Green Synthesis of CuO/TiO_2 Composite for Hybrid Supercapacitor Application

Abebe Wolelaw Yitbarek

A Thesis Submitted to the Department of Materials Science and Engineering,

College of Mechanical, Chemical and Materials Engineering

Presented in Partial Fulfillment of the Requirement for the Degree of Master's in Materials Science and Engineering

Office of Graduate Studies

Adama Science and Technology University

May, 2025

Adama, Ethiopia

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Declaration

I hereby declare that this Master's Thesis entitled **"Green Synthesis of CuO/TiO_2 Composite for Hybrid Supercapacitor Application"** is my work and it has not been submitted for the award of any academic degree, diploma, or certificate in any other university. All sources of materials that are used for this thesis have been duly acknowledged through citation.

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I/we, the advisors of the thesis entitled **“Green Synthesis of CuO/TiO_2 Composite for Hybrid Supercapacitor Application”** and developed by Abebe Wolelaw; hereby certify that the recommendations and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis.

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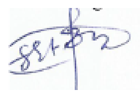
______________________		______________
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We, the undersigned, members of the Board of Examiners of the thesis by Abebe Wolelaw, have read and evaluated the thesis entitled "**Green Synthesis of CuO/TiO_2 Composite for Hybrid Supercapacitor Application**" and examined the candidate during open defense. This is, therefore, to certify that the thesis is accepted for partial fulfillment of the requirements of the degree of Master of Science in material science and engineering.

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LIST OF ACRONYMS

BET	Brunauer, Emmett, and Teller
CV	Cyclic Voltammetry
EDLC	Electrical Double Layer Capacitor
EIS	Electrochemical Impedance Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
GCD	Galvanostatic Charge-Discharge
Rct	Charge Transfer Resistance
SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction

ABSTRACT

In recent years, supercapacitors have gained significant attention due to their high power density, long cycle life, and ability to bridge the power/energy gap between traditional capacitors and batteries. Composite electrode materials have shown exceptional electrochemical properties, leading to the development of high-performance supercapacitors. This study introduces a green synthesis method for titanium oxide (TiO_2) and copper oxide (CuO), along with their binary composites, CuO/TiO_2, in varying weight ratios for potential supercapacitor applications. The synthesis process utilized Stephania abyssinica (S. abyssinica) plant extract as a natural reducing and capping agent. The synthesized materials were characterized their structural, morphological, thermal, surface properties, and functional groups using various techniques. This included X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric/differential thermal analysis (TGA/DTA), Brunauer-Emmett-Teller (BET) surface area analysis, and Fourier-transform infrared spectroscopy (FTIR). Electrochemical properties were assessed through cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS). The results indicated that the green-synthesized TiO_2, CuO, and CuO/TiO_2 composite exhibit hybrid-type supercapacitive behavior. Among the composites, the CuO/TiO_2 with a 70:30 weight ratio (TC3) demonstrated the highest specific capacitance (593.8 Fg^{-1}), enhanced surface area (102.84 m^2g^{-1}), and superior cycling stability (98.7% after 2500 cycles), surpassing the individual metal oxide electrodes. These findings suggest that the CuO/TiO_2 (TC3) composite is a promising candidate for environmentally friendly and efficient supercapacitor electrode applications.

Keywords: S.abyssinica; Green Synthesis; TiO_2; CuO; CuO/TiO_2 Composite; Supercapacitor; Energy Storage

CHAPTER ONE

INTRODUCTION

1.1 Background

Over the next few years, world energy consumption is expected to double (Kober et al., 2020). This raise is due to several key factors. Population growth comes in first place that leads to more people needing energy for necessary needs like heating, transportation, household usage, and appliances. Rapid urbanization, and industrialization will significantly raise energy use for manufacturing, construction, transportation infrastructure, and powering buildings in densely populated areas (Gielen et al., 2019). Industries are shifting from fossil fuels to electricity, due to increasing the power demand. In addition climate change poses a constant threat, requiring significant investments in energy efficiency and renewable sources to address its impacts (Jie et al., 2023). In addition, public awareness of global warming has risen due to our reliance on non-renewable energy and the depletion of natural resources.

Many developed countries are shifting focus to renewable energy alternatives (solar energy, hydrothermal, wind energies) because of these concerns (Amin et al., 2022). Solar, hydrothermal, and wind energies are abundant, environmentally friendly, and clean, but their variability makes it difficult to ensure consistent power output (Shamet et al., 2025; Sharma, 2024). To address the challenges of renewable energy, energy storage technologies such as batteries, capacitors, and supercapacitors, are crucial. These technologies help to maintain a clean and reliable energy grid and meet peak energy demands (Maghami et al., 2024).

Supercapacitors are energy storage systems, that can be utilized as a promising alternative to batteries in areas demanding high power delivery, stable, and rapid charge discharge cycles, and low overall energy storage requirements (Yaseen et al., 2021). These devices have several additional advantages, including low internal resistance, a wide operational temperature range, and high efficiency in energy transfer (Oyedotun & Mamba, 2024).

However, it is important to acknowledge their drawback, supercapacitors offer a relatively low energy density compared to other storage solutions (Dutta et al., 2023).

As compared to many types of supercapacitor electrodes, such as carbon-based, and conducting polymer, transition metal oxides (TMOs) based supercapacitors, show excellent capacitive behavior for pseudocapacitor applications due to their fast and reversible redox reactions with the electrolyte (Lukatskaya et al., 2023), and higher energy density compared to carbon and conducting polymer-based materials. However, high-cost of synthesis, low stability, and poor electrical conductivity limits their commercial applications.

Therefore, researchers directed their attention to inexpensive and non-toxic metal oxides such as, copper oxide CuO, TiO_2, MnO_2, and SnO_2 (Ruman et al., 2024; Ullah et al., 2023) and on their synthesis methods. From these lists, TiO_2 has gained attention as a promising electrode material for supercapacitors due to its natural abundance, chemical stability, tunable characteristics, and supportive structure it helps to form hetero-structure with other metal oxides (Parangi & Mishra, 2021; Salari et al., 2012). Its low cost, non-toxic nature and environmental friendliness further enhance its usefulness.

However, the main challenges regarding to TiO_2 are poor electrical conductivity, and low specific capacitance (Raj & Prasanth, 2018). To address this problem, making composite CuO with TiO_2 could be a useful strategy to study the synergetic effect of both oxides. Because CuO is a promising material owing to its high natural abundance, and good electrical conductivity (Saleem et al., 2024; Sidiqi et al., 2024), it has good pseudocapacitive performance, helping this material a promising material for efficient supercapacitor technologies. For instance, Researchers are addressing these issues through various strategies. Such as, depositing manganese dioxide (MnO_2) onto TiO_2 nanotube arrays via hydrothermal synthesis, which significantly boosts the areal capacitance (Zhang et al., 2019). Another approach involves creating hybrid nanocomposites, such as graphene oxide and TiO_2 (GO-TiO_2), which exhibit high areal specific capacitance and excellent cycling stability (Badoni et al., 2025).

In addition, now a days, very concerning issue that hindering the widespread application of TMOs based supercapacitors is their synthesis method (Meena et al., 2024). In the last decade, several physical and chemical methods such as thermal decomposition (Nandagudi et al., 2022), chemical vapor deposition (Sun et al., 2021), electrochemical deposition, sol-gel (Owens et al., 2016), and co-precipitation have been used to synthesis. But they are expensive, time taking, consumes high energy, release hazardous by products, toxic, and their disposal contaminates the environment and presents various disadvantages (Kurniawan et al., 2025).

So, the replicable strategy to address this drawback is green synthesis methods that are becoming more and more popular for producing nanoparticles because of their sustainable, improved surface morphology, high surface area, and environmentally friendly nature. it is known by its speed (Dheyab et al., 2024), enhanced surface area (Rani & Kumar, 2024), enhanced surface morphology, affordability, and environmental safety. From well know reducing agents plant-mediated metal oxide synthesis is especially advantageous since it produces stable nanoparticles while inhibiting aggregation (Munir et al., 2021).

Plant extracts contain phytochemicals that act as reduce, and stabilizing agent. Main phytochemicals that act as reducing and stabilizing agents are organic molecules such as flavonoids (Murti et al., 2021), alkaloids (Smolobochkin et al., 2024), phenolic (Haydari et al., 2023), terpenoids, proteins, and polysaccharides that contain functional groups of hydroxyl, carboxyl, and amine. These groups donate electrons for metal ion reduction and adsorb on the surface of nanoparticles to avoid agglomeration. Reducing and stabilizing agents double the effect of allowing green, and efficient nanoparticle synthesis under mild conditions.

S. Abyssinica plant extract that act as capping and reducing agent is best candidate in green synthesis. The dominant which are rich in functional groups of hydroxyl, carboxyl, and amine (Adugna et al., 2024; Haitosa et al., 2022).

Green-synthesized nanoparticles are increasingly important in various fields, for instance, energy harvesting technologies, catalysis, sensing, drug delivery, environmental remediation, and electronics (Kirubakaran et al., 2025). It is cost effective and environmentally friendly because it reduces the use of high temperature, pressure and hazardous chemical used to reduce metallic salts to their oxide form. For example, The green synthesized ZnO-activated carbon nanocomposite exhibited a specific capacitance of 184.8 F/cm² at a scan rate of 5 mV/s, indicating its potential as a supercapacitor electrode material (Raja et al., 2019). Green synthesized CuO/NiO nanocomposite indicated high specific capacitance of 1072 F/g, and It retained 72% capacitance after 4000 cycles, indicating excellent cyclic stability (Da'na et al., 2024).

In this work, titanium dioxide (TiO_2), copper oxide (CuO), and CuO/TiO_2 binary composite with varied weight percentage (50:50, 60:40, and 70:30) assigned as TC1, TC2, and TC3 respectively, were synthesized by simple and green approach, by introducing S. abyssinica plant extract as capping and reducing agent, followed by dip coating (immersion) rout of synthesis was used to fabricate working electrodes. Characterization of materials properties of TiO_2, CuO, and binary composite by using TGA/DTA, XRD, FTIR, and BET techniques, followed by optimization of electrochemical properties of TiO_2, CuO, and its binary composite using CV, GCD, and EIS was done. The overall results showed that CuO/TiO_2 binary composite has improved electrochemical characteristics, such as better surface area, and as result higher specific capacitance and better cycling stability as compared to pristine. In the end, these green-synthesized materials' encouraging electrochemical performance points to a feasible route toward more efficient and sustainable supercapacitor electrodes, facilitating the shift to greener energy solutions.

1.2 Statement of the Problem

The raise of the world's need for energy forces the researchers to tackle the problem of sustainable and high-performance energy storage systems. One of the solutions is in the supercapacitors which are of great help for their fast charging/discharging feature and long-life cycle. As compared to carbon, and conducting polymer-based supercapacitors, the transition metal oxides (TMOs) based are still the best choice, which are very popular electrode materials used for supercapacitor application, and among these TiO_2 and CuO, are attractive because they are not expensive, have tunable proprieties, nontoxic, are able to form heterostructure, and have pseudocapacitive properties. However, TiO_2 has low areal capacitance, low electrical conductivity (Mahmood & Hussain, 2025), and low specific capacitance (Jena et al., 2024), and limited pseudocapacitive behavior (Tuersun et al., 2025). To address this problem, making a composite of CuO with TiO_2 could be a useful strategy to study the synergetic effect of both oxides. Since, CuO is a promising material owing to its high natural abundance, and good electrical conductivity (Saleem et al., 2024; Sidiqi et al., 2024), helping this material a promising material for efficient supercapacitor technologies.

In addition, conventional physical and chemical synthesis methods such as sol-gel, hydrothermal, chemical vapor deposition, and co-precipitation are expensive, time-consuming (slow process), release hazardous by products, needs high temperature and pressure, and their disposal contaminates the environment (Kurniawan et al., 2025). Therefore, the replicable strategy to address this drawback is green synthesis methods that are becoming more and more popular for synthesizing metal oxide composites since, it is sustainable, cost effective, ecological, and not hazardous by-products, aligns with green technology, and are environmentally friendly nature. Due to its speed, enhancing surface area, enhancing surface morphology, affordability, and environmental safety, plant-mediated composite synthesis is especially advantageous since it produces stable nanoparticles while inhibiting aggregation (Munir et al., 2021).

1.3 Objective

1.3.1 General Objective

The general objective of this thesis work is the green synthesis of CuO/TiO_2 Composite for hybrid supercapacitor application.

1.3.2 Specific Objective

- To extract S. abyssinica plant extract
- To synthesize S. abyssinica plant extract-mediated TiO_2, CuO, and CuO/TiO_2 binary composites.
- To characterize properties of pristine TiO_2, CuO, and CuO/TiO_2 binary composites by using XRD, FTIR, SEM, BET, and TGA/DTA techniques.
- To investigate and optimize the electrochemical performance of pristine TiO_2, CuO, and CuO/TiO_2 binary composites using CV, GCD, and EIS.

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1.4 Significance of the Study

This research is notable in transferring renewable and more efficient energy storage technologies to higher stages by executing an ecological method of metal oxide-based material synthesis. The introduction of S. abyssinica plant extract as a natural reducing and capping agent takes care of the growing concerns of the environmental issues associated with traditional chemical synthesis methods. Such methods generally employ toxic reagents, are characterized by high energy consumption, and lead to the creation of hazardous by-products.

What is more, the design of CuO/TiO_2 composites through that approach contributes not just to the materials' electrochemical performance but also gives an idea of the combined action of two transition metal oxides; hence the specific capacitance is improved, and cycling stability, and surface area are better by this principle, which is important for the great supercapacitor electrodes. The partnership of green chemistry with energy-saving applications is educational and offers also practical advantages in the field of renewable energy technologies.

Besides, the findings of the research work suggest that there is a potential for plant-mediated synthesis that can be a source of high-quality nanocomposites, thereby, this in turn leads to engaging in further research in this direction. The results of this study confirm the worldwide endeavors for sustainable energy solutions, and at the same time, it is a very promising scalable and eco-friendly supercapacitor development that can drive the rescue of energy crises and can help to reduce the usage of fossil fuels.

1.5 Scope of the Study

The focus of this work is on green synthesis, the characterization of materials property, and the electrochemical assessment of pristine TiO_2, CuO, and their binary composite (CuO/TiO_2) for supercapacitor application. The study uses the extract of S. abyssinica plant as a natural reducing and capping agent to develop a new, cost-effective, and ecological way which allows the green synthesis of particles. The synthesized materials are thoroughly analyzed to determine their crystalline structure, morphology, thermal, and surface properties, surface area analysis, and electrochemical properties. This included (XRD), (SEM), (TGA/DTA), (BET), and (FTIR). Electrochemical properties were assessed through cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS). The main attention is drawn from the improved performance of the CuO/TiO_2 composite, where the 70:30 CuO to TiO_2 ratio has proven to be the best candidate regarding specific capacitance, surface area, and cycling stability as compared to pristine.

CHAPTER TWO

LITERATURE REVIEW

2.1 Global Energy Status

The welfare, economic, and developmental states of societies are based on energy. Fossil fuels, notably oil, coal, and natural gas, account for around 85% of the primary energy used by humans and are the predominate primary energy sources (Kalair et al., 2021). Concerns regarding energy resource depletion, supply constraints, and adverse environmental effects (ozone layer depletion, global warming, climate change, etc.) have already been brought up by the world’s rapidly expanding energy use (Ristinen et al., 2022). Our continued reliance on non-renewable energy sources and the accelerating depletion of natural resources have heightened public awareness of global warming (Abdisattar et al., 2022; Yi et al., 2023). This growing concern has prompted a paradigm shift in many countries, with a renewed focus on developing renewable energy solutions.

Solar and wind energy, for example, offer significant advantages, they are both clean and abundant. However, their inherent variability presents a challenge. The unpredictable nature of these sources makes it difficult to consistently generate optimal power output. This is where energy storage systems play a vital role. These systems are crucial for not only meeting peak energy demands but also for maintaining a clean and stable energy grid (Abdallaoui et al., 2020; Amin et al., 2022).

In the last few decades, energy storage technologies have come to play an important role as far as the electric grid is concerned. The fact that there are a growing number of different applications that need a specific power or voltage level in a short amount of time is one of the key causes of this. A set of techniques and tools used to store energy is known as an energy storage system. Later on, the stored energy can be used to carry out beneficial tasks. Despite not being energy sources, energy storage technologies offer significant benefits that enhance supply reliability, stability, and power quality (Abdisattar et al., 2022; Choudhury, 2022).

The challenges of practical electric vehicles and utility used have been met by substantial advancements in battery technologies. Modern, non-polluting uninterruptible power supplies employ flywheel technology. In order to store energy for power quality applications, advanced capacitors are being studied. Utility applications are drawing attention to superconducting energy storage devices, which are still in the prototype stage (Ribeiro et al., 2001).

2.2 Electrochemical Energy Storage Technologies

2.2.1 Batteries

An electrochemical battery is made up of two or more cells that can transform chemical energy into electrical energy. These serve as tools for storing and converting energy. For a battery to operate smoothly, electrodes such as, the metal zinc, lead, and lithium need to have high surface areas, strong electrical conductivity, and compatibility with the electrolyte. Primary batteries, like lithium batteries, and secondary batteries, like lithium-ion batteries, are two different types of batteries. The latter is rechargeable, but the former is metallic. Li-ion batteries are not as energy dense as non-rechargeable batteries, but they still provide a high load current (Gao et al., 2022). Finally, electrical energy storage system bosting superior energy and power capabilities would transform energy production, transmission, and consumption. In the electrical power industry, dependable power systems remain essential for consumers, industries, and defense force (Aghmadi & Mohammed, 2024; Rajaperumal & Columbus, 2025).

2.2.2 Fuel Cell

Fuel cells change chemical energy into electricity as needed. In fuel cells, the anode undergoes oxidation, the cathode undergoes reduction, and the electrolyte facilitates current flow through ion conduction (Dwivedi, 2020). In contrast to batteries, fuel cells receive their oxidants and fuel from external sources. Like internal combustion engines, fuel cell function only with a continuous fuel supply.

2.2.3 Supercapacitor

The mechanism of energy storage in supercapacitors (SCs), also known as electric double layer capacitor (EDLC) or ultracapacitors, involves a simple charge separation at the interface between the electrode and the electrolyte. This allows the devices to store and deliver energy at relatively higher rates than batteries SC have a very high capacity and low internal resistance (Yadlapalli et al., 2022). An electrolyte, two electrodes, and a separator that electrically isolates the two electrodes make up a SC. The most crucial element of a SC is the electrode material. When compared to other energy storage technologies, SC have a number of advantages, including a long lifespan, high power, flexible packaging, a wide temperature range (-40 to 70 ˚C), low maintenance, and low weight (Olabi et al., 2022; Zhang & Chen, 2024).

The majority of renewable energy sources, with the exception of bio-fuels, are supplied as electricity. A dependable technological platform for electrochemical storage, such as batteries, fuel cells, and electrochemical supercapacitors, has been in high demand (Amer et al., 2025). Beyond low energy density, recent developments in supercapacitors concerning electrode materials and electrolytes have the ability to bridge the gap between current electrolyte capacitors technology and that of batteries, and fuel cells.

SCs have emerged as viable options in a variety of industries that demand high energy throughput (hybrid electric vehicles) and stable energy throughput (sensitive automation, computer chips, and portable electronic devices), in line with resent technological advancements in electric-powered devices in terms of cycle life, charge time, and specific power (Chaudhary et al., 2024).

2.3 Evolution of Supercapacitor Technologies

As early as 1879, a German physicist named Helmholtz proposed a supercapacitor with a farad level, which is an electrochemical component that stores energy by polarizing electrolytes (Zawawi, 2023). By 1957, an American named Becker applied for a patent on an electrochemical capacitor using activated carbon with a high specific surface area as an electrode material (Scibioh & Viswanathan, 2020). Since then, supercapacitors have entered the development stage and are now widely utilized in industry and household appliances due to ongoing advancements in critical technologies in materials and processes, as well as ongoing improvements in product quality and performance (Conway, 2013).

The rapid growth in demand for more efficient energy storage systems has driven intensive research in nanoscale materials, resulting in substantial improvements in both energy and power densities of supercapacitors (Yadlapalli et al., 2022). In recent years, supercapacitors have gained significant attention due to their potential to address the challenges posed by the depletion of fossil fuels and environmental pollution (Muzaffar et al., 2024).

The development of advanced functional materials for supercapacitors has become crucial in meeting the increasing energy storage demands of portable electronics and hybrid electric vehicles. As research continues to focus on improving energy density and exploring new electrode materials and electrolytes, supercapacitors are poised to play a vital role in sustainable energy storage solutions for the future (Dar et al., 2024). the following figure summarizes the overall evolution of supercapacitor by tracing back from capacitor to major research hots spots on energy storage technology (supercapacitor) in 21st century.

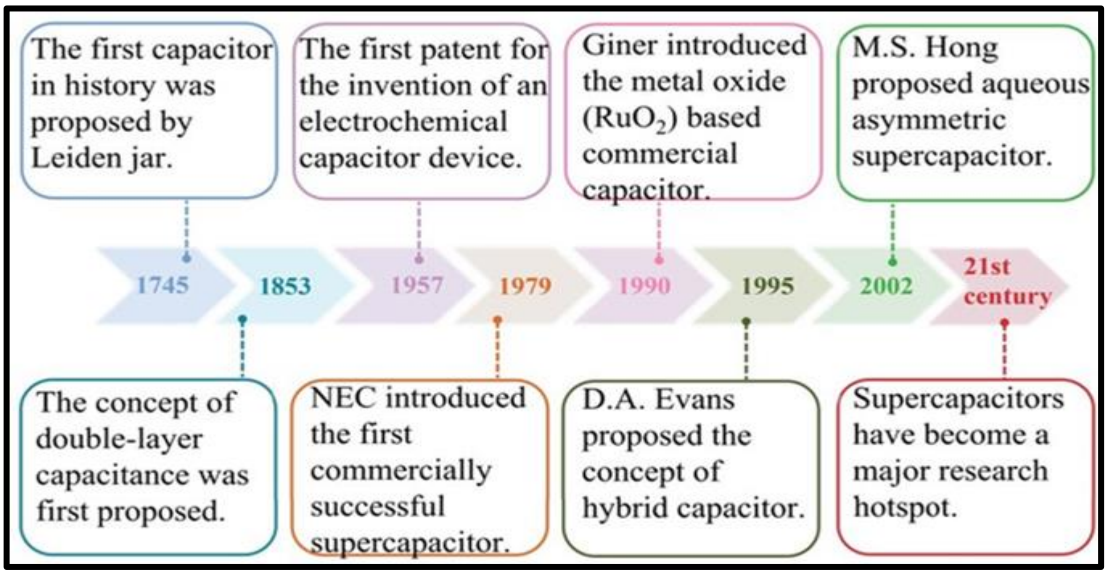

Figure 2. 1: Development histories of Supercapacitors (Yang et al., 2023).

2.4 Basic Parameters of Supercapacitors

2.4.1 Capacitance

Capacitance is the capacity of capacitors to store charges per unit of voltage. It is expressed as the capacitor's stored charge (Q) divided by the voltage (V) across it (Radi & Rasmussen, 2024).

$$C = \frac{Q}{V} \qquad 2.1$$

2.4.2 Energy Density

The energy density of a capacitor is defined as the amount of energy (E) it retains per unit volume or per unit mass (Yadlapalli et al., 2022). Typically, the energy density parameter is stated in watt hours per liter (Wh/L) or watt hours per kilogram (Wh/Kg). A device with a high energy density may store a lot of energy per unit size or weight, which is typical for applications requiring long-term energy storage, such as electric cars and cell phones. The supercapacitor's energy density is provided as:

$$\boldsymbol{E = \frac{1}{2} CV^2} \qquad 2.2$$

Where E, energy density, C is specific capacitance, and V is potential window

Therefore, the energy density can be expressed as:

$$\boldsymbol{u = \frac{E}{V} = \frac{1}{2} \varepsilon E^2} \qquad 2.3$$

2.3.3 Power Density (p)

Power density is power per unit volume. Where Power is the rate of energy transfer or conversion, measured in watts per kilogram (W/kg). High power density means the system can deliver its energy very rapidly, which is ideal for applications needing quick power, for example, to start a car or power a camera flash (Brooks et al., 2024). When a capacitor is discharging energy, the power can be defined as the way in which the energy changes over time (t):

$$\boldsymbol{P = \frac{dE}{dt}} \qquad 2.4$$

Batteries commonly give a higher energy density for longer storage time, whereas capacitor operates at high power density, allowing for rapid energy release (Yadlapalli et al., 2022). As a result, there is a trade-off between the two, improving one frequently impairs the other. Enhancing energy and power densities in supercapacitors has been the focus of recent research. Techniques like using materials with a large surface area, optimizing electrode structures with specific pore sizes, improving electrolytes by increasing ionic concentration or using those that permit higher operating voltages, and creating hybrid systems that combine various energy storage technologies are some of the strategies developed. Energy and power densities in energy storage solutions are intended to be efficiently balanced using these methods (Mitali et al., 2022).

2.5 The Charge Storage Mechanisms of Supercapacitors

The two main charge storage techniques used by supercapacitors are faradaic and non-faradaic. The electrostatic double-layer capacitance (EDLC) also known as a non-faradaic mechanism uses a purely physical approach to store charge (Rajapriya et al., 2023). The electrolyte ions and the electrode material do not exchange electrons. Applying a voltage causes the ions in the electrolyte solution to go across the separator and into the porous structure of the electrode that is oppositely charged. This double layer, which is made up of distinct positive and negative charges, is what gives the supercapacitor its electrostatic energy storage capability. Carbon-based materials are typically used as electrodes in EDLCs, which are supercapacitors that only use this non-faradaic process (Forouzandeh et al., 2020; Kothandam et al., 2023). Unlike the non-faradaic mechanism, the faradaic mechanism depends on electron transfer events that take place at the electrode-electrolyte interface. Three main processes, such as, electrosorption, redox (reduction-oxidation) reactions, and intercalation (shown in figure 2.2 below), combine to enable the storage of electrical energy in pseudocapacitor. The pseudocapacitive electrodes used in supercapacitors that use this faradaic process are usually made of conducting polymers or transition metal compounds (Ehsani et al., 2019; Naskar et al., 2021).

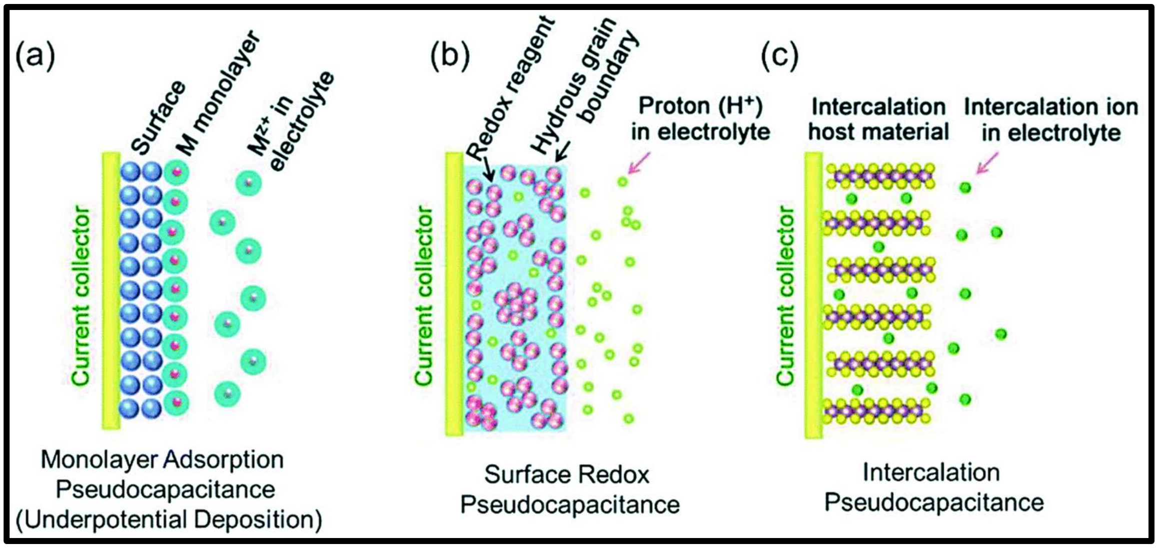

Figure 2. 2: Pseudocapacitance charge storage mechanisms are categorized into three types: Under potential deposition (a), Redox reactions (b), and (c) Intercalation/de-intercalation.

(a). Under potential Deposition: This involves the deposition of a single layer of metal ions on another metal at a potential higher than their redox potential, which is a rare phenomenon.

(b). Redox Reactions: This is the most common mechanism for pseudocapacitive charge storage. It involves the adsorption of ions on or near the material's surface through Faradaic redox reactions, mainly in aqueous electrolytes like H_2SO_4 and KOH. The electrochemical behavior of materials using this mechanism resembles that of EDLCs, showing quasi-rectangular CV curves, and quasi-triangular GCD curves. However, charge storage occurs through both double-layer formation and surface redox reactions (Ishita et al., 2023).

(c). Intercalation/De-intercalation: This mechanism involves ions being inserted into and removed from the material's structure during charge and discharge cycles. Intercalation pseudocapacitance involves the insertion of ions into the layers of redox-active materials, primarily occurring in non-aqueous electrolytes. Unlike surface redox processes, this mechanism uses the bulk of the material for charge storage. Materials that exhibit intercalation pseudocapacitance include transition metal oxides (such as MoO_3 and TiO_2) and transition metal sulfides (like MoS_2 and TiS_2) (Liu et al., 2020).

2.6 Classification of Supercapacitors

Supercapacitors can be broadly classified into three main groups for easier understanding as in **Figure 2.3**. These categories are asymmetric supercapacitors, symmetric supercapacitors, and hybrid supercapacitors (Maghami et al., 2024; Zhang & Chen, 2024). This classification emphasizes the significance of electrode materials, cell designs, and basic operating principles like chemical or physical processes, or both. Researchers and engineers can create supercapacitors that are suited for particular uses by identifying these important categories and the fundamental elements that affect them. Navigating the complex world of supercapacitor technology is made easier with the help of this classification scheme.

2.6.1 Asymmetric Supercapacitors

Asymmetric capacitors (ASCs) are a special kind of energy storage device that maximizes performance by strategically designing its electrodes. ASCs use electrodes with intentionally different capacitances, in contrast to traditional or symmetric supercapacitors, which use electrodes with comparable properties (Sadavar et al., 2023).

2.6.2 Symmetric Supercapacitors

Symmetric supercapacitors are a type of Electric Double-Layer Capacitor (EDLC) characterized by having identical electrode materials. Usually, both electrodes are made from the same material, like activated carbon, and have similar designs and mass loading. This uniformity ensures that the charge storage mechanism, whether physical (like electrostatic attraction) or chemical (involving redox reactions), functions consistently on both electrodes (Zhai et al., 2022).

There are three main types of carbon-based materials used for EDLC electrodes (Wang et al., 2021):

a. Carbon foams, carbon aerogels, and carbide-derived carbon (CDC) (Lee & Park, 2020).
b. Carbon nanotubes (CNTs) and graphene.
c. Activated carbon (AC)

2.6.3 Hybrid Supercapacitor

Hybrid supercapacitors are advanced energy storage devices that combine different electrode materials and chemistries to improve performance (Gao et al., 2023; Iqbal & Aziz, 2022). This design aims to overcome the limitations of traditional supercapacitors by leveraging the strengths of each component.

The main goal of hybrid supercapacitor research is to narrow the performance gap between conventional supercapacitors and electrochemical batteries. By carefully choosing and combining electrode materials, researchers seek to boost energy density, power capability, and cycle life while also reducing costs.

Three primary categories of hybrid supercapacitors have emerged:

a. Composite supercapacitors (Zhong et al., 2022)
b. Battery-like supercapacitors
c. Hybrid electrolytic capacitors.

Hybrid supercapacitors combine two different types of electrodes to enhance performance. One electrode uses pseudocapacitive behavior, which involves Faradaic reactions, while the other relies on capacitive behavior through an electric double layer. This mix allows hybrid supercapacitors to take advantage of both types, often achieving better performance than each component alone (Azizi et al., 2024; Muzaffar et al., 2019).

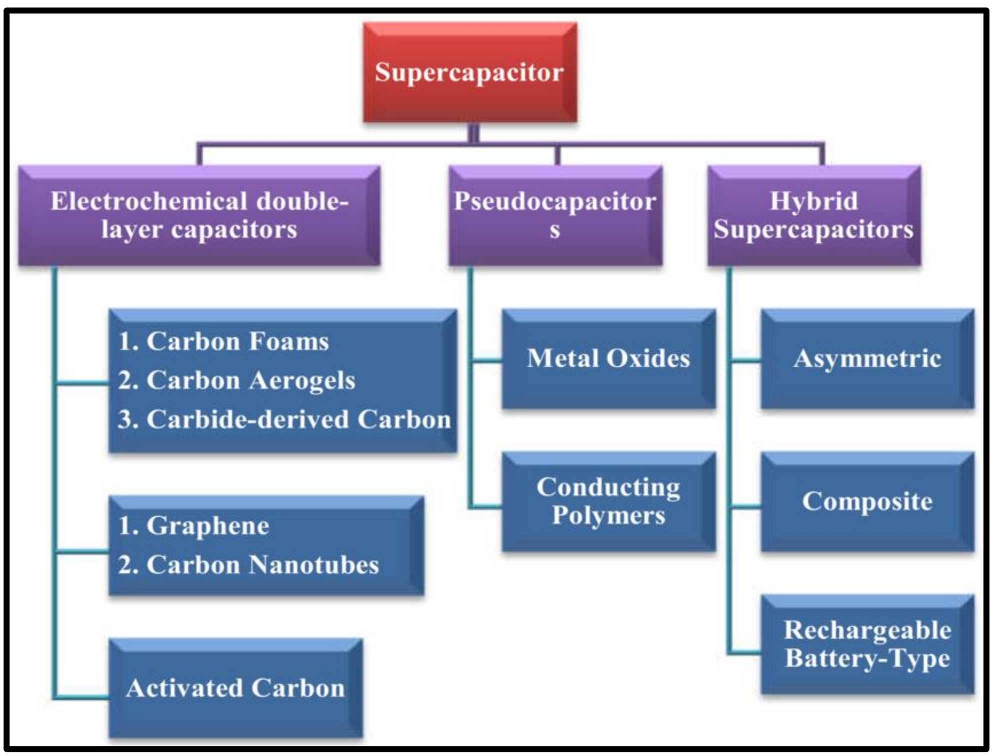

Figure 2. 3: General types and classification of (Czagany et al., 2024)

2.7 Components of Supercapacitors

2.7.1 Electrodes

Supercapacitors store energy in their electrodes, which can be made from materials like carbon or metal oxides. When a potential is applied, it accumulates an electrical charge, which is crucial for its energy storage capabilities (Abdel Maksoud et al., 2021). To ensure efficient energy transfer in supercapacitors, the electrode material should have high electrical conductivity. This allows for smooth electron flow between the electrode and the external circuit, enhancing power delivery.

The essential conditions for standard electrodes are as follows (Rehman et al., 2022). (1) Specific Surface Area: A larger surface area exposes more of the electrode material to the electrolyte, increasing charge accumulation at the interface (Li et al., 2021). This enhanced interaction improves both the specific capacitance and energy density of the electrode material. (2) The porosity of an electrode material, including pore size and distribution, greatly affects its electrochemical performance, especially specific capacitance and rate capability. For optimal performance, pore sizes should be larger than electrolyte ions to allow effective adsorption on the electrode surface, which is key for charge storage in supercapacitors (Zhang et al., 2022).

2.7.2 Electrolyte

The electrolyte is a vital part of electrochemical energy storage systems, greatly affecting the cell's efficiency and performance. It influences capacitance, energy density, power density, rate capability, cycle life, and safety, while also balancing charge between the electrodes. Choosing the right electrolyte is crucial because it impacts the electrode's and electrolyte's interface. However, an ideal electrolyte that meets all supercapacitor needs has not yet been found. The basic requirements for electrolytes in these devices are outlined as follows:

The conductivity of the electrolyte is crucial for supercapacitor performance. A highly conductive electrolyte allows for faster ion transport between electrodes, improving power density and rate capability. Like sulfuric acid (H_2SO_4) and potassium hydroxide (KOH) typically have higher conductivity than non-aqueous ones due to their lower viscosity, which enables easier ion movement (Periasamy & Chavli, 2025). The general trend in specific conductivity is $H_2SO_4 > KOH > KCl > Na_2SO_4$. Additionally, smaller ions tend to have higher mobility, further enhancing conductivity (Hegde & Bhat, 2024).

The size of ions in the electrolyte greatly affects supercapacitor performance. Smaller ions have better mobility, allowing them to diffuse more easily into the electrode's pore structure and adsorb onto its surface. This improved interaction leads to higher capacitance and better supercapacitor rate capability (Hegde & Bhat, 2024).

An ideal electrolyte must easily dissociate into ions when dissolved, which reduces internal resistance in supercapacitors and boosts performance (Nordness & Brennecke, 2020).

Electrochemical stability is vital for the safety and performance of supercapacitors. This stability is influenced by two main factors, how the electrolyte interacts with the electrode material and the inherent properties of the electrolyte's components (Hegde & Bhat, 2024).

From the listed electrolytes potassium hydroxide (KOH) typically has higher conductivity than non-aqueous ones due to their lower viscosity, which enables easier ion movement (Periasamy & Chavli, 2025).

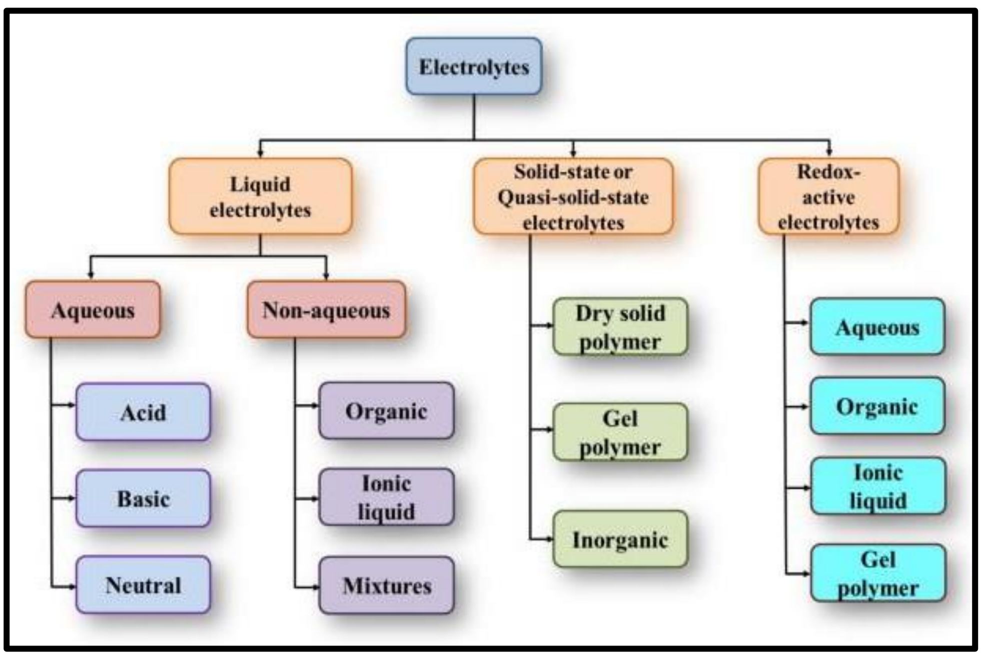

Figure 2. 4: The three major types of electrolytes which are applicable in supercapacitors (Bhat et al., 2022)

2.7.3 Separator

A separator is an essential component of a supercapacitor, serving as a barrier between the two electrodes to prevent short circuits while allowing ions to move freely. An ideal separator should possess several key characteristics; it must provide electrical insulation to stop direct contact between electrodes, exhibit high porosity to enable efficient ion movement, and demonstrate chemical inertness to remain stable in the electrolyte (Zhigalenok et al., 2024).

2.7.4 Current Collector

The current collector is vital for supercapacitor operation as it facilitates the transport of electrons between the electrode and the external circuit, requiring several key attributes to function effectively (Abdisattar et al., 2022). High electrical conductivity is essential to ensure efficient electron flow and reduce resistance, while corrosion resistance helps maintain the collector's integrity in harsh environments. Additionally, mechanical strength is necessary to provide structural support to the cell, and compatibility with various electrode and electrolyte materials is crucial for optimal performance. For this application nickel foam which is a very porous, and metal material produced mainly from nickel is the best candidate for this application. It is extensively applied in electrochemical applications owing to its superior, 3D interconnected porous structure, electrical conductivity, and chemical stability (Ratsoma et al., 2023).

2.8 Most Common Electrode Materials for Supercapacitors

2.8.1 Carbon Based

Carbon-based materials are the predominant choice for electrodes in commercially available supercapacitors. This preference is primarily due to their exceptional properties. Carbon electrodes are renowned for their cost-effectiveness, excellent corrosion resistance, superior cyclic stability, extended lifespan, and wide operating temperature range. These attributes, coupled with their high electronic conductivity, make them ideal candidates for energy storage applications (Ajmal et al., 2024). The emergence of three-dimensional carbon nanostructures, such as activated carbon, carbide-derived carbon, and templated carbon, which possess large surface areas and porous architectures, is anticipated to hold significant promise for supercapacitor applications. However, on the flip side, their specific capacitance is constrained at high current densities, primarily due to their relatively low conductivity and the presence of micro-pores (Arumugam et al., 2023).

2.8.2 Conducting Polymer as an Electrode Material

Among the most used conductive polymers for energy storage electrodes are Polypyrrole (PPy) (Sumdani et al., 2022), polyaniline (PANI) (Agobi et al., 2019), Polythiophene (PTh) (Shindalkar et al., 2023), poly(3,4-ethylenedioxythiophene) (PEDOT) (Obeidat & Rastogi, 2023), and poly(ionic liquid) (PIL). These materials are favored for their high charge density, ease of production, and cost-effectiveness, making them suitable for pseudocapacitor applications.

a. Polythiophene (PTh)
b. Polyaniline (PANi)
c. Polypyrrole (Ppy)

These polymers possess unique electrochemical properties that enable them to store and release energy through redox reactions, leading to enhanced energy density and power capability compared to traditional capacitors.

2.8.3 Transition Metal Oxides (TMOs)

The metal oxides are also suitable for electrochemical capacitors owing to their high specific capacitance and low resistance. The transition metal oxides, including manganese oxide (MnO_2), nickel oxide (NiO), and ruthenium dioxide RuO_2, possess the advantage of enhanced energy density and chemical stability compared to carbon materials. Even though RuO_2 exhibits superior performance, its cost and environmental concerns limit its use. The blend of metal oxides in a nanocomposite state shows interactions that are not only able to further augment the entire supercapacitor performance. The electrochemical performance is boosted by metal oxide blending via both the enhancement in the electrochemically active surface area and the enhancement in charge transfer efficiency (Joysi et al., 2024).

2.8.3.1 Ruthenium Oxide RuO_2

Ruthenium dioxide RuO_2 is a leading material for energy storage due to its remarkable properties. It has excellent redox activity, a wide electrochemical potential window, and high electrical conductivity. These qualities allow RuO_2 to serve effectively as an electrode in supercapacitors, enabling fast and efficient energy storage and release. Its large potential window also means it can store a significant amount of energy per unit mass (Banik et al., 2023). Additionally, RuO_2's reversible redox reactions guarantee its performance and longevity throughout time. Kim et al. (Park et al., 2004) used the electrostatic spray deposition approach to successfully construct a thin film ruthenium oxide electrode. RuO_2 particles might be carefully deposited onto a substrate using this technique. With an average specific capacitance of 650 F/g, the resultant electrode showed promise for energy storage applications. RuO_2 has several benefits, but its high cost is still a problem. The goal of ongoing research is to create more economical synthesis techniques and investigate substitute materials that can take advantage of RuO_2's advantages without incurring related costs. Ruthenium dioxide is expected to have a significant impact on the development of energy storage technologies in the future as researchers in this area continue to make progress.

2.8.3.2 Nickel Oxide (NiO)

Nickel oxide (NiO) is a promising electrode material due to its availability, affordability, environmental friendliness, and stability. Researchers have been working to improve its performance by changing its structure and shape. For example, Zheng et al. used a hydrothermal method to create nanostructured NiO in unique sandwich and cauliflower-like forms. This new shape improved the electrode's performance, allowing it to retain 91.6% of its initial capacitance after 1000 charge-discharge cycles, showing its potential for long-term energy storage. Patil et al. used a chemical method to create nickel oxide thin films on glass. They first made nickel hydroxide films, which were then heated to 623 K (Salokhe et al., 2021). This heating changed the hydroxide into cubic nickel oxide and created a honeycomb-like structure. The resulting NiO electrodes showed a specific capacitance of up to 167 F/g, making them strong candidates for energy storage applications.

2.8.3.3 Titanium dioxide (TiO_2)

Titanium dioxide (TiO_2) has gained attention as a promising electrode material for supercapacitors due to its high surface area, porosity, mechanical strength, and excellent transport properties (Parangi & Mishra, 2021). Its low cost, non-toxic nature and environmental friendliness further enhance its appeal. However, TiO_2 faces challenges like poor conductivity and low areal-specific capacitance (Raj & Prasanth, 2018). Researchers are addressing these issues through various strategies. One effective method is depositing manganese dioxide (MnO_2) onto TiO_2 nanotube arrays via hydrothermal synthesis, which significantly boosts areal capacitance (Zhang et al., 2019). Another approach involves creating hybrid nanocomposites, such as graphene oxide and TiO_2 (GO-TiO_2), which exhibit high areal-specific capacitance and excellent cycling stability(Badoni et al., 2025). Their versatility allows for various combinations with other materials, paving the way for high-performance energy storage solutions.

2.8.3.4 Copper Oxide (CuO)

Copper oxide-based nanocomposites have shown promising potential as electrode materials for supercapacitors due to their high theoretical specific capacitance, low cost, and eco-friendliness (Sayyed et al., 2023). Several studies have explored different copper oxide composites for supercapacitor applications, demonstrating impressive electrochemical performance. A chitosan-based hybrid nanocomposite incorporating copper oxide (CuO) and zinc oxide (ZnO) nanoparticles exhibited excellent electrochemical properties, including a high specific capacitance of 638.3 F/g and 86.98% capacity retention after 5000 cycles at 1 A/g current density (Gouda et al., 2024). Similarly, a CuS-graphene oxide (CuS-GO) nanocomposite electrode showed a specific capacitance of 250 F/g at 0.5 A/g current density and 70% capacitance retention after 5000 charge-discharge cycles (Lu et al., 2024). The integration of copper oxide with other materials, such as graphene oxide or other metal oxides, can further improve the overall performance of supercapacitor electrodes, making them promising candidates for future energy storage devices.

2.8.3.5 TMO Composites for Supercapacitor

The increasing need for sustainable and efficient energy-storage systems of compact sizes accelerated the research on supercapacitors. Among diverse electrode materials, transition metal oxides have, in recent years, stood out based on their huge theoretical capacitance, variable oxidation states, and proneness to environmental degradation (Ahmad et al., 2024). However, their inherent limitations of low conductivity, rate capability, and cycling instability have come in the way of practical applications (Liang et al., 2021). Research thus involves TMO-based composites in which metal oxides get so combined with conductive materials (carbon, polymers, or other TMOs) that the overall performance gets boosted. For instance, MnO_2/graphene composites synthesized via a hydrothermal method, achieve a specific capacitance of 310 F/g at 1 A/g, with good cycling stability (92% after 5000 cycles) (Qian, 2017). (Shanmugam et al., 2022) developed NiO/rGO composites through a facile solvothermal route and achieved a capacitance of 456 F/g at 1 A/g, with improved rate capability and cycle life. (Madian et al., 2018) synthesized a TiO_2/graphene composite with a specific capacitance of 215 F/g and 95% retention after 2000 cycles, highlighting the synergistic effect of TiO_2 and graphene. (Anandhi et al., 2022) prepared TiO_2/MnO_2 core-shell nanorods and reported a capacitance of 378 F/g, attributing the improvement to the increased active surface area and redox activity of MnO_2. (Zhang et al., 2016) prepared TiO_2/PANI nanocomposites that delivered 412 F/g with good rate capability and 85% retention after 1000 cycles.

2.9 Synthesize Methods

There are various ways of synthesizing transition metal oxide nanocomposites but they mostly come under two groups. Such as the, bottom-up approach and top-down approach, and physical, chemical, and biological (green) approaches (as shown in figure). In the bottom-up approach, size and properties are fully controlled by the production of nanoparticles from atomic dimensions using processes like spinning, chemical vapor deposition (CVD), pyrolysis, sol-gel techniques, and biosynthesis. Conversely, starting with big materials, the top-down technique disassembles them into tiny nanoparticles. Each method has advantages and the choice is based on the properties needed of the nanomaterials (Guo et al., 2015).

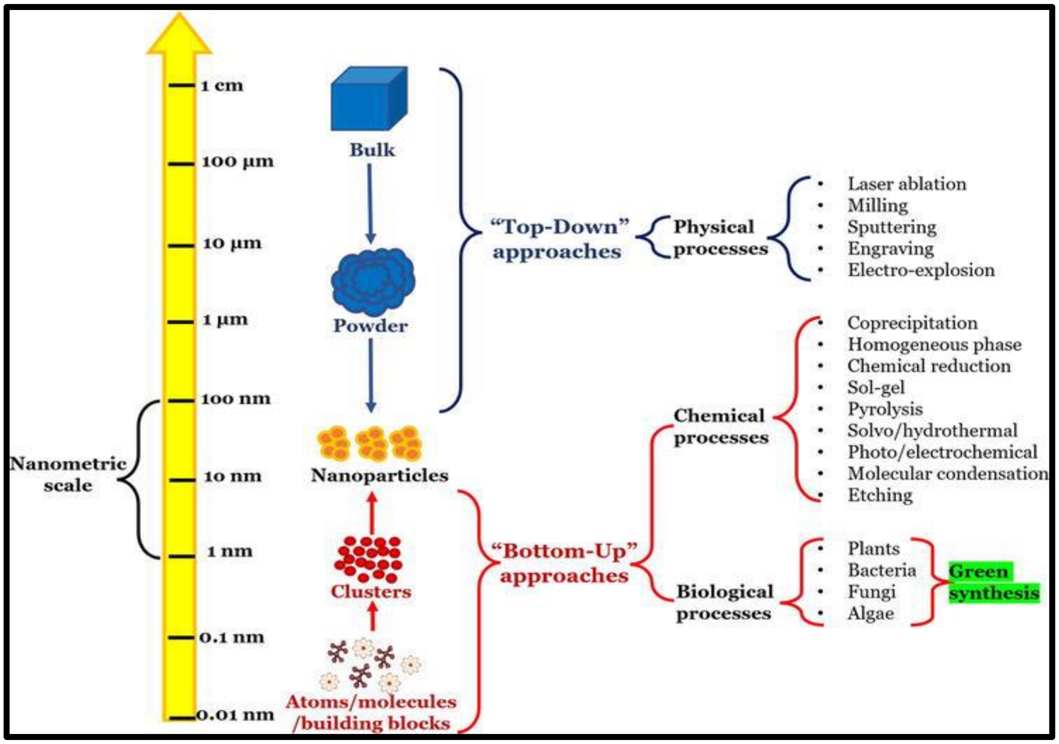

Figure 2. 5: Wide varieties of nanoparticle synthesis approaches and methods (Álvarez-Chimal & Arenas-Alatorre, 2023)

2.9.1 Sol-gel Method

Sol-gel processing is a low-temperature, inexpensive, and easy means of material production through by initially creating a gel that offers uniformity and eliminates the need for atomic motion in solid-state processes (Owens et al., 2016). Metal alkoxides are usually applied as precursor materials since they are in liquid or easily vaporizable solid forms, which enable filtration and lead to high-purity oxide materials required for electroceramics (Roy, 2016). However, such alkoxides are costly and also release huge quantities of alcohol upon heating, necessitating careful safety measures. The process involves the preparation of a solution of the intended starting materials, which is hydrolyzed and condensed to give a homogeneous gel that, after drying and calcination, provides the final product oxide. In addition, the alkoxides can be mixed with alcohol in order to create multi-component oxides, and when there are no alkoxides, other materials like acetates can be used as salts (Abdisattar et al., 2022; Roy, 2016).

2.9.2 Co-precipitation

Chemical precipitation synthesis also referred to as the chemical bath deposition (CBD) process carries out chemical reactions with the precursors in an open container at comparatively low temperatures of reaction conditions to ultimately yield monomeric building units that sub and then come together to create the resulting compounds. Most surfactants and precipitating agents are employed to control the orientation and rate of growth formation of nanocrystals (Bakshi, 2016). Co-precipitation has been widely used to synthesize metal oxide-containing hybrids due to its simplicity and cost-effectiveness. Proposed a straightforward, scalable, and cost-effective approach to synthesize high-performance supercapacitor electrode materials (Patil & Jagadale, 2023).

Traditional synthesis approaches of metal oxides, particularly transition metal oxides (TMOs), include both chemical and physical methods such as sol-gel (Owens et al., 2016), co-precipitation (Patil & Jagadale, 2023), hydrothermal/solvothermal synthesis (Nandagudi et al., 2022), chemical vapour deposition (CVD) (Sun et al., 2021), and thermal decomposition (Sahoo et al., 2024). Generally speaking, although these processes will be associated with a very well-structured and crystalline material, they tend to be arduous to perform and have high synthesis temperatures, dangerous chemicals, or dangerous organic solvents.

To illustrate this serious set of problems associated with these approaches includes expensive precursors as sol-gel with calcination, a hydrothermal process operating at high pressure and energy consumption, and CVD and thermal decomposition with toxic byproducts. All of which indicates a process that will be unnecessary cost, considerable energy, and bad for the environment prohibiting potential wide-scale applicability and green synthesis. On the other hand, the green synthesis has been identified and promoted as a more environmentally friendly and sustainable approach to nanomaterial synthesis (Idoko et al., 2024; Kharissova et al., 2019). In essence, a biologically-based green synthesis of nanomaterial-based supercapacitors involves use of biological systems mostly plant extracts containing natural phytochemicals (as flavonoids, alkaloids, phenolic, terpenoids, proteins, etc.) that act as capping agents, stabilizing agents, and reducing agents that help to create nanoparticles.

2.9.3 Green Synthesis Method

Green synthesis is the development of new chemical technologies that aim to minimize or avoid toxic chemicals in the design, production, and utilization of chemical products (Idoko et al., 2024; Kharissova et al., 2019). The main reason the world is focusing on renewable energy sources is to reduce the release of toxic chemicals, to minimize the depletion of natural resources, and to create clear and sustainable environment for the future.

Paul J. Anastas, one of the founding pillars of green chemistry, has defined this strategy as an intellectual framework to address the treatment of potential byproducts as a component of synthetic methodology design through the use of alternative tools and techniques to reduce environmental pollution (Murphy, 2020; Nowak et al., 2023).

Along the way, green synthesis is gaining traction, in which several plants, algae, or microbial species like fungi and bacteria are used to prepare nanoparticles. Natural source-derived compounds like terpenes, polyphenols, and proteins are essential in the synthesis (Salem & Fouda, 2021).

The most important parameters that threaten nanoparticle size, and shape are the concentration of metal ions, pH, reaction time, and temperature (Azad et al., 2023; Jameel et al., 2020). In green synthesis there are four main stages the initial stage (selection of the reaction medium and precursors), the second stage (chemical reduction of metal ions and activation), the third stage (formation of small nanoparticles into large aggregates), and finally (ultimate stabilization and shaping of nanoparticles) (Álvarez-Chimal & Arenas-Alatorre, 2023)

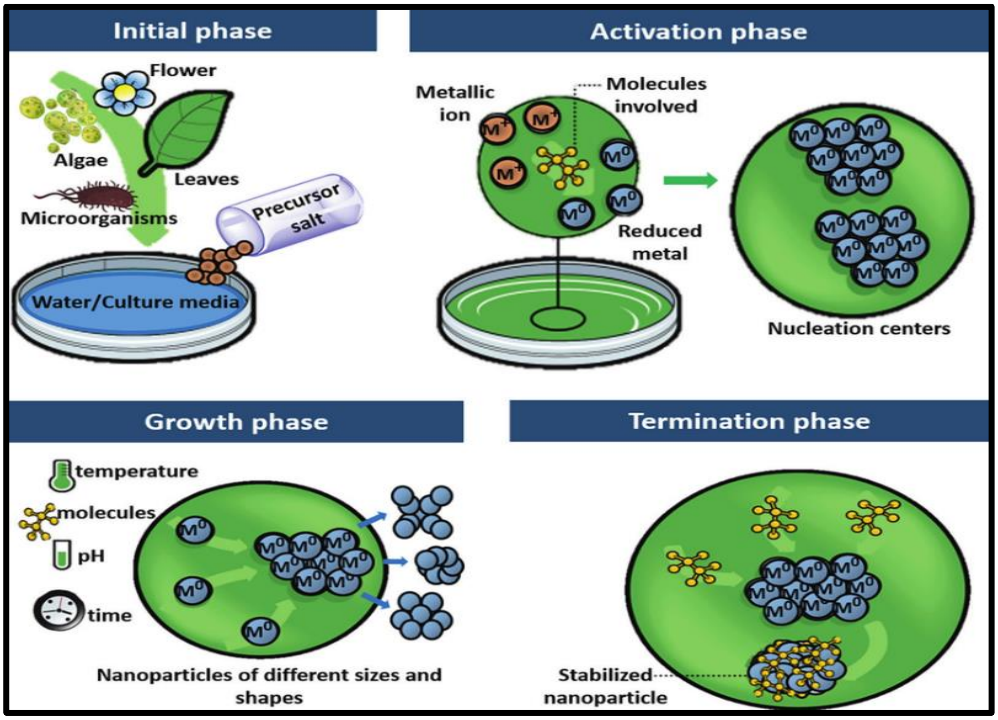

Figure 2. 6: The green synthesis process typically involves four phases (stages) (Álvarez-Chimal & Arenas-Alatorre, 2023).

2.9.3.1 Resources for the Synthesis of Nanoparticles

Plant Extracts

Plant-based use for nanoparticle synthesis is a green, hot, and non-toxic process that removes toxic compounds, hence quicker and less expensive compared to microbial synthesis (Alsaiari et al., 2023). Plant species have varied compounds such as terpenes, flavonoids, and proteins that help in reducing metal ions and stabilizing nanoparticles (Shafey, 2020). There are three synthesis processes: intracellular, extracellular, and phytochemical-mediated (Ankamwar et al., 2020). The intracellular process needs growth factors under strict control to synthesize the nanoparticles within plant cells. The extracellular process, the most popular among them, is the approach of preparing a plant extract and employing a metal salt precursor and is easy and effective to perform in one step. The phytochemicals-mediated process is identical to the extracellular process with only isolated phytochemical compounds for greater control but at more complexity and steps.

Table 2. 1: Summary of green synthesized metal oxides, and metal oxide composite electrode materials for supercapacitor applications

Sample No	Electrode material	Extract type	Specific capacitance	Stability (%/cycle)	Electrolyte	Power density (WKg^{-1})	Reference
1	CuO-GO	Camellia sinensis	82.1	98	Na_2SO_4	-	(Ravichandran et al., 2022)
2	CuO-rGO	Mentha piperita	137	-	Na_2SO_4	12,000	(Sudhakar et al., 2017)
3	NiO	Aloe barbadense miller	752	95	KOH	-	(Kundu et al., 2017)
5	Cu_2O	Ocimum tenuiflorum	87	74	Na_2SO_4	737	(Nwanya et al., 2019)
6	Cu_2O/rGO	Punica granatum	195	79	KOH	4114	(Kumar et al., 2016)
7	ZnO-rGO	Citrus limon	180	80	KCl	-	(Jayaprakash & Kannappan, 2022)
8	ZnO	Aloe vera	535	92	H_2SO_4	65.624	(Yadav et al., 2022)
9	ZnO-GO	Azadirachta indica	523.4	86	KOH	-	(Bishwakarma et al., 2023)

2.10 Synthesis Methods for Electrode Materials

2.10.1 Hydrothermal

The hydrothermal process enables chemical reactions in an aqueous solution. side sealed container above solution critical point to form different Nanomaterials (Byrappa & Adschiri, 2007). The procedure is straightforward, and the post-synthetic Interventions are comparatively less complicated when compared to other solution-focused technologies. In addition, the benefits of hydrothermal synthesis include ease of use, affordability, and eco-friendliness. Furthermore, the sample’s morphology and structure can be easily adjusted by adjusting the temperature, time, and solution concentration (El-Khawaga et al., 2023; Ndlwana et al., 2021).

2.10.2 Electrodeposition

Electroplating, also referred to as electrodeposition, is an electrochemical process that forms metals and metal-based alloys as a thin film coating on the electrically conducting substrate by reducing cations that are moving towards the cathode under the influence of an electric field (Mohapatra et al., 2024). The thickness of the deposited film is controlled by varying the electrode potential and current density (Mohapatra et al., 2024).

2.10.3 Dip Coating (Dip Immersion) Synthesis

Dip coating synthesis is a valuable method in the synthesis of electrode material for supercapacitor application. Dip coating synthesis is a convenient and effective approach to designing high-performance electrodes with large surface area and electrochemical activity.

CHAPTER THREE

EXPERMENTAL METHODOLOGY

3.1 Green Synthesis

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3.2 Chemicals and Reagents

The chemicals and reagents used in this work were deionized water (DI), titanium tetrafluoride (TiF4) (96%, Sigma Aldrich, Germany), reduced graphene oxide (rGO), isopropyl (96%, Alpha Chemika, India), sodium hydroxide (NaOH) (98%, Luba, India), copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$) (96%, Alpha Chemika, India), acetone (99%), absolute ethanol, hydrochloric acid (HCl) (37%, Alpha Chemika, India), %5 Nafion, platinum coated counter electrode (Solaronix, Switzerland), ethanol (99.8%), and S.Abyssinica extract. All the chemicals and reagents were used as received without further purification.

3.3 Methodology

3.3.1 Preparation of the Plant Extracts

The S. abyssinica plants were collected in the fields of the Zygam, Awi Zone, Ethiopia. The leaves were washed with DI water, and then they were dried within a week. The dry leaves were then crushed (using a blender) and stored in an airtight container. The plant extracts of S. abyssinica plant given at (figure 3.1) were prepared in a 500 mL bicker containing 250 hot DI water as reported by (Altemimi et al., 2017; Cao et al., 2025; Ramirez-Rodrigues et al., 2011). A total of 15 g S. abyssinica plant powder was added and further heated at 80◦C for 15 min. The resulting extract was cooled (at room temperature) and then filtrated. The extracts were reserved for further use.

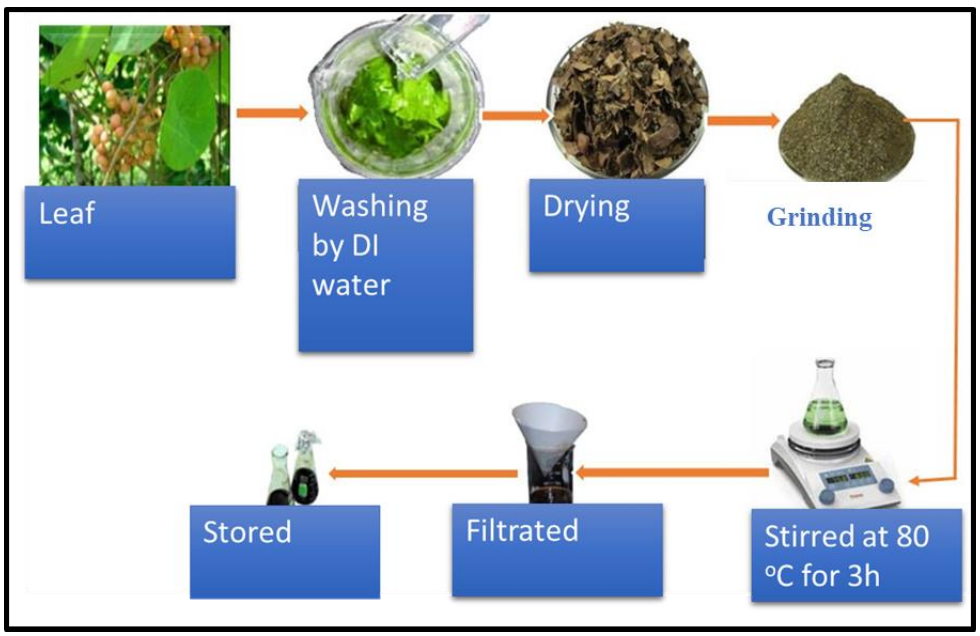

Figure 3. 1: Schematic representation of S. abyssinica plant extraction

3.3.2 Synthesis of S. abyssinica-Mediated CuO

An optimized amount of 50 mL S. abyssinica extract was added to 2 g in 50 mL DI water of copper (II) nitrate trihydrate while continuously stirring at 60 ^{o}C and stayed for 2h as given in (Bouafia et al., 2020) with slight modification. Following this it was washed by centrifuging the paste seven times, five times by DI water and twice by ethanol as referred. Then the collected paste was added to the bicker and put into a drying oven at 100 ◦C. Following this, the paste was collected into a ceramic crucible and heated in a muffle furnace at 400 ◦C for 2 h (Berra et al., 2018). Finally, a black powder was obtained, and the product was carefully collected and ground for characterization as shown Figure 3.2 below.

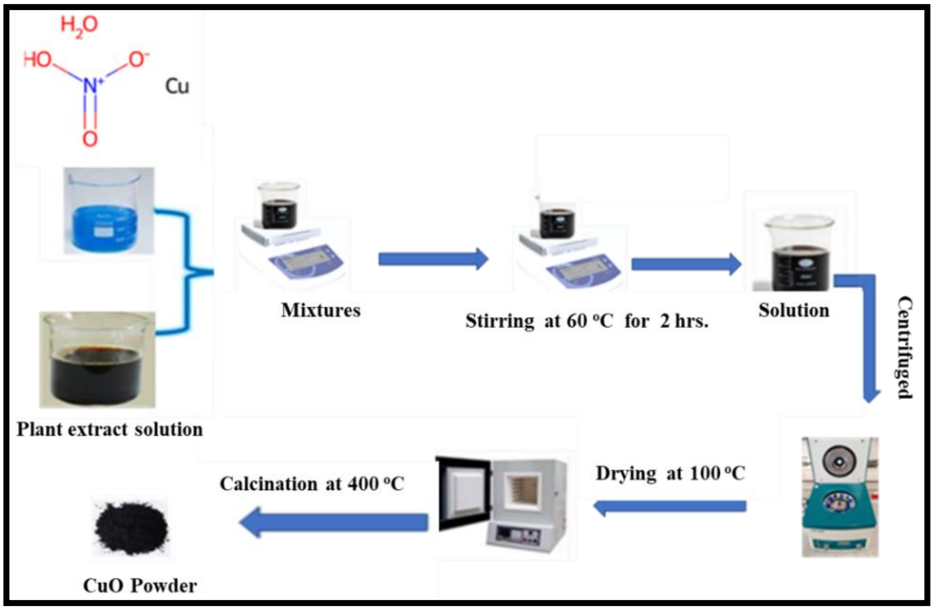

Figure 3. 2: Green synthesis of CuO

3.3.3 Synthesis of S. abyssinica-Mediated TiO_2

A 50 mL of titanium tetrafluoride (TiF_4) in an isopropyl solution was mixed with an aliquot amount of 50 ml plant extracts. After 12 hours of stirring and homogenizing the mixture followed by filtration. It was then washed and centrifuged, and rinsed five times with deionized water and twice with ethanol followed by drying in the oven at 100 °C by following (Rao et al., 2015). and the produced particles were calcined In a muffle furnace with a heating rate of 10 °C/min, for three hours at 400 °C and ground using a mortar and pestle (Bopape et al., 2023). The product was gathered, crushed, and stored for later. the Figure 3.3 below indicates the whole synthesis steps.

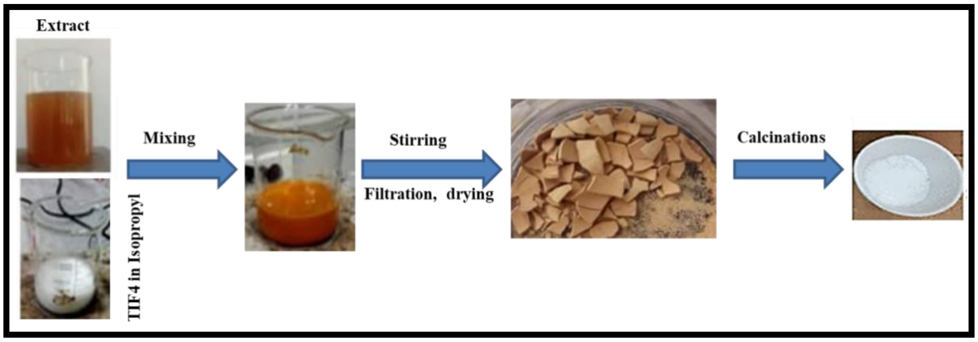

Figure 3. 3: Green synthesis of TiO_2

3.3.4 Synthesis of S. abyssinica-Mediated CuO/TiO_2

The CuO/TiO_2 were synthesized (Scheme 3) by adding an aliquot of 50 mL of the S. Abyssinia to the Cu $(NO_3)_2{\cdot}3H_2O$ and TiF4 separately. The mixture was heated at 80 ◦C for an hour to produce a paste. It was then washed and centrifuged, and rinsed five times with deionized water and twice with ethanol followed by drying in the oven at 100 ^{o}C by following. The paste was then transferred into a crucible and calcined in a furnace for 4 h at 500 ° C referring (Bopape et al., 2023). The products were collected and crushed for further characterization and applications.

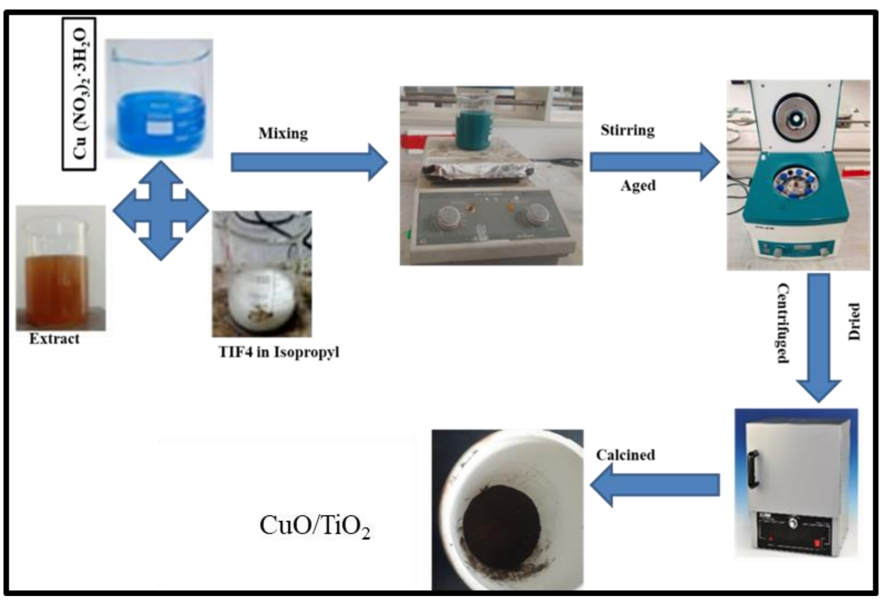

Figure 3. 4: Green synthesis of CuO/TiO_2 (TC1, TC2, and TC3)

3.3.5 Electrode preparation

In the beginning the nickel foam (1 cm^2) is subjected to sonication with 0.1 M HCl for 15 min followed by washing with ethanol and acetone, and finally dried in the oven. The supercapacitor electrodes were synthesized by preparing a slurry of green synthesized active materials such as, TiO_2, CuO, and CuO/TiO_2, with varied weight percentages (TC1, TC2, and CT3), reduced graphene oxide (rGO), and 5% Nafion with ratio of 80:10:10 respectively, in absolute ethanol. Reduced graphene oxide provided electrical conductivity, while 5% Nafion acted as a binder for adhesion. Then the slurry was coated onto treated Ni foam by dip immersion into prepared slurry. The electrodes were then dried at 80 degrees Celsius for 15 min to remove residual solvent and solidify the active materials as referred to in the work of (Shah et al., 2022).

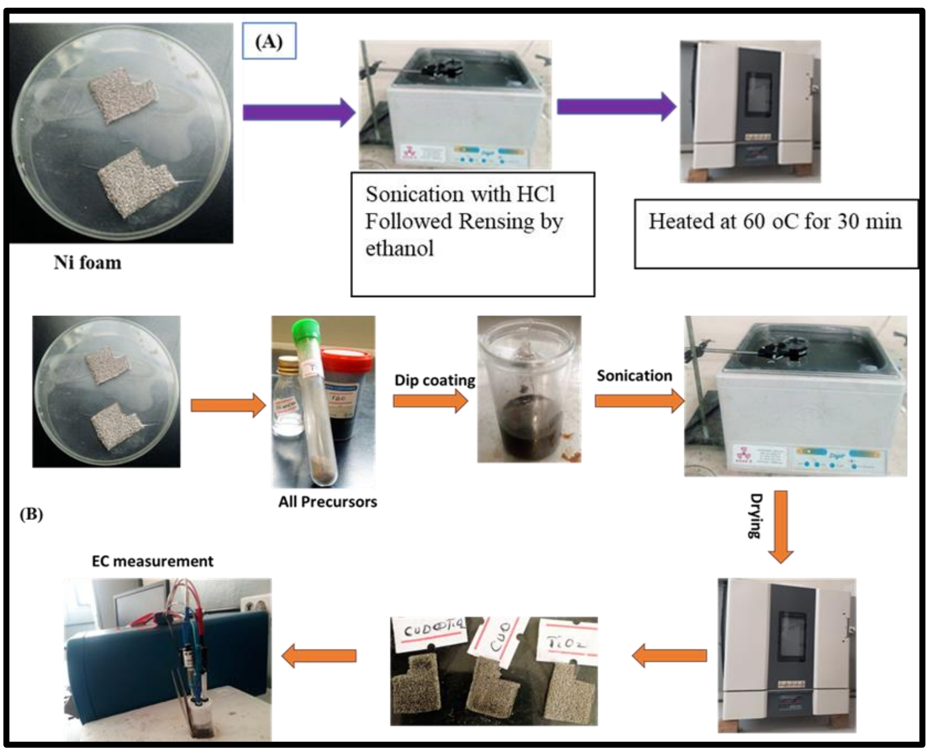

Figure 3. 5: Pretreatment of Ni foam (A), and dip coating deposition of the working electrodes (B)

3.4 Instrumentation and Measurements

A comprehensive characterization of green synthesized TiO_2, CuO, and CuO/TiO_2 nanocomposites was conducted to evaluate their structural, compositional, and electrochemical properties. Scanning electron microscopy (SEM) and X-ray powder diffraction (XRD) determined crystallographic structures and phase compositions. Electrochemical tests employed a three-electrode setup in a 2M KOH electrolyte, with cyclic voltammetry (CV) evaluating electrochemical reversibility, specific capacitance, and rate capability, highlighting redox processes and charge storage mechanisms. Galvanostatic charge-discharge (GCD) tests assessed specific capacitance and energy density at varying current densities, revealing charge/discharge behavior and self-discharge rates. Finally, electrochemical impedance spectroscopy (EIS) examined charge transfer kinetics and interfacial resistance, providing valuable insights into the materials' performance for supercapacitor applications.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Structural Analysis

4.1.1 XRD Analysis

Phase composition and average crystallinity of the pristine TiO_2, CuO, and composite CuO/TiO_2 (TC1, TC2, and TC3) were investigated by using XRD, as illustrated in Figure 4.1. The successful production of the pristine and composite is confirmed by the distinct peaks in the diffraction pattern that correspond to anatase TiO_2, CuO, and CuO/TiO_2.

The table below summarizes the x-ray diffraction angles, miller indices and average crystallite size of the synthesized TiO2 anatase phase that is confirmed by JCPDS Card no. 00-021-1272 (Li et al., 2014).

Table 4. 1: The table below summarizes the x-ray diffraction angles, miller indices, and average crystallite size of synthesized TiO_2

Sample	2 thetas (degree)	Miller indices	Mean crystallite size (nm)
TiO_2	25.3	(101)	9.28
	38.1	(004)	
	48.1	(200)	
	54.0	(105)	
	62.8	(204)	
	69.1	(220)	
	70.5	(215)	
	75.3	(224)	

Whereas CuO exhibits peaks at 32.5 ^{o}, 35.5 ^{o}, 38.7 ^{o}, 48.7 ^{o}, 53.2 ^{o}, 58.3 ^{o}, 61.5 ^{o}, 66.2 ^{o}, 68.0 ^{o}, and 75.1 ^{o} with corresponding crystal planes at (110), (002), (111), (112), (020), (202), (113), (310), (220), and (004) which is confirmed by (JCPDS Card no. 00-048-1548 as referred from (Mouruj & Al-Aubydi, 2009).

CuO/TiO_2 is confirmed to be incorporated into the composite by a peak at 25.3, 35.5, 38.7, 47.93, 58.33, 61.71, and 75.18. In general, the XRD data show that the binary composite retains its crystalline structures in TiO_2, CuO, and CuO/TiO_2 indicating its effective production and structural integrity. The mean crystallite size was calculated using the Scherer formula (Fatimah et al., 2022) Eq (4.1),

$$\boldsymbol{D} = \frac{\boldsymbol{k\lambda}}{\boldsymbol{\beta \, cos\theta}} \tag{4.1}$$

Where D is the average crystallite size, k (is Scherer constant) = 0.9, λ is the wavelength of the X-ray source (0.1541 nm), β is the full width at half maximum (FWHM) and θ is the half diffraction angle. The average crystallite for TiO_2, CuO, and CuO/TiO_2 was calculated to be 9.28 nm, 20.16 nm, and 12.26 nm respectively.

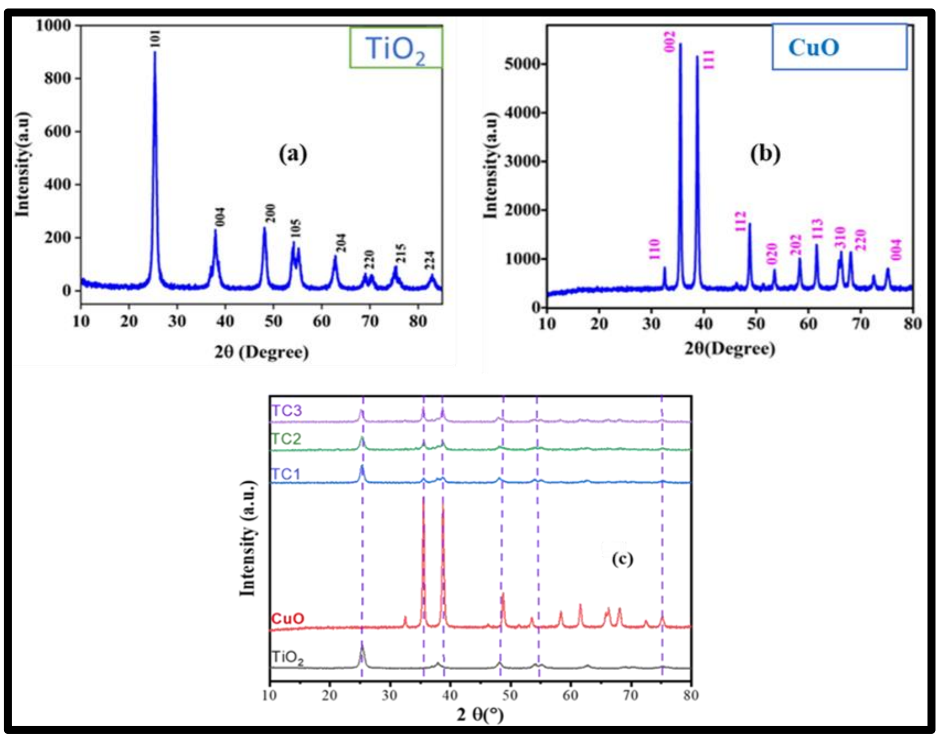

Figure 4. 1: XRD schematic representation of TiO_2 (a), CuO (b), and the all five materials including CuO/TiO_2 binary composites (TC1, TC2 and TC3) (c)

4.1.2 SEM Analysis

The surface morphologies of the synthesized samples examined using scanning electron microscopy (SEM) are displayed in Figure 4.2. The TiO_2 powder (Figure 4.2a) exhibited a highly aggregated morphology with spherical particle structures, forming porous agglomerates, which are favorable for high surface area applications (Ajith et al., 2025). In contrast, the CuO sample (Figure 4.2b) displayed a flake-like structure with loosely aggregated particles. This morphology promotes efficient electron pathways and enhances conductivity (Purushothaman et al., 2014). The CuO/TiO_2 composite (Figure 4.2c) revealed a heterogeneous texture, where CuO flakes appear to be embedded or anchored onto the TiO_2 particle matrix. This integrated structure suggests strong interfacial contact between the two components, which is critical for synergistic effects in hybrid supercapacitor applications (Millán-Ocampo et al., 2025).

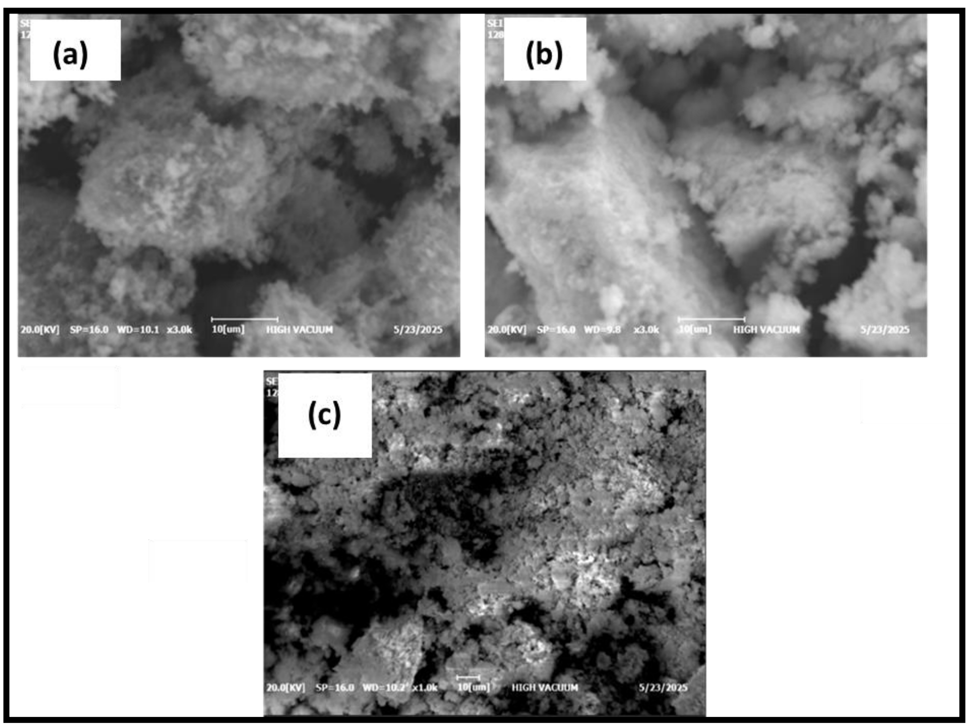

Figure 4. 2: SEM analysis of TiO_2 (a), CuO (b), and CuO/TiO_2

4.1.2.1 EDX Result of CuO/TiO_2

The EDX (Energy Dispersive X-ray Spectroscopy) spectrum of the CuO/TiO_2 composite reveals the elemental composition and confirms the successful integration of copper oxide and titanium dioxide in the sample. The x-axis represents energy in keV, and the y-axis shows counts per second, corresponding to the intensity of emitted X-rays at each energy level. Notable peaks are observed at approximately 0.5 keV, 0.95 keV, 2.0 keV, 4.5 keV, and 8.0 keV. The peak at 0.5 keV corresponds to the Kα line of oxygen, confirming the presence of oxygen, which is expected in both CuO and TiO_2 (Roy, 2016). The peak at 0.95 keV is attributed to the Lα line of copper, while the prominent peak at 8.0 keV represents the Kα line of copper, both confirming the presence of Cu from CuO (El-Seidy et al., 2024; Sahai et al., 2016). Peaks at 2.0 keV (Kα) and 4.5 keV (Kβ) are characteristic of titanium, indicating the presence of Ti from TiO_2 (Mokoena, 2016).

An additional peak near 2.2 keV is marked with a question mark, suggesting an unidentified signal. This could be due to a sum peak, background interference, an overlapping minor impurity, or a Cu Kα escape peak (Mokoena, 2016). Overall, the EDX analysis confirms the presence of Cu, Ti, and O in the sample, consistent with a CuO/TiO_2 composite. For further insight, elemental mapping and standard calibration could enhance the understanding of elemental distribution and concentration within the sample.

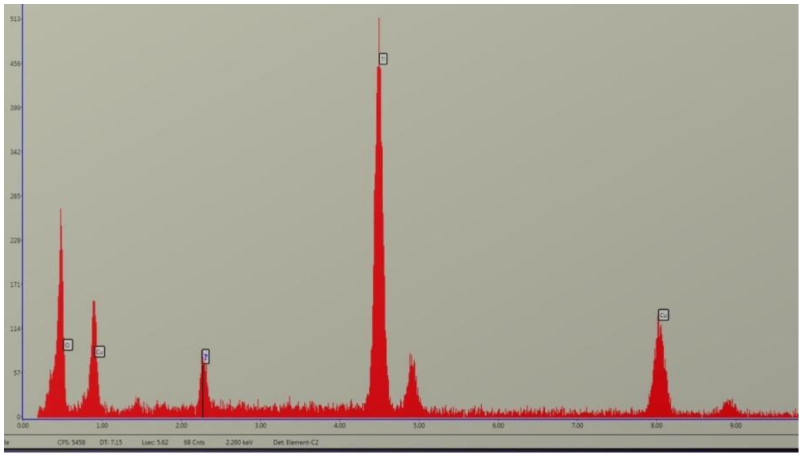

Figure 4.2.1: EDX analysis of CuO/TiO_2

4.2 FTIR Analysis

The FTIR spectra of plant extract Figure 4.3a, measured in the range of 4000-400 cm^{-1}, reveal several key features. for instance, Peaks between 3400-3100 cm^{-1} indicate hydroxyl group stretching, characteristic of polyphenolic compounds (Krysa et al., 2022). Whereas Peak around 2919.19 cm^{-1} indicates characteristics of C-H stretching vibrations, which exist in saturated hydrocarbons (Agarwal et al., 2021). Peaks at 1607.39 cm^{-1} this peak corresponds to C=C and C=O stretching vibrations, which exist in alkenes and aromatic compounds (Dev & Mukadam, 2025). Additionally, a phenolic C-O bending vibration is observed around 1248.66-1025.53 cm^{-1} (Tejedor-Tejedor et al., 1990).

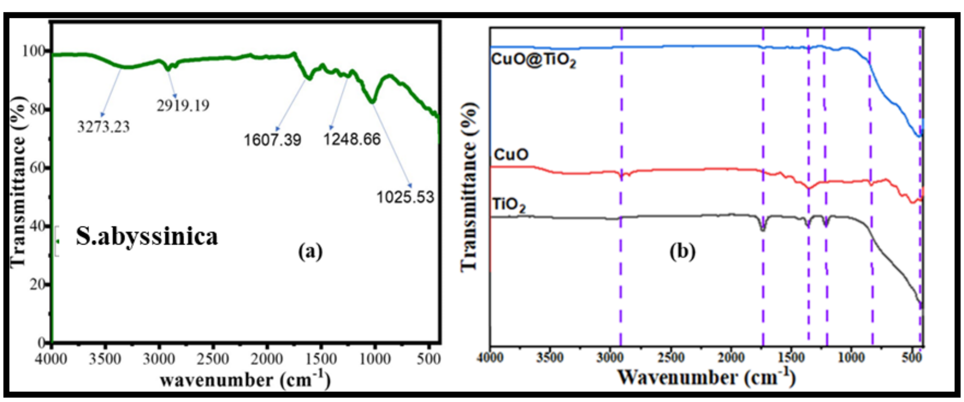

Figure 4. 3: FTIR absorption spectra plot of S. Abyssinica plant extract (a), and pristine TiO_2, CuO, and CuO/TiO_2

In the FTIR spectrum of metal-oxide composites figure 4.3b, several key features can be identified that reveal the components present. For TiO_2 A broadband typically indicates the stretching vibrations of surface hydroxyl groups (Ti-OH) and adsorbed water molecules, with a specific band around 1630 cm^{-1} associated with the bending vibrations of these water molecules (Bezrodna et al., 2004; Watkins, 2016). Characteristic TiO_2 generally appears in the range of 400-800 cm^{-1}, corresponding to Ti-O stretching vibrations (Paramasivam et al., 2022), while copper oxide (CuO) exhibits characteristic stretching vibrations in the range of 400-600 cm^{-1} (Gherasim et al., 2022). Observing these spectral regions is crucial for detecting both metal oxides within the composite material. The peak observed at around 650 cm^{-1} corresponds to the Ti-O-O stretching vibration bond in the composite. Furthermore, the spectra revealed two additional distinct bands below 500 cm^{-1} associated with metal-oxygen (M-O) bond vibrations. The vibrational bands all suggest both Ti-O vibrational stretching and Cu-O stretching vibration bonds (Abouri et al., 2024; Yitagesu et al., 2024), indicating the successful incorporation of CuO into TiO_2. Additionally, shifts in peak positions compared to those of individual TiO_2 and CuO may indicate chemical interactions or bonding at the interface between the components, suggesting the formation of Ti-O-Cu bonds and highlighting the interactions within the composite that can influence its properties and potential applications.

4.3 Brunauer, Emmett, and Teller Analysis (BET)

BET analysis is a technique used to measure the surface area of materials. The specific surface area of the CuO/TiO_2 composite was obtained to be 102.83 m^2/g, which is higher as compared the to specific surface area of TiO_2 (78.2 m_2/g), and CuO (84.06 m^2/g). A higher surface area provides more surface-active sites for the adsorption of more ions resulting in a more efficient supercapacitive process application in supercapacitors (Boutaleb et al., 2022; Jena et al., 2024).

Table 4. 2: BET data of three samples (TiO_2, CuO, and CuO/TiO_2)

Materials	Specific Surface Area (m^2/g)
TiO_2 particles	78.92
CuO particles	84.06
CuO/TiO_2 (70:30) Composite	102.84

4.4 TGA /DTA Analysis

The thermal decomposition properties of green synthesized CuO/TiO_2 composites shown at (figure 4.4b) were evaluated using thermogravimetric analysis (TGA/DTA) from 25 °C to 800 °C. The large endothermic peak in the DTA, which shows the elimination of volatile substances, clearly corresponds to the initial weight loss in the TGA. The abrupt exothermic peak in the DTA, which indicates the combustion of organic matter, is correlated with the weight loss in the TGA between approximately 150 and 350 °C (Abouri et al., 2024). The large endothermic decline in the DTA and the plateau in the TGA between about 350 and 550 °C may be signs of a phase shift. Higher-temperature reactions or structural alterations have been suggested by the minor weight loss and exothermic tendency at about 550 °C (Abouri et al., 2024).

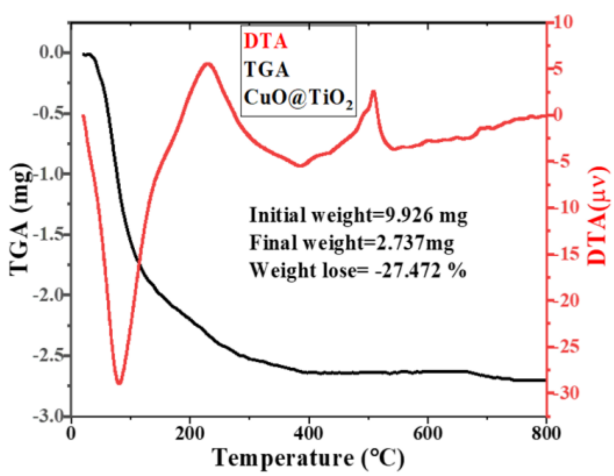

Figure 4. 4: TGA/DTA analysis of CuO/TiO_2

4.5 Electrochemical Characterization

4.5.1 Cyclic Voltammetry (CV)

In CV, the potential of the working electrode is gradually increased from a negative to a positive value and then reversed back to the starting point. This process occurs within a defined range known as the "potential window". As the potential changes, various electrochemical processes, such as redox reactions, ion adsorption/desorption, and double-layer capacitance, take place at the electrode-electrolyte interface, involving the flow of ions and electrons (Adarakatti, 2025). The resulting current is measured and plotted against the potential, creating a "voltammogram." This allows for the observation of both forward and reverse electrochemical reactions, providing insights into the material's electrochemical behavior.

Here in, the performance of the TiO_2, CuO, and CuO/TiO_2 with different weight percentage TC1, TC2, and TC3 electrodes was examined by conducting CV measurements in a 2M KOH electrolyte solution. This electrolyte was selected due to its good electrical conductivity, which allows for a better efficiency of electrodes (Wee et al., 2010). As shown in the Figure 4.5, CV measurement of all five electrodes at a scan rate ranging from 5-200 mV/s, within a voltage window of 0 to 0.7 V was conducted. In order to evaluate the rate capabilities and stability, demonstrating the electrodes' relative super capacitive capability was measured. A distinctive feature that denotes normal capacitive behavior is the quasi-rectangular form displayed by each of these curves. This form indicates that these electrodes' charge storage mechanism is redox (reduction oxidation) reaction, which is in line with supercapacitors' ideal behavior, which stores charges at the electrode-electrolyte interface by faradaic reactions (Attia et al., 2022; Li et al., 2024).

Copper oxide (CuO) typically exhibits pseudocapacitive behavior in alkaline electrolytes like KOH due to Faradaic redox reactions occurring at the electrode surface (Endut et al., 2013).

$CuO + OH^- \rightleftharpoons CuOOH + e^-$

This reaction involves the oxidation of Cu (II) in CuO to Cu (III) in CuOOH. The reverse reaction occurs during the reduction process.

TiO_2, particularly in its anatase form, can undergo intercalation and de-intercalation of ions from the electrolyte, contributing to charge storage. In KOH, this could involve potassium ions (K^+) (Bhat et al., 2022).

The area under the CV curve of the TC3 with weight percentage of 70:30 electrodes is large indicating superior charge storage capacity. This enhancement is due to the synergetic effect of CuO and TiO_2 (Shah et al., 2022). For example, TiO_2 provides structural support and protects the composite from degradation during prolonged cycling, while CuO improves overall electrochemical activity of the composite due to more active sites it has (Shah et al., 2022), and their composite enhance surface area and electron transport which leads to enhanced electrochemical property.

The voltammogram shows constant shape that implication of the electrode can maintain its charge storage capabilities even during quick cycles of charge and discharge. The electrode's capacitive behavior and electrochemical durability are confirmed by this quasi-rectangular profile at different scan rates. Negligible degradation over time makes it appropriate for high-power applications (Khot & Kiani, 2022).

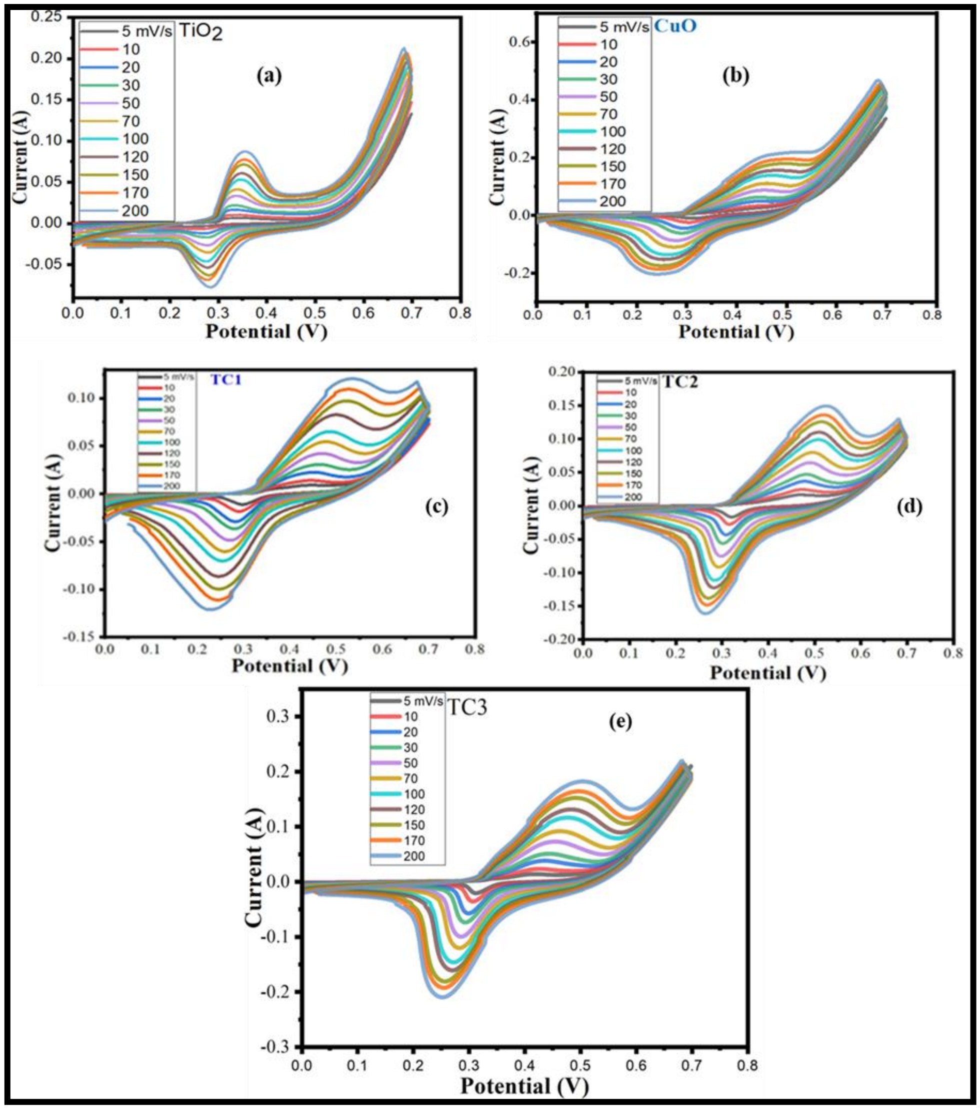

Figure 4. 5: CV plot of five electrodes, pristine TiO_2 (a), CuO (b), and binary composite TC1 (c), TC2 (d), and TC3 (e).

To summarize CV analysis finds the TC3 binary composite electrode to be far better performing than its binary and pristine counterparts. Its higher CV curve area and stable capacitive nature at different scan rates reveal its good rate capability, outstanding electrochemical stability, and higher charge storage capacity. As an energy storage material, the composite has enormous potential in high-power density applications and fast charge-discharge applications. The improved performance of and TC3 is mainly due to their synergy, highlighting the significance of material design in future supercapacitors.

4.5.2 Galvanostatic Charge Discharge (GCD)

GCD analysis is a kind of electrochemical technique that is widely applied in the investigation of the charge storage characteristics of devices such as batteries and supercapacitors. This technique is based on the application of a constant current to the electrode and the simultaneous recording of the voltage response over time in the course of both charging and discharging (Adarakatti, 2025). The obtained potential-time plots bear extremely significant features in the form of specific capacitance, energy density, power density, and internal resistance. The presence of an almost symmetrical triangular form in the curve suggests a perfect capacitive behavior, while any deviations may intimate resistive or pseudocapacitive properties (Mathis et al., 2019). GCD analysis is a very popular tool to determine the efficiency, robustness, and actual performance of electrode materials.

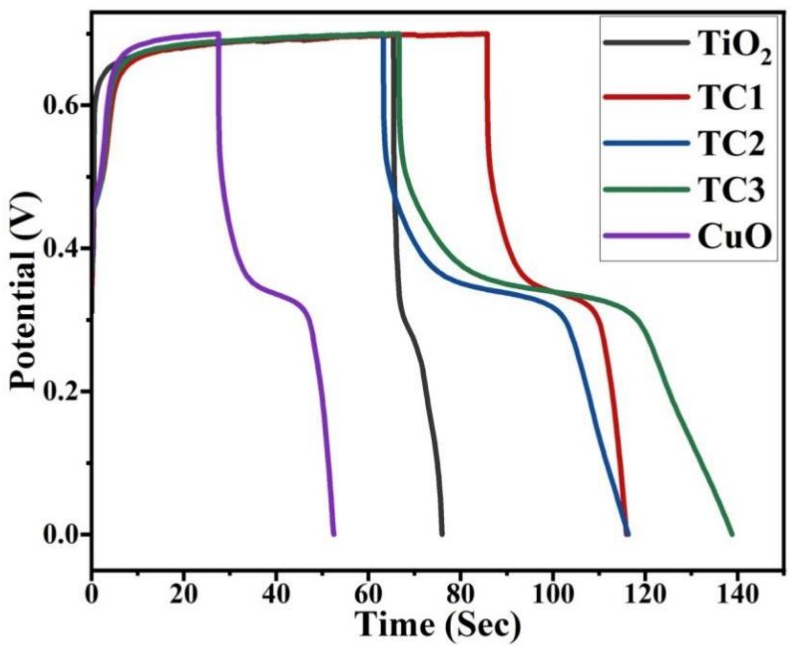

Figure 4. 6: GCD plot of five electrodes, pristine TiO_2, CuO, and binary composites TC1, TC2, and TC3 at current density 5A/g.

As shown in Figure 4.6 GCD experiments were conducted to evaluate the electrochemical characteristics of TiO_2, CuO, TC1, TC2, and TC3 electrodes at a current density of 5 A/g within a potential range of 0 to 0.7V.

According to the GCD analysis, the TC3 electrode has a higher energy storage capacity than the remaining electrodes since it shows a noticeably longer discharge time as compared to the rest of the electrodes used. The binary composite structure's synergistic effects are the cause of this improved performance (Shah et al., 2022). TC3 offer a large surface area as compared to pristine TiO_2 and CuO, and effective electron transport because, TiO_2 improves structural integrity and, and CuO improves conductivity and speeds up faradaic reactions. When combined, these elements enable better charge transport and storage, which improves electrochemical performance.

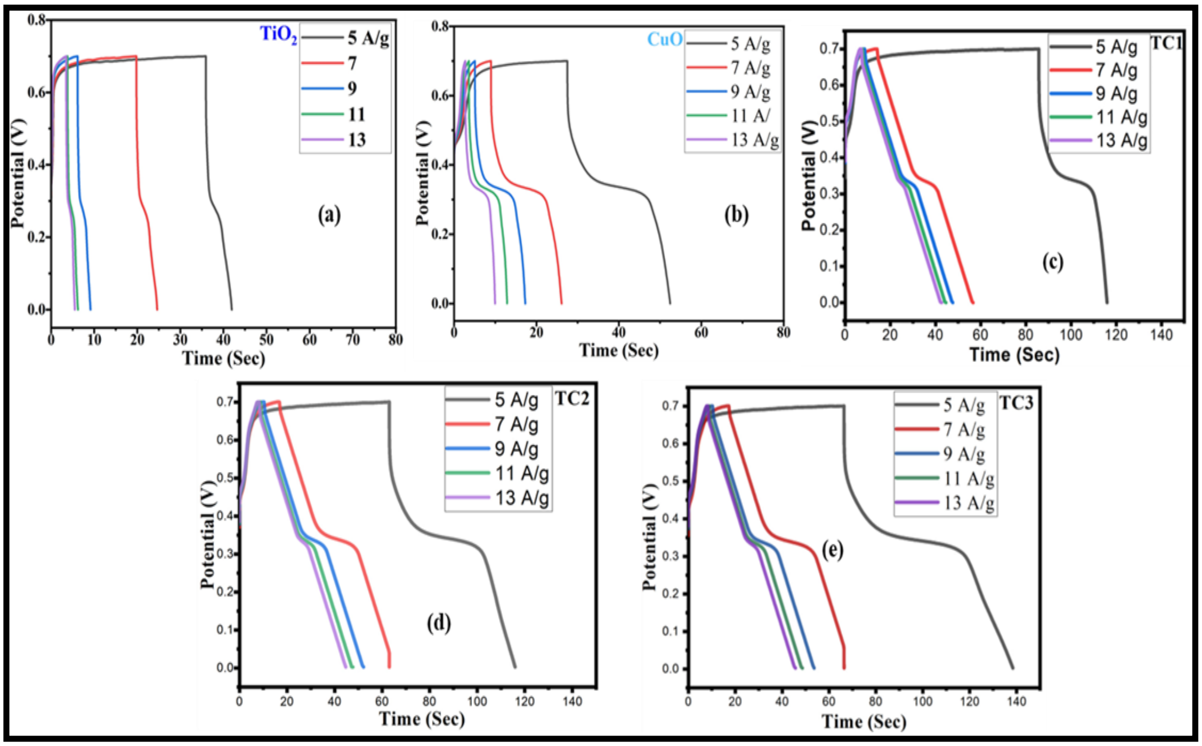

Figure 4. 7: Schematic representation GCD plot of five electrodes, pristine TiO_2 (a), CuO (b), and binary composite TC1 (c), TC2 (d), and TC3 (e).

Based on the GCD test, the TC3 electrode has a much greater discharge time than the rest of electrodes.

This indicates that the electrode has a higher energy storage capacity since it is capable of storing and delivering more charge in the same potential window. The galvanostatic charge-discharge diagram illustrates that TC3 composite material has the largest charge storage capacity among the electrodes studied (TiO_2, CuO, TC1, and TC2). TiO_2 improves structural whereas, CuO adds conductivity large faradic reaction, and both of which work together to improve charge storage and transfer efficiency. These synergistic effects of the binary composite structure are responsible for this improved performance. While all materials have predominantly capacitive behavior with a certain resistive loss and potential pseudocapacitive contribution, the extended discharge time of TC3 proves it to be the optimal choice for supercapacitor application in this series of experiments.

Key parameters that can be derived from GCD graph are:

Specific capacitance (Gravimetric or Areal):

For discharge profile specific capacitance can be calculated as follows (Czagany et al., 2024): eq 4.2 and 4.3

$$\text{Gravimetric capacitance (F/g)} \quad C_g = \frac{I.\Delta t}{m.\Delta V} \qquad 4.2$$

$$\text{Areal capacitance (F/cm}^2\text{)} \quad C_g = \frac{I.\Delta t}{A.\Delta V} \qquad 4.3$$

Where: I=discharge current (A), Δt=discharge time (s), ΔV=discharge voltage (V), A=area of active electrode (cm^2), and m=mass of active electrode (g).

Here in, the Gravimetric capacitance of all working electrodes was calculated by Appling above equation. The highest calculated value of specific capacitance for each of five electrodes are 593.8 (F/g) for TC3, 437.4 (F/g) for TC2, 248.2 (F/g) for TC1, 205.7 (F/g) for CuO, and 86.2 (F/g) for TiO_2. From this TC3 593.8 (F/g) is leading recorded value.

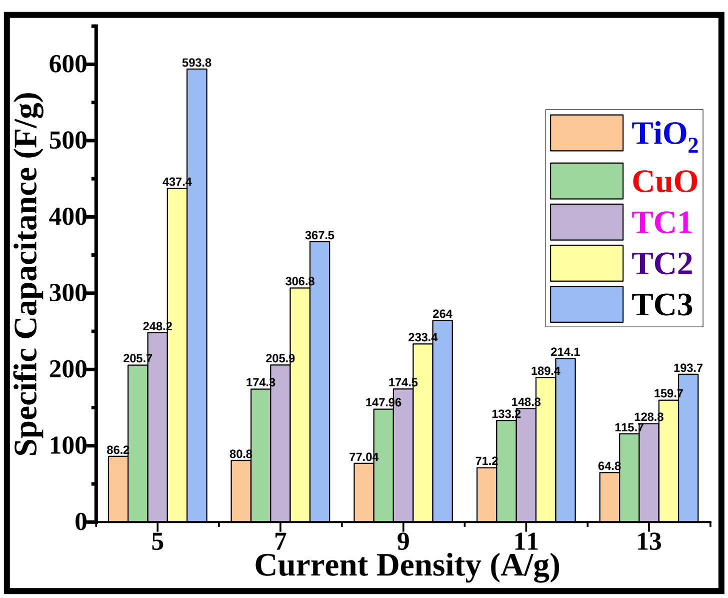

Figure 4. 8: Comparison of specific capacitance of five electrodes at different current density

4.5.3 Electrochemical Impedance Spectroscopy (EIS)

The electrochemical impedance spectroscopy (EIS) was conducted to understand better the kinetics of electron transfer and ion diffusion into the electrode materials. EIS test, performed in the frequency range from 100 kHz (high frequency) to 10 mHz (low frequency) in 2MKOH.

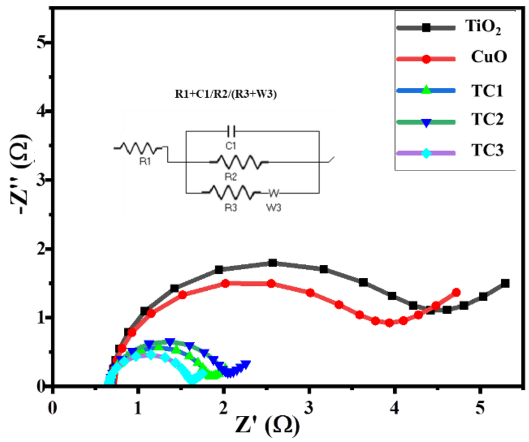

Figure 4. 9: Schematic representation Nyquist diagram for five electrodes TiO_2, CuO, TC1, TC2, and TC3;

The results are depicted in Figure 4.9. The Nyquist plot displays the real and imaginary parts of impedance for pristine $TiO_{2,}$ CuO, and TC1, TC2, and TC3 electrodes and provides insights into their charge transfer and ion diffusion properties. As indicated the resistance of TC3 is lowest as compared to others which gives information that TC3 has better capacitance value.

4.6 Stability Test

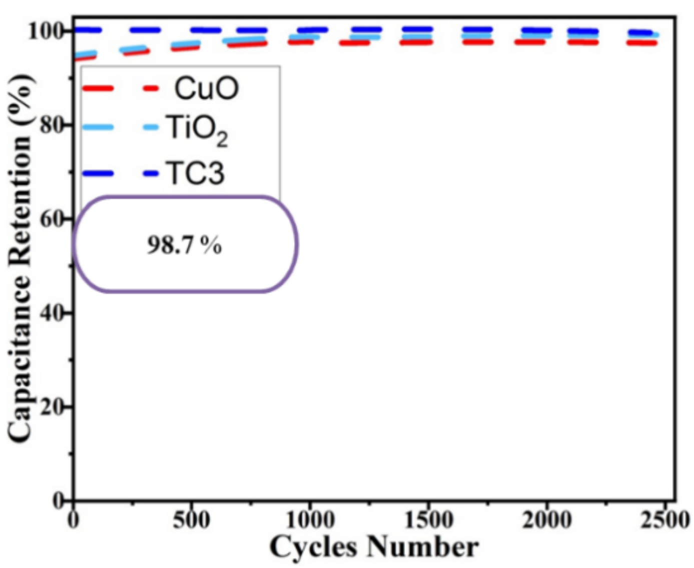

Figure 4. 10: Cycling performance of three electrodes TiO_2, CuO, CuO/TiO_2

This is a plot of capacitance retention (%) versus cycle number for three supercapacitor electrode materials: TC3, TiO_2, and CuO to evaluate their cyclic stability to 2500 charge/discharge cycles. The plot shows that TC3 is a highly stable supercapacitor electrode material and may be a good candidate to be used in long-life energy storage devices. Its excellent retention of 98.7% to 2500 cycles confirms its long-term stability to repeated electrochemical stress.

Table 4. 3: Provides a detailed comparison between the synthesized CuO/TiO_2 (TC3) and CuO and TiO_2 based composite electrodes.

Electrode Materials	Methodology	Specific capacitance (F/g)	Stability (%/cycle num)	References
CuO/Polyaniline	In situ polymerizations	185	75% capacitance retention)	(Gholivand et al., 2015)
CuO/rGO	Hydrothermal	326	-	(Purushothaman et al., 2014)
CuO/TiO_2 Nanocomposites	Wet chemical method	553	96% (after 10,000 cycles)	(Shah et al., 2022)
$Cu/CuO/PCNF/TiO_2$ Hybrid Composite	Electrospinning followed by hydrothermal technique	530	78.8% (after 10,000 cycles)	(Lal et al., 2019)
$PANI@TiO_2$-CuO Ternary Composite	Facile method (TiO_2-CuO) followed by in-situ polymerization of aniline	-	87.5% (after 1500 cycles at 1.0 A g^{-1})	(Boutaleb et al., 2022)
$CuO/Pt-TiO_2$ NTs	Electrodeposition-thermal oxidation method	423	93% (after 5000 cycles)	(Attou et al., 2019)
CuO/Biochar Composite (CuO@BC)	Hydrothermal carbonization	353	-	(Ahmed Alsharif et al., 2023)
CuO/TiO_2 nanocomposite	**Green Synthesis**	**593.8**	**98.7 % after 2500 cycles**	**This work**

Table 5.1 provides a detailed comparison between the synthesized CuO/TiO_2 (TC3) electrodes and previously reported TiO_2, CuO based binary or ternary electrodes, and synthesis method the used further showing the performance characteristics and expected improvements of the present composite. Thus, lesser resistance values of the composite combined with faster charge transfer kinetics and enhanced ion diffusion ability provide the CuO/TiO_2 (TC3) composite great potential as a superior electrode for the next generation of supercapacitors and other energy storage devices.

CHAPTER FIVE

5.1 Conclusion

This study successfully demonstrated the green synthesis of CuO, TiO_2, and CuO/TiO_2 using S. abyssinica plant extract as a natural reducing and capping agent. The synthesized materials were thoroughly characterized using XRD, FTIR, SEM, BET, and electrochemical techniques. Among the composites, CuO/TiO_2 with a 70:30 ratio (TC3) exhibited superior electrochemical performance, including higher specific capacitance of (593.8 F/g), better surface area of (102.94 m^2/g), and enhanced cycling stability of (98.7 % after 2500 cycles), energy density of (20.1 Wh/kg), and power density of (1010.3 W/kg) compared to individual CuO and TiO_2 electrodes. This improvement is attributed to the synergistic effect between the metal oxides, and enhanced porosity. The findings underscore the potential of environmentally friendly green synthesis routes for producing efficient and sustainable electrode materials for energy storage applications, particularly supercapacitors. Overall, this research contributes to the advancement of cost-effective, eco-friendly energy storage solutions vital for future renewable energy systems.

5.2 Recommendation

To enhance the electrochemical performance of CuO/TiO_2 electrode material in the practical application of supercapacitors, several avenues can be explored. The following recommendations can be implemented to ensure the completion of the research work. Additionally, there are further recommendations for utilizing CuO/TiO_2 for photo catalyst dye degradations.

- ✓ In this study, the composite electrode materials have a lower conductivity property so by adding carbon based materials and making it a ternary composite the specific capacitance can be enhanced more than the two composites.
- ✓ For which instead of water-based electrolyte system, using the organic solvent-based electrolyte system, e.g. Acetonitrile + $TBAPF_6$ in order to increase the energy density of the supercapacitor.
- ✓ Since the electrode material is important, synthesizing by using porous materials like metallic-organic framework (MOF) can also be beneficial for the performance of supercapacitor.

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