powder showed larger reflectance in the UV region than visible. Moreover, the composite samples have relatively smaller reflectance in the UV region than the bare samples. It is due to the smaller dual band gap of Co<sub>3</sub>O<sub>4</sub> and has a relatively smaller reflectance in the UV-Vis region than ZnO & Sn-ZnO. In this study, the optical bandgap of ZnO negligibly decreased when Sn substitutionally doped into the lattice of ZnO, i.e., bare ZnO = 3.20 eV and the doped one 3.12 eV; it might be due to the incorporation of a small dopant amount (Ahamed *et al.*, 2021). The doping of Sn<sup>4+</sup> in ZnO host also induced a donor level near the conduction band and increases the electron density in it.

The Co<sub>3</sub>O<sub>4</sub>/ZnO composite exhibited a decreasing optical band gap, i.e., 2.37 eV, compared to bare Co<sub>3</sub>O<sub>4</sub> = 2.78 eV and ZnO = 3.20 eV, as shown in figure 26 (a, b, and d). Moreover, the optical band gap decreased to 2.23 eV for the Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO composite, as shown in figure 26 (e). This decrease in band gap could be due to the partial incorporation of Co ions in place of vacancies or Zn interstitials in the ZnO and the lower dual band gap of Co<sub>3</sub>O<sub>4</sub>. The lower band gap ( $E_g = 1.56$  eV) associated with the charge transfer from O<sup>2-</sup> to the level of Co<sup>3+</sup> located between the conduction and valance band, and the larger band gap is related to O<sup>2-</sup> to Co<sup>2+</sup> band to band charge transfer (Lakehal *et al.*, 2018). Co<sub>3</sub>O<sub>4</sub> has a very good light absorbing ability in a visible light spectrum region so that when coupled it with Sn-ZnO the light absorbing capacity could be increased and recombination rate of carriers might be reduced which is the major problem to use pristine oxides for photocatalysis. Moreover, the lower band gap of Co<sub>3</sub>O<sub>4</sub> might play a great role in reducing the bandgap of Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite, and therefore it could be a best photocatalyst. In addition to the Uv-DRS analysis, the Uv-visible absorbance measurement in figure 27 indicates that Sn-ZnO

nanoparticles,  $\text{Co}_3\text{O}_4/\text{ZnO}$ , and  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  composites show a red shift (or band gap narrowing) (Ameen *et al.*, 2012; Selvinsimpson *et al.*, 2021). This means that  $\text{Co}_3\text{O}_4/\text{ZnO}$  and  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  composites absorb light in the visible spectral region. Therefore, an energy level created near the conduction band of the materials enhances the density of the photogenerated carriers, increases visible light absorption capacity and improves the charge carriers' kinetics, and it enable redox reactions to happen more quickly, which improves the efficiency of a photocatalyst in the photocatalytic process. As a result, the  $\text{Co}_3\text{O}_4/\text{ZnO}$  and  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposites could show high photocatalytic performance.

The band gap for  $\text{SnO}_2$ , 5%  $\text{CuO-SnO}_2$ , and 10 %  $\text{CuO-SnO}_2$  and 15%  $\text{CuO-SnO}_2$  were 3.55 eV, 3.48 eV, 3.23 eV and 3.26 eV respectively as indicated in figure 27 (a-e). The band gap decreases with the increase of Cu ion dopant concentration 5%  $\text{CuO-SnO}_2$ , and 10 %  $\text{CuO-SnO}_2$  agreed with previous reports (Sagadevan *et al.*, 2019) and slightly increased for 15%  $\text{CuO-SnO}_2$  due to a slight increase of the crystalline size. The decrease of bandgap could be due to the formation of acceptor levels near the valance band and formation of more defects on the surface. The decrease in band gap facilitates the flow of charges, and enhances the electrical conductivity of the synthesized electrode materials for a good supercapacitor. Figure 27 (f) shows the absorbance as a function of wavelength for graphene oxide (GO) and reduced graphene oxide (rGO). The UV visible spectroscopic analysis exhibited a maximum absorbance wavelength for GO and rGO are 230 nm and 265 nm respectively. This result further confirmed that Graphite is transformed into GO and then GO was hydrothermally reduced to rGO.

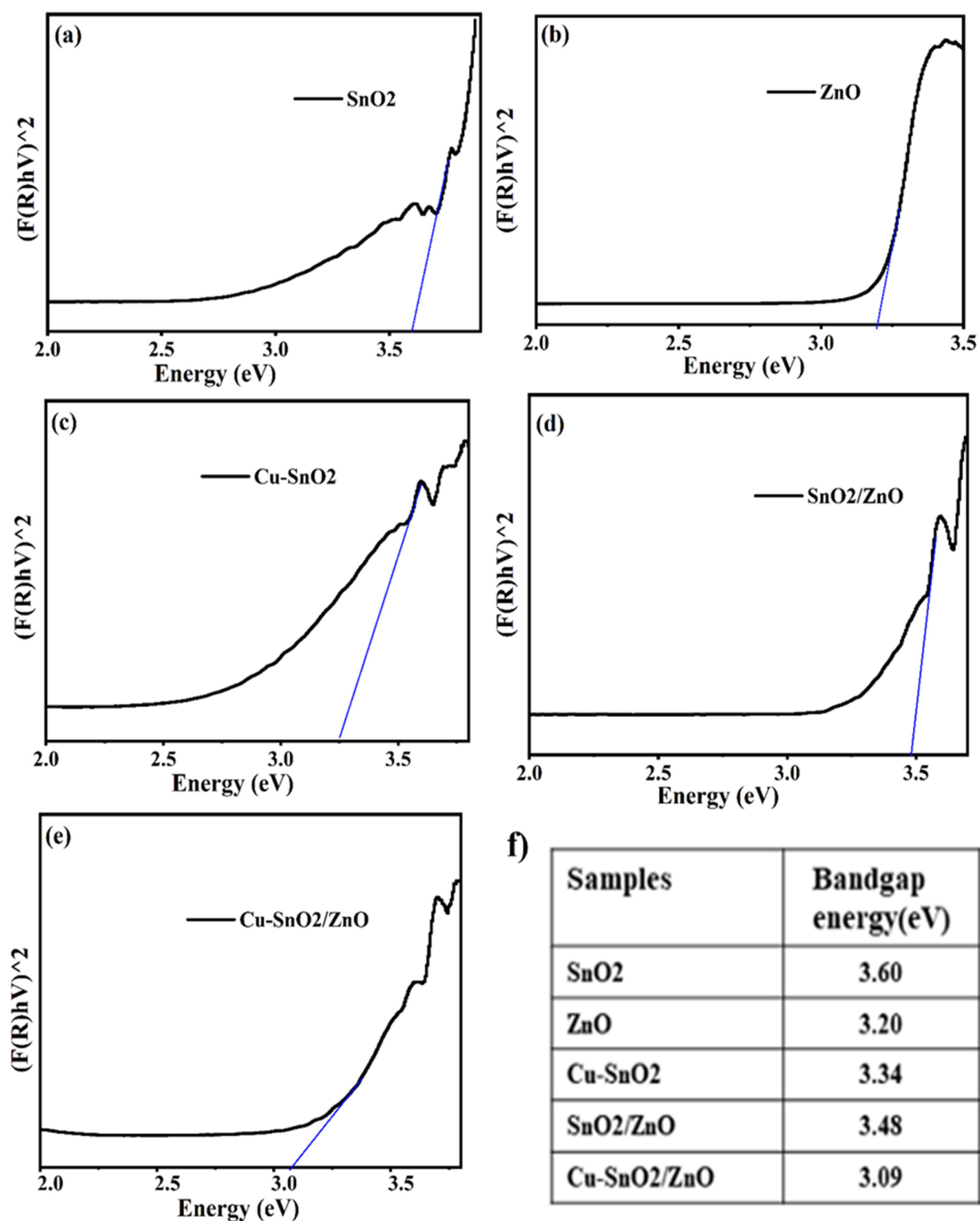


Figure 24: Plots of  $(F(R)h\nu)^2$  versus photon energy( $h\nu$ ) obtained from UV-DRS of (a) SnO<sub>2</sub>, (b) ZnO, (c) Cu-SnO<sub>2</sub>, (d) SnO<sub>2</sub>/ZnO, (e) Cu-SnO<sub>2</sub>/ZnO nanocomposites, and (f) optical band gaps of synthesized samples calcined at 500 °C.

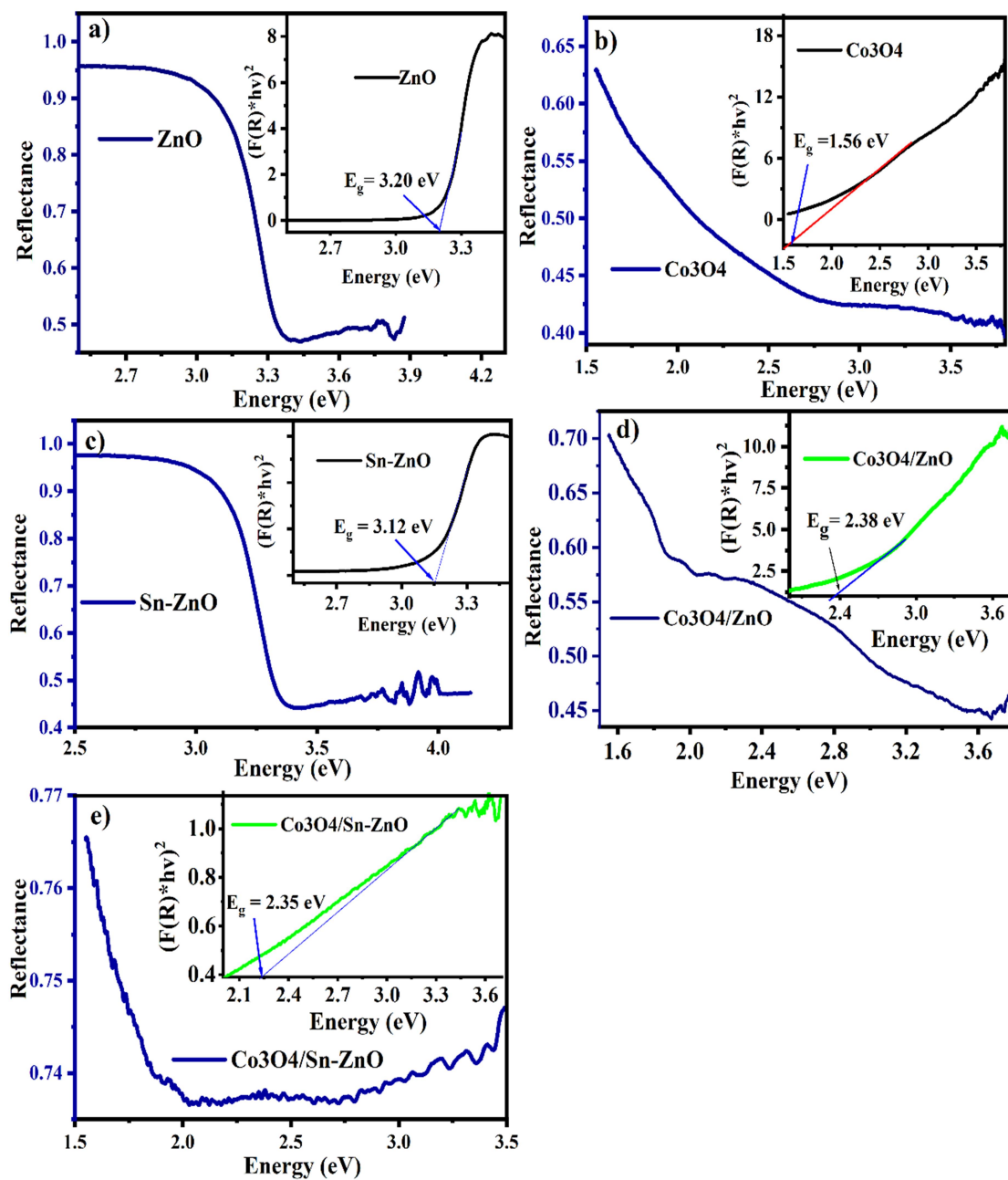


Figure 25: Plots of reflectance and  $(F(R)hv)^2$  versus photon energy( $h\nu$ ) of (a) ZnO (b) Co<sub>3</sub>O<sub>4</sub> (c) Sn-ZnO and (d) Co<sub>3</sub>O<sub>4</sub>/ZnO and (e) Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite, and f) FTIR spectra of ZnO, Co<sub>3</sub>O<sub>4</sub>, Sn-ZnO, Co<sub>3</sub>O<sub>4</sub>/ZnO and Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposites.



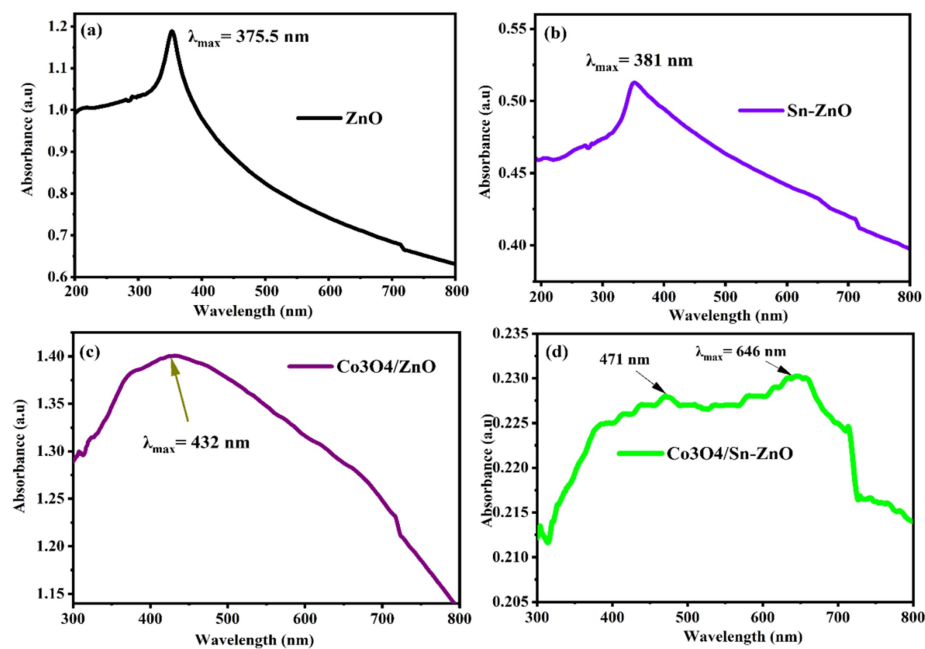


Figure 26: UV-visible absorbance spectra of ZnO and Sn-ZnO nanoparticles, and  $\text{Co}_3\text{O}_4/\text{ZnO}$  and  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposites.

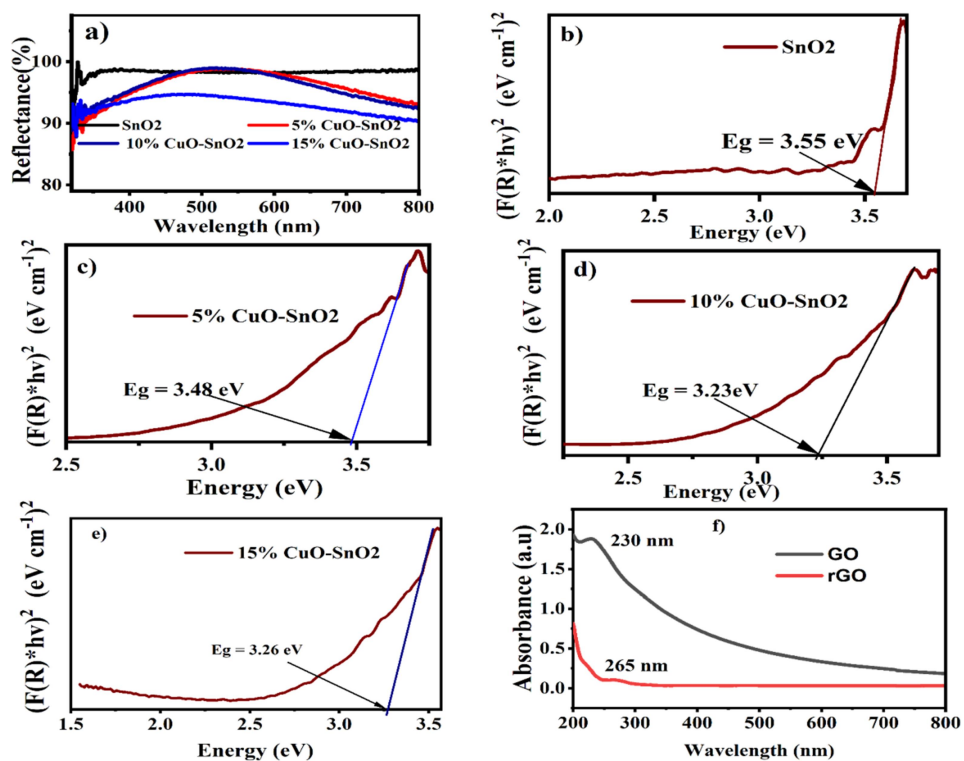


Figure 27: UV-visible diffusive reflectance spectra of a) pure  $\text{SnO}_2$  nanoparticle, b) 5%  $\text{CuO-SnO}_2$  nanoparticle, c) 10%  $\text{CuO-SnO}_2$  nanoparticle, and d) 15%  $\text{CuO-SnO}_2$  nanocomposite, e) UV absorbance of GO and rGO.

#### 4.3 FTIR Analysis of Cu-SnO<sub>2</sub>/ZnO, Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO and CuO-SnO<sub>2</sub>/rGO Nanocomposite

The functional groups and their bonds, and compositions of the synthesized samples were investigated using FTIR spectroscopy. The FTIR spectroscopy measurement showed, in figure 28 (a), the spectra of ZnO, Cu-SnO<sub>2</sub>, SnO<sub>2</sub>/ZnO, and Cu-SnO<sub>2</sub>/ZnO nanocomposites have strong and broad bands at 3496 cm<sup>-1</sup>, 3380 cm<sup>-1</sup>, 3483 cm<sup>-1</sup>, and 3485 cm<sup>-1</sup> peaks that are related to O-H stretching of water molecules reabsorbed on the surface of the synthesized materials, and the strong stretching at 2340 cm<sup>-1</sup> assigned to CO<sub>2</sub> (O = C = O) introduced from the ambient environment (Asaithambi *et al.*, 2021). The absorption of ZnO, SnO<sub>2</sub>/ZnO and Cu-SnO<sub>2</sub>/ZnO nanocomposites at 908 cm<sup>-1</sup>, 906 cm<sup>-1</sup> and 916 cm<sup>-1</sup> corresponds to tetrahedral Zn<sup>2+</sup> ion respectively (Motelica *et al.*, 2023). In Cu-SnO<sub>2</sub> nanoparticles, the absorptions observed at the wavenumber of 1741 cm<sup>-1</sup>, 1367 cm<sup>-1</sup> and 1220 cm<sup>-1</sup> due to C = O, C-O and C-OH stretching respectively (Khatoon *et al.*, 2020). The O-Sn-O stretching vibrations were detected at 461 cm<sup>-1</sup> in SnO<sub>2</sub>, 460 cm<sup>-1</sup> in Cu-SnO<sub>2</sub>, 462 cm<sup>-1</sup> in SnO<sub>2</sub>/ZnO, and 465 cm<sup>-1</sup> in Cu-SnO<sub>2</sub>/ZnO nanocomposite (Felcia & Gnanam, 2017). The FTIR spectra's detection of O-Sn-O and Zn<sup>2+</sup> bonding might further confirm the formation of crystalline phase of the composite as confirmed from XRD results (Felcia & Gnanam, 2017; Horti *et al.*, 2018).

In FTIR spectra demonstrated in figure 28 (b), O-H vibrations of water molecules occurred at 3492.52 cm<sup>-1</sup> and stretching of CO<sub>2</sub> molecules at 2336.83 cm<sup>-1</sup> for ZnO, Co<sub>3</sub>O<sub>4</sub>, Sn-ZnO, Co<sub>3</sub>O<sub>4</sub>/ZnO, and Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite (Bashir *et al.*, 2022). In the FTIR spectra of Co<sub>3</sub>O<sub>4</sub> nanoparticles, stretching vibration occurred at 1617.97 cm<sup>-1</sup>. In Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite, the peaks at 451 cm<sup>-1</sup> and 661 cm<sup>-1</sup> represent stretching vibrations of Co-O and Co-O-Co of Co<sub>3</sub>O<sub>4</sub> nanoparticles, respectively (Prabaharan *et al.*, 2017), 420.41 cm<sup>-1</sup> represents Zn-O (Devi *et al.*, 2019), and 908.27 cm<sup>-1</sup> corresponding to Sn-O (Elci *et al.*, 2018). The FTIR result confirms that the presence of all the expected compositions of Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite.

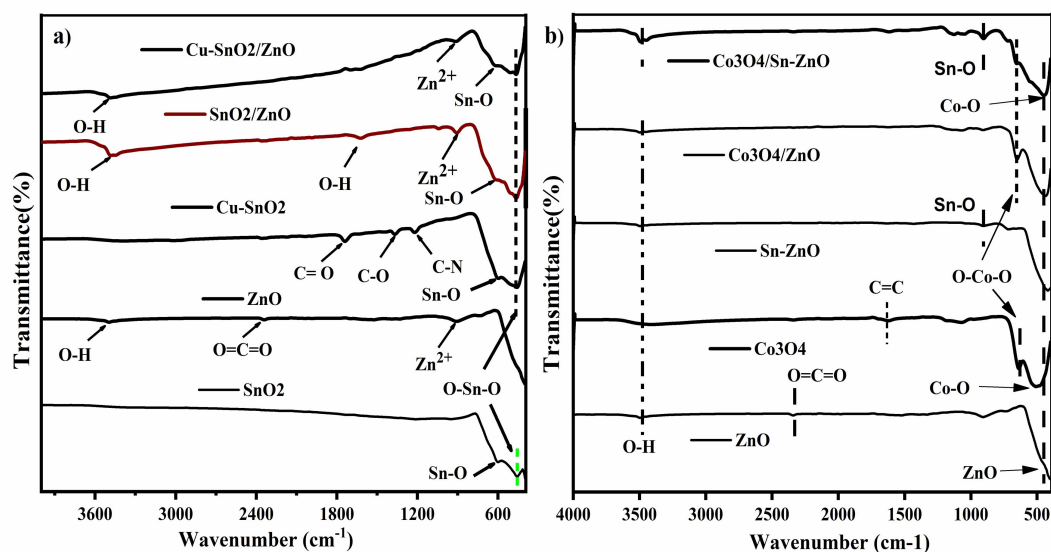


Figure 28: The FTIR spectra of the synthesized samples (a-b).

#### 4.4 PL Analysis Cu-SnO<sub>2</sub>/ZnO, Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO and CuO-SnO<sub>2</sub>/rGO Nanocomposites

The photoluminescence analysis was carried out to identify the emission peaks associated with band-to-band transitions and band-to-defect levels of the photogenerated electrons in the synthesized nanomaterials. The PL spectra shown in figure 29 (a) of SnO<sub>2</sub>, ZnO, Cu-SnO<sub>2</sub>, SnO<sub>2</sub>/ZnO, and Cu-SnO<sub>2</sub>/ZnO nanocomposites were measured at an excitation wavelength of 325 nm. These PL spectra shows emission peaks at 360 nm which is near-to-absorption band edge and minor emission peaks at 378 nm, 411 nm and 482 nm attributed to defects energy level between the bands (Asaithambi *et al.*, 2020). The PL spectra showed that the primary peak of ZnO found in the UV region at 390 nm corresponds to the band-to-band transition, while minor peaks at 416 nm and 441 nm are produced due to induced defects energy states (M. Ramesh *et al.*, 2014). The PL intensities and photogenerated carrier recombination of the Cu-SnO<sub>2</sub>, SnO<sub>2</sub>/ZnO, and Cu-SnO<sub>2</sub>/ZnO nanocomposites all reduced. These decrease in PL intensity and recombination rate of carriers were due geometrical distortions, oxygen vacancies, and an increase in dislocation density in Cu-SnO<sub>2</sub>/ZnO nanocomposite confirmed from the XRD analysis. As a result, the photocatalytic performance could be enhanced.

The PL spectra of ZnO and Sn-ZnO nanoparticles, and Co<sub>3</sub>O<sub>4</sub>/ZnO and Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite were measured at an excitation wavelength of 325 nm and shown in figure 29 (b). The photoluminescence intensity of ZnO nanoparticles is higher than that of Sn-ZnO

nanoparticles,  $\text{Co}_3\text{O}_4/\text{ZnO}$ , and  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite. The higher intensity indicates that the recombination rate might be higher in ZnO than in Sn-ZnO,  $\text{Co}_3\text{O}_4/\text{ZnO}$ , and  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite. In the PL spectra of ZnO, the most intense peak at 390 nm in the UV region corresponds to the band-to-band transition. The weak intensity peaks observed in the visible region at 416 nm and 440 nm might be due to oxygen vacancies, Zn interstitials, or defects (Saikia *et al.*, 2014). In the Sn-doped ZnO nanoparticle, the peak at 356 nm corresponds to a band-to-band transition, whereas the peak at 385 nm could correspond to a transition from the dopant ( $\text{Sn}^{+4}$ ) level to the valance band. When Sn was added to ZnO, the intensity was quenched. This means the substitutional doping of  $\text{Sn}^{+4}$  into the ZnO lattice reduces the band to band as well as the band to defect recombination of photogenerated charge carriers. Moreover, the simultaneous incorporation of  $\text{Co}_3\text{O}_4$  and  $\text{Sn}^{+4}$  into ZnO further quenched the intensity of ZnO, indicating that the separation of photogenerated charge carriers had properly improved. Thus, we conclude that the photocatalytic efficiencies of  $\text{Co}_3\text{O}_4/\text{ZnO}$  and  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposites are better than those of ZnO and Sn-ZnO nanoparticles.

The PL spectra of 5% Cu-SnO<sub>2</sub>, 10 % Cu-SnO<sub>2</sub> and 10 % CuO-SnO<sub>2</sub>, and CuO-SnO<sub>2</sub>/rGO (1% & 2 %) hybrid composite are given in figure 29 (c). In PL spectra, the peak at 360 nm ascribed to the band to band transition of electrons in the synthesized samples whereas other visible peaks observed at 410 nm, 487 nm, might be created due to oxygen vacancies or defects which results the band to defect level, band to acceptor level, or from defect to valance band. The defect could be oxygen vacancies, interstitials, and donor and acceptor levels. In PL analysis, the simultaneous incorporation of CuO and reduced graphene oxide consistently quenched the PL intensity of the host SnO<sub>2</sub>. This might facilitate the redox reaction taking place at the electrode of the supercapacitor, and confirmed that reduction-oxidation reaction could be easily occurred on the electrode so that the pseudocapacitive behavior improved when 10% CuO-SnO<sub>2</sub>/rGO (1% & 2%) hybrid composite used.

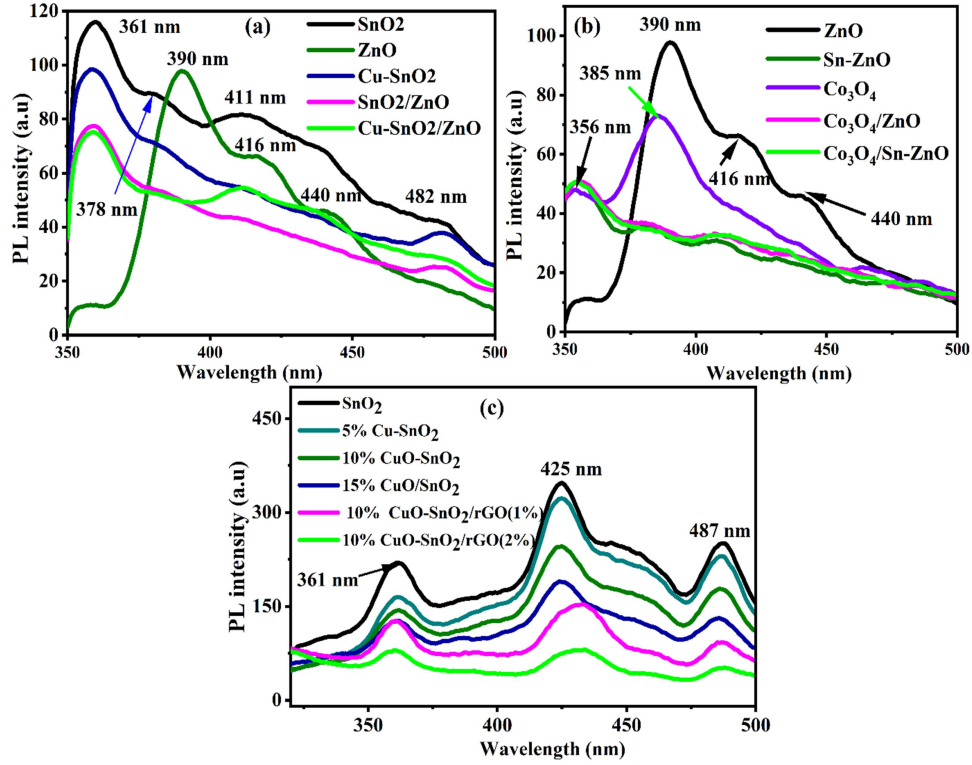


Figure 29: The photoluminescence spectra of the synthesized samples dispersed in DMSO and excited at a wavelength of  $\lambda_{ex} = 325$  nm (a & b) and  $\lambda_{ex} = 265$  nm (c).

#### 4.5 SEM and EDS Analysis of Cu-SnO<sub>2</sub>/ZnO and Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO Nanocomposites

SEM analysis was used to investigate the surface morphology of the synthesized nanomaterials. Figure 30 (a-f) shows SEM images of the synthesized SnO<sub>2</sub>, ZnO, and Cu-SnO<sub>2</sub>, SnO<sub>2</sub>/ZnO, and Cu-SnO<sub>2</sub>/ZnO samples. The morphology of pristine SnO<sub>2</sub> is altered by doping Cu ions and adding ZnO. In SnO<sub>2</sub> nanoparticles, Cu-SnO<sub>2</sub>, SnO<sub>2</sub>/ZnO, and Cu-SnO<sub>2</sub>/ZnO composites, smaller and bigger grains with various irregular morphologies were observed. The bigger grains could be due to the aggregation of smaller crystallites. The EDS measurements for elemental analysis of the synthesized Cu-SnO<sub>2</sub>/ZnO nanocomposite are shown in figure 31 (a). The EDS spectra of the composite show the existence of Cu, Sn, Zn, and O. Moreover, EDS elemental mapping of the sample shows that the Cu, Sn, Zn, and O atoms were present over the whole surface of the Cu-SnO<sub>2</sub>/ZnO nanocomposite, as shown in figure 31 (b-f). Both EDS and elemental mapping assured the formation of the Cu-SnO<sub>2</sub>/ZnO composite. In EDS spectra, the absence of impurities is consistent with XRD result.

The morphology of ZnO, Co<sub>3</sub>O<sub>4</sub> and Sn-ZnO nanoparticles, Co<sub>3</sub>O<sub>4</sub>/ZnO and Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposites observed by SEM are shown in figure 32. Figure 32 (a) depicts agglomerated spherical ZnO nanoparticles. Figure 32 (b) shows agglomerated spherical Co<sub>3</sub>O<sub>4</sub> nanoparticles; figure 32 (c) shows aggregated particles of Sn-ZnO; and figure 32 (d) depicts that the spherical and rode-like morphologies were observed in the Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite. Aggregation and agglomeration of particles are also observed on the surface of the Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite. The EDS spectra in figure 32 (f) indicated that all of the components of the Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposites were present in the spectra with no extraneous impurities. In the EDS spectra, tin (Sn), zinc (Zn), cobalt (Co), and oxygen (O) are identified. This verifies that the atoms were present as expected during the synthesis. Furthermore, the purity of peaks in the EDS spectrum was consistent with the tidy XRD pattern produced for the nanocomposite. In the Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite, the individual color mappings of O, Sn, Zn, and Co are shown in figure 32 (h–k). Platinum (Pt) peaks might be introduced during coating for EDS sample preparation. All these constituent atoms are distributed uniformly across the surface of the Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite. This also provides further confirmation for the formation of a Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite.

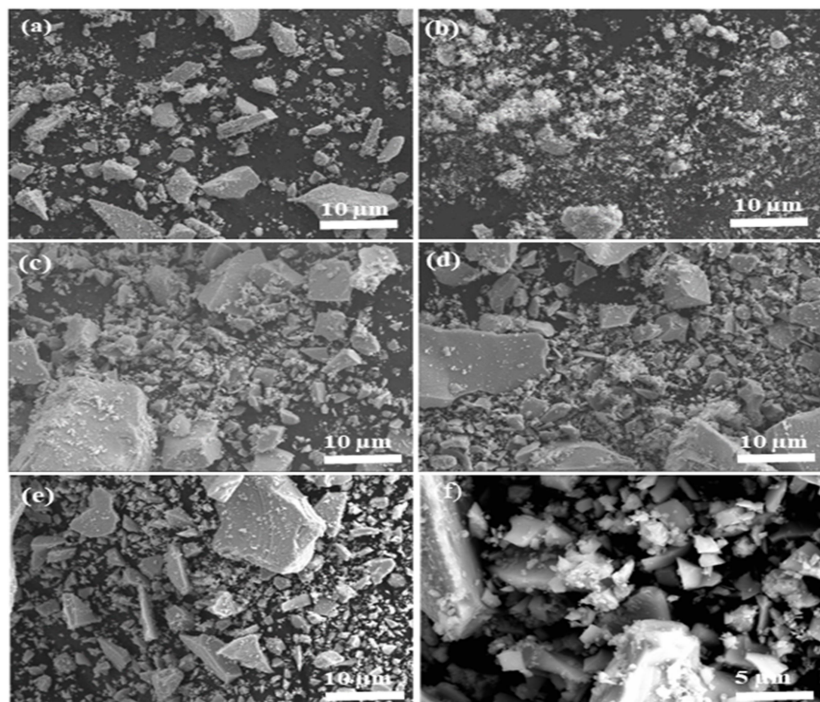


Figure 30: SEM images of magnification of 1.00 K × (a) SnO<sub>2</sub> nanoparticles, (b) ZnO nanoparticles, (c) Cu-SnO<sub>2</sub> nanoparticles, (d) SnO<sub>2</sub>/ZnO nanocomposite and (e & f) Cu-SnO<sub>2</sub>/ZnO nanocomposite at different scale.



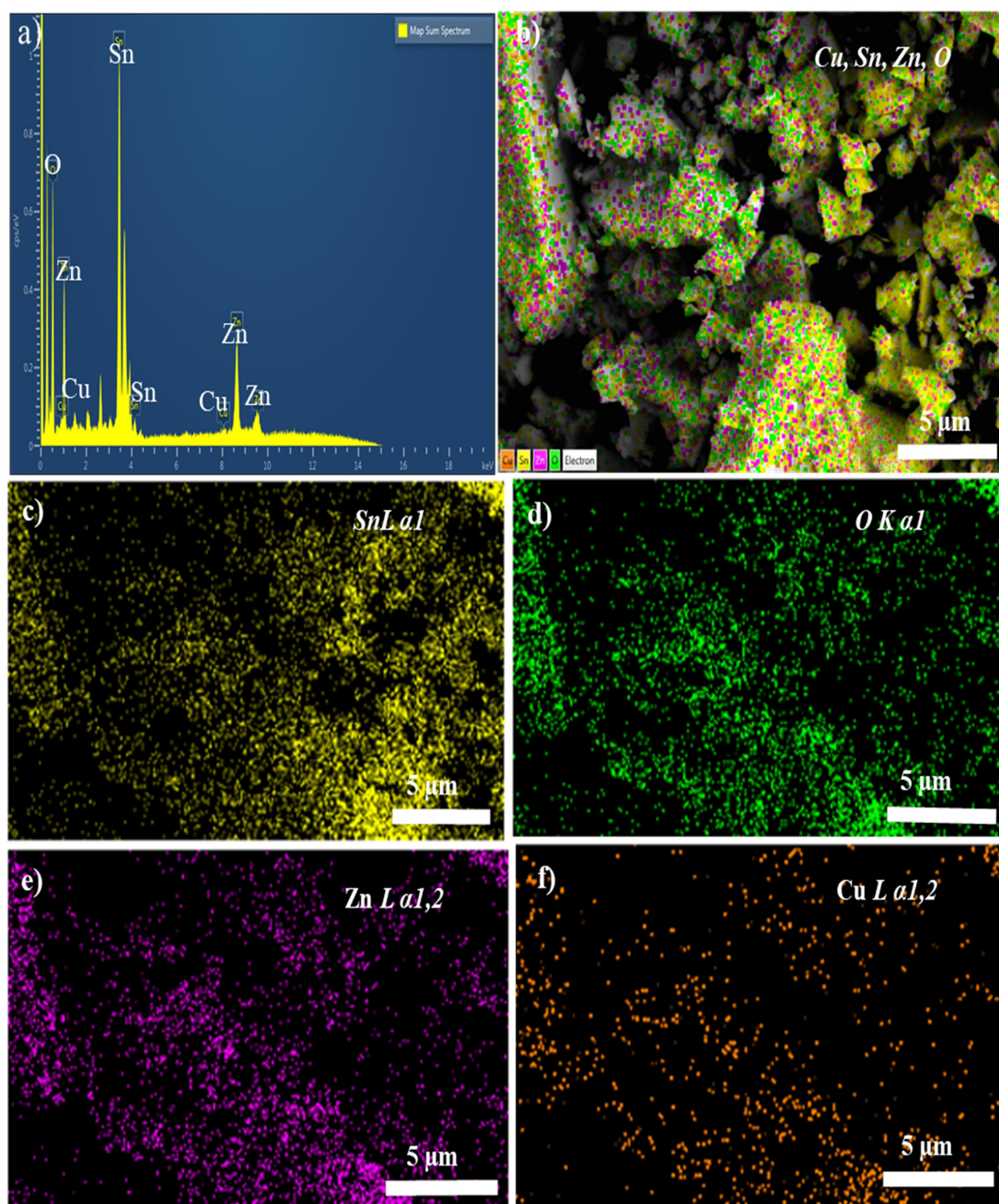


Figure 31: (a) EDS spectra and (b-f) elemental mapping of the synthesized Cu-SnO<sub>2</sub>/ZnO composite samples.

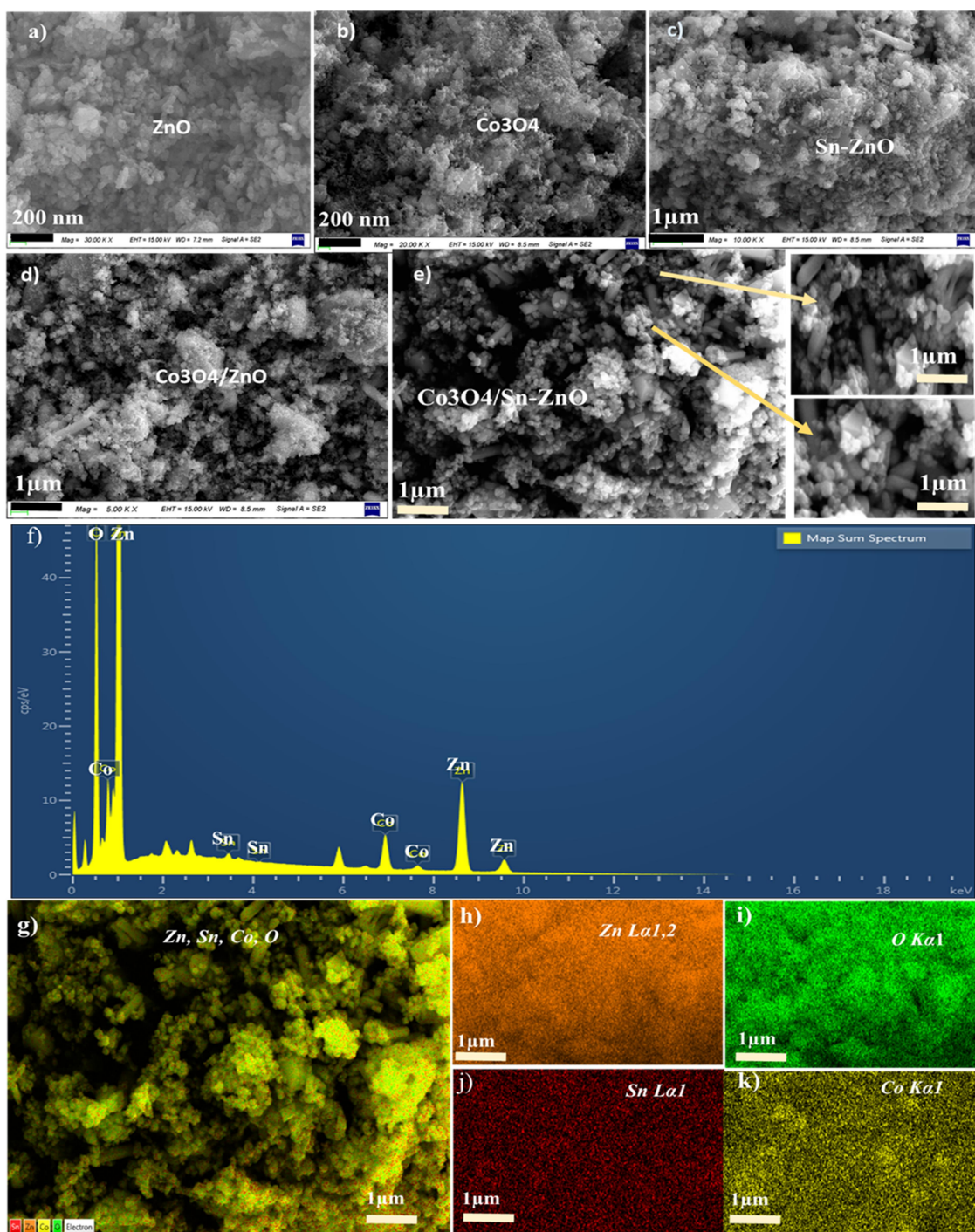


Figure 32: SEM images of (a) ZnO nanoparticles, (b) Co<sub>3</sub>O<sub>4</sub> nanoparticles, (c) Sn-ZnO nanoparticles, and (d) Co<sub>3</sub>O<sub>4</sub>/ZnO and (e) Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite, (f) EDS spectra and (g) elemental mapping distribution of Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite (h) Tin (Sn) (i) Cobalt (Co) (j) Zinc (Zn) (k) Oxygen (O).



#### 4.6 TEM and HRTEM Analysis Cu-SnO<sub>2</sub>/ZnO and Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO Nanocomposite

The high-resolution transmission electron microscope image of the sample is displayed in figure 33(a-c). These HRTEM images clearly showed tetragonal and hexagonal structures of SnO<sub>2</sub> and ZnO, respectively, which agrees with the XRD result. The parallel lattice fringes with d-spacings equal to 2.65 Å and 2.86 Å correspond to the (101) crystal plane of the tetragonal SnO<sub>2</sub> and (100) plane of the hexagonal ZnO, respectively, as shown in figure 33 (c-e). The values of d-spacing determined from the inverse fast Fourier transform (IFFT) profile using Gatan digital micrograph software, and the SnO<sub>2</sub> (101) sample profile is shown in figure 33 (f). The HRTEM images showed that Cu-SnO<sub>2</sub>/ZnO nanocomposite contains different grains sizes indicating that it is a polycrystal. In Cu-SnO<sub>2</sub>/ZnO nanocomposite, the smaller size corresponds to Cu-SnO<sub>2</sub> whereas the larger size represents the ZnO nanoparticles. This was because in addition to the impact of Cu ion the high activation energy of SnO<sub>2</sub> restricts its nanograins growth whereas the grain size of ZnO was bigger due to its low activation energy as reported in literature (Hong *et al.*, 2021). In figure 33 (g), the small angle electron diffraction (SAED) fringes further confirmed that Cu-SnO<sub>2</sub>/ZnO nanocomposite is a polycrystalline material. The interplanar spacings of 0.265 nm and 0.286 nm matched with miller indices of tetragonal rutile SnO<sub>2</sub> (101) shown in figure 33 (d) and ZnO (100) in figure 33 (e). This further confirms the XRD results.

The TEM image of Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite is given in figure 34 (a). The average particle size estimated was about 45 nm, and the particle size distribution ranges from 21 nm to 79 nm, as shown in figure 34 (b). The TEM and HRTEM images in figure 34 (c and d) depict that the crystal phases of both Co<sub>3</sub>O<sub>4</sub> and ZnO are presented in the Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite. The cubic spinel and hexagonal wurtzite structures correspond to Co<sub>3</sub>O<sub>4</sub> and ZnO, respectively. The co-existence of both Co<sub>3</sub>O<sub>4</sub> and ZnO phases assured the formation of Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite, which agreed very well with the XRD result. In the small area electron diffraction (SAED) in figure 34 (d (inset)), the bright ring-like fringes confirm that the nanocomposite is polycrystalline. The FFT and IFFT of ZnO and Co<sub>3</sub>O<sub>4</sub> nanoparticles with the corresponding lattice spacing given in figure 34 (e and f) are obtained from the HRTEM image given in figure 34 (d). In figure 34 (e (inset)), the lattice distortion observed from the IFFT image might be the effect of Sn<sup>4+</sup> as a dopant. The lattice spacing estimated from the HRTEM image agrees with the XRD result.

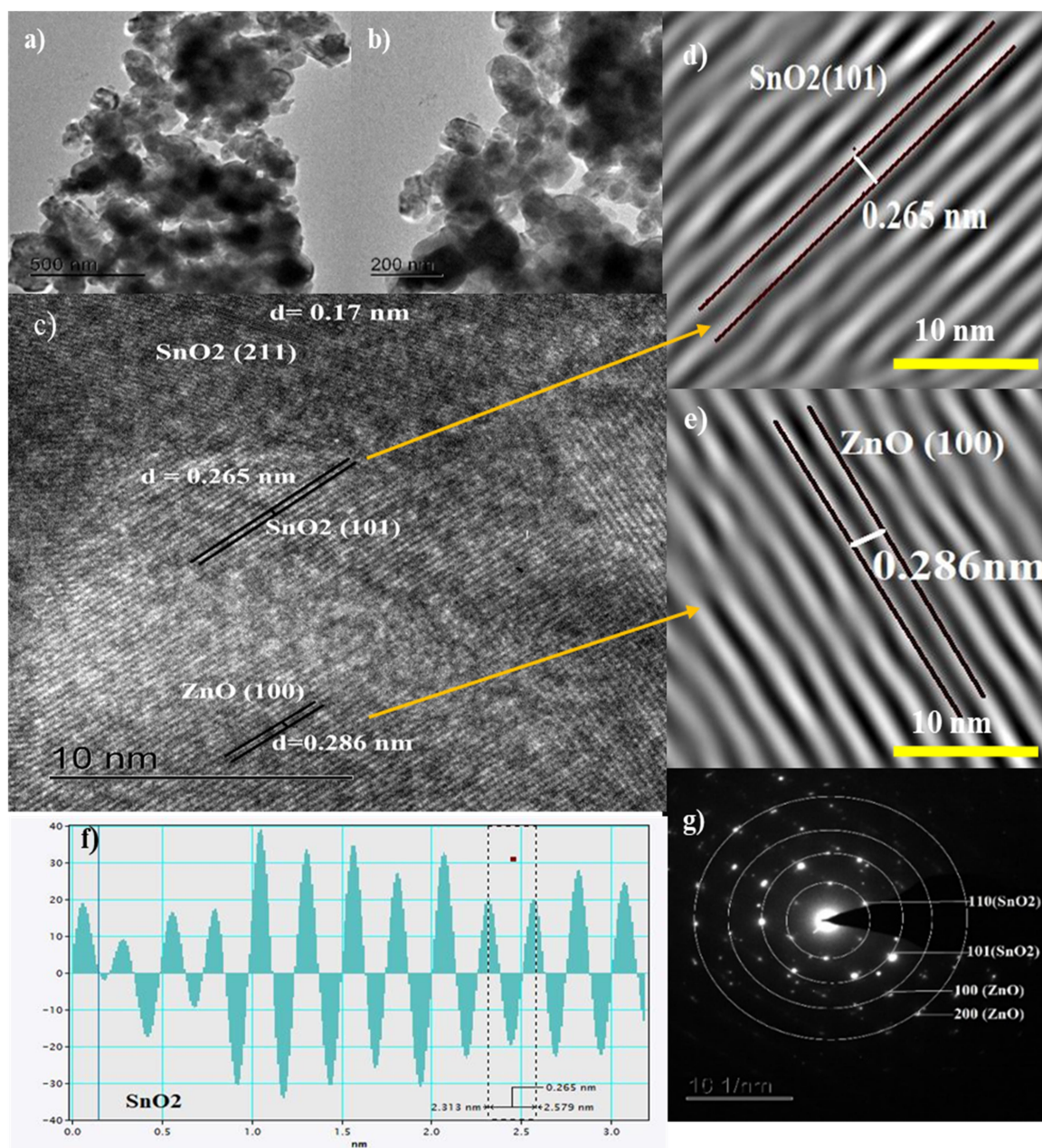


Figure 33: TEM images of Cu-SnO<sub>2</sub>/ZnO nanocomposites: (a-b) at different magnification scale, (c) Corresponding high-resolution TEM image or magnified fringes, (d) FFT with d-spacing of SnO<sub>2</sub> (101), (e) FFT with d-spacing of ZnO (100), (f) profile of IFFT of SnO<sub>2</sub>(101) and (g) SAED pattern.

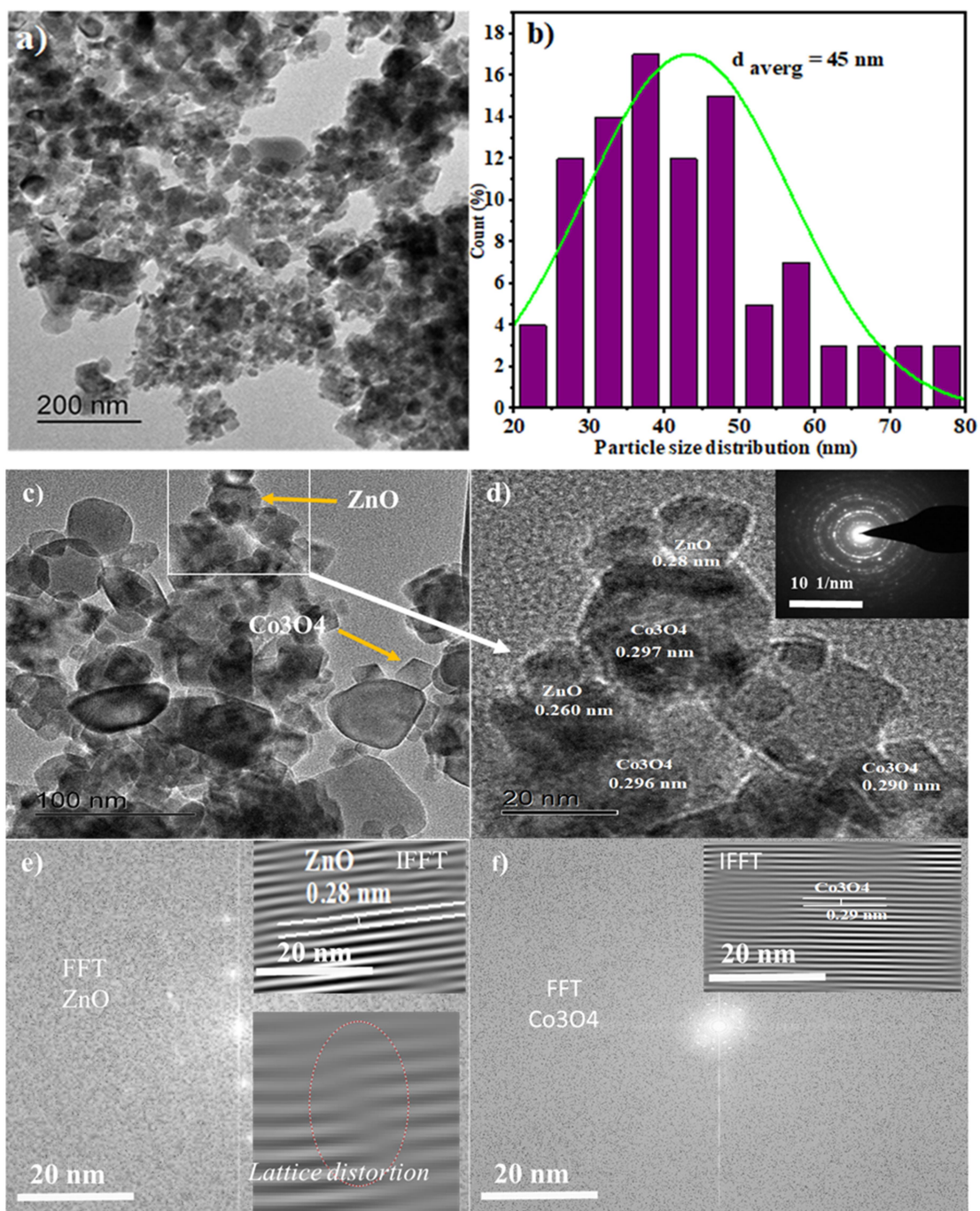


Figure 34: (a) TEM image and (b) histogram of particle size distribution fitted with a Gaussian distribution curve for  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite; (c & d) high-resolution transmission electron microscope (HRTEM) image at different magnification scales; and selected area electron diffraction (SAED) inset in (d), and FFT and their corresponding IFFT of (e) ZnO and (f)  $\text{Co}_3\text{O}_4$  of  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite.

## 4.7 Cu-SnO<sub>2</sub>/ZnO Composite Photocatalyst for Degradation of Methylene Blue Dye

The photocatalytic activity of SnO<sub>2</sub>, Cu-SnO<sub>2</sub>, SnO<sub>2</sub>/ZnO, and ZnO/Cu-SnO<sub>2</sub> nanocomposite were studied after optimization of the pH and catalyst dosage using methylene blue under illumination of visible light. The optimization was first done for Cu-SnO<sub>2</sub>/ZnO nanocomposite which is the narrower bandgap photocatalyst. Using the collected spectroscopic data, the photocatalytic efficiency of the methylene blue dye for the photocatalysts were calculated using (eq. (3.16)). Moreover, using the Langmuir-Hinshelwood model, the photocatalytic rate constant values of the photocatalysts at low MB concentrations was determined by using eq. (3.17).

### 4.7.1 Optimization of Operational Factors for Cu-SnO<sub>2</sub>/ZnO Composite Photocatalyst

#### 4.7.1.1 Effect of pH

The adsorption of MB dye molecules on the Cu-SnO<sub>2</sub>/ZnO photocatalyst surface may be affected by pH variations. The photocatalytic experiment was performed in the acidic, neutral, and basic where the pH is 4, 7, and 10, respectively. Figure 35 (a-c) shows the absorbance vs. wavelength of MB dye at the pH of 4, 7, and 10 solutions. When the light illumination time gets longer during the photocatalysis the absorbance peak decreases more for the solution with pH 10; it confirms that the concentration of MB dye decreases as shown in figure 35(d). The photocatalytic efficiency is linearly increased with light irradiation time for pH values of 4, 7, and 10, as shown in figure 36 (a-c). The degradation efficiency of Cu-SnO<sub>2</sub>/ZnO nanocomposite for degradation of MB dye is 41.4, 48, and 78% for pH 4, 7, and 10, respectively.

Figure 36 (d) also displays the photocatalytic degradation rate constants. The photocatalytic efficiency and rate constant are higher at the pH equal to 10 compared to 4 and 7. The high degradation efficiency for the cationic MB dye at a pH of 10 was due to the formation of more OH<sup>-</sup> radicals in the solution. Moreover, Due to electrostatic forces and the positive charge on the surface of MB dye, the dye adsorption on the surface of the catalyst and degradation may occur more in basic media than in neutral or acidic media.



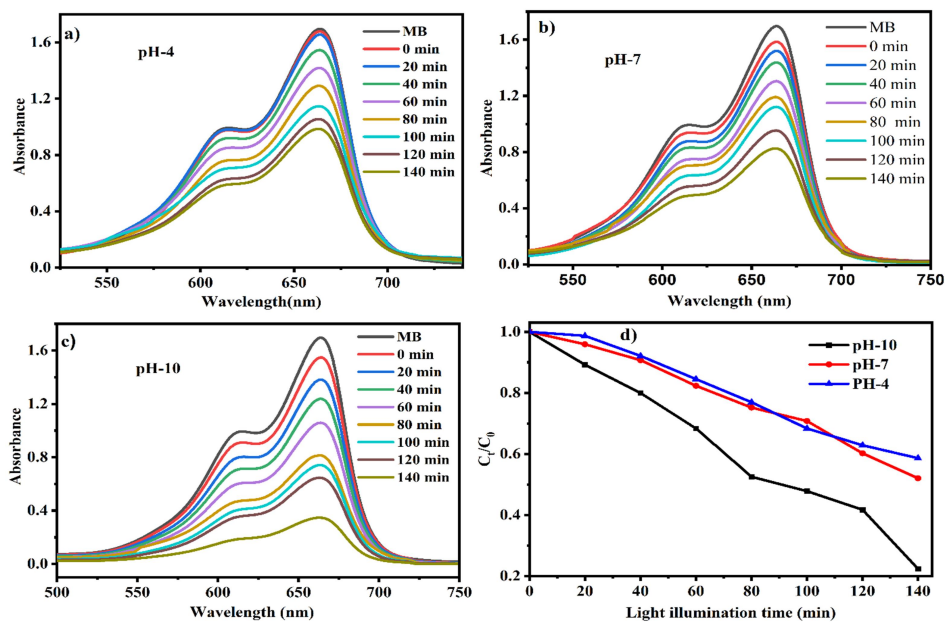


Figure 35: UV-vis spectra of MB dye solutions in 20 min intervals at (a) pH = 4, (b) pH = 7, and (c) pH = 10; (d) photocatalytic degradation of MB versus light illumination time up to 140 min at pH 4, 7 and 10.

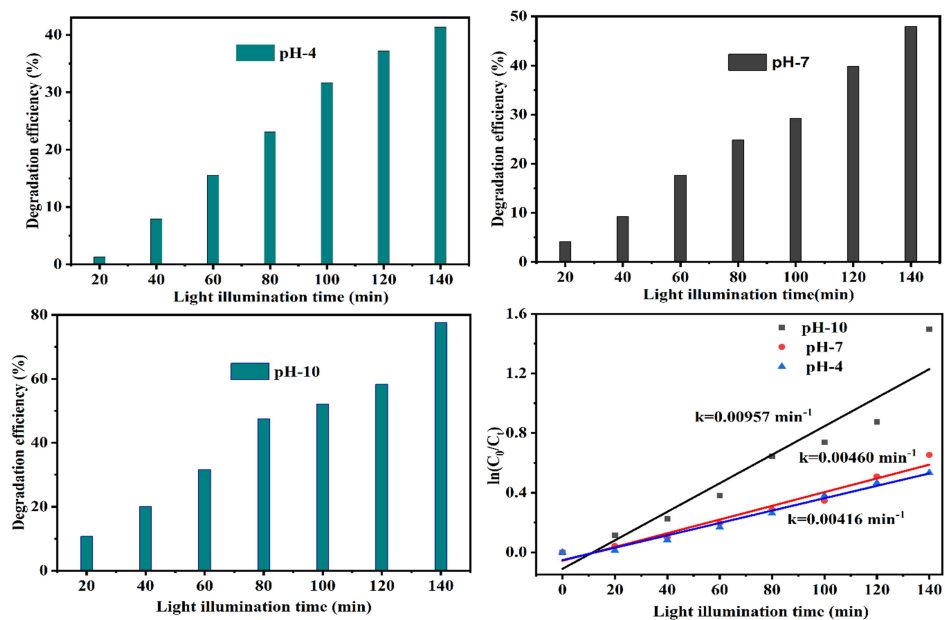


Figure 36: Degradation efficiency of MB dye at the value of (a) pH=4 (b) pH=7 (c) pH=10 for the Cu-SnO<sub>2</sub>/ZnO photocatalyst, and (d) graph of  $\ln(C_0/C_t)$  versus light illumination time for 4, 7 and 10 of Cu-SnO<sub>2</sub>/ZnO photocatalysts.

#### 4.7.1.2 Effect of Catalyst Dosage

Figure 37 (a-d) shows the photocatalytic MB dye degradation at various catalyst doses measured for 140 min of visible light irradiation. The MB dye absorbance peak gradually decreases as the illumination time gets longer. The photocatalytic degradation efficiency for Cu-SnO<sub>2</sub>/ZnO catalyst dosages of 15 mg, 30 mg, and 50 mg is 63.4%, 69.3 %, and 78 %, respectively. The slope of the linearly fitted graph versus light illumination time, in figure 38 (d), yields the photocatalytic degradation rate constants of Cu-SnO<sub>2</sub>/ZnO photocatalyst for 15 mg, 30 mg, and 50 mg catalyst dose given as 0.00670 min<sup>-1</sup>, 0.00842 min<sup>-1</sup>, and 0.00957 min<sup>-1</sup>, respectively. The photocatalytic degradation effectiveness increased as the catalyst dose increased due to the density of active site enhancement in the Cu-SnO<sub>2</sub>/ZnO photocatalyst absorption and charge carrier density (Thota *et al.*, 2014). Moreover, more electrons generated in the conduction band result in more formation of oxygenated species, and more holes created in the valance band also result in more concentration of OH<sup>-</sup> radicals on the Cu-SnO<sub>2</sub>/ZnO photocatalyst surface. Therefore, this enhancement of the density of the active site and photogenerated charge carrier results in enhanced dye degradation performance for MB dye.

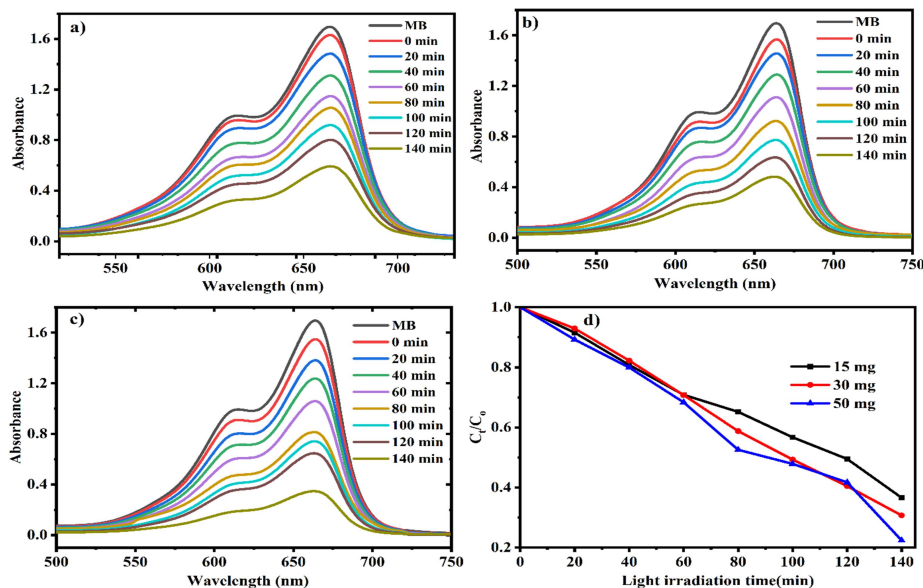


Figure 37: UV-vis absorbance spectra shows the effect of catalyst dose on the degradation of MB for (a) 15 mg (b) 30 mg and (c) 50 mg of Cu-SnO<sub>2</sub>/ZnO composite catalyst, and (d) graph of maximum absorbance versus light illumination time in minutes for 15 mg, 30 mg and 50 mg of Cu-SnO<sub>2</sub>/ZnO composite catalyst.

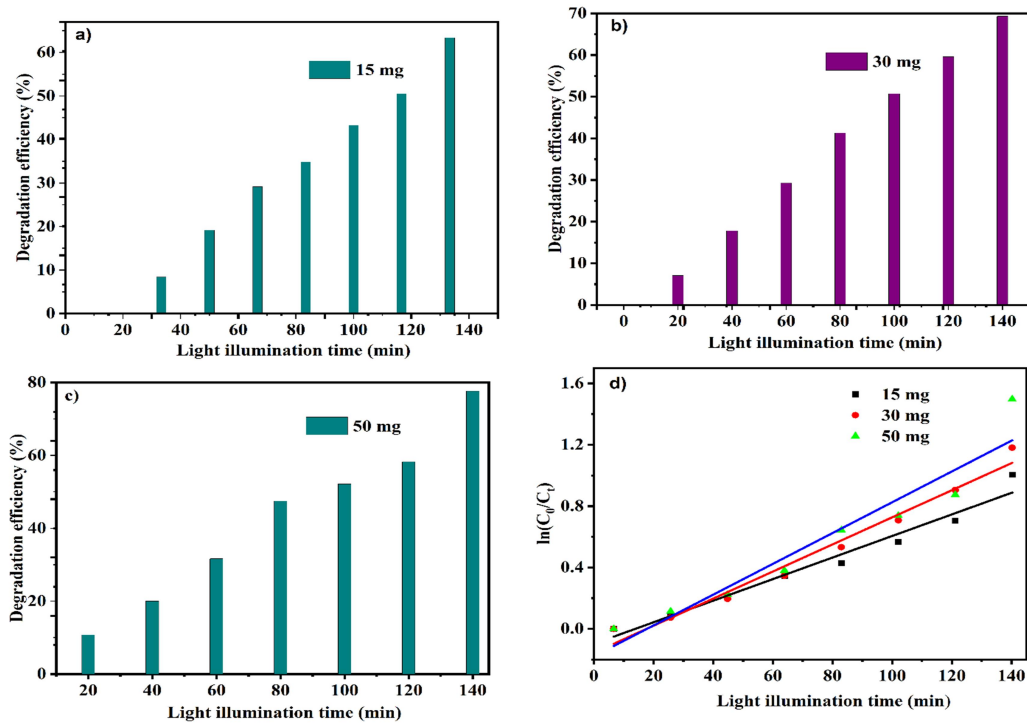


Figure 38: Degradation efficiency of MB dye for (a) 15 mg, (b) 30 mg, (c) 50 mg Cu-SnO<sub>2</sub>/ZnO photocatalyst, and (d) graph of  $\ln(C_0/C_t)$  vs light illumination time for 15 mg, 30 mg and 50 mg of Cu-SnO<sub>2</sub>/ZnO photocatalysts.

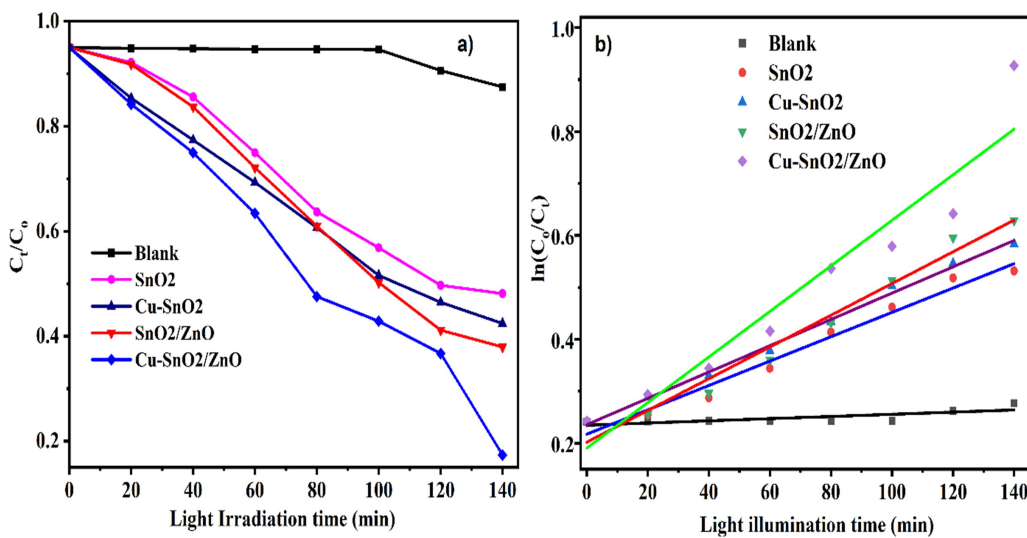


Figure 39:(a) Plot of  $C_0/C_t$  versus light illumination time and (b) plot of  $\ln(C_0/C_t)$  versus light illumination time for blank (without catalyst) and samples SnO<sub>2</sub>, Cu-SnO<sub>2</sub>, SnO<sub>2</sub>/ZnO and Cu-SnO<sub>2</sub>/ZnO photocatalysts.

#### 4.7.2 Degradation Kinetics of Cu-SnO<sub>2</sub>/ZnO Composite Photocatalyst

The photocatalytic activity of SnO<sub>2</sub>, Cu-SnO<sub>2</sub>, SnO<sub>2</sub>/ZnO, and Cu-SnO<sub>2</sub>/ZnO nanocomposites were investigated. In the blank experiment, illuminated without catalyst, depicted in figure 39 (a & b) black color curve, the degradation of MB dye was low and not significantly degraded after 140 min implying that the photolysis process has a negligible contribution to the removal of methylene blue dye. Moreover, the dark reaction with the catalyst was also poor, which indicates the adsorption of MB dye in the photocatalyst surface is small. Light reaction with the presence of the catalyst, in figure 39 (a & b), shows a higher degradation rate of MB dye.

Up on addition of SnO<sub>2</sub>, Cu-SnO<sub>2</sub>, SnO<sub>2</sub>/ZnO, and Cu-SnO<sub>2</sub>/ZnO nanocomposite photocatalysts with the assistance of visible light, the absorbance peak of MB dye at 664 nm was slowly quenched with increasing light irradiation time. Cu-SnO<sub>2</sub> nanoparticles, SnO<sub>2</sub>/ZnO, and Cu-SnO<sub>2</sub>/ZnO nanocomposite photocatalyst showed higher degradation efficiencies and degradation rate constants than the pristine SnO<sub>2</sub> as indicated in Table 4 (Asaithambi *et al.*, 2021). The Cu-SnO<sub>2</sub>/ZnO nanocomposite revealed a higher degradation efficiency of 78 % after an illumination time of 140 minutes than others. It might be the formation of defects in the host materials than others, as confirmed by the XRD and PL analysis. Moreover, the Cu ion in the host decreases the crystallite size and bandgap, increases the density of defects, and improves the Cu-SnO<sub>2</sub>/ZnO photocatalytic MB dye degradation activities.

Table 4: Shows the photocatalytic efficiency and the degradation rate constants for SnO<sub>2</sub>, Cu-SnO<sub>2</sub> and SnO<sub>2</sub>/ZnO and Cu-SnO<sub>2</sub>/ZnO photocatalysts.

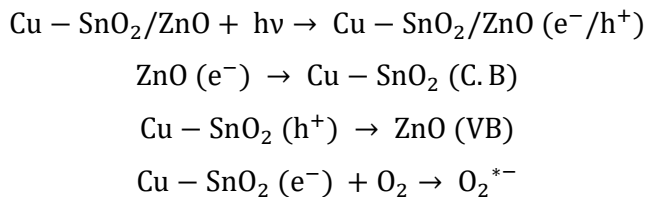
| Photocatalysts           | Photocatalytic efficiency (%) | Photodegradation rate constant, k ( x 10 <sup>-4</sup> min <sup>-1</sup> ) |
|--------------------------|-------------------------------|----------------------------------------------------------------------------|
| Blank (without catalyst) | 7.5                           | 4.573                                                                      |
| SnO <sub>2</sub>         | 47                            | 51.2                                                                       |
| Cu-SnO <sub>2</sub>      | 53                            | 55.3                                                                       |
| SnO <sub>2</sub> /ZnO    | 57                            | 66.7                                                                       |
| Cu-SnO <sub>2</sub> /ZnO | 78                            | 95.7                                                                       |



### 4.7.3 Degradation Mechanism of Cu-SnO<sub>2</sub>/ZnO Nanocomposite Photocatalyst

The proposed photocatalytic MB dye degradation mechanism for the best photocatalyst, Cu-SnO<sub>2</sub>/ZnO nanocomposite, is given in figure 40. The band edge position values of Cu-SnO<sub>2</sub> and ZnO can be calculated using equations (4.18 & 4.19) (Asaithambi *et al.*, 2021). The summarized  $X, E_g, E_{VB}$  and  $E_{CB}$  values are given in Table 5. Based on these calculated values, the MB dye degradation mechanism was proposed. It has been known that the negative charges carriers (or electrons) could be transferred from low potential to high potential whereas the positive charge carriers (or holes) move in the opposite directions. Therefore, the conduction band edge potential of ZnO ( $-0.31\text{ eV}$ ) and Cu-SnO<sub>2</sub> ( $-0.080\text{ eV}$ ) causes the electrons to move from the conduction band of ZnO to the conduction band of Cu-SnO<sub>2</sub> whereas the high valance band edge potential of SnO<sub>2</sub> ( $3.42\text{ eV}$ ) and ZnO ( $2.89\text{ eV}$ ) causes the holes to diffuse towards the valance band of ZnO. The decrease of rapid carrier recombination results from the trapping of electrons at the conduction band of Cu-SnO<sub>2</sub> and holes at the valance band of ZnO. Doping Cu ions into SnO<sub>2</sub> reduces its band gap, which in turn facilitates the formation of electron-hole pairs when the catalyst is exposed to visible light. Moreover, Cu-SnO<sub>2</sub> has a higher valance band edge potential than ZnO, therefore the holes never diffuse back into the valance band and instead these carriers on the valance band side undergone a reaction with water to form OH<sup>-</sup> radical on the surface of ZnO.

Figure 40 shows that during the photocatalytic reaction, the oxygen molecules received from the air or water combine with the freely mobile photogenerated electrons in Cu-SnO<sub>2</sub> to form peroxide radicals O<sub>2</sub><sup>\*-</sup>. This reaction is known as reduction reaction. While the photogenerated holes in the valance band of ZnO react with water produces H<sup>+</sup> and OH<sup>\*</sup> in a chemical reaction known as reduction reaction. The hydroxyl radicals are a stronger degrading species having a high redox potential nearly equals to valance band edge potential ( $2.89\text{ eV}$ ). The summarized charge transfer and creation mechanisms of the active degrading species or the redox reaction during the photocatalytic processes are given below:



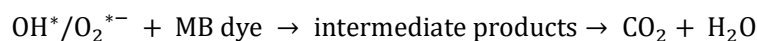
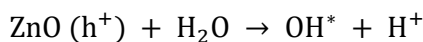


Table 5: Shows the absolute electronegativity(X), band gap energy  $E_g$  calculated from UV-DRS spectra, the conduction band ( $E_{CB}$ ) and valance band ( $E_{VB}$ ) edge potentials for  $\text{SnO}_2$ ,  $\text{Cu-SnO}_2$  and  $\text{ZnO}$ .

| Catalysts         | X(eV) | $E_g$ (eV) | $E_{VB}$ (eV) | $E_{CB}$ (eV) |
|-------------------|-------|------------|---------------|---------------|
| ZnO               | 5.79  | 3.20       | 2.89          | -0.31         |
| $\text{SnO}_2$    | 6.25  | 3.60       | 3.55          | -0.05         |
| $\text{Cu-SnO}_2$ | 6.25  | 3.34       | 3.42          | -0.08         |

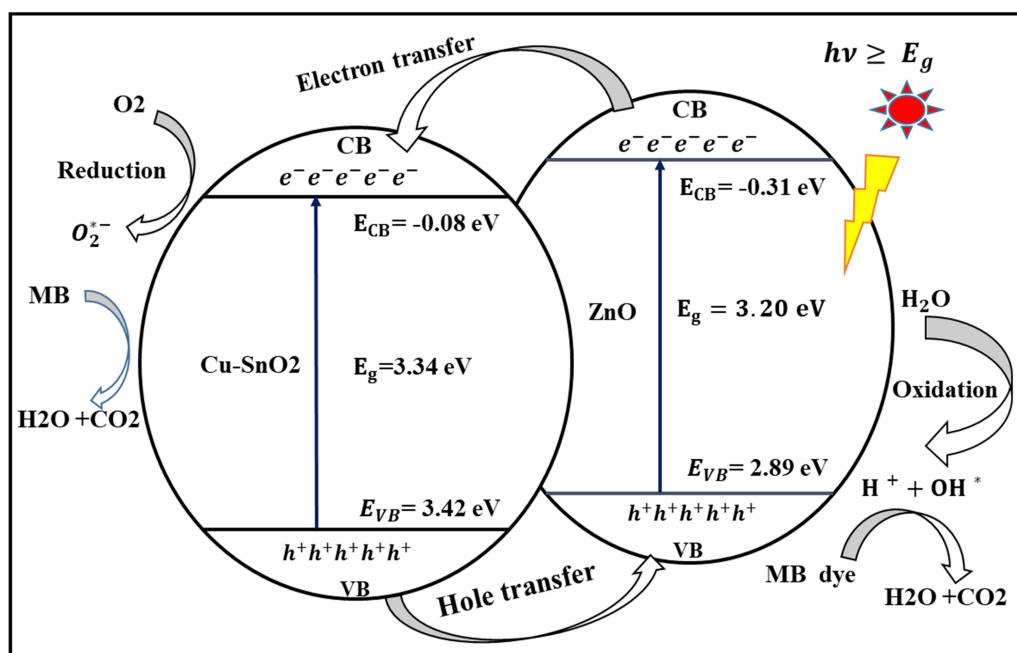


Figure 40: Proposed Photocatalytic mechanism for the MB dye degradation using  $\text{Cu-ZnO/SnO}_2$  photocatalyst.

#### 4.8 Photocatalytic Performance of $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$ Nanocomposite Photocatalyst

##### 4.8.1 Photocatalytic Efficiency and Degradation Rate Constants of synthesized Nanocomposites

The photocatalytic performance measurement was performed using 30 mg of catalysts and a 10 ppm MB dye concentration at room temperature in a basic medium (pH = 9) to identify

the best catalyst. Among all the synthesized samples  $\text{Co}_3\text{O}_4/\text{ZnO}$  and  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite shown the highest degradation performance and optimization was done only for the best  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite catalyst. The absorbance versus wavelength recorded using UV-visible spectroscopy during the photocatalytic degradation process of MB dye is given in figure 41. In photolysis (without catalyst), the absorbance was not decreased, suggesting that MB dye did not degrade by illumination of visible light alone in 100 minutes of illumination time, as depicted in figure 41 (a) (Krobthong *et al.*, 2023). The adsorption of MB dye on the ZnO and  $\text{Co}_3\text{O}_4$  surface was lower than that of Sn-ZnO nanoparticles and  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite when stirred for 40 minutes in the dark. Actually, no significant difference was recorded in adsorbing MB dye on the surface of the synthesized samples in dark. As observed in figure 41 (b-f), the decrease in absorbance of MB dye was higher in  $\text{Co}_3\text{O}_4/\text{ZnO}$  and  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite than in ZnO,  $\text{Co}_3\text{O}_4$  and Sn-ZnO nanoparticles under irradiation of visible light for 100 minutes. From the graph shown in figure 42 (a), a higher decrease in the concentration of MB dye was observed in Sn-ZnO nanoparticles,  $\text{Co}_3\text{O}_4/\text{ZnO}$ , and  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite as compared to pure ZnO and  $\text{Co}_3\text{O}_4$  nanoparticles. Figure 42 (b & c) also showed that the photocatalytic efficiencies for all synthesized samples increase with irradiation time. Using equation (3.16), the photocatalytic efficiency of ZnO,  $\text{Co}_3\text{O}_4$  and Sn-ZnO nanoparticles,  $\text{Co}_3\text{O}_4/\text{ZnO}$ , and  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite is given as 50.33 %, 65.94 %, 75.33 %, 93.76 %, and 94.32 %, respectively.

Moreover, using the Langmuir-Hinshelwood model, the photocatalytic rate constant values of the photocatalysts at low MB concentrations were determined by using equation (3.17). The graph of  $\ln(C_0/C_t)$  versus light illumination time of blank (without catalyst), ZnO,  $\text{Co}_3\text{O}_4$ , Sn-ZnO,  $\text{Co}_3\text{O}_4/\text{ZnO}$ , and  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite is given in figure 42 (d). The degradation rate constants obtained from the slope of the linearly fitted graph are given as  $0.0000381 \text{ min}^{-1}$ ,  $0.00662 \text{ min}^{-1}$ ,  $0.01152 \text{ min}^{-1}$ ,  $0.01443 \text{ min}^{-1}$ ,  $0.02599 \text{ min}^{-1}$ , and  $0.02844 \text{ min}^{-1}$  for blank (without catalyst), ZnO,  $\text{Co}_3\text{O}_4$ , Sn-ZnO nanoparticles,  $\text{Co}_3\text{O}_4/\text{ZnO}$ , and  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposites, respectively. The highest photocatalytic efficiency and rate constant obtained for  $\text{Co}_3\text{O}_4/\text{ZnO}$  and  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite were due to the narrower band gap and higher quenching of the photoluminescence intensity. The narrow bandgap obtained from Uv-DRS was associated with the harvesting of more visible light, whereas the higher quenching of intensity observed in PL confirmed a lower recombination rate of charge carriers. The efficiency of  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposites catalyst was

excellent compared with the reported literatures as indicated in Table 6. Therefore, it can be used as an alternative photocatalyst for MB dye removal from waste water.

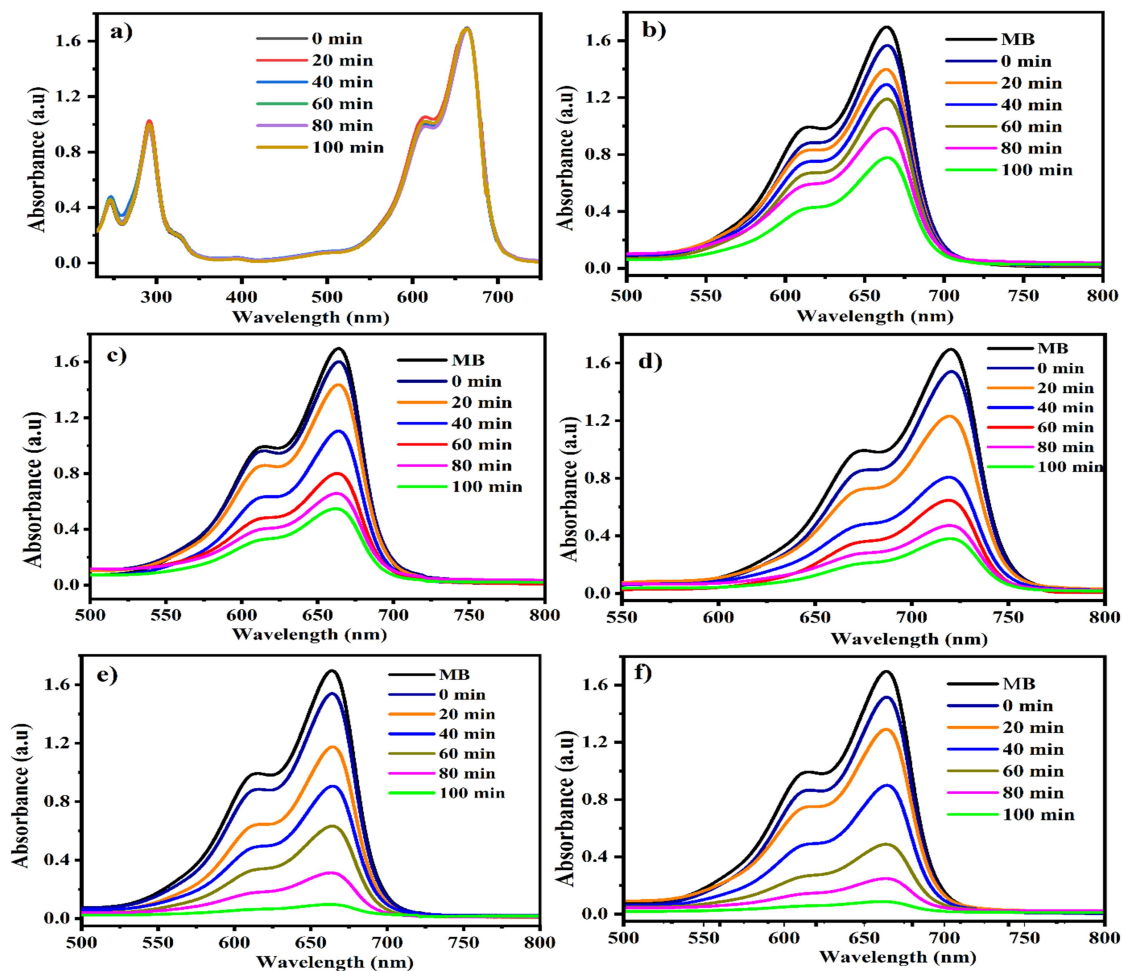


Figure 41: Plots of Uv-visible absorbance versus wavelength of (a) blank (without catalyst), and (b) ZnO, (c)  $\text{Co}_3\text{O}_4$ , (d) Sn-ZnO, (e)  $\text{Co}_3\text{O}_4/\text{ZnO}$  and (f)  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite using 30 mg catalyst and 100 mL of 10 ppm dye concentration at a pH of 9 under visible light irradiation for 100 minutes at room temperature.

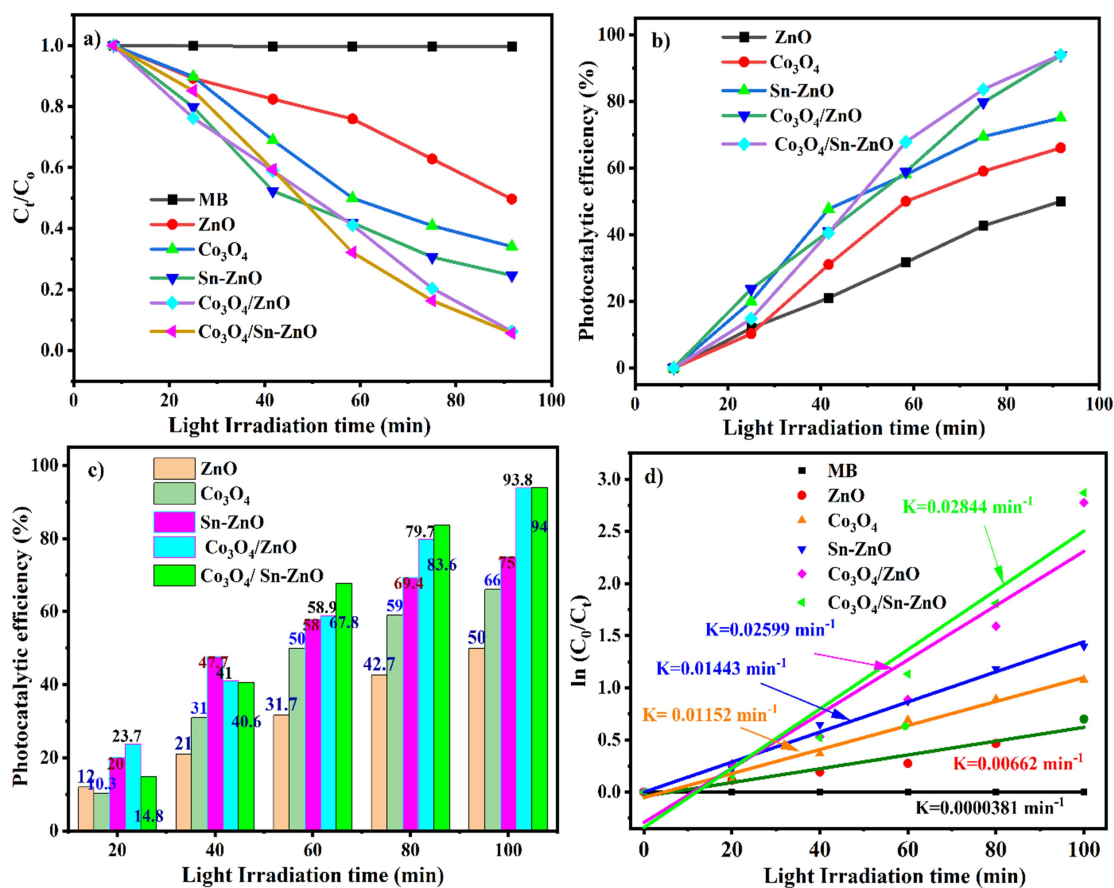


Figure 42: Plots of (a)  $C_t/C_0$  versus light illumination time, (b and c), photocatalytic efficiency versus light irradiation time, and (d)  $\ln(C_0/C_t)$  versus light illumination time of blank (without catalyst), ZnO, Co<sub>3</sub>O<sub>4</sub>, Sn-ZnO, Co<sub>3</sub>O<sub>4</sub>/ZnO and Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite using 30 mg catalyst, 100 mL of 10 ppm dye concentration and pH value of 9 for visible light irradiation time of 100 minutes at room temperature.

## 4.8.2 Optimization of Photocatalytic Factors in Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO Nanocomposite Photocatalyst

### 4.8.2.1 Effect of pH

The pH value of the solution is one of the operational parameters in photocatalytic activity that impacts the adsorption of the target synthetic dye, and it determines the surface charge of the Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite catalyst. Figure 43 (a-e) shows the relationship between pH and the photocatalytic performance of the Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO catalyst for the degradation of MB dye in 100 minutes of visible light irradiation. The adsorption capacity of MB dye on the

surface of the  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite catalyst was higher compared to the pH values of 5 and 7 as obtained from the adsorption-desorption analysis in the dark for 40 minutes. At pH = 5 (acidic medium), the surface of the catalyst is positively charged, and only weak electrostatic attraction occurred between the MB dye and the catalyst surface, resulting in poor adsorption capacity and photocatalytic efficiency.

In the case of pH = 7, due to an equal amount of positive and negative charges, both electrostatic repulsion and attraction of the MB dye occurred on the surface of the  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite catalyst. These results in a better adsorption capacity and photocatalytic efficiency of MB dye compared to a pH of 5 by the  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite catalyst. However, at pH of 9, when MB is dissolved in distilled water, a strong Coulombic attraction occurs on the negatively charged  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite catalyst's surface, but at higher pH, the recombination rate of charge carriers might be increased results in the photocatalytic efficiency to be deteriorated (Prabakaran & Pillay, 2019). Therefore, the photocatalytic efficiency at pH 5, 7, and 9 are given as 51.1%, 75.4%, and 94.3%, respectively. Moreover, the degradation rate constant of the MB dye by the  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite catalyst was determined by the Langmuir-Hinshelwood model using equation (4.16) from the slope of the linearly fitting graph of  $\ln(C_0/C_t)$  versus light irradiation time shown in figure 43 (f). The rate constants for  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite catalyst are  $0.00775 \text{ min}^{-1}$ ,  $0.01493 \text{ min}^{-1}$ , and  $0.02844 \text{ min}^{-1}$  at pH of 5, 7 and 9 respectively. The higher rate constant was obtained for pH 9 compared to 5 and 7. This means that a faster photocatalytic reaction or rapid decomposition of MB dye was occurred for  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite catalyst at this pH value compared to 5 and 7.

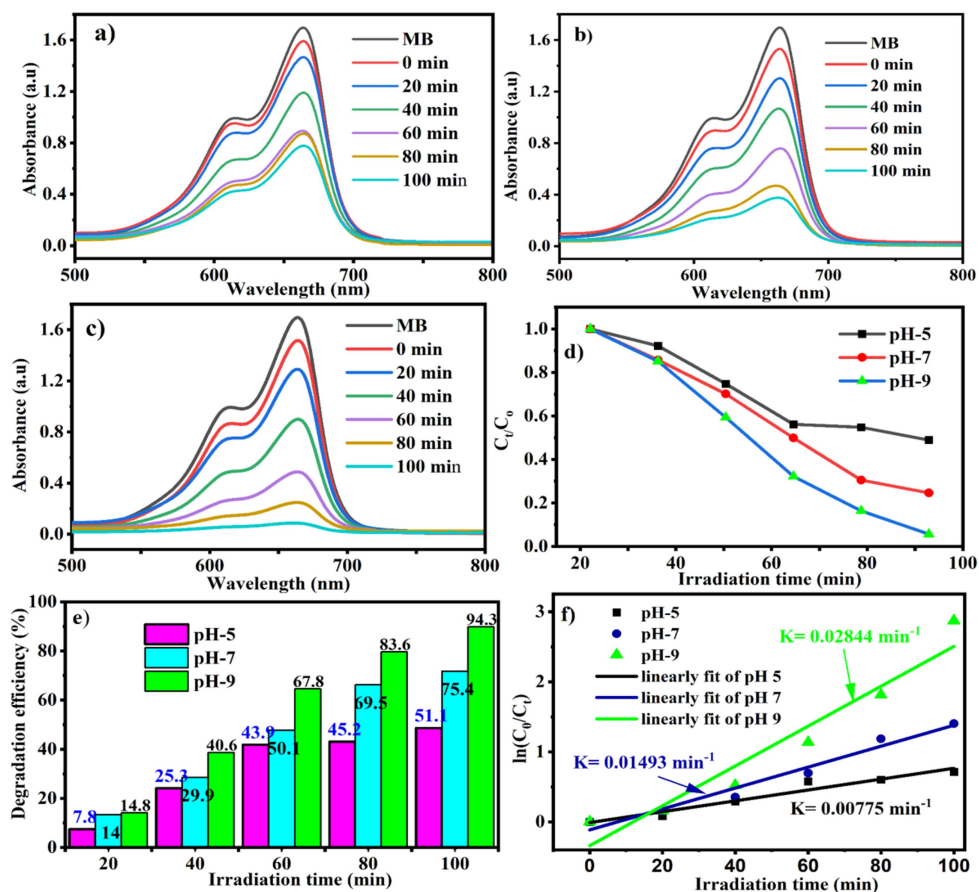


Figure 43: Effect of variation of pH value on the photocatalytic degradation performance of MB dye at (a)  $pH = 5$ , (b)  $pH = 7$ , (c)  $pH = 9$ , (d)  $C_t/C_0$  versus light irradiation time, (e) histogram of degradation efficiency versus light irradiation time, and (f)  $\ln(C_0/C_t)$  versus light irradiation time using 30 mg  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite catalyst and 10 ppm dye concentration under visible light irradiation for 100 minutes at room temperature.

#### 4.8.2.2 Effect of Catalyst Dosage

It is also one of the major operational parameters that strongly affect the photocatalytic performance of the  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite catalyst for the degradation of MB dye under visible light exposure in terms of its adsorption of the dye molecules and light absorption capacity. Figure 44 (a-e) shows the effect of variation of catalyst dosage on the degradation efficiency of MB dye at a pH value of 9 for 100 minutes of light irradiation at room temperature. The addition of 30 mg, 60 mg and 90 mg in a 100-mL dye solution for photocatalytic reactions in a reactor results in a photocatalytic efficiency of 94.3 %, 95.1%, and 90 %, respectively. There has been no significant difference observed in photocatalytic



efficiency between the 30 mg and 60 mg catalyst dosages, but a low efficiency was recorded for the 90 mg  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite catalyst. This might be due to the poor adsorption of dyes on the surface of the catalyst and the poor light penetration through the mixed solution of 90 mg  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  photocatalyst and dye solution (Adeel *et al.*, 2021; Goswami, 2020). The higher photocatalytic efficiency of 60 mg  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite photocatalyst could be due to better adsorption and good light absorption capacity during the photocatalytic reaction. The rate constants for 30 mg, 60 mg, and 90 mg obtained from the slope of the graph indicated in figure 44 (f) are given as  $K = 0.02844 \text{ min}^{-1}$ ,  $K = 0.03251 \text{ min}^{-1}$  and  $K = 0.02373 \text{ min}^{-1}$  respectively. The rate constant of 60 mg is higher compared to 30 mg and 90 mg catalyst dosages. This means that at this optimal catalyst dosage, the faster degradation of the MB dye was recorded.

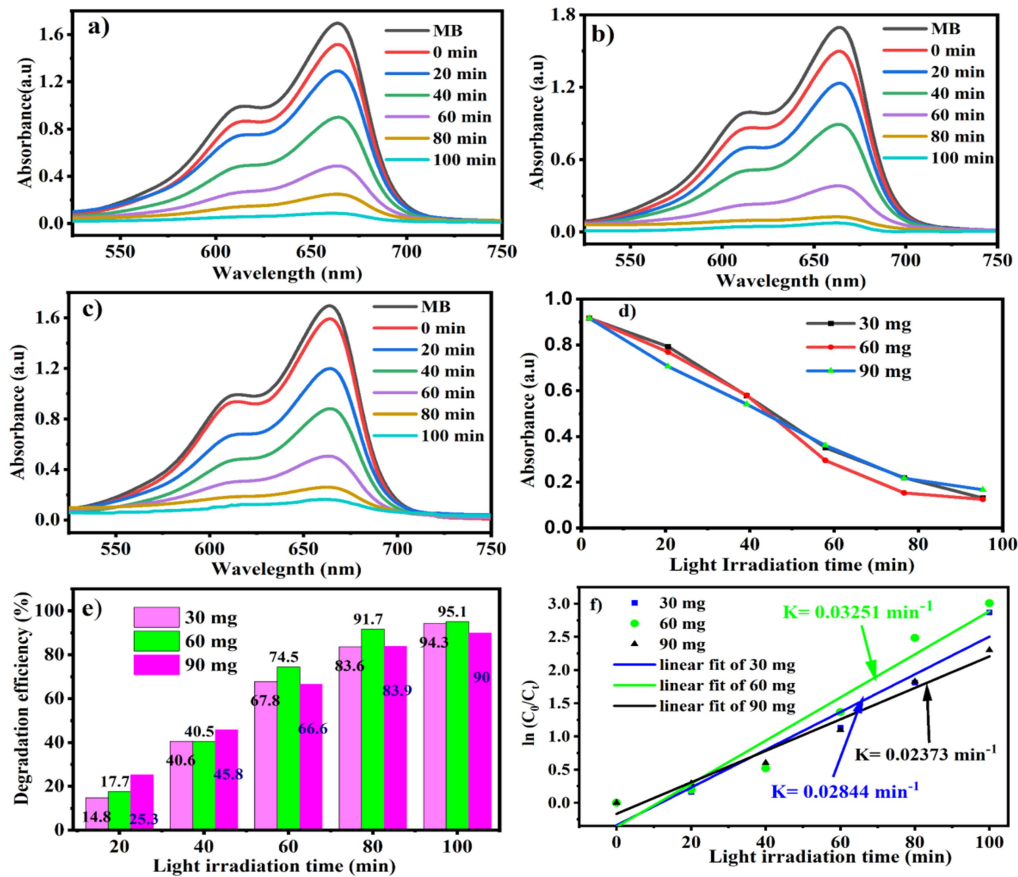


Figure 44: Effect of variation of catalyst dosage on the photocatalytic degradation performance of MB dye at (a) 30 mg, (b) 60 mg, (c) 90 mg, (d)  $C_t/C_0$  versus light irradiation time, (e) histogram of degradation efficiency versus light irradiation time, and (f)  $\ln(C_0/C_t)$  versus light irradiation time using 10 ppm dye concentration at a pH of 9 under visible light irradiation for 100 minutes at room temperature.



Table 6: Shows comparison of the present work with the previously reported results.

| Photocatalysts                          | Synthesis method | Catalyst (mg) | MB Dye (ppm) | Light used | Irradiation time (min) | Efficiency (%) | Ref.                             |
|-----------------------------------------|------------------|---------------|--------------|------------|------------------------|----------------|----------------------------------|
| 2% Ag-ZnO                               | Green method     | 79            | 1            | sun        | 30                     | 95             | (Jarvin <i>et al.</i> , 2022)    |
| 1% Ag-ZnO                               | Sol-gel          | 100           | 10           | uv light   | 15                     | 97.1           | (Zhu <i>et al.</i> , 2021)       |
| Cu-ZnO                                  | Hydrothermal     | 50            | 5            | uv light   | 120                    | 94             | (Khalid <i>et al.</i> , 2022)    |
| 4% Ag-ZnO                               | Co-precipitation | 100           | 50           | visible    | 100                    | 95             | (Shelar <i>et al.</i> , 2020)    |
| 2%Fe-ZnO                                | Sol-gel          | 100           | 10           | uv light   | 140                    | 92             | (Isai & Shrivastava, 2019)       |
| 4% Sn-ZnO                               | Co-precipitation | 25            | 20           | sun light  | 180                    | 94.5           | (Venkatesh <i>et al.</i> , 2021) |
| 5wt % CuO/ZnO                           | Mechano-chemical | 20            | 10           | solar      | 120                    | 98             | (Sakib <i>et al.</i> , 2019)     |
| CuO/TiO <sub>2</sub> /ZnO               | Sol-gel          | 20            | 20           | visible    | 120                    | 98             | (Taufik <i>et al.</i> , 2017)    |
| ZnO-Sb (1%)                             | Sonochemical     | 30            | 10           | solar      | 120                    | 91             | (Modi <i>et al.</i> , 2023)      |
| ZnO/Eu <sub>2</sub> O <sub>3</sub> /NiO | Combustion       | 30            | 5            | sun        | 150                    | 98             | (Shubha <i>et al.</i> , 2021)    |
| Cu-SnO <sub>2</sub> /ZnO                | Sol-gel          | 50            | 10           | visible    | 140                    | 78             | This work                        |
| Co <sub>3</sub> O <sub>4</sub> /Sn-ZnO  | Sol-gel          | 60            | 10           | visible    | 100                    | 95.1           |                                  |

#### 4.8.3 Quenching Experiment

Quenching experiment was performed for Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite catalyst to identify the main degrading active radical species in photocatalytic decomposition of MB dye. In photocatalytic reaction photogenerated charge carriers such as electrons and holes are produced in the conduction and valance bands respectively. These carriers could generate active degrading species in a redox reaction if they get enough redox potential. The degrading active radicals which could be produced are hydroxyl radicals (OH<sup>\*</sup>), superoxide anion radical (O<sub>2</sub><sup>\*-</sup>), electron (e<sup>-</sup>) and hole (h<sup>+</sup>). In this quenching experiment, isopropanol alcohol, ethylenediaminetetra-acetic acid (EDTA-2Na) and silver nitrate (AgNO<sub>3</sub>) were used as hydroxyl radical (OH<sup>\*</sup>), hole (h<sup>+</sup>) and electron (e<sup>-</sup>) trapping agents respectively. As indicated in figure 45 (a & b) electrons (e<sup>-</sup>) (52.82 %) and hydroxyl radicals (OH<sup>\*</sup>) (67.35

%) plays the major role whereas holes ( $h^+$ ) (86.52 %) plays a minor role in degrading MB dye.

#### 4.8.4 Photocatalytic Mechanism of $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$ Nanocomposite Photocatalyst

The mechanisms of charge transfer and production of the active degrading species or redox reaction during photocatalytic activities are given in figure 46. The band edge location values of ZnO and  $\text{Co}_3\text{O}_4$  can be determined from equations (3.18 and 4.19). The summarized values of the synthesized samples are given in Table 7. In Sn-doped ZnO nanoparticles, a donor level is induced near the conduction band of ZnO, and extra electrons are injected into its conduction band. Moreover, the density of electrons increases, and the Fermi level shifts upward to the conduction band of n-type ZnO.  $\text{Co}_3\text{O}_4$  is a p-type semiconductor. The coupling of these semiconductors produces a  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite catalyst. The photocatalytic degradation mechanism of the  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite photocatalyst for the removal of MB dye is given in figure 45. When visible light is produced from a 150-watt tungsten halogen lamp irradiated on  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite, electron-hole pairs are generated on its surface. The electrons could be transferred from a lower to a higher band edge potential, but holes move from a higher to a lower band edge potential. Therefore, in this composite, when electrons are generated and excited by the conduction band of ZnO, in return, the holes generated in its valence band move to the valence band of  $\text{Co}_3\text{O}_4$ , whereas the electrons generated in the conduction band of  $\text{Co}_3\text{O}_4$  move to the conduction band of ZnO. The photogenerated electrons in the conduction band of ZnO produce peroxide radicals due to a reduction reaction with oxygen molecules ( $\text{O}_2$ ) from air, and the holes in the valence band of  $\text{Co}_3\text{O}_4$  produce radicals by an oxidation reaction with water ( $\text{H}_2\text{O}$ ). The reaction of these highly active radicals with MB dye results in the MB dye degrading into  $\text{CO}_2$  and water. The charge transfer and production mechanisms of the active degrading species, or redox reaction, during photocatalytic activities are given as follows:

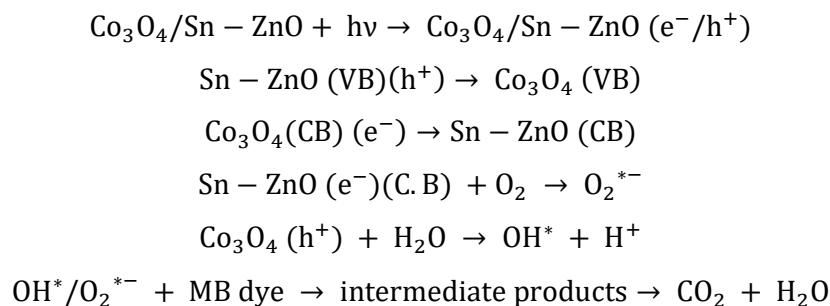


Table 7: The absolute electronegativity ( $X$ ), band gap energy ( $E_g$ ), the valance band ( $E_{VB}$ ) and conduction band ( $E_{CB}$ ) edge potentials for  $\text{Co}_3\text{O}_4$  and  $\text{ZnO}$  are summarized as follows.

| Catalysts               | $X(\text{eV})$ | $E_g(\text{eV})$ | $E_{VB}(\text{eV})$ | $E_{CB}(\text{eV})$ |
|-------------------------|----------------|------------------|---------------------|---------------------|
| $\text{ZnO}$            | 5.790          | 3.20             | 2.89                | -0.32               |
| $\text{Co}_3\text{O}_4$ | 5.42           | 2.78             | 2.33                | -0.45               |

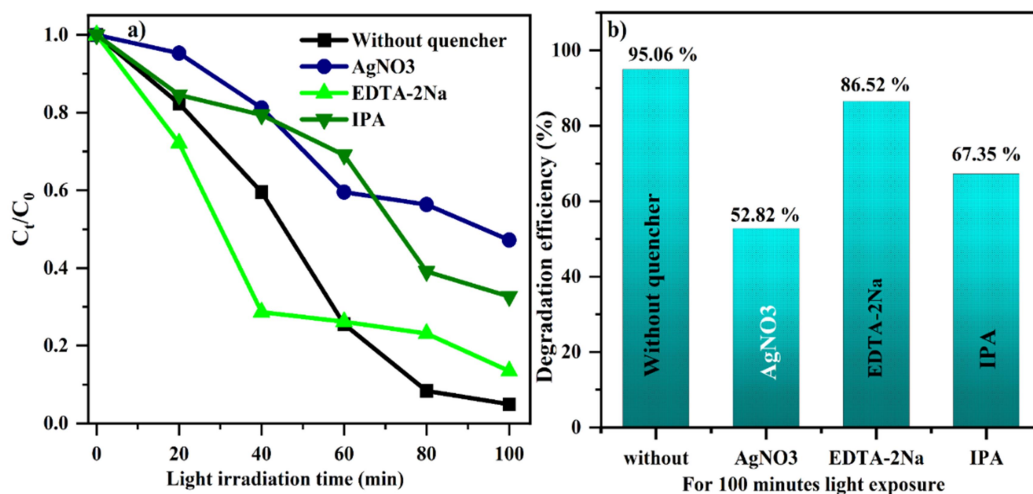


Figure 45: Effect of adding various quenchers on the photocatalytic efficiency of MB dye using  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite under visible light irradiation for 100 minutes at room temperature (a)  $C/C_0$  versus light irradiation time (b) histogram of degradation efficiency versus light irradiation time using 10 ppm dye concentration at a pH of 9.

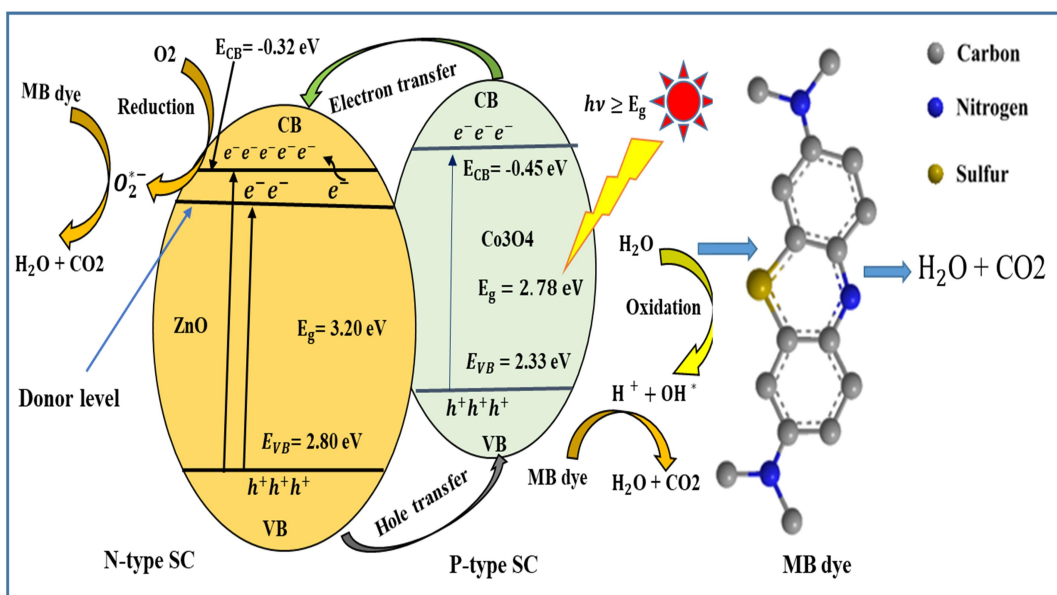


Figure 46: The photocatalytic degradation mechanism of  $\text{Co}_3\text{O}_4/\text{Sn-ZnO}$  nanocomposite photocatalyst for removal MB dye from polluted water in aqueous basic medium.

## 4.9 Electrochemical Characterization of Supercapacitor

### 4.9.1 Cyclic Voltammetry (CV) Analysis

In electrochemical analysis, optimization of the potential window plays a great role to enhance the performance of the given working electrode for the corresponding electrolyte used. The cyclic voltammetry analysis was done for 10 % CuO-SnO<sub>2</sub>/rGO composite in KOH electrolyte at the fixed scan rate of 30 mV/s as indicated in figure 46. The best potential window was between the ranges between 0-0.60 V, and therefore the CV and GCD analysis were performed based on this potential window interval.

In CV results shown in figure 48 (a-f), the curves shows quasi-rectangular curves represents a pseudocapacitive behavior with redox peaks between 0.54–0.69 V for oxidative reactions and 0.12–0.37 V for reductive reaction (Morka & Ujihara, 2023)(Rafique *et al.*, 2023). In this curves, the peak current increases as the scanning rate increases because the rate of diffusion is greater than the rate of adsorption or redox reaction. Hence, at higher scanning rate more electrolytes reach at the electrolyte-electrode interface with faster speed but only few ions could transfer charges (Shameem *et al.*, 2024). As given in Table 8 and figure 49 (b), with the same conditions the specific capacitance decreased as the scanning rate increased and high specific capacitance achieved at lower scanning rate due to favorable adsorption of ions into pores of the working electrode.

Based on the CV curves, the highest calculated specific capacitance of 185 F/g, 239 F/g, 254 F/g, 429 F/g, 614 F/g and 513 F/g were obtained for pristine SnO<sub>2</sub>, 5% CuO-SnO<sub>2</sub>, 10% CuO-SnO<sub>2</sub>, 15% CuO-SnO<sub>2</sub>, 10 % CuO-SnO<sub>2</sub>/(1%) rGO and 10 % CuO-SnO<sub>2</sub>/(2%) rGO hybrid composite respectively at a fixed scanning rate of 5 mV/s. The specific capacitance of these synthesized electrode materials for various scanning rates (5-40 mV/s) was calculated using equation 3.20 and are given in Table 8. Moreover, the comparison of CV curves for all electrode materials at fixed scanning rate of 50 mV/s given in figure 49 (a) indicates greater surface areas generated under CV curves for modified electrode materials indicates a highest specific capacitance compared to the nickel foam substrate and pristine SnO<sub>2</sub>.

Table 8: Shows the specific capacitance trend corresponding to the scanning rate of the electrode materials.

| Scanning rate (mV/s) | Specific capacitance (F/g) in KOH electrolyte |                        |                         |                          |                                    |                                    |
|----------------------|-----------------------------------------------|------------------------|-------------------------|--------------------------|------------------------------------|------------------------------------|
|                      | SnO <sub>2</sub>                              | 5% Cu-SnO <sub>2</sub> | 10% Cu-SnO <sub>2</sub> | 15% CuO-SnO <sub>2</sub> | 10% CuO-SnO <sub>2</sub> /rGO (1%) | 10% CuO-SnO <sub>2</sub> /rGO (2%) |
| 5                    | 185                                           | 217                    | 254                     | 239                      | 362                                | 307                                |
| 10                   | 175                                           | 215                    | 248                     | 192                      | 318                                | 280                                |
| 20                   | 170                                           | 205                    | 217                     | 184                      | 261                                | 248                                |
| 30                   | 157                                           | 185                    | 200                     | 167                      | 212                                | 214                                |
| 40                   | 148                                           | 168                    | 181                     | 156                      | 177                                | 186                                |

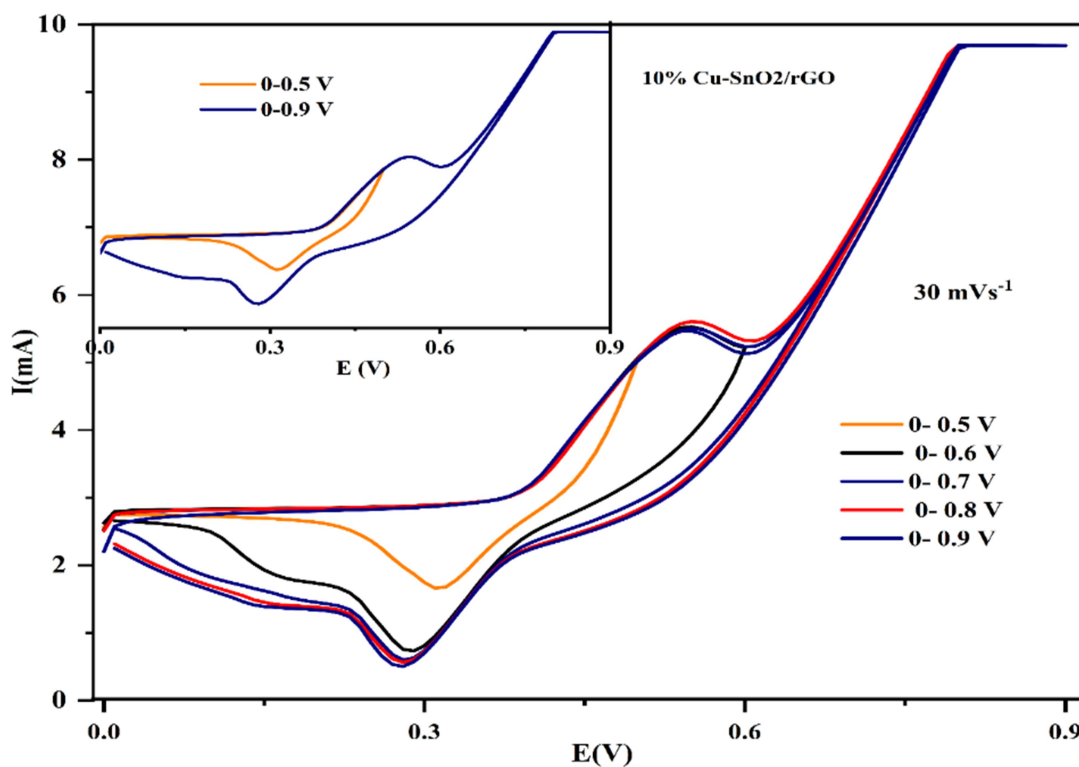


Figure 47: Optimization of the upper limits of the cyclic voltammetry potential window for 10% CuO-SnO<sub>2</sub>/rGO (2%) composite at a fixed scan rate of 30 mV/s.

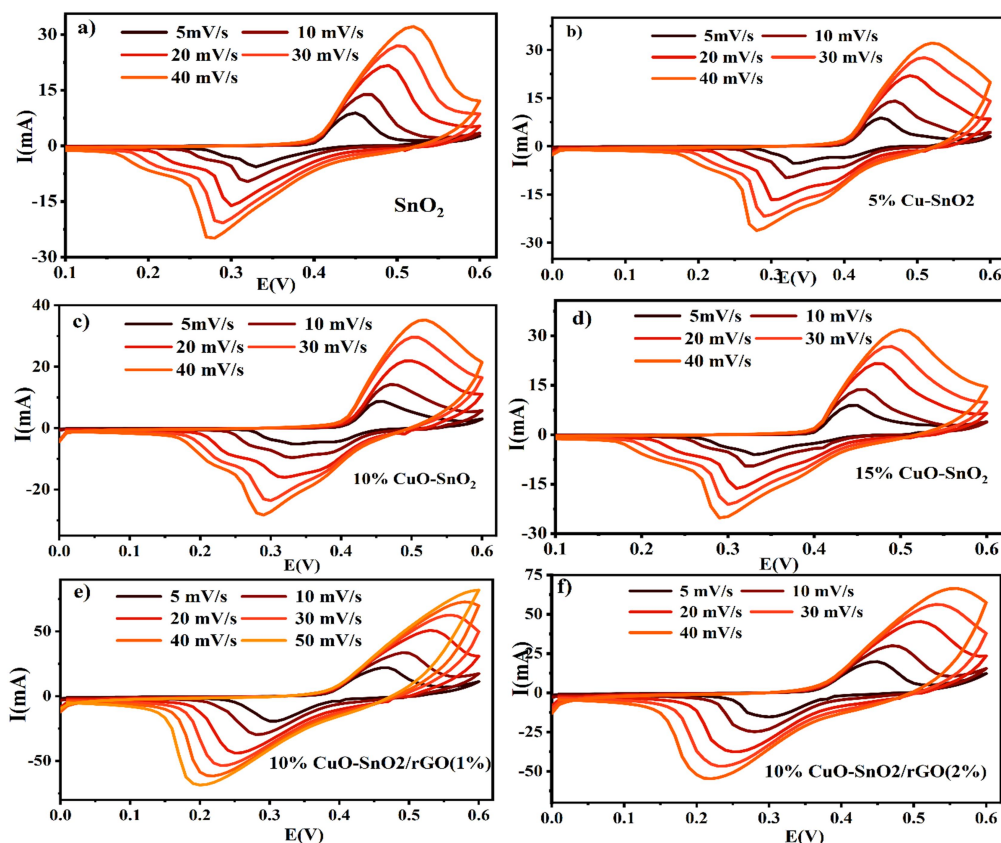


Figure 48: CV curves for (a) pristine  $\text{SnO}_2$  NPs, (b) 5%  $\text{CuO-SnO}_2$  NPs, (c) 10%  $\text{CuO-SnO}_2$  NPs, and (d) 15 %  $\text{CuO-SnO}_2$ , (e) 10 %  $\text{CuO-SnO}_2$ /(1%) rGO and (f) 10 %  $\text{CuO-SnO}_2$ /(2%) rGO hybrid composite in KOH electrolyte.

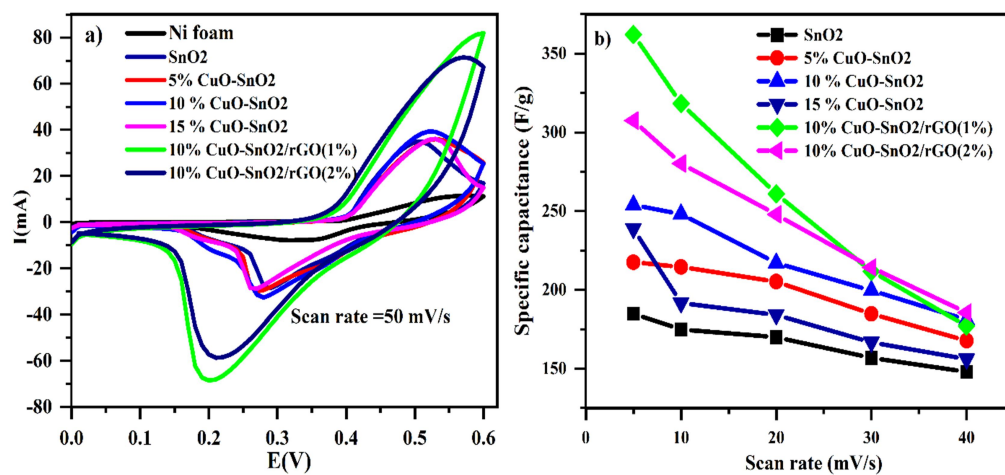


Figure 49: (a) Comparative curves of all the synthesized samples aforementioned at a fixed scan rate of 50 mV/s, and (b) Specific capacitance versus scanning rate between 5 mV/s to 40 mV/s for pristine  $\text{SnO}_2$  and modified electrode materials in KOH electrolyte.

#### 4.9.2 Galvanostatic Charge-Discharge (GCD) Analysis

Figure 50 (a-f) Shows the GCD curves of the synthesized electrode materials in the potential window ranges of 0 to 0.55 V at current densities (1-5 A/g). The nonlinear charge-discharge curves further confirmed the pseudocapacitive behavior of the SnO<sub>2</sub> based electrode materials as explained in CV analysis. Using equation (3.21), the specific capacitance calculated from GCD curves were 201 F/g, 255 F/g, 342 F/g, 365 F/g, 627 F/g and 416 F/g for pristine SnO<sub>2</sub>, 5% CuO-SnO<sub>2</sub>, 10% CuO-SnO<sub>2</sub>, 15%CuO-SnO<sub>2</sub>, 10% CuO-SnO<sub>2</sub>/(1%) rGO and 10%CuO-SnO<sub>2</sub>/(2%) rGO nanohybrid composite respectively at the current density of 1A/g. As indicated in Table 9 the specific capacitance calculated from GCD curves were consistent with the specific capacitance obtained from the CV curves. The relationship between specific capacitance and current density is given in figure 50 (a). The specific capacitance of the synthesize electrode material decreases with increasing the current density because of insufficient time for the electrolytic ions to penetrate into the pores of the synthesized electrode materials. The Ragone plot for energy density versus power density illustrated in figure 50 (b), exhibited that it is possible to enhance the energy density of the synthesized electrode materials with reduction of power density. In other words, a maximum power density was achieved at a current density of 5 A/g with a lower energy density. The known relationship of various energy storage devices based on energy density versus power density is demonstrated in figure 51 (b) for comparison.

We conclude that from both CV and GCD analysis methods, the addition of copper ion and copper oxide (CuO) into the SnO<sub>2</sub> host enhances the specific capacitance, energy density and power density of it. Moreover, reduced graphene oxide was added to the CuO-SnO<sub>2</sub> electrode material for further improvement of the performance of the supercapacitor. The highest specific capacitance was obtained for 10% CuO-SnO<sub>2</sub>/(1%) rGO and 10 %CuO-SnO<sub>2</sub>/(2%) rGO hybrid composite. This is because of addition of reduced graphene oxide (rGO) that could facilitate charge transfer efficiency and adsorption of electrolytic ions on the surface of the electrode due to its high specific surface area, large pore size and high electrical conductivity. Moreover, the enhancement of the specific capacitance in the synthesized hybrid composite ascribed to the simultaneous incorporation of both Cu and rGO which inhibits the grain growth, produces more active sites, shorten the transport path of electrolytic ions, increased the surface area, and narrowing the band gap to facilitate the charge transfer rate and increased the electrical conductivity. Publish articles given Table 11 confirms that

our results are comparable with reported results, and different strategies could be implemented to improve the performance of the working electrode materials for supercapacitor application. For instance, Asaithambi *et al.* 2020 reported that Fe and Cu doped  $\text{SnO}_2$  synthesized by a simple coprecipitation method exhibited a specific capacitance of 270 F/g and 251 F/g respectively, with a capacitance retention of 98% after 2000 charge-discharge cycles due to better electrical conductivity, high specific surface area and low resistance of electrolytic ions compared to the pristine  $\text{SnO}_2$  (197 F/g) (Asaithambi *et al.*, 2020). He also reported enhanced specific capacitance of 348 F/g at a current density of 1 A/g for  $\text{Fe-SnO}_2@\text{CeO}_2$  nanocomposite in KOH electrolyte. The enhancement of specific capacitance might be credited for fast electrolyte ion transport, lower crystallite size or shorten ions transport distance, lower energy band gap and higher electrical conductivity, more active sites, enhanced electronic and ionic conductivities when both Fe and Ce incorporated into  $\text{SnO}_2$  to produce  $\text{Fe-SnO}_2@\text{CeO}_2$  composite electrodes (Asaithambi *et al.*, 2021). Kumar *et al.*, 2020 also reported that hydrothermally synthesized  $\text{CeO}_2\text{-SnO}_2/\text{rGO}$  nanocomposite electrodes exhibited a high capacitance of 156 F/g at a current density of 0.5 A/g with capacitance retention of 98% after 1000 cycles attributed to the addition of both Ce and reduced graphene oxide (rGO) (Kumar *et al.*, 2020).

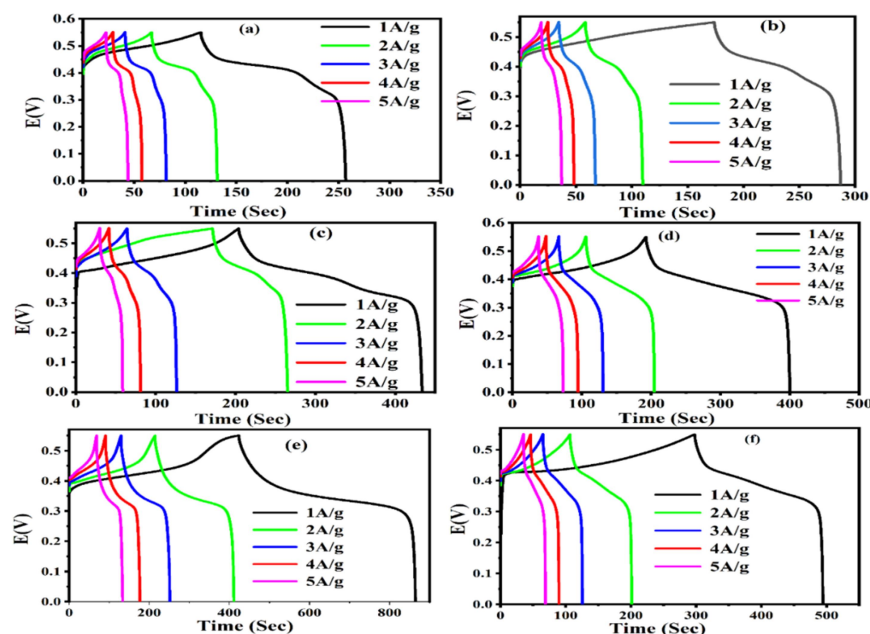


Figure 50: Galvanostatic charge-discharge (GCD) with mixed mode analysis of a) Pristine  $\text{SnO}_2$  (b) 5%  $\text{CuO-SnO}_2$  NPs (c) 10%  $\text{CuO-SnO}_2$  NPs (d) 15 %  $\text{CuO-SnO}_2$  NPs (e) 10 %  $\text{CuO-SnO}_2$ / (1%) rGO hybrid composite and (f) 10 %  $\text{CuO-SnO}_2$ / (2%) rGO nanohybrid composite.



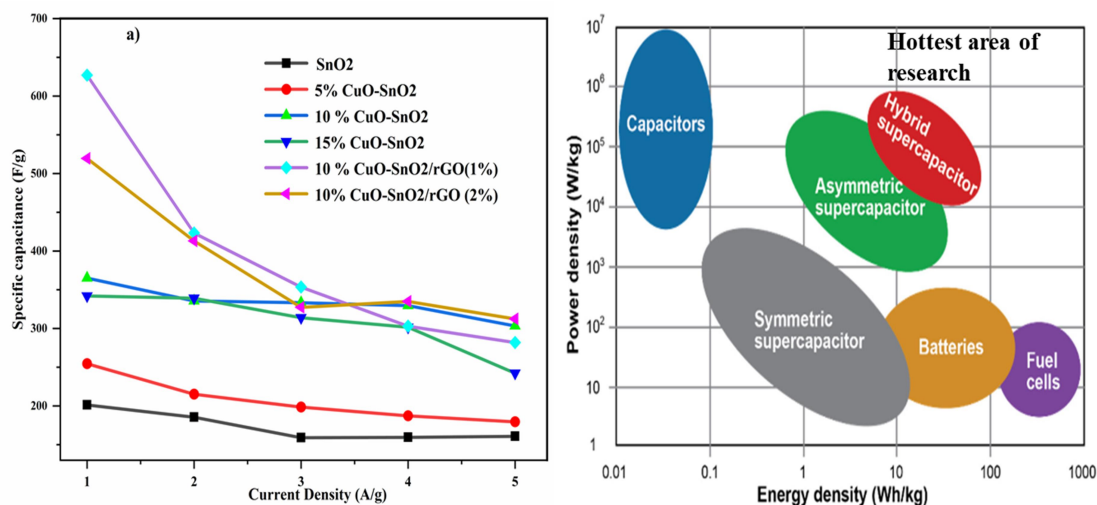


Figure 51: (a) Specific capacitance versus current density of the synthesized electrode materials obtained from GCD, and (b) Ragone plot for comparison of the types of supercapacitors with batteries and fuel cells based on their energy and power density (Vandeginste, 2022).

Table 9: shows specific capacitance values of the electrode materials calculated from GCD curves at current densities of 1 to 5 A/g in a potential window range of 0-0.55 V.

| Current density (A/g) | Specific Capacitance (F/g) in KOH electrolyte |                        |                         |                          |                                   |                                   |
|-----------------------|-----------------------------------------------|------------------------|-------------------------|--------------------------|-----------------------------------|-----------------------------------|
|                       | SnO <sub>2</sub>                              | 5% Cu-SnO <sub>2</sub> | 10% Cu-SnO <sub>2</sub> | 15% CuO-SnO <sub>2</sub> | 10%CuO-SnO <sub>2</sub> /rGO (1%) | 10%CuO-SnO <sub>2</sub> /rGO (2%) |
| 1                     | 201                                           | 255                    | 365                     | 342                      | 627                               | 416                               |
| 2                     | 186                                           | 215                    | 336                     | 339                      | 423                               | 330                               |
| 3                     | 159                                           | 199                    | 333                     | 314                      | 354                               | 327                               |
| 4                     | 160                                           | 188                    | 330                     | 302                      | 303                               | 268                               |
| 5                     | 161                                           | 180                    | 303                     | 242                      | 282                               | 250                               |

Table 10: The energy density and power density of the electrode materials at fixed current density of 1 A/g.

| Electrode materials                | Specific Capacitance (F/g) | Energy density (Wh/Kg) | Power density (W/kg) |
|------------------------------------|----------------------------|------------------------|----------------------|
| SnO <sub>2</sub>                   | 201                        | 8.84                   | 281                  |
| 5% Cu-SnO <sub>2</sub>             | 255                        | 10.97                  | 279                  |
| 10% Cu-SnO <sub>2</sub>            | 342                        | 15.82                  | 289                  |
| 15% CuO-SnO <sub>2</sub>           | 365                        | 16.4                   | 284.5                |
| 10% CuO-SnO <sub>2</sub> /rGO (1%) | 784                        | 34.9                   | 283                  |
| 10%CuO-SnO <sub>2</sub> /rGO (2%)  | 416                        | 17.65                  | 277                  |

Table 11: Comparisons of specific capacitance of synthesized electrode materials with reported Literatures results.

| Electrode materials                     | Potential window (V) | Electrolyte (KOH) | Current density (A/g) | Specific Capacitance (F/g) | Reference                         |
|-----------------------------------------|----------------------|-------------------|-----------------------|----------------------------|-----------------------------------|
| SnO <sub>2</sub>                        | 0-0.50               | 1 M               | 0.25                  | 28.21                      | (S. Kumar <i>et al.</i> , 2022)   |
| SnO <sub>2</sub>                        | 0-0.65               | 1M                | 1                     | 143.5                      | (Kang <i>et al.</i> , 2019)       |
| Hollow-SnO <sub>2</sub>                 | 0-0.65               | 1M                | 1                     | 332.7                      |                                   |
| Fe-SnO <sub>2</sub>                     | 0-0.55               | 2 M               | 0.5                   | 270                        | (Asaithambi <i>et al.</i> , 2020) |
| Cu-SnO <sub>2</sub>                     | 0 -0.55              | 2 M               | 0.5                   | 251                        |                                   |
| CeO <sub>2</sub> -SnO <sub>2</sub> /rGO | 0 - 0.50             | 3 M               | 0.5                   | 156                        | (Kumar <i>et al.</i> , 2020)      |
| Fe-SnO <sub>2</sub> /CeO <sub>2</sub>   | 0 - 0.50             | 2 M               | 1                     | 348                        | (Asaithambi <i>et al.</i> , 2021) |
| SnO <sub>2</sub> - MoS <sub>2</sub>     | 0 - 0.60             | 3 M               | 1                     | 102                        | (K. Rafique <i>et al.</i> , 2023) |
| NGO/SnO <sub>2</sub>                    | -0.2-0.80            | 6 M               | 4                     | 378                        | (S. Ramesh <i>et al.</i> , 2019)  |
| 15% CuO-SnO <sub>2</sub>                | 0-0.55               | 1 M               | 1                     | 365                        | This work                         |
| 10% CuO-SnO <sub>2</sub> /rGO (1%)      | 0-0.55               | 1 M               | 1                     | 784                        |                                   |
| 10%CuO-SnO <sub>2</sub> /rGO (2%)       | 0-0.55               | 1 M               | 1                     | 416                        |                                   |

## 5. CONCLUSION

The Cu-SnO<sub>2</sub>/ZnO and Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite photocatalysts were synthesized using a one-step facile sol-gel synthesis method and evaluated for their photocatalytic activity to remove methylene blue dye under visible light irradiation, and hydrothermally synthesized CuO-SnO<sub>2</sub>/rGO hybrid composite was studied for supercapacitor applications. XRD analysis revealed that the tetragonal rutile SnO<sub>2</sub> and hexagonal wurtzite ZnO coexist in the synthesized Cu-SnO<sub>2</sub>/ZnO composite. Hexagonal structured ZnO and cubic spinel structure of Co<sub>3</sub>O<sub>4</sub> were fused together to form Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite. In CuO-SnO<sub>2</sub>/rGO hybrid monoclinic CuO and tetragonal SnO<sub>2</sub> were amalgamated to produce it. The crystal size decreases and defect density increases in Cu-SnO<sub>2</sub>/ZnO composite. In Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite, the crystal size increased when Co<sub>3</sub>O<sub>4</sub> coupled with Sn-ZnO as full width at half maxima (FWHM) decreased. In CuO-SnO<sub>2</sub>/rGO hybrid composite, the crystallite size decreased when CuO and rGO added into SnO<sub>2</sub> host. In Cu-SnO<sub>2</sub>/ZnO composite, the band gap decreases when Cu ion doped into SnO<sub>2</sub> and coupled with ZnO. The red shift in the Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite indicates the reduction of its band gap. In all composites, the recombination rate of photogenerated charge carriers of the composites were decreased, as confirmed by the PL results. The FTIR measurement identifies the functional groups of the synthesized nanomaterials. The EDS analysis confirmed that in Cu-SnO<sub>2</sub>/ZnO and Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO composites all the component elements were present in it without any impurities. The TEM and HRTEM images confirmed that the structure of Cu-SnO<sub>2</sub>/ZnO and Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO composites is in good agreement with the XRD results. The lattice spacing determined by the HRTEM is also in excellent agreement with the XRD results. In both composite photocatalysts, increase of surface area, narrowing of bandgap and a reduction in the fast recombination rate results in an increase of the photocatalytic efficiency. The donor level and the induced distortions or defects also trap electrons when they return back to their earlier positions. The Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite photocatalyst could be recommended as an alternative low cost high performance photocatalytic material for practical applications. On the other hand, in cyclic voltammetry analysis of 10% CuO-SnO<sub>2</sub> shows pseudocapacitive behavior, and 10% CuO-SnO<sub>2</sub>/rGO (1%) and 10% CuO-SnO<sub>2</sub>/rGO (2 %) hybrid composites were hybrid type. Both CV and GCD analysis confirmed that 10% CuO-SnO<sub>2</sub>/rGO (1%) hybrid composite exhibited the highest specific capacitance and energy density compared to pristine SnO<sub>2</sub>.

## 6. RECOMMENDATION AND FUTURE WORK

- ◆ Cu-SnO<sub>2</sub>/ZnO and Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposites can be recommended for gas sensor, electrochemical sensor and energy storage application such as batteries.
- ◆ CuO-SnO<sub>2</sub>/rGO hybrid composite also recommended for further investigation in other application areas such as photocatalytic materials, gas sensor, electrochemical sensor, and batteries, water filtration, heavy metal adsorption, antibacterial and anticancer applications.

## 7. LIST OF PUBLICATIONS

- ◆ Zewdu Weldemichael Zena, Lemma Teshome Tufa, Dinsefa Mensur Andoshe, Abebe Belay Gemta and Francis Birhanu Dejene, (2023). Single step facile synthesis of Cu-SnO<sub>2</sub>/ZnO nanocomposite photocatalyst for methylene blue dye degradation in aqueous solution, *Phys. Scr.* **98** (105974), <https://doi.org/10.1088/1402-4896/acfa44>
- ◆ Zewdu Weldemichael Zena, Dinsefa Mensur Andoshe, Lemma Teshome Tufa, Abebe Belay Gemta and Francis Birhanu Dejene, (2024). High performance Co<sub>3</sub>O<sub>4</sub>/Sn-ZnO nanocomposite photocatalyst for removal of methylene blue dye, *Phys. Scr.* **99** (045934), <https://doi.org/10.1088/1402-4896/ad2f8f>

## 8. REFERENCE

- Abbasi, S., & Hasanpour, M. (2017). The effect of pH on the photocatalytic degradation of methyl orange using decorated ZnO nanoparticles with SnO<sub>2</sub> nanoparticles. *Journal of Materials Science: Materials in Electronics*, 28(2), 1307–1314.
- Abdelkader, E., Nadjia, L., & Rose-noe, V. (2016). Adsorption of Congo red azo dye on nanosized SnO<sub>2</sub> derived from sol-gel method. *International Journal of Industrial Chemistry*, 7(March), 53–70.
- Adeel, M., Saeed, M., Khan, I., Muneer, M., & Akram, N. (2021). Synthesis and Characterization of Co–ZnO and Evaluation of Its Photocatalytic Activity for Photodegradation of Methyl Orange. *ACS Omega*, 6(2), 1426–1435.
- Adéla Jiříčková, Ondřej Jankovský, Z. ěek S. and D. S. (2022). Synthesis and Applications of Graphene Oxide. *Materials*, 15(920), 1–21.
- Ahamed, M., Akhtar, M. J., Khan, M. A. Ma., & Alhadlaq, H. A. (2021). SnO<sub>2</sub>-doped ZnO/reduced graphene oxide nanocomposites: Synthesis, characterization, and improved anticancer activity via oxidative stress pathway. *International Journal of Nanomedicine*, 16(15 June), 89–104.
- Ahmed, A., Siddique, M. N., Alam, U., Ali, T., & Tripathi, P. (2018). Improved Photocatalytic Activity of Sr doped SnO<sub>2</sub> Nanoparticles: A role of Oxygen Vacancy. *Applied Surface Science*, 463,(1), Pp. 976-985.
- Ahmed, M. A., & Adel, M. (2023). Photocatalysts : Synthesis , Photocatalytic Applications , and Challenges. *RSC Advances*, 13(1), 421–439.
- Akhil, K., Jayakumar, J., Gayathri, G., & Khan, S. S. (2016). Effect of various capping agents on photocatalytic , antibacterial and antibio fi lm activities of ZnO nanoparticles. *Journal of Photochemistry & Photobiology, B : Biology*, 160(July), 32–42.
- Al., K. P., Manop, D., Tanghengjaroen, C., Palakawong, W., & Ayuthaya, N. (2020). Crystal Structure, Lattice Strain, Morphology, and Electrical Properties of SnO<sub>2</sub> Nanoparticles Induced by Low Calcination Temperature. *Advances in Materials Science and Engineering*, 2020(1), 1–10.
- Alam, S. N., Sharma, N., & Kumar, L. (2017). Synthesis of Graphene Oxide ( GO ) by Modified Hummers Method and Its Thermal Reduction to Obtain Reduced Graphene Oxide. *Graphene*, 6(1), 1–18.
- Albero, J., Mateo, D., & Garc, H. (2019). Graphene-Based Materials as Efficient Photocatalysts for Water Splitting. *Molecules*, 24(906), 1–21.

- Ali, M. H. H., Goher, M. E., Al, A. D. G., Siliem, A., & Sayed, M. El. (2022). A facile method for synthesis rGO/Ag nanocomposite and its uses for enhancing photocatalytic degradation of Congo red dye. *SN Applied Sciences*, 4(276), 1–15.
- Ali, M. M., Haque, J., Kabir, M. H., Kaiyum, M. A., & Rahman, M. S. (2021). Nano synthesis of ZnO–TiO<sub>2</sub> composites by sol-gel method and evaluation of their antibacterial , optical and photocatalytic activities. *Results in Materials*, 11(September), 100199.
- Aliyev, E., Filiz, V., Khan, M. M., Lee, Y. J., Abetz, C., & Abetz, V. (2019). Structural Characterization of Graphene Oxide : Surface Functional Groups and Fractionated Oxidative Debris. *Nanomaterials*, 9(1180), 1–15.
- Alshammari, B. H., Lashin, M. M. A., Mahmood, M. A., Al-mubaddel, F. S., Ilyas, N., Rahman, N., Sohail, M., Khan, A., Abdullaev, S. S., & Khan, R. (2023). Organic and inorganic nanomaterials: fabrication, properties and applications. *RSC Advances*, 13(20), 13735–13785.
- Ameen, S., Akhtar, M. S., Seo, H., Soon, Y., & Shik, H. (2012). Influence of Sn doping on ZnO nanostructures from nanoparticles to spindle shape and their photoelectrochemical properties for dye sensitized solar cells. *Chemical Engineering Journal*, 187(1), 351–356.
- Amirtharaj, S. N., & Mariappan, M. (2021). A facile synthesis of interconnected CuO nanosheets : a promising electrode material for supercapacitor application. *Applied Physics A*, 127(7), 1–10.
- Aragón, F. F. H., Villegas-Lelovsky, L., J. I. Castillo-Llanos, C. M. S., Solis, J. L., Peralta-Alarcón, G. H., Pacheco-Salazar, D. G., & Morais, P. C. (2023). Cu-doped SnO<sub>2</sub> nanoparticles: size and antibacterial activity investigations. *RSC Advances*, 13(41), 28482–28492.
- Aroob, S., Carabineiro, S. A. C., Taj, M. B., Bibi, I., Raheel, A., Javed, T., Yahya, R., Alelwani, W., Verpoort, F., Kamwilaisak, K., & Al-farraj, S. (2023). Green Synthesis and Photocatalytic Dye Degradation Activity of CuO Nanoparticles. *Catalysts*, 13(502), 1–18.
- Asaithambi, S., Sakthivel, P., Karuppaiah, M., Balaji, V., Yuvakkumar, R., & Ravi, G. (2021). Visible light induced photocatalytic performance of Mn-SnO<sub>2</sub>@ZnO nanocomposite for high efficient cationic dye degradation. *Journal of Materials Science: Materials in Electronics*, 32(17), 22168–22186.
- Asaithambi, S., Sakthivel, P., Karuppaiah, M., Balamurugan, K., & Yuvakkumar, R. (2021).

- Synthesis and characterization of various transition metals doped SnO<sub>2</sub>@MoS<sub>2</sub> composites for supercapacitor and photocatalytic applications. *Journal of Alloys and Compounds*, 853, 157060.
- Asaithambi, S., Sakthivel, P., Karuppaiah, M., Sankar, G. U., & Balamurugan, K. (2020). Investigation of electrochemical properties of various transition metals doped SnO<sub>2</sub> spherical nanostructures for supercapacitor applications. *Journal of Energy Storage*, 31(April), 101530.
- Asaithambi, S., Sakthivel, P., Karuppaiah, M., Yuvakkumar, R., Balamurugan, K., Ahamad, T., Khan, M. A. M., Ramalingam, G., Mohammed, M. K. A., & Ravi, G. (2021). Preparation of Fe-SnO<sub>2</sub>@CeO<sub>2</sub> nanocomposite electrode for asymmetric supercapacitor device performance analysis. *Journal of Energy Storage*, 36(102402), 1–15.
- Asaithambi, S., Sakthivel, P., Karuppaiah, M., Yuvakkumar, R., Velauthapillai, D., Ahamad, T., Khan, M. A. M., Mohammed, M. K. A., Vijayaprabhu, N., & Ravi, G. (2021). The bifunctional performance analysis of synthesized Ce doped SnO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> composites for asymmetric supercapacitor and visible light photocatalytic applications. *Journal of Alloys and Compounds*, 866(February), 158807.
- Aval, L. F., Ghoranneviss, M., & Pour, G. B. (2018). High-performance supercapacitors based on the carbon nanotubes, graphene and graphite nanoparticles electrodes. *Heliyon*, 4(September), e00862.
- Aziz, M., Abbas, S. S., Rosemaria, W., & Baharom, W. (2013). Size-controlled synthesis of SnO<sub>2</sub> nanoparticles by sol – gel method. *Materials Letters*, 91(15), 31–34.
- Babu, B., Kadam, A. N., Ravikumar, R. V. S. S. N., & Byon, C. (2017). Enhanced visible light photocatalytic activity of Cu-doped SnO<sub>2</sub> quantum dots by solution combustion synthesis. *Journal of Alloys and Compounds*, 703(5May), 330–336.
- Bahishti, A. A., & Majid, A. (2017). Intensity Dependent Photoconductivity in ZnO Nanostructured Film Intensity Dependent Photoconductivity in ZnO Nanostructured Film. *Advanced Nano Research Volume*, 1(1), 23–30.
- Balık, M., Bulut, V., & Erdogan, I. Y. (2018). Optical , structural and phase transition properties of Cu<sub>2</sub>O , CuO and Cu<sub>2</sub>O/CuO: Their photoelectrochemical sensor applications. *International Journal of Hydrogen Energy*, 44(34), 18744–18755.
- Bárdos, E., Krisztina, A., Pap, Z., Baia, L., & Garg, S. (2019). Applied Surface Science The effect of the synthesis temperature and duration on the morphology and photocatalytic activity of BiOX ( X = Cl , Br , I ) materials. *Applied Surface Science*, 479(15 June),

745–756.

- Bashir, Saiqa Awan, M. S., Farrukh, Muhammad Akhyar Naidu, Ravi Khan, Shahzad Akbar Rafique, Nagina Ali Hayat Shaista, H., Imran Khan, I., Hussain, M. Z. K., & Zubair, M. (2022). In-vivo ( Albino Mice ) and in-vitro Assimilation and Toxicity of Zinc Oxide Nanoparticles in Food Materials. *International Journal of Nanomedicine*, 17(July), 4073–4085.
- Bayda, S., Adeel, M., Tuccinardi, T., Cordani, M., & Rizzolio, F. (2020). The History of Nanoscience and Nanotechnology: From Chemical – Physical Applications to Nanomedicine. *Molecules*, 25(112), 1–15.
- Benzait, Z., Chen, P., & Trabzon, L. (2021). Enhanced synthesis method of graphene oxide. *Nanoscale Advances*, 3(1), 223–230.
- Bhise, S. C., Awale, D. V, Vadiyar, M. M., & Patil, S. K. (2017). Facile synthesis of CuO nanosheets as electrode for supercapacitor with long cyclic stability in novel methyl imidazole-based ionic liquid electrolyte. *Journal of Solid State Electrochemistry*, 21(9), 2585–2591.
- Boon, C., Yong, L., & Wahab, A. (2018). A review of ZnO nanoparticles as solar photocatalysts: Synthesis, mechanisms and applications. *Renewable and Sustainable Energy Reviews*, 81(part-1), 536–551.
- Campo, C. M., Rodríguez, J. E., & Ramírez, A. E. (2016). Thermal behaviour of romarchite phase SnO in different atmospheres: a hypothesis about the phase transformation. *Heliyon*, 2(May), e00112.
- Chauhan, A., Verma, R., Batoo, K. M., Kumari, S., Kalia, R., Kumar, R., Hadi, M., Raslan, E. H., & Imran, A. (2021). Structural and optical properties of copper oxide nanoparticles: A study of variation in structure and antibiotic activity. *Journal of Materials Research*, 36(7), 1–14.
- Chen, W., Hu, Z., & Chen, Y. (2018). Synthesis of SnO<sub>2</sub>/RGO nanocomposite and its superior capacitive performance as supercapacitor electrode materials. *Optoelectronics and Advanced Materials – Rapid Communications*, 12(3), 211–221.
- Chen, Y. (2021). Effects of Reaction Temperature on the Photocatalytic Activity of TiO<sub>2</sub> with Pd and Cu Cocatalysts. *Catalysts*, 11(966), 1–12.
- Chiu, H., & Yeh, C. (2007). Hydrothermal Synthesis of SnO<sub>2</sub> Nanoparticles and Their Gas-Sensing of Alcohol. *Journal of Physical Chemistry C*, 111(20), 7256–7259.
- Choi, K., Kim, H., Kim, K., Liu, D., Cao, G., & Lee, J. (2010). C<sub>2</sub>H<sub>5</sub>OH sensing characteristics of various Co<sub>3</sub>O<sub>4</sub> nanostructures prepared by solvothermal reaction.



*Sensors & Actuators: B. Chemical*, 146(1), 183–189.

- Cui, X., Zheng, Y. F., Zhou, H., Yin, H. Y., & Song, X. C. (2015). The effect of synthesis temperature on the morphologies and visible light photocatalytic performance of Ag<sub>3</sub>PO<sub>4</sub>. *Journal of the Taiwan Institute of Chemical Engineers*, 000(October), 1–7.
- Dar, R. A., & Zubair, M. (2022). Effect of pH variations on structural and morphological properties of ZnO nanocrystals. *The European Physical Journal Plus*, 137(1093), 1–7.
- Das, D., & Jyoti, B. (2023). Synthesis , characterization and biological applications of cobalt oxide ( Co<sub>3</sub>O<sub>4</sub> ) nanoparticles. *Chemical Physics Impact*, 6(November), 100137.
- Das, P., Ibrahim, S., Chakraborty, K., Ghosh, S., & Pal, T. (2024). Stepwise reduction of graphene oxide and studies on defect - controlled physical properties. *Scientific Reports*, 14(294), 1–10.
- Deng, Z., Ma, Z., Li, Y., Li, Y., Chen, L., Yang, X., & Wang, H. (2018). Boosting Lithium-Ion Storage Capability in CuO Nanosheets via Synergistic Engineering of Defects and Pores. *Frontiers in Chemistry*, 6(September), 1–9.
- Devi, D., Jagriti, T., Niroj, G., & Sahu, K. (2019). Effect of induced defects on the properties of ZnO nanocrystals : surfactant role and spectroscopic analysis. *SN Applied Sciences*, 1(May), 1030.
- Devi, S. A. J. M. (2023). Experimental Investigation on Structural, Optical, Electrical and Magnetic Properties of Copper Oxide Nanoparticles. *Proceedings of the National Academy of Sciences, India Section A: Physical Sciences*, 94(February), 153–160.
- Dhinakar, K. G., & Meenakshi, T. S. S. (2016). Structural , optical and impedance properties of SnO<sub>2</sub> nanoparticles. *Journal of Materials Science: Materials in Electronics*, 27(June), 5818–5824.
- Dhineshbabu, N. R., & Vetumperumal, V. R. N. N. R. (2016). Study of structural and optical properties of cupric oxide nanoparticles. *Applied Nanoscience*, 6(6), 933–939.
- Długosz, O., & Banach, M. (2021). ZnO – SnO<sub>2</sub> – Sn nanocomposite as photocatalyst in ultraviolet and visible light. *Applied Nanoscience*, 11(5), 1707–1719.
- Dong, H., & Hu, W. (2013). Springer Handbook of Nanomaterials. In *Organic Nano* (pp. 905–939).
- Dulta, K., Ko, G., Chauhan, P., Jasrotia, R., Chauhan, P. K., & Ighalo, J. O. (2022). Multifunctional CuO nanoparticles with enhanced photocatalytic dye degradation and antibacterial activity. *Sustainable Environment Research*, 32(2), 1–15.
- Ejsmont, A., & Goscińska, J. (2023). Hydrothermal Synthesis of ZnO Superstructures with Controlled Morphology via Temperature and pH Optimization. *Materials*, 16(4), 1641.

- Elci, A., Demirtas, O., Ozturk, I. M., Bek, A., & Esenturk, E. N. (2018). Synthesis of tin oxide-coated gold nanostars and evaluation of their surface-enhanced Raman scattering activities. *Journal of Materials Science*, 53(24), 6–9.
- Faustova, Z. V., & Slizhov, Y. G. (2017). Effect of Solution pH on the Surface Morphology of Sol – Gel Derived Silica Gel. *Inorganic Materials*, 53(3), 287–291.
- Felcia, E. B., & Gnanam, K. D. (2017). Synthesis and Characterization of SnO<sub>2</sub> Nanoparticle by Microwave Assisted Hydrothermal Method. *Journal of Applied Physics*, e-ISSN: 22(February), 98–104.
- Fuku, X., Thovhogi, N., & Maaza, M. (2018). Photocatalytic Effect of Green Synthesised CuO Nanoparticles on Selected Environmental Pollutants and Pathogens. *AIP Conference Proceedings*, 1962(1), 040006.
- Gan, Y. X., Jayatissa, A. H., Yu, Z., Chen, X., & Li, M. (2020). Editorial Hydrothermal Synthesis of Nanomaterials. *Journal of Nanomaterials 2020*, 2020(editorial), 1–3.
- Gao, L., Pang, C., He, D., Shen, L., Gupta, A., & Bao, N. (2015). Synthesis of Hierarchical Nanoporous Microstructures via the Kirkendall Effect in Chemical Reduction Process. *Scientific Reports*, 5(March), 1–12.
- Gardey, M. C., Fernández, M. E., Rapp, D., Pinto, M., Elisa, M., Lassa, M. S., Martín, J. M., Lascalea, G. E., & Vázquez, P. G. (2015). Combustion synthesis of ultrafine powders of Co<sub>3</sub>O<sub>4</sub> for selective surfaces of solar collectors. *Procedia Materials Science*, 9, 230–238.
- Geng, J., Ma, C., Zhang, D., & Ning, X. (2020). Facile and fast synthesis of SnO<sub>2</sub> quantum dots for high performance solid-state asymmetric supercapacitor. *Journal of Alloys and Compounds*, 825(5), 153850.
- Giannakou, P. (2020). *Printed Transition Metal Oxide Electrochemical Capacitors for Energy Harvesting Applications*.
- Gomathi, E., Jayapriya, M., & Arulmozhi, M. (2021). Environmental benign synthesis of tin oxide ( SnO<sub>2</sub> ) nanoparticles using Actinidia deliciosa ( Kiwi ) peel extract with enhanced catalytic properties. *Inorganic Chemistry Communications*, 130(January), 108670.
- Goswami, M. (2020). Enhancement of photocatalytic activity of synthesized Cobalt doped Zinc Oxide nanoparticles under visible light irradiation. *Optical Materials*, 109(November), 110400.
- Guo, W., Zhou, Q., Zhang, J., Fu, M., Radacsi, N., & Li, Y. (2019). Sensors and Actuators B : Chemical Hydrothermal synthesis of Bi-doped SnO<sub>2</sub> / rGO nanocomposites and the

- enhanced gas sensing performance to benzene. *Sensors & Actuators: B. Chemical*, 299(April), 126959.
- Gutiérrez-pineda, E., Subrati, A., & Rodríguez-presa, M. J. (2023). Electrochemical Exfoliation of Graphene Oxide: Unveiling Structural Properties and Electrochemical Performance. *Chemistry A European Journal*, 29(66), e202302450.
- Habte, A. T., & Ayele, D. W. (2019). Synthesis and Characterization of Reduced Graphene Oxide ( rGO ) Started from Graphene Oxide ( GO ) Using the Tour Method with Different Parameters. *Advances in Materials Science and Engineering*, 1, 1–9.
- Hakim, A., Rahim, A., Ramli, N., Nurashikin, A., Firdaus, M., & Wahab, A. (2021). Supercapacitor performance with activated carbon and graphene nanoplatelets composite electrodes , and insights from the equivalent circuit model. *International Journal of Nanoelectronics and Materials*, 15(2), 139–154.
- Halvaeifard, R., & Sharifnia, S. (2018). The effect of surfactants on the photocatalytic performance of BiOCl-ZnO nanoparticles in the degradation of an organic pollutant. *Korean Journal of Chemical Engineering*, 35(3), 770–776.
- Hamrouni, A., Moussa, N., Parrino, F., Di, A., Houas, A., & Palmisano, L. (2014). Sol – gel synthesis and photocatalytic activity of ZnO – SnO<sub>2</sub> nanocomposites. *Journal of Molecular Catalysis A : Chemical*, 390(August), 133–141.
- Han, C., Wang, X., Peng, J., Xia, Q., Chou, S., Cheng, G., & Huang, Z. (2021). Recent Progress on Two-Dimensional Carbon Materials for Emerging Post-Lithium ( Na<sup>+</sup> , K<sup>+</sup> , Zn<sup>2+</sup> ) Hybrid Supercapacitors. *Polymers*, 13(13), 1–22.
- Haruna, A., Abdulkadir, I., & Idris, S. O. (2020). Effect of annealing temperature on the synthesis and photocatalytic properties of nanoparticle synthesized by sol-gel method. *Beni-Suef University Journal of Basic and Applied Sciences*, 9(8), 1–8.
- Hayes, W. I., Joseph, P., & Mughal, M. Z. (2015). Production of reduced graphene oxide via hydrothermal reduction in an aqueous sulphuric acid suspension and its electrochemical behaviour. *Journal of Solid State Electrochemistry*, 19(February), 361–380.
- He, S., Hou, P., Petropoulos, E., Feng, Y., & Yu, Y. (2018). High Efficient Visible-Light Photocatalytic Performance of Cu/ZnO/rGO Nanocomposite for Decomposing of Aqueous Ammonia and Treatment of Domestic Wastewater. *Frontiers in Chemistry*, 6(June), 1–13.
- Hong, P., Ngoc, N., Viet, L., & Manh, C. (2021). Comparative study on the gas-sensing performance of ZnO/ SnO<sub>2</sub> external and ZnO – SnO<sub>2</sub> internal heterojunctions for ppb H<sub>2</sub>S and NO<sub>2</sub> gases detection. *Sensors and Actuators : B . Chemical*, 334(December

- 2020), 129606.
- Horti, N. C., Kamatagi, M. D., Patil, N. R., Wari, M. N., & Inamdar, S. R. (2018). Optik Photoluminescence properties of SnO<sub>2</sub> nanoparticles: Effect of solvents. *Optik*, 169(May), 314–320.
- Hu, Y., & Gao, H. (2023). Chemical synthesis of reduced graphene oxide: a review. *Minerals and Mineral Materials*, 2(8), 1–14.
- Huang, M., Li, F., Dong, F., Zhang, X., & Li, L. (2015). MnO<sub>2</sub>-based nanostructures for high-performance supercapacitors. *Journal of Materials Chemistry A: Materials for Energy and Sustainability*, 3, 21380–21423.
- Iqbal, M. Z., Zakar, S., & Haider, S. S. (2020). Role of aqueous electrolytes on the performance of electrochemical energy storage device. *Journal of Electroanalytical Chemistry*, 858, 113793.
- Isai, K. A., & Shrivastava, V. S. (2019). Photocatalytic degradation of methylene blue using ZnO and 2 % Fe –ZnO semiconductor nanomaterials synthesized by sol–gel method: a comparative study. *SN Applied Sciences*, 1(10), 1–11.
- Ismail, M., Gul, S., Khan, M. A., & Khan, M. I. (2016). Plant Mediated Green Synthesis of Anti-Microbial Silver Nanoparticles — A Review on Recent Trends. *Reviews in Nanoscience and Nanotechnology*, 5(2), 119–135.
- Jaafar, E., Kashif, M., Sahari, S. K., & Ngaini, Z. (2018). Study on Morphological, Optical and Electrical Properties of Graphene Oxide (GO) and Reduced Graphene Oxide (rGO). *Materials Science Forum*, 917(January), 112–116.
- Jalal, N. I., Ibrahim, R. I., & Oudah, M. K. (2021). A review on Supercapacitors: types and components A review on Supercapacitors: types and components. *Journal of Physics: Conference Series*, 1973 012015.
- Jalil, M. A., Khan, M. N. I., Mandal, S., Chowdhury, F., & Hossain, M. M. (2023). Impact of reaction temperatures on the particle size of V<sub>2</sub>O<sub>5</sub> synthesized by facile hydrothermal technique and their auspicious photocatalytic performance in dye degradation. *AIP Advances*, 13(1), 1–19.
- Jangir, L. K., Kumari, Y., Kumar, A., Kumar, M., & Awasthi, K. (2017). Investigation of luminescence and structural properties of ZnO nanoparticles, synthesized with different precursors. *Material Chemistry Frontiers*, 1(7), 1413–1421.
- Janotti, A., & Walle, C. G. Van De. (2014). Fundamentals of zinc oxide as a semiconductor. *Reports on Progress in Physics*, 72(12), 29.
- Jarvin, M., Kumar, · Sundararajan Ashok, Rosaline, D. R., Foletto, E. L., Dotto, G. L., &

- Inbanathan, S. S. R. (2022). Remarkable sunlight-driven photocatalytic performance of Ag-doped ZnO nanoparticles prepared by green synthesis for degradation of emerging pollutants in water. *Environmental Science and Pollution Research*, 29, 57330–57344.
- Jayah, N. A., Yahaya, H., Mahmood, M. R., Terasako, T., Yasui, K., & Hashim, A. M. (2015). High electron mobility and low carrier concentration of hydrothermally grown ZnO thin films on seeded a -plane sapphire at low temperature. *Nanoscale Research Letters*, 10(7), 0–10.
- Ji, D., & Kim, J. (2024). Trend of Developing Aqueous Liquid and Gel Electrolytes for Sustainable, Safe, and High - Performance Li-Ion Batteries. *Nano-Micro Letters*, 16(2), 1–18.
- Jiang, L., Roh, H., Caliskan, S., Qin, F., & Lee, J. (2020). Pseudocapacitance of Chemically Stable MnO<sub>2</sub> -NiO Mixture Layer on Highly Conductive Sb doped SnO<sub>2</sub> Nanowire Arrays. *Materials Science and Engineering:B*, 260(October), 114637.
- Jiang, L., Sun, G., Zhou, Z., Sun, S., Wang, Q., Yan, S., Li, H., Tian, J., Guo, J., Zhou, B., & Xin, Q. (2005). Size-Controllable Synthesis of Monodispersed SnO<sub>2</sub> Nanoparticles and Application in Electrocatalysts. *Journal of Physical Chemistry B*, 109(18), 8774–8778.
- Jin, C., Cheng, Y., Liu, W., & Lv, Y. (2022). Preparation of ZnO-GO nanocomposites and their properties. *In E3S Web of Conferences*, 341, 01001.
- Jones, F., Tran, H., Lindberg, D., Zhao, L., & Hupa, M. (2013). Thermal Stability of Zinc Compounds. *Energy and Fuels*, 27(10), 5663–5669.
- Kachere, A. R., Kakade, P. M., Kanwade, A. R., Dani, P., Mandlik, N. T., Rondiya, S. R., Dzade, N. Y., Jadkar, S. R., & Bhosale, S. V. (2022). Zinc Oxide/Graphene Oxide Nanocomposites: Synthesis , Characterization and Their Optical Properties. *ES Materials and Manufacturing*, 16, 19–29.
- Kadinskaya, S. A., Kondratev, V. M., Kindyushov, I. K., Koval, O. Y., Yakubovsky, D. I., Kusnetsov, A., Lihachev, A. I., Nashchekin, A. V, Akopyan, I. K., Serov, A. Y., Labzovskaya, M. E., Mikushev, S. V, Novikov, B. V, Shtrom, I. V, & Bolshakov, A. D. (2023). Deep-Level Emission Tailoring in ZnO Nanostructures Grown via Hydrothermal Synthesis. *Nanomaterials*, 13(1), 58.
- Kahouadji, B., Guerbous, L., Boukerika, A., Doli, S. D., & Jovanovi, D. J. (2017). Sol gel synthesis and pH effect on the luminescent and structural properties of YPO<sub>4</sub>: Pr<sup>3+</sup> phosphors. *Optical Materials*, 70(August), 138–143.
- Kai, C., Kwok, G., Wang, Y., Shu, X., & Yu, K. M. (2023). Conversion of p-type SnO to n-type SnO<sub>2</sub> via oxidation and the band offset and rectification of an all-Tin oxide p-n

- junction structure. *Applied Surface Science*, 627(1 August), 157295.
- Kammakakam, I., Baig, N., & Falath, W. (2021). Nanomaterials: a review of synthesis methods, properties, recent progress, and challenges. *Materials Advances*, 2(6), 1821–1871.
- Kang, Y., Li, Z., Xu, K., He, X., Wei, S., & Cao, Y. (2019). Hollow SnO<sub>2</sub> nanospheres with single-shelled structure and the application for supercapacitors. *Journal of Alloys and Compounds*, 779(30 March), 728–734.
- Karmaoui, M., Jorge, A. B., Mcmillan, P. F., Aliev, A. E., Pullar, R. C., & Tobaldi, D. M. (2018). One-Step Synthesis, Structure, and Band Gap Properties of SnO<sub>2</sub> Nanoparticles Made by a Low Temperature Nonaqueous Sol – Gel Technique. *ACS Omega*, 3(10), 13227–13238.
- Khajuee, S., & Memarian, N. (2021). Hydrothermal synthesis of ultrafine SnO<sub>2</sub> nanospheres: effect of reaction time on physical properties. *The European Physical Journal Plus*, 136, 592.
- Khalid, Awais Ahmad, P., Khan, Abdulhameed Muhammad, Saleh Khandaker, Mayeen Uddin Alam, Md. Mottahir Asim, Mohd Din, I. U., Chaudhary, Ratiram G. Kumar, Dileep Sharma, R., & Iqbal, Faruque Mohammad Rashed Emran, T. Bin. (2022). Effect of Cu Doping on ZnO Nanoparticles as a Photocatalyst for the Removal of Organic Wastewater. *Bioinorganic Chemistry and Applications*, 2022, 12.
- Khan, I. Saeed K. Zekker, I. Zhang, B. Hendi, A. H., Ahmad, A. Ahmad, S., Zada, N. Ahmad, H. Shah, L. A., & Shah, T. I. K. (2022). Review on methylene blue: Its properties, uses, toxicity and photodegradation. *Water*, 14(2), 242.
- Khan, S., Zulfiqar, S., Khan, T., Khan, R., Khan, M., & Ali, S. (2019). Investigation of structural , optical, electrochemical and dielectric properties of - SnO<sub>2</sub>/ GO nanocomposite. *Journal of Materials Science: Materials in Electronics*, 30(11), 10202–10210.
- Khatoon, Z., Fouad, H., Seo, H. K., Hashem, M., Ansari, Z. A., & Ansari, S. G. (2020). Feasibility study of doped SnO<sub>2</sub> nanomaterial for electronic nose towards sensing biomarkers of lung cancer. *Journal of Materials Science: Materials in Electronics*, 31(August), 15751–15763.
- Khuc, Q. T., Vu, X. H., & Dang, D. V. (2010). The influence of hydrothermal temperature on SnO<sub>2</sub> nanorod formation. *Advances in Natural Sciences: Nanoscience and Nanotechnology*, 1(2), 1–5.
- Kim, S., Lee, S., & Park, S. (2022). Recent Advanced Supercapacitor : A Review of Storage

- Mechanisms , Electrode Materials , Modification , and Perspectives. *Nanomaterials*, 12(20), 3708.
- Kim, S. P., Choi, M. Y., & Choi, H. C. (2016). Photocatalytic activity of SnO<sub>2</sub> nanoparticles in methylene blue degradation. *Materials Research Bulletin*, 74(February), 85–89.
- Klingshirn, C. (2007). ZnO: From basics towards applications. *Basic Solid State Physics*, 244(9), 3027–3073.
- Kong, F., Li, Y., Shang, C., & Liu, Z. (2019). Stability and Phase Transition of Cobalt Oxide Phases by Machine Learning Global Potential Energy Surface [Research-article]. *The Journal of Physical Chemistry C*, 123, 17539–17547.
- Kong, X., Hu, Y., & Pan, W. (2017). Effect of Reaction Time on the Morphology and Photocatalytic Property of ZnO Nanoparticles. *Key Engineering Materials*, 726(January), 365–369.
- Koshy, J., Chandran, A., Samuel, S., George, K. C., Koshy, J., Chandran, A., Samuel, S., & George, K. C. (2014). Optical properties of SnO<sub>2</sub> nanoparticles. *AIP Conf. Proc.*, 1620(1), 192–196.
- Krobthong, S., Rungsawang, T., & Wongrerkdee, S. (2023). Comparison of ZnO Nanoparticles Prepared by Precipitation and Combustion for UV and Sunlight-Driven Photocatalytic Degradation of Methylene Blue. *Toxics*, 11, 266.
- Kumar, G. S., Reddy, S. A., & Maseed, H. (2020). Facile hydrothermal synthesis of ternary CeO<sub>2</sub> – SnO<sub>2</sub>/rGO nanocomposite for supercapacitor application. *Functional Materials Letters*, 13(2), 1–7.
- Kumar, N., Setshedi, K., Masukume, M., & Sinha, S. (2022). Facile scalable synthesis of graphene oxide and reduced graphene oxide: comparative investigation of different reduction methods. *Carbon Letters*, 32(4), 1031–1046.
- Kumar, N., & Srivastava, V. C. (2018). Simple Synthesis of Large Graphene Oxide Sheets via Electrochemical Method Coupled with Oxidation Process [Research-article]. *ACS Omega*, 3(August), 10233–10242.
- Kumar, S., Adinarayana, G., Somala, R., Sankar, S., & Mohamed, S. (2022). Evaluation of pH Effect of Tin Oxide (SnO<sub>2</sub>) Nanoparticles on Photocatalytic Degradation , Dielectric and Supercapacitor Applications. *Journal of Cluster Science*, 33(4), 1635–1644.
- Lakehal, A., Bedhiaf, B., Bouaza, A., Benhebal, H., Ammari, A., & Dalache, C. (2018). Structural, optical and electrical properties of Ni-doped Co<sub>3</sub>O<sub>4</sub> prepared via Sol-Gel technique. *Materials Research*, 21(3).
- Lamba, R., Umar, A., Mehta, S. K., & Kansal, S. K. (2015). ZnO doped SnO<sub>2</sub> nanoparticles

- heterojunction photo-catalyst for environmental remediation. *Journal of Alloys and Compounds*, 653(25 December), 327–333.
- Lee, H., Huat, C., Lim, J., Low, M. J., Murukeshan, V. M., & Kim, Y. (2018). Flexible and stretchable micro GO/rGO optical structures by femtosecond laser photoreduction. *Conference Preceeding*, 10520, 1–8.
- Li, J., Xiao, Z., Hu, W., Zhou, X., & Zheng, X. (2013). Improved photocatalytic performance of ZnO prepared by sol–gel method with the assistance of CTAB. *Materials Letters*, 91, 301–303.
- Liang, M., Zhao, M., Wang, H., Wang, F., & Song, X. (2018). Excellent cycling stabilities of a novel calliandra-like Co<sub>3</sub>O<sub>4</sub> acted as anode materials for the lithium-ion battery. *Journal of Energy Storage*, 17(March), 311–317.
- Liang, Y., & Fang, B. (2013). Hydrothermal synthesis of SnO<sub>2</sub> nanorods: Morphology dependence, growth mechanism and surface properties. *Materials Research Bulletin*, 48(10), 4118–4124.
- Lim, I., Guzm, C. A., Anaya-esparza, L. M., & Rico, J. L. (2022). Effect of the Precursor on the Synthesis of ZnO and Its Photocatalytic Activity. *Inorganics*, 10(2), 17.
- Ling, V., Siong, E., Tai, X. H., Lee, K. M., & Juan, J. C. (2020). Unveiling the enhanced photoelectrochemical and photocatalytic properties of reduced graphene oxide for photodegradation of methylene blue dye. *RSC Advances*, 10(62), 37905–37915.
- Liu, J., Wang, D., Wang, M., & Chen, J. (2016). Uniform Two-Dimensional Co<sub>3</sub>O<sub>4</sub> Porous Sheets: Facile Synthesis and Enhanced Photocatalytic Performance. *Chemical Engineering Technology*, 39(5), 891–898.
- Liu, Y., & Chen, Y. (2016). Synthesis of large scale graphene oxide using plasma enhanced chemical vapor deposition method and its application in humidity sensing. *Journal of Applied Physics*, 119(10), 103301.
- Lobnik, A., Turel, M., Urek, S. K., & Kosak, A. (2010). Nanostructured Materials Use in Sensors: Their Benefits and Drawbacks. *In Book: Carbon and Oxide Nanostructures*, 5(August), 307–354.
- Look, D. C., Claflin, B., Alivov, Y. I., & Park, S. J. (2004). The future of ZnO light emitters. *Physica Status Solidi C: Conferences*, 201(10), 2203–2212.
- Lu, Y., Deng, B., Liu, Y., Wang, J., Tu, Z., Lu, J., Xiao, X., & Xu, G. (2020). Nanostructured Co<sub>3</sub>O<sub>4</sub> for achieving high-performance supercapacitor. *Materials Letters*, 285(15 February), 129101.
- M, N., Francisco, P., & Gonz, C. (2022). Eco-Friendly Approach for Graphene Oxide



- Synthesis by Modified Hummers Method. *Materials*, 15(20), 7228.
- Malik, S., & Muhammad, K. (2023). Nanotechnology : A Revolution in Modern Industry. *Molecules*, 28(661), 1–26.
- Mandi, V., Kurajica, S., Plodinec, M., & Panži, I. (2022). Thermal Stability and Utilization of 1D-Nanostructured Co<sub>3</sub>O<sub>4</sub> Rods Derived by Simple Solvothermal Processing. *Catalysts*, 12(10), 1162.
- Marcano, D. C., Kosynkin, D. V., Berlin, J. M., Sinitskii, A., Sun, Z., Slesarev, A., Alemany, L. B., Lu, W., & Tour, J. M. (2010). Improved Synthesis of Graphene Oxide. *ACS Nano*, 4(8), 4806–4814.
- Mary, A. J. C., Bose, A. C., Mary, A. J. C., & Bose, A. C. (2017). Facile Synthesis of ZnCo<sub>2</sub>O<sub>4</sub>/rGO Nanocomposite for Effective Supercapacitor Application. *AIP Conference Proceedings*, 1832(1), 050093.
- Mbongo, A. K., & Mata, G. N. (2019). Gamma - radiation induced synthesis of spinel - Co<sub>3</sub>O<sub>4</sub> nanoparticles. *SN Applied Sciences*, 1(4), 1–9.
- Mbuyazi, T. B., & Ajibade, P. A. (2023). Influence of Different Capping Agents on the Structural , Optical, and Photocatalytic Degradation Efficiency of Magnetite ( Fe<sub>3</sub>O<sub>4</sub> ) Nanoparticles. *Nanomaterials*, 13(14), 2067.
- Mei, X., Meng, X., & Wu, F. (2015). Hydrothermal method for the production of reduced graphene oxide GO colloidal solution GO lamellar solid sample for conductivity test. *Physica E: Low-Dimensional Systems and Nanostructures*, 68(April), 81–86.
- Mekuye, B., & Abera, B. (2023). Nanomaterials : An overview of synthesis, classification , characterization , and applications. *Nano Select*, 4(8), 486–501.
- Meng, J., Yang, Z., Chen, L., Qin, H., & Cui, F. (2020). Energy storage performance of CuO as a cathode material for aqueous zinc ion battery. *Materials Today Energy*, 15(March), 100370.
- Modi, S., Yadav, V. K., Amari, A., & Alyami, A. Y. (2023). Photocatalytic Degradation of Methylene Blue Dye from Wastewater by Using Doped Zinc Oxide Nanoparticles. *Water*, 15(12), 2275.
- Modi, S., Yadav, V. K., Amari, A., Alyami, A. Y., Yousef, A., Gacem, A., Fulekar, Harharah, H. N., & Hiranman, M. (2023). Photocatalytic Degradation of Methylene Blue Dye from Wastewater by Using Doped Zinc Oxide Nanoparticles. *Water*, 15(12), 2275.
- Mondal, A., Prabhakaran, A., Gupta, S., & Subramanian, V. R. (2021). Boosting Photocatalytic Activity Using Reduced Graphene Oxide (RGO)/Semiconductor Nanocomposites : Issues and Future Scope. *ACS Omega*, 6(13), 8734–8743.

- Moosavifard, S. E., El-kady, M. F., Rahmanifar, S., Kaner, R. B., & Mousavi, M. F. (2015). Designing 3D highly ordered nanoporous CuO electrodes for high-performance asymmetric supercapacitors Designing 3D highly ordered nanoporous CuO electrodes for high- performance asymmetric supercapacitors. *ACS Appl Mater Interfaces*, 7(8), 4851–4860.
- Moradpoor, Hedaiat Safaei, Mohsen Rezaei, Farzad Golshah, Amin Jamshidy, Ladan Hatam, Reza Abdullah, R. S. (2019). Optimisation of Cobalt Oxide Nanoparticles Synthesis as Bactericidal Agents. *J Med Sci.*, 7(17), 2757–2762.
- Morka, T. D., & Ujihara, M. (2023). Enhanced Performance of WO<sub>3</sub>/SnO<sub>2</sub> Nanocomposite Electrodes with Redox-Active Electrolytes for Supercapacitors. *International Journal of Molecular Sciences*, 24(7), 6045.
- Motelica, L., Oprea, O., Vasile, B., & Ficai, A. (2023). Antibacterial Activity of Solvothermal Obtained ZnO Nanoparticles with Different Morphology and Photocatalytic Activity against a Dye Mixture : Methylene Blue , Rhodamine B and Methyl Orange. *International Journal of Molecular Sciences*, 24(6), 5677.
- Mubeen, K., Irshad, A., Safeen, A., Aziz, U., & Safeen, K. (2023). Band structure tuning of ZnO/CuO composites for enhanced photocatalytic activity. *Journal of Saudi Chemical Society*, 27(3), 101639.
- Mun, H., Yang, H., Park, J., Ju, C., & Char, K. (2015). High electron mobility in epitaxial SnO<sub>2</sub> – x in semiconducting regime. *APL Mater.*, 3(March), 076107.
- Munguti, L., & Dejene, F. (2021). Materials Science in Semiconductor Processing Effects of Zn:Ti molar ratios on the morphological , optical and photocatalytic properties of ZnO-TiO<sub>2</sub> nanocomposites for application in dye removal. *Materials Science in Semiconductor Processing*, 128(January), 105786.
- Mustapha, S., Ndamitso, M. M., Abdulkareem, A. S., Tijani, J. O., & Ajala, D. T. S. A. O. (2020). Application of - TiO<sub>2</sub> and ZnO nanoparticles immobilized on clay in wastewater treatment : a review. *Applied Water Science*, 10(1), 1–36.
- Nagarjuna, Y., Hsiao, Y., Albadarin, N. A., & Takriff, M. S. (2017). Synthesis CuO-ZnO nanocomposite and its application as an antibacterial agent. *OP Conf. Series: Materials Science and Engineering*, 172.
- Naqvi, S. H., & Badshah, N. (2013). Sn doping induced enhancement in the activity of ZnO nanostructures against antibiotic resistant S . aureus bacteria. *International Journal of Nanomedicine*, 8(2013), 3679–3687.
- Ni, X., Chen, C., Wang, Q., & Li, Z. (2019). One-step hydrothermal synthesis of SnO<sub>2</sub> -

- MoS<sub>2</sub> composite heterostructure for improved visible light photocatalytic performance. *Chemical Physics*, 525(May), 110398.
- Nikiforov, A., Timofeev, V., Mashanov, V., Azarov, I., Loshkarev, I., Volodin, V., Gulyaev, D., Chetyrin, I., & Korolkov, I. (2020). Applied Surface Science Formation of SnO and SnO<sub>2</sub> phases during the annealing of SnO (x) films obtained by molecular beam epitaxy. *Applied Surface Science*, 512(October 2019), 145735.
- Nishina, Y., & Eigler, S. (2020). Chemical and Electrochemical Synthesis of Graphene Oxide Chemical and Electrochemical Synthesis of Graphene Oxide - A Generalized View. *Nanoscale*, 12(24), 12731–12740.
- Olusakin, P., Oladiran, T., Oyinkansola, E., Joel, O., Oladoye, P. O., Oladiran, A. T., Omotola, E. O., & Oyewola, O. J. (2022). Results in Engineering Methylene blue dye : Toxicity and potential elimination technology from wastewater. *Results in Engineering*, 16(September), 100678.
- Pal, B., Yang, S., & Ramesh, S. (2019). Electrolyte selection for supercapacitive devices : A critical review. *Nanoscale Advances*, 1(10), 3807–3835.
- Palai, A., Panda, N. R., Sahoo, M. R., & Sahu, D. (2021). Study on the electronic band structure of ZnO – SnO<sub>2</sub> heterostructured nanocomposites with mechanistic investigation on the enhanced photoluminescence and photocatalytic properties. *Journal of Materials Science: Materials in Electronics*, 33(April), 9599–9615.
- Panda, A. M. H. S. (2023). A review on electrolytes for supercapacitor device. *Discover Materials*, 3(29), 1–27.
- Pathak, M., Bhatt, D., Bhatt, C., & Bohra, S. (2024). High Energy Density Supercapacitors : An Overview of Efficient Electrode Materials , Electrolytes , Design , and Fabrication. *The Chemical Record*, 24(e202300236), 1–37.
- Pavithra, N. S., Manukumar, K. N., Viswanatha, R., & Nagaraju, G. (2021). Combustion-derived CuO nanoparticles: Application studies on lithium-ion battery and photocatalytic activities. *Inorganic Chemistry Communications*, 130(4), 108689.
- Pazouki, S., & Memarian, N. (2021). Optik Effects of Hydrothermal temperature on the physical properties and anomalous band gap behavior of ultrafine SnO<sub>2</sub> nanoparticles. *Optik*, 246(37), 167843.
- Peddi, P., Ptsrk, P. R., Rani, N. U., & Tulasi, S. L. (2021). Green Synthesis, Characterization, antioxidant , antibacterial, and photocatalytic activity of Suaeda maritima ( L .) Dumort aqueous extract-mediated copper oxide nanoparticles. *Journal of Genetic Engineering and Biotechnology*, 19(1), 131.

- Perumal, V., Uthrakumar, R., Chinnathambi, M., Inmozhi, C., Robert, R., Rajasaravanan, M. E., Raja, A., & Kaviyarasu, K. (2023). Electron-hole recombination effect of SnO<sub>2</sub> – CuO nanocomposite for improving methylene blue photocatalytic activity in wastewater treatment under visible light. *Journal of King Saud University - Science*, 35(1), 102388.
- Perveen, S., & Akhyar, M. (2017). Influence of lanthanum precursors on the heterogeneous La/SnO<sub>2</sub> – TiO<sub>2</sub> nanocatalyst with enhanced catalytic activity under visible light. *Journal of Materials Science: Materials in Electronics*, 28(August), 10806–10818.
- Pham Van Tuan, , Le Trung Hieu<sup>1</sup>, Vu Thi Tan, Tran Thi Phuong , Tran Thi Quỳnh Hoa, T., & Khiem, N. (2019). The dependence of morphology, structure, and photocatalytic activity of SnO<sub>2</sub>/rGO nanocomposites on hydrothermal temperature. *Materials Research Express*, 6(10), 106204.
- Pinto, A. H., Nogueira, A. E., Dalmaschio, C. J., Frigini, I. N., Almeida, J. C. De, Ferrer, M. M., Berengue, O. M., Gonçalves, R. A., & Mendonça, V. R. De. (2022). Doped Tin Dioxide (d-SnO<sub>2</sub>) and Its Nanostructures: Review of the Theoretical Aspects , Photocatalytic and Biomedical Applications. *Solids*, 3(2), 327–360.
- Pirgholi-givi, G., Farjami-shayesteh, S., & Azizian-kalandaragh, Y. (2019). The influence of irradiation intensity and stirring rate on the photocatalytic activity of titanium dioxide nanostructures prepared by the microwave-assisted method for photodegradation of MB from water. *Physica B: Physics of Condensed Matter*, 578(1 February), 411886.
- Poh, T. Y., Nur, A., Mohamed, B., Aogáin, M. Mac, & Kathawala, M. H. (2018). Inhaled nanomaterials and the respiratory microbiome: clinical, immunological and toxicological perspectives. *Particle and Fibre Toxicology*, 15(46), 1–16.
- Prabaharan, D. D. M., Sadaiyandi, K., Mahendran, M., & Sagadevan, S. (2017). Precipitation method and characterization of cobalt oxide nanoparticles. *Applied Physics A*, 123(4), 1–6.
- Prabakaran, E., & Pillay, K. (2019). Synthesis of N-doped ZnO nanoparticles with cabbage morphology as a catalyst for the efficient photocatalytic degradation of methylene blue under UV and visible light. *RSC Advances*, 9(13), 7509–7535.
- Prakash, K., Kumar, P. S., Pandiaraj, S., & Saravanakumar, K. (2016). Controllable synthesis of SnO<sub>2</sub> photocatalyst with superior photocatalytic activity for the degradation of methylene blue dye solution. *Journal of Experimental Nanoscience*, 11(14), 1138–1155.
- Priyadharsini, C. I., Anbarasan, P. M., Aroulmoji, V., Siva, V., Priyadharsini, C. I., Anbarasan, P. M., Aroulmoji, V., & Synthesize, V. S. (2021). Investigations of Cobalt Oxide Nanoparticles to Supercapacitor. *Aegaeum Journal*, 8(8), 750.

- Rafique, K., Zia, M., Shah, U., Shah, A., Sana, M., Shah, U., Hou, H., Sajjad, M., Arif, M., Ahmad, S. A., & Hassan, N. (2023). Electrochemical performance evaluation of a newly developed ZnS – SnO<sub>2</sub> composite in an aqueous electrolyte. *Journal of Materials Science: Materials in Electronics*, 34(24), 1–13.
- Rafique, M., Tahir, M. B., Rafique, M. S., & Hamza, M. (2020). History and fundamentals of nanoscience and nanotechnology. In *Nanotechnology and Photocatalysis for Environmental Applications*. Elsevier Inc.
- Raha, S., & Ahmaruzzaman, M. (2022). ZnO nanostructured materials and their potential applications: progress, challenges and perspectives. *Nanoscale Advances*, 4(8), 1868–1925.
- Raizada, P., Sudhaik, A., Patial, S., Hasija, V., Aslam, A., Khan, P., Singh, P., Gautam, S., Kaur, M., & Nguyen, V. (2020). Engineering nanostructures of CuO-based photocatalysts for water treatment: Current progress and future challenges. *Arabian Journal of Chemistry*, 11(November), 8424–8457.
- Ramesh, M. (2021). CuO as efficient photo catalyst for photocatalytic decoloration of wastewater containing Azo dyes. *Water Practice and Technology*, 16(4), 1078–1090.
- Ramesh, M., Anbuvaran, M., & Viruthagiri, G. (2014). Green synthesis of ZnO nanoparticles using Solanum nigrum leaf extract and their antibacterial activity. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 136, Part(5 February), 864–870.
- Ramesh, S., Yadav, H. M., Lee, Y., Hong, G., Kathalingam, A., Sivasamy, A., Kim, H., Kim, H. S., & Kim, J. (2019). Porous materials of nitrogen doped graphene oxide @ SnO<sub>2</sub> electrode for capable supercapacitor application. *Scientific Reports*, 9(12622), 1–10.
- Ramzan, M., & Ashraf, S. (2019). Synthesis of Co<sub>3</sub>O<sub>4</sub> Nano Aggregates by Co-precipitation Method and its Catalytic and Fuel Additive Applications. *Open Chemistry*, 17(1), 865–873.
- Rana, P. S. (2023). Influence of CTAB surfactant on the various properties of CdO nanoparticles and their application in field of dye degradation. *Journal of Water and Environmental Nanotechnology*, 8(2), 190–205.
- Raship, N. A., Sahdan, M. Z., Adriyanto, F., Nurfazliana, M. F., & Bakri, A. S. (2017). Copper Oxide Films Prepared by Dip Coating Technique. *AIP Conf. Proc.*, 1788(1), 030121.
- Ray, S. C. (2016). Application and Uses of Graphene Oxide and Reduced Graphene Oxide. In *In book: Applications of Graphene and Graphene-Oxide Based Nanomaterials* (Issue

December, pp. 39–55).

- Roberts, M. W., Clemons, C. B., Wilber, J. P., Young, G. W., Buldum, A., & Quinn, D. D. (2014). Continuum Plate Theory and Atomistic Modeling to Find the Flexural Rigidity of a Graphene Sheet Interacting with a Substrate. *Journal of Nanotechnology*, 23(May), 8.
- Rocha, I. L., González, C. A. G., Esparza, L. M. A., Toledo, R. R., Rico, J. L., Vargas, O. A. G., & Larios, A. P. (2022). Effect of the Precursor on the Synthesis of ZnO and Its Photocatalytic Activity. *Inorganics*, 10(16), 1–18.
- Sagadevan, S., Chowdhury, Z. Z., Johan, M. R. Bin, Aziz, F. A., Roselin, L. S., Podder, J., Lett, J. A., & Selvin, R. (2019). Cu-Doped SnO<sub>2</sub> Nanoparticles: Synthesis and Properties. *Journal of Nanoscience and Nanotechnology*, 19(11), 7139–7148.
- Sahu, K., Satpati, B., & Mohapatra, S. (2021). Facile fabrication of CuO nanosheets for photocatalytic applications. *Applied Physics A*, 127(5), 361.
- Saikia, L., Bhuyan, D., Saikia, M., & Malakar, B. (2014). Photocatalytic performance of ZnO nanomaterials for self sensitized degradation of malachite green dye under solar light. *Applied Catalysis A: General*, 490(25 January), 42–49.
- Sakib, A. A. M., Masum, S. M., Hoinkis, J., Islam, R., & Molla, M. A. I. (2019). Synthesis of CuO/ZnO Nanocomposites and Their Application in Photodegradation of Toxic Textile Dye. *Journal of Composite Science*, 3(3), 91.
- Saleem, S., Jabbar, A. H., Jameel, M. H., Rehman, A., Kareem, Z. H., Abbas, A. H., Gha, Z., & Razzaq, S. A. (2022). Enhancement in structural , morphological and optical properties of copper oxide for optoelectronic device applications. *Nanotechnology Reviews*, 11(1), 2827–2838.
- Sali, S., & Mackey, H. R. (2019). Effect of Graphene Oxide Synthesis Method on Properties and Performance of Polysulfone-Graphene Oxide Mixed Matrix Membranes. *Nanomaterials*, 9(5), 769.
- Sarmah, S., & Kumar, A. (2010). Optical Properties of SnO<sub>2</sub> Nanoparticles. *Indian Journal of Physics*, 84(September), 1211–1221.
- Sayyed, S. G., Shaikh, A. V., Shinde, U. P., Hiremath, P., & Naik, N. (2023). Copper oxide-based high-performance symmetric flexible supercapacitor: potentiodynamic deposition. *Journal of Materials Science: Materials in Electronics*, 34(17), 1–14.
- Schmiedova, V., Pospisil, J., Kovalenko, A., Ashcheulov, P., Fekete, L., Cubon, T., Kotrusz, P., Zmeskal, O., & Weiter, M. (2017). Physical Properties Investigation of Reduced Graphene Oxide Thin Films Prepared by Material Inkjet Printing. *Journal of*

- Nanomaterials*, 2017(31 December), 1–8.
- Schorr, N. B., Arnot, D. J., Bruck, A. M., Gallaway, J. W., & Lambert, T. N. (2021). Copper Oxide Cathodes for Rechargeable Alkaline Zinc Batteries. *Proposed for Presentation at the MRS Fall Meeting Held December 6-8, in Boston, MA US*.
- Sedira, S., & Mendaci, B. (2020). Hydrothermal synthesis of spherical carbon nanoparticles ( CNPs ) for supercapacitor electrodes uses. *Materials for Renewable and Sustainable Energy*, 9(1), 1–9.
- Selvinsimpson, Steplinpauselvin Gnanamozhi, P Pandiyan Govindasamy, V.Mani Habila, Mohamed A. Najla, AlMasoud Chen, Y. (2021). Synergetic effect of Sn doped ZnO nanoparticles synthesized via ultrasonication technique and its photocatalytic and antibacterial activity. *Environmental Research*, 197(June), 111115.
- Sennu, P., Madhavi, S., Aravindan, V., & Lee, Y. (2020). Co<sub>3</sub>O<sub>4</sub> Nanosheets as Battery-Type Electrode for High-Energy Li-Ion Capacitors: A Sustained Li-Storage via Conversion Pathway. *ACS Nano*, 14(8), 10648–10654.
- Shameem, A. S., Murugan, A., Siva, V., Palanisamy, G., Kim, I., Lee, J., & Paramasivam, S. (2024). A High-Performance Supercapacitor Based on Hierarchical template-Free Ni/SnO<sub>2</sub> Nanostructures via Hydrothermal Method. *Materials*, 17(8), 1894.
- Sharma, D. K., Shukla, S., Sharma, K. K., & Kumar, V. (2020). A review on ZnO : Fundamental properties and applications. *Materials Today: Proceedings*, 49(Part 8), 3028–3035.
- Sharma, M., Adalati, R., Kumar, A., Chawla, V., & Chandra, R. (2021). Elevated performance of binder-free Co<sub>3</sub>O<sub>4</sub> electrode for the supercapacitor applications. *Nano Express*, 2(1), 010002.
- Sharma, S., & Chand, P. (2023). Supercapacitor and electrochemical techniques : A brief review. *Results in Chemistry*, 5(March), 100885.
- Sharma, V., Sharma, J. K., Kansay, V., Dutt, V., Sharma, A., Kumar, S., Sharma, A. K., & Bera, M. K. (2023). The effect of calcination temperatures on the structural and optical properties of zinc oxide nanoparticles and their influence on the photocatalytic degradation of leather dye. *Chemical Physics Impact*, 6(March), 100196.
- Shelar, S. G., Mahajan, K. V., Patil, S. P., & Sonawane, G. H. (2020). Effect of doping parameters on photocatalytic degradation of methylene blue using Ag doped ZnO nanocatalyst. *SN Applied Sciences*, 2(5), 820.
- Shewale, P. S., & Yun, K. (2020). Synthesis and characterization of Cu-doped ZnO / RGO nanocomposites for room-temperature H<sub>2</sub> S gas sensor. *Journal of Alloys and*

*Compounds*, 837, 155527.

- Sheyda Fakhri-Mirzanagh, Kobra Ahadzadeh-Namin, Gholamreza Pirgholi Givi, Javid Farazin, Y. A.-K. (2020). The effect of capping agent on the structural, optical properties and photocatalytic activity of MgO nanostructures. *Physica B: Physics of Condensed Matter*, 583(January), 412064.
- Shittu, H. A., Adedokun, O., Kareem, M. A., Bello, I. T., & Arumugam, S. (2023). Effect of Low-Doping Concentration on Silver-Doped SnO<sub>2</sub> and its Photocatalytic Applications. *Biointerface Research in Applied Chemistry*, 13(2), 165.
- Shubha, J. P., Adil, S. F., Khan, M., Hatshan, M. R., & Khan, A. (2021). Facile Fabrication of a ZnO/Eu<sub>2</sub>O<sub>3</sub>/NiO-Based Ternary Heterostructure Nanophotocatalyst and Its Application for the Degradation of Methylene Blue. *ACS Omega*, 6(5), 3866–3874.
- Sivasubramanian, S. P., & Vhanbatte, S. (2019). *Graphene Oxide a Promising Material – A Review*. July.
- Song, J., Hua, L., Shen, Q., Wang, F., & Zhang, L. (2015). Effect of pH Value on the Properties of SnO<sub>2</sub> Nano-Crystalline for Dye Sensitized Solar Cells. *Key Engineering Materials*, 633(7 November), 273–276.
- Srivastava, A. K., Tawale, J. S., Verma, R., Agarwal, D., Sharma, C., Kumar, A., & Gupta, M. K. (2022). Morphological evolution driven semiconducting nanostructures for emerging solar, biological and nanogenerator applications. *Materials Advances*, 3(22), 8030–8062.
- Su, D., Xie, X., Dou, S., & Wang, G. (2014). CuO single crystal with exposed {001} facets - A highly efficient material for gas sensing and Li-ion battery applications. *Scientific Reports*, 4(5753), 1–9.
- Tadyszak, K., & Wychowanec, J. K. (2018). Biomedical Applications of Graphene-Based Structures. *Nanomaterials*, 8(11), 944.
- Tai, X. H., Chook, W., Lai, W., Lee, K. M., & Juan, J. C. (2019). Effective photoreduction of graphene oxide for photodegradation of volatile organic compounds. *RSC Advances*, 9(31), 18076–18086.
- Tao, L., Shengjun, L., Bowen, Z., Bei, W., Dayong, N., Zeng, C., Ying, Y., & Ning, W. (2015). Supercapacitor electrode with a homogeneously Co<sub>3</sub>O<sub>4</sub> coated multiwalled carbon nanotube for a high capacitance. *Nanoscale Research Letters*, 10(208), 1–8.
- Tarek, Y. A., Shakil, R., Reaz, A. H., Roy, C. K., Barai, H. R., & Firoz, S. H. (2022). Wrinkled Flower-Like rGO intercalated with Ni(OH)<sub>2</sub> and MnO<sub>2</sub> as High-Performing Supercapacitor Electrode. *ACS Omega*, 7(23), 20145–20154.



- Taufik, A., Albert, A., & Saleh, R. (2017). Sol-gel synthesis of ternary CuO/TiO<sub>2</sub>/ZnO nanocomposites for enhanced photocatalytic performance under UV and visible light irradiation. *Journal of Photochemistry & Photobiology, A: Chemistry*, 344(1 July), 149–162.
- Thota, S., Tirukkovalluri, S. R., & Bojja, S. (2014). Visible Light Induced Photocatalytic Degradation of Methyl Red with Codoped Titania. *Journal of Catalysts*, 2014, 1–7.
- Toloman, D., Popa, A., Stefan, M., Silipas, T. D., Suci, R. C., Barbu-tudoran, L., & Pana, O. (2020). Enhanced photocatalytic activity of Co doped SnO<sub>2</sub> nanoparticles by controlling the oxygen vacancy states. *Optical Materials*, 110(September), 110472.
- Tripathi, S. K., Kaur, R., & Rani, M. (2015). Fabrication and electrical characterization of memristor with TiO<sub>2</sub> as an active layer. *AIP Conference Proceedings*, 1661(1), 110027.
- Tryba, B., Tygielska, M., Wróbel, R., Żołnierkiewicz, G., & Guskos, N. (2016). Influence of pH of sol-gel solution on phase composition and photocatalytic activity of TiO<sub>2</sub> under UV and visible light. *Materials Research Bulletin*, 84(December), 152–161.
- Uddin, M. T., Hoque, M. E., & Bhoomick, M. C. (2020). Facile one-pot synthesis of heterostructure SnO<sub>2</sub>/ZnO photocatalyst for enhanced photocatalytic degradation of organic dye. *RSC Advances*, 10(40), 23554–23565.
- Ullah, E., Ahmad, S. A., Zia, M., Shah, U., Arif, M., Khan, M. I., Hou, M., Guo, S., Shah, A., & Sajjad, M. (n.d.). *Pr ep rin t n ot pe er r Pr rin t n ed*.
- Ullah, E., Zia, M., Shah, U., Awais, S., & Arif, M. (2023). Fabrication of 1.6 V asymmetric supercapacitor in an aqueous electrolyte using a CuO-SnO<sub>2</sub> composite and activated carbon electrodes Fabrication of 1.6 V asymmetric supercapacitor in an aqueous electrolyte using a CuO-SnO<sub>2</sub> composite and activated car. *Materials Today Communications*, 37(August), 106889.
- Umar, A., Raut, S. D., Ibrahim, A. A., Algadi, H., Albargi, H., Alsaiani, M. A., Akhtar, M. S., & Qamar, M. (2021). Electrochimica Acta Perforated Co<sub>3</sub>O<sub>4</sub> nanosheets as high-performing supercapacitor material. *Electrochimica Acta*, 389(48), 138661.
- Ungeheuer, K., Marszalek, K. W., & Mitura-nowak, M. (2022). Influence of Cr Ion Implantation on Physical Properties of CuO Thin Films. *International Journal of Molecular Sciences*, 23(9), 4541.
- Vandeginste, V. (2022). *applied sciences A Review of Fabrication Technologies for Carbon*.
- Velardi, L., Scrimieri, L., Serra, A., Manno, D., & Calcagnile, L. (2020). Effect of temperature on the physical , optical and photocatalytic properties of - TiO<sub>2</sub> nanoparticles. *SN Applied Sciences*, 2(4), 1–6.

- Venkatesh, N., Aravindan, S., Ramki, K., Murugadoss, G., Thangamuthu, R., & Sakthivel, P. (2021). Sunlight-driven enhanced photocatalytic activity of bandgap narrowing Sn-doped ZnO nanoparticles. *Environmental Science and Pollution Research*, 28(13), 16792–16803.
- Vennela, A. B., Mangalaraj, D., Muthukumarasamy, N., Agilan, S., & Hemalatha, K. V. (2019). Structural and Optical Properties of Co<sub>3</sub>O<sub>4</sub> Nanoparticles Prepared by Sol-gel Technique for Photocatalytic Application. *International Journal of Electrochemical Science*, 14(4), 3535–3552.
- Vetter, S., Haffer, S., Wagner, T., & Tiemann, M. (2015). Nanostructured Co<sub>3</sub>O<sub>4</sub> as a CO gas sensor: Temperature-dependent behavior. *Sensors & Actuators: B. Chemical*, 206, 133–138.
- Viet, P. Van, Thi, C. M., & Hieu, L. Van. (2016a). The High Photocatalytic Activity of SnO<sub>2</sub> Nanoparticles Synthesized by Hydrothermal Method. *Journal of Nanomaterials*, 2016.
- Viet, P. Van, Thi, C. M., & Hieu, L. Van. (2016b). The High Photocatalytic Activity of SnO<sub>2</sub> Nanoparticles Synthesized by Hydrothermal Method. *International Journal of Industrial Chemistry*, 7, 53–70.
- Vignesh, K., Rajarajan, M., & Suganthi, A. (2014). Visible light assisted photocatalytic performance of Ni and Th co-doped ZnO nanoparticles for the degradation of methylene blue dye. *Journal of Industrial and Engineering Chemistry*, 20(5), 3826–3833.
- Wang, Y., Bai, X., Luo, Z., & Fu, L. (2020). High specific energy of CuO as a thermal battery cathode. *International Journal of Electrochemical Science*, 15(10), 10406–10411.
- Wasly, H. S., El-sadek, M. S. A., & Henini, M. (2018). Influence of Reaction Time and Synthesis Temperature on Physical Properties of ZnO Nanoparticles Synthesized by Hydrothermal Method. *Applied Physics A*, 124(1), 12.
- Yadav, K., Kumar, P., Teja, D. R., Chakraborty, S., Chakraborty, M., Mohapatra, S. S., Sahoo, A., Chou, M. M. C., Liang, C., & Hang, D. (2023). A Review on Low-Dimensional Nanomaterials: Nanofabrication, Characterization and Applications. *Nanomaterials*, 13(160), 1–44.
- Yi-feng, L. I., Jian-feng, H., Li-yun, C. A. O., & Jian-peng, W. U. (2012). Effect of pH Value on Preparation of La<sub>2</sub>CuO<sub>4</sub> Microcrystallites Synthesized by Sol-Gel Process. *Key Engineering Materials*, 515, 231–234.
- Yu, K., Shi, J., Zhang, Z., Liang, Y., & Liu, W. (2013). Synthesis, characterization, and photocatalysis of ZnO and er-doped ZnO. *Journal of Nanomaterials*, 2013(75), 75.

- Yuasa, M., Suematsu, K., Yamada, K., Kida, T., Yamazoe, N., & Shimanoe, K. (2016). Thermally stable SnO<sub>2</sub> nanocrystals : Synthesis and application to gas sensors. *Crystal Growth and Design*, 16(8), 4203–4208.
- Zaaba, N. I., Foo, K. L., Hashim, U., Tan, S. J., Liu, W., & Voon, C. H. (2017). Synthesis of Graphene Oxide using Modified Hummers Method : Solvent Influence. *Procedia Engineering*, 184(5934), 469–477.
- ZabnAllah M. Alaizeri, Hisham A. Alhadlaq, Saad Aldawood, M. J. A. and M. A. (2022). One - Pot Synthesis of SnO<sub>2</sub> -rGO Nanocomposite for Enhanced Photocatalytic and Anticancer Activity. *Polymers*, 14(10), 2036.
- Zhang, H., Xu, P., Ni, Y., Geng, H., Zheng, G., Dong, B., & Jiao, Z. (2014). In situ chemical synthesis of SnO<sub>2</sub>/reduced graphene oxide nanocomposites as anode materials for lithium-ion batteries. *Journal of Materials Research*, 29(5), 617–624.
- Zhang, J., Cui, Y., & Shan, P. G. (2018). Metal oxide nanomaterials for pseudocapacitors. *ACS Applied Materials Interfaces*, 7(8), 4851–4860.
- Zhang, L., Hui, K. N., Hui, K. S., Chen, X., & Chen, R. (2016). Role of graphene on hierarchical flower-like NiAl layered double hydroxide-nickel foam-graphene as binder-free electrode for high-rate hybrid supercapacitor. *International Journal of Hydrogen Energy*, 41(22), 9443–9453.
- Zhang, L., Zeng, Z., Shi, J., & Gao, K. (2023). Growth and optical properties of ZnO nanorods on the full surface of porous silicon by sol – gel method and oil bath method. *Journal of Nanophotonics*, 17(2), 1–10.
- Zhang, S., Zhang, B., Sun, G., Li, Y., Zhang, B., & Wang, Y. (2019). One-step synthesis of Ag / SnO<sub>2</sub> / rGO nanocomposites and their trimethylamine sensing properties. *Materials Research Bulletin*, 114(June), 61–67.
- Zhang, W., Feng, L., Chen, H., & Zhang, Y. (2019). Hydrothermal Synthesis of SnO<sub>2</sub> Nanorod as Anode Materials for Lithium-Ion Battery. *Nano*, 14(9), 1–9.
- Zhang, X., Sun, J., Chen, T., Xiang, C., Zhao, Y., & Zhang, N. (2022). Hydrothermal synthesis of Pd - doped rGO/ZnO - SnO<sub>2</sub> nanocomposites for efficient hydrogen detection. *Ionics*, 28(6), 1–9.
- Zhang, Y., Liu, M., & Sun, S. (2020). The preparation and characterization of SnO<sub>2</sub>/rGO nanocomposites electrode materials for supercapacitor. *Advanced Composites Letters*, 29(391), 1–7.
- Zhang, Z., Wen, Z., & Zhu, L. (2015). Gas sensors based on ultrathin porous Co<sub>3</sub>O<sub>4</sub> nanosheets to detect acetone at low temperature. *RSC Advances*, 5(74), 59976–59982.

- Zheng, J. P., Cygan, P. J., & Jow, T. R. (1995). Hydrous Ruthenium Oxide as an Electrode Material for Electrochemical Capacitors. *ChemInform*, 26(47), 98–102.
- Zhou, Q., Xu, L., Umar, A., Chen, W., & Kumar, R. (2017). Pt nanoparticles decorated SnO<sub>2</sub> nanoneedles for efficient CO gas sensing applications. *Sensors & Actuators: B. Chemical*, 256(March), 656–664.
- Zhou, T., Zhang, T., Deng, J., Zhang, R., Lou, Z., & Wang, L. (2017). P-type Co<sub>3</sub>O<sub>4</sub> nanomaterials-based gas sensor : Preparation and acetone sensing performance. *Sensors & Actuators: B. Chemical*, 242(April), 369–377.
- Zhu, Xiaodong Wang, J., Yang, Daixiong Liu, J., & He, Lili Tang, Mao Feng, Wei Wu, X. (2021). Fabrication, characterization and high photocatalytic activity of Ag–ZnO heterojunctions under UV-visible light. *RSC Advances*, 11(44), 27257–27266.
- Zhu, S., & Wang, D. (2017). Photocatalysis : Basic Principles, Diverse Forms of Implementations and Emerging Scientific Opportunities. *Advanced Energy Materials*, 7(23), 1700841.
- Zou, X., Dong, X., Wang, L., Ma, H., Zhang, X., & Zhang, X. (2014). Preparation of Ni Doped ZnO-TiO<sub>2</sub> Composites and Their Enhanced Photocatalytic Activity. *International Journal of Photoenergy*, 11, 8.