

ENHANCED SUPERCAPACITOR PERFORMANCE OF CeO_2 MODIFIED WITH Co_3O_4 USING A FACILE HYDROTHERMAL ROUTE

Submitted in partial fulfillment of the requirements for the award of
Master of Science degree in Physics

By

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**INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)**

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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of S.Sivaramalakshmi (41590019) who carried out the project entitled "ENHANCED SUPERCAPACITOR PERFORMANCE OF CeO_2 MODIFIED WITH Co_3O_4 USING A FACILE HYDROTHERMAL ROUTE" under my supervision from November 2022 to May 2023.

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I S.Sivaramalakshmi hereby declare that the Project Report entitled ENHANCED SUPERCAPACITOR PERFORMANCE OF CeO_2 MODIFIED WITH Co_3O_4 USING A FACILE HYDROTHERMAL ROUTE done by me under the guidance of Dr. M. Dakshana (Internal), Department of Physics, Sathyabama Institute of Science and Technology, Chennai is submitted in partial fulfilment of the requirements for the award of Master of Science Degree in Physics.

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SIGNATURE OF THE CANDIDATE

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ABSTRACT

Due to the increasing demand for sustainable clean energy storage systems, there is an urge for the development of high-energy and power-density electrode materials. Among the various materials, n-type CeO_2 has more attention due to good reversibility and excellent stability, biosensors, photocatalysts, photovoltaics, and optoelectronics. Apart from the appreciable characteristics of CeO_2 , there is some limitation to promoting the metal oxide for further applications, mainly lower electrical conductivity and wide bandgap ($\sim 3.5\text{eV}$). To enhance electrical conductivity and surface activity, various metal oxides are used to combine with CeO. In this work, the properties of Cerium are enhanced by combining with Co_3O_4 forming a novel CeO-CoO nanocomposite prepared by hydrothermal route. The prepared CeO_2 -CoO nanocomposite was characterized using advanced studies for understanding the crystal structure, morphology, and optical property of the CeO-Co₂O₄ nanocomposite. The developed CeO_2 -CoO nanocomposite showed high specific surface area, enhanced specific capacitance, and good reversible redox reactions. The high specific capacitance of CeO_2 -Co₂O₂ nanocomposite shows that the modified electrode has potential application for the fabrication of high power and energy storage devices.

Keywords: Nanocomposite, supercapacitor, band gap, CV, TEM

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CHAPTER-1

Chapter-1 starts with a brief introduction of the metal oxide nanostructures. In addition to this, a short review of the targeted applications, i.e., supercapacitor applications, of this project was also discussed in this chapter. Finally, the chapter describes the importance of the project

CHAPTER-1

1. Introduction:

1.1 Nanomaterials

Nanomaterials have gained prominence in technological advancements due to their variety of tunable physical, chemical, and biological properties with embellished performance over their bulk counterparts. The nanoparticles and nanostructured materials is an active one in terms of research due to its wide variety of potential applications [1]. In principle, nanomaterials are smaller than 100 nm at least on one dimension. It exhibits different physicochemical properties based on size and shape compared to bulk materials. By modifying the shape and size of nanomaterials at the nanoscale, these materials produce a unique character with appreciable capabilities. There are many different shapes of nanomaterials, including nanorods, nanoparticles, and nanosheets. Based on the dimensions of the nanoscale they are classified as Zero-dimensional nanomaterials (0-D), one-dimensional nanomaterials (1-D), Two-dimensional nanomaterials (2-D), and Three dimensional or bulk nanomaterials (3-D) as displayed in Fig.1.1 [2]. In zero dimension, nanomaterials are measured within the nanoscale its dimension is not more than 100 nm. In one dimension, nanomaterial measurement is outside the nanoscale this includes nanotubes, nanorods, and nanowires and possess unique features that can provide a high accessible surface area-to-volume ratio. In two dimensional structure, only two dimensions are in the nanoscale range, and the remaining one dimension is outside of it. They include nanofilms, nanolayers, and nanocoatings. In three dimensions, these nanomaterials are not in the nanoscale range. That means in three arbitrary dimensions they are >100 nm scale. These include nanocomposites, core shells, multi nanolayers, bundles of nanowires, and bundles of nanotube [3].

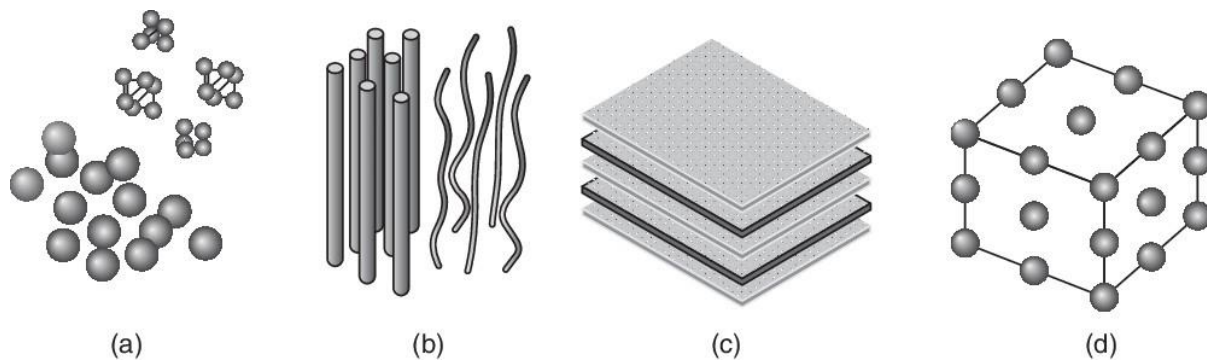


Fig1.1 (a) zero dimension, (b) one dimension, (c) two dimension, (d) three dimension

Based on their morphology, size, properties, and constituents, nanomaterials are classified into different types they are carbon-based nanomaterials, inorganic-based materials, organic-based materials, and composite-based materials. Carbon-based nanomaterials contain carbon and are found in morphologies such as spheres, ellipsoids, or hollow tubes. Inorganic materials include metals and metal oxide-based nanoparticles such as RuO_2 , MnO_2 , NiO , etc, and it also includes semiconductors such as silicon and ceramics. Organic-based nanomaterials are mostly made from organic matter. In composite-based nanomaterial, the composite may be any combination of metal-based, carbon-based, or organic-based nanomaterials with any form of ceramic, metal or polymer bulk material [4]. There are various preparation methods for nanoparticles they are Bottom-up technique, Top-down technique, Chemical reaction technique and Combination technique [5].

1.2 Metal oxide:

Metal oxide has been attracted because of its changes in electrical, optical, and magnetic properties include with chemical and physical stability. Metal oxide nanoparticles have a variety of applications such as electrochemical capacitors. In recent times transition metal oxide-based electrochemical capacitors have attracted more attention due to its unique properties, high theoretical capacitance, variable oxidation state and existence of a double-layer charge storage mechanism yet lags from providing high energy density values [6]. To upgrade the energy density and specific capacitance, various other materials are involved which are as follows,

(i) Carbon materials are low cost and have good electrical conductivity but it suffers from low specific capacitance,

(ii) polymers have immense specific capacitance and extreme conductivity, yet their cycle life is excessively poor.

Compared to the above two types of materials, transition metal oxides have multiple oxidation states and fast redox reactions. Which in turn offers high specific capacitance and excellent conductivity [7]. The design of metal oxide material in terms of fabrication of novel nanostructures, composition, oxygen vacancies, and electroconductivity has boosted the chemical and physical performances of metal oxide regarding their electrical conductivity, specific surface area, electro-active sites, and chemical stability [8]. The well-known metal oxides are ruthenium oxide (RuO_2), cobalt oxide (Co_3O_4), manganese oxide (MnO_2), and vanadium oxide (V_2O_5), these materials have high theoretical specific capacitance [9]. Among these materials, RuO_2 has been an amorphous potential candidate for electrochemical capacitors and it achieves higher energy density and power density compared to the other EDLCs and conducting polymer-based pseudocapacitors, but the only limitation is cost-effective, resource affluence, and toxic nature limit its broad applications. In order to replace RuO_2 , other metal oxides such as CeO_2 , Co_3O_4 , NiO , and MnO_2 are being investigated [10].

1.3 Cerium Oxide

Cerium is a rare earth element that is enforced today in many fields of applications such as magnetism, alloys, catalysis, and electrochemical capacitors [11]. In particular, CeO_2 has been utilized as an electrode material for supercapacitors due to its excellent redox properties, abundance in nature, and low toxicity [12]. Because of its outstanding redox properties, it is used as a promising electrode for supercapacitors, CeO_2 has been proven as a conducive and convenient electrode for supercapacitors [13]. Cerium typically crystallizes in oxide form as CeO_2 , which has the common oxidation state of +4. A facile transition between the +4 and +3 oxidation states is possible, resulting in oxygen vacancies. Because of its oxygen storage and release capability, it becomes a good candidate for a variety of applications. This oxygen

vacancy is created by the loss of oxygen from the lattice, which determines the conductivity of the material. According to the literature, rare earth oxide supercapacitors have been reported in only a few cases [14].

1.4 Cobalt Oxide

Nanoparticles of Co_3O_4 serve as active sites for redox reactions, which results in high specific capacitance [15]. It is noticeable that Co_3O_4 has the same admirable electrochemical potential as ruthenium compounds with a theoretical capacitance of up to 3650 F g^{-1} [16]. Co_3O_4 is considered as an ideal material due to its good cycle life, fast ion diffusion, effective transportation of electrons, its high specific capacitance, and electrochemical stability making it as a suitable pseudo-capacitor electrode material [17]. However, due to limited potential, energy density and small cycling stability, the study of new cobalt oxide composite materials for the supercapacitor has been thoroughly investigated. The different methods of preparation for Co_3O_4 have been established in recent years. For example, Shinde et al. [18] prepared Co_3O_4 thin films via the spray pyrolysis method.

1.5 CeO₂/Co₃O₄ Nanocomposite

CeO_2 is one of the actively researched materials due to its high oxygen storage capacity, ecologically friendly nature, and moderately priced with strong redox characteristics. However, its conductivity and structural stability are poor due to the expansion of lattice during the diminish of Ce^{4+} to Ce^{3+} . Hence, CeO_2 is not applicable as a stand-alone electrode material so hybrid materials are used to enhance its conductivity and structural stability [16]. Based on the electrical conductivity nature, redox activity Co_3O_4 is considered as a suitable material to enhance the properties of CeO_2 . Jiewu Cui et al [19] reported that $\text{Co}_3\text{O}_4/\text{CeO}_2$ hybrid materials are auspicious candidates for supercapacitor applications. In this work, we report the synthesis of CeO_2 nanoparticles and $\text{CeO}_2/\text{Co}_3\text{O}_4$ nanocomposite as an electrode material for enhanced supercapacitor application via a facile hydrothermal route.

1.6 Supercapacitor

It has been visibly seen that the accelerated production and use of fossil fuels have a great impact on the environment. This in turn escalated the demand for batteries, supercapacitors, and fuel cells. Supercapacitors have drawn a lot of attention in comparison to other types of rechargeable energy storage systems because of their numerous advantages like their extended lifespan, high power density, high specific capacitance, high availability, and reliability, quick charging and discharging capabilities, etc. Supercapacitors show extensive applicability in electrical vehicles, transportation, and Industrial machinery [20]. In recent days supercapacitor technology has undergone considerable development and research due to its potential to allow the advancement of energy storage technology. Supercapacitors employ high surface area and thin dielectric layers. They exhibit capacitance that is higher than traditional capacitors. When compared to the conventional capacitor energy storage device in terms of their high-power capability and charging-discharging cycles. Supercapacitors have a higher power rating than rechargeable batteries and can store a lot more charge, however, supercapacitors have low energy density than the batteries and fuel cells.

For applications requiring an energy supply for long periods of time, this calls for coupling with batteries or other power sources. As a result, it would be advantageous to increase the supercapacitor's energy density than batteries. which is one of the main causes of the recent spike in interest of supercapacitor technology research and the development of a variety of materials and synthesis techniques which is appropriate for supercapacitor applications [21].

Supercapacitors work is very similarly to batteries, In supercapacitors energy storage mechanism purely depends on movement of charges and electrochemical redox activity. Supercapacitors are constructed from an electrolyte, two electrodes, and a separator that allows the transfer of ions while providing insulation between the electrodes. For supercapacitor electrodes, various types of materials such as carbon material, polymers, and metal oxides have been used [22].

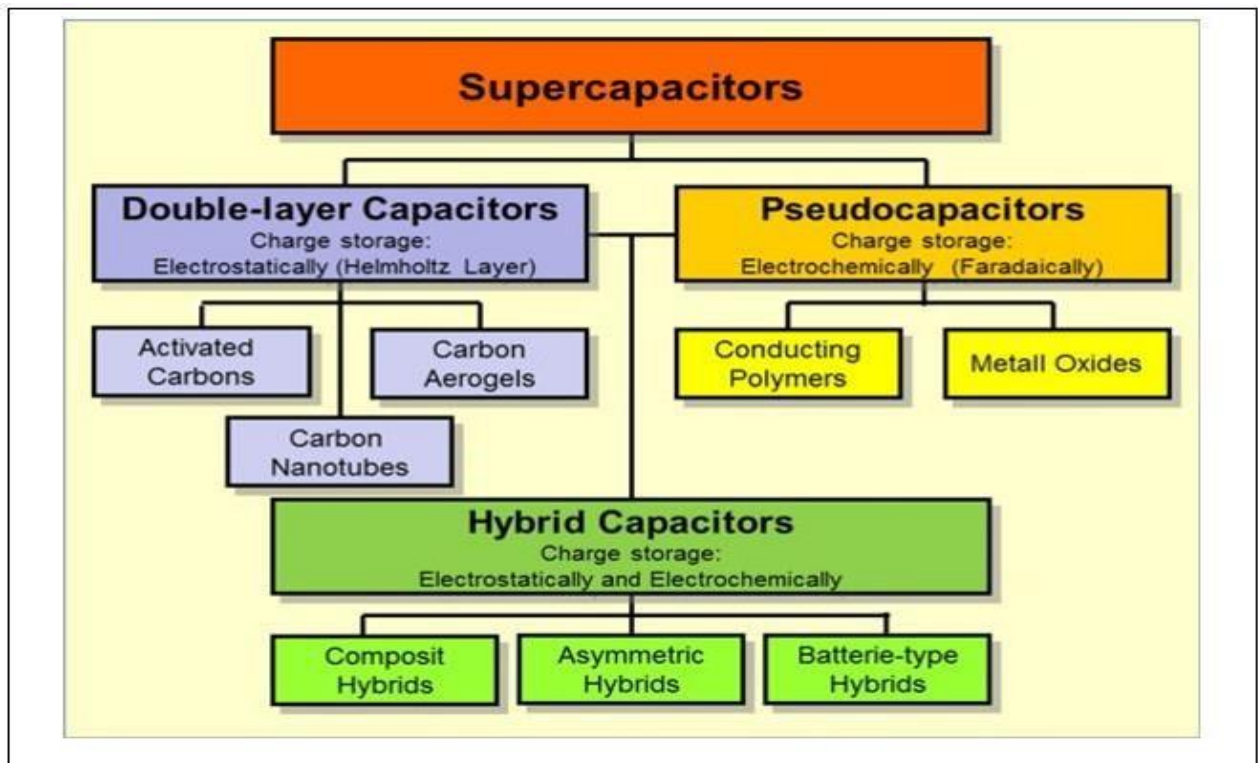


Fig.1.2 shows the supercapacitor types

Relying on energy storage technologies supercapacitors are classified into three types, they are Electric double-layer capacitors (EDLC) and faradaic supercapacitors (FS), sometimes known as pseudo capacitors and hybrid types as depicted in Fig.1.2 [23]

1.6.1 Electrochemical double layer supercapacitor (EDLC) :

In EDLCs, the charge storage and release mechanism are based on the nanoscale charge separation at the electrochemical interface formed between an electrolyte and electrodes. In EDLC the charge storage mechanism is a non-faradaic process and no redox reactions are involved. Here there is no transport of charge between the electrodes and electrolyte, due to this there are no chemical charges possible hence it is known as non-faradaic process. So the charge storage in EDLCs is very highly reversible. When the potential is applied, the charges are assembled on the surface of the electrodes. Following the unusual attraction between the unlike

charges, ions are diffused into the pores of active electrode materials by diffusion from the liquid electrolyte solution. In this way every electrode builds up a double layer of charges, resulting in an increase in surface area and a decrease in electrode distance. It allows EDLCs to get high energy density, and high cyclic stability in comparison with conventional capacitors. The electrochemical characteristics of EDLCs remain stable for a great number of charge-discharge cycles. But they offer a very low power density compare to pseudocapacitor electrode material. By changing the nature of electrodes, we can change the electrochemical performance of EDLCs. Generally, for EDLC carbon based materials are used as electrode materials and H_2SO_4 , KOH , NaOH , and Na_2SO_4 are used as electrolytes [24]. Figure1.3 represents the construction and charge storage mechanism of EDLC type storage device [25].

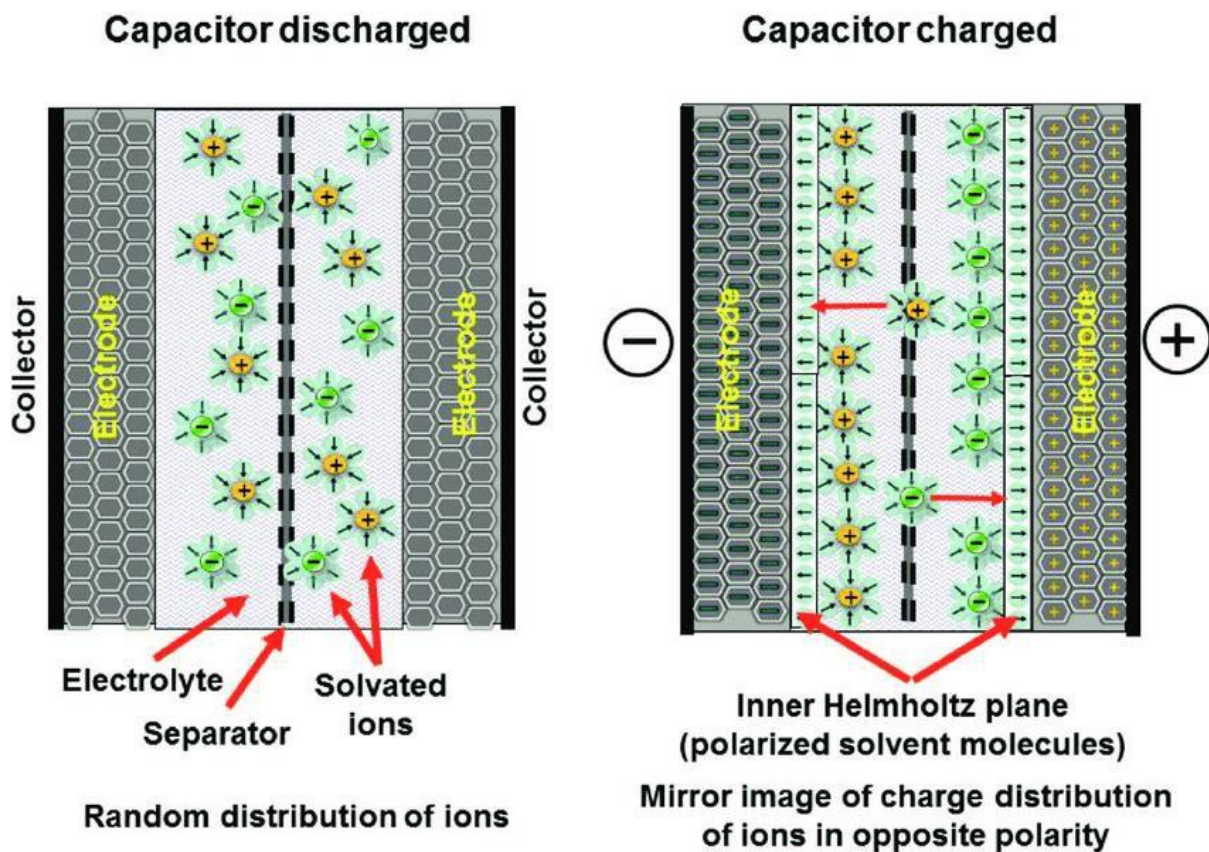


Fig1.3 shows the construction and charge storage mechanism of EDLC

1.6.2 Pseudocapacitor :

Pseudocapacitors store the charge through the faradaic process by transferring the charge between electrode materials and electrolytes. As displayed in Fig1.4 [25]. It occurs from the reversible redox reaction in the near-surface of active electrode materials or on the surface. The interaction between the electrolyte and electrode materials includes the faradaic reaction. It is also called as charge transfer reaction. In pseudocapacitance, the faradaic reactions depend on the voltage. The charge diffusion occurs in the faradaic reaction resulting in a voltage-dependent capacitive behavior. Redox or pseudocapacitors are achieved through oxidation-reduction reactions, electro sorption, and the intercalation process. To develop the pseudocapacitors three types of electrochemical processes were applied. They are redox reactions involving the ions from electrolytes, surface adsorption of ions from the electrolyte, and doping-undoping of active ions into electrode materials. By the faradaic process, pseudocapacitors obtain higher energy densities and higher capacitance compared to EDLCs. The pseudocapacitive electrode material has high conductivity in all cases in order to donate and collect the electron current. Most commonly used electrode materials are Conducting polymers or transition metal oxide-based materials and sulfides. Conducting polymers give high conductivity which in turn provides high capacitance. They show low ESR values due to their high conductivity. The main advantage of the conducting polymer is its processability. Transition metal oxides based electrodes have high conductivity. Due to their micropores, the electrode materials give a relatively high surface area. It allows the distribution of the ions to and from the electrodes in a cell. The specific capacitance of the material is dependent on its surface area. By several orders of magnitude over the double-layer capacitance, the pseudocapacitors offers the specific capacitance value [24].

Pseudocapacitance with specifically adsorbed ions

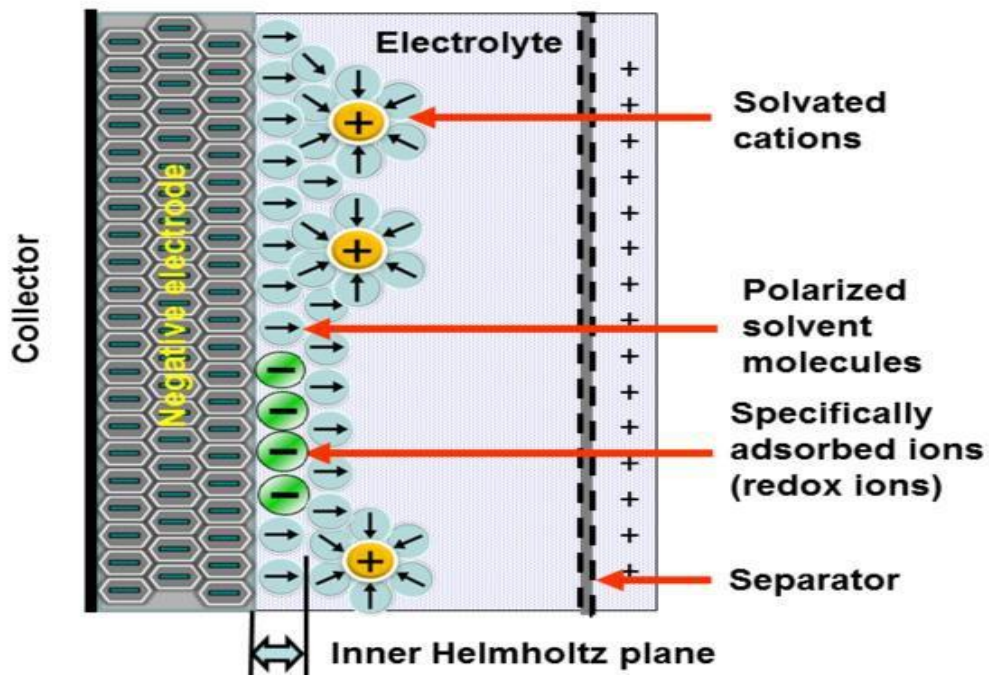


Fig1.4 shows the charge storage mechanism of pseudocapacitors

1.6.3 Hybrid Supercapacitor:

By using one electrode made of double-layer carbon materials and one electrode made of pseudocapacitance materials, hybrid capacitors can store charge using both faradic and non-faradaic processes. Hybrid capacitors have a higher energy and power density than EDLCs without sacrificing cyclic stability or cost-effectiveness. In the last ten years, the majority of hybrid supercapacitors have used nickel oxide (NiO) as the pseudocapacitance material in the positive electrode. Although hybrid capacitors energy density may be somewhat higher than that of EDLCs, their nonlinear charged-discharge behavior places restrictions on their performance. The efforts are concentrated on three distinct types of hybrid supercapacitors, which are distinguished by electrode configuration, battery, asymmetric, and composite types. The metal oxide or conducting polymer polymers are combined with carbon-based compounds to create composite electrodes. This involves simultaneous physical and chemical charge storage processes in a single electrode.

By coupling an EDLC electrode with a pseudocapacitors electrode, asymmetric cells offer both faradaic and non-faradaic mechanisms as depicted in Fig1.5 [26]. In particular, the pairing of an activated charcoal negative electrode with a conducting polymer positive electrode has drawn more attention. In comparison to EDLCs, asymmetric supercapacitors that connect these two electrodes have higher energy and power densities and better cycling stability than pseudocapacitors. In comparison to EDLCs, asymmetric supercapacitors that connect these two electrodes have higher energy and power densities and better cycling stability than pseudocapacitors [24].

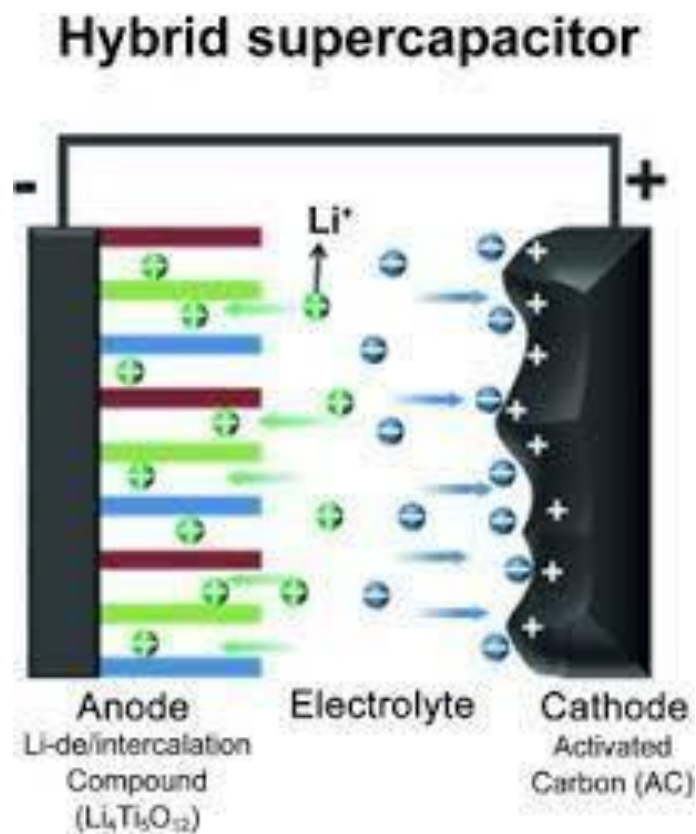


Fig1.5 Pictorial representation of the working of hybrid supercapacitor.

Chapter-2

Literature Survey

In the last two decades, nanoscience has been an exciting area of research as much of application point of view as fundamental research.

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3. Bortamuly, R., Konwar, G., Boruah, P. K., Das, M. R., Mahanta, D., & Saikia, P. (2020). y, two nano-ceria-based composites were developed to use as electrode materials in supercapacitor applications. The composites were synthesized by combining ceria with conductive polyaniline (PANI) and doped with HCl and p-toluene sulfonic acid (PTSA). The materials were characterized by FTIR spectroscopy, SEM, XRD, and XPS techniques. Electrochemical studies were performed by cyclic voltammetry, galvanometric charge-discharge, and AC impedance spectroscopy.
4. Lu, Z., Yang, Q., Zhu, W., Chang, Z., Liu, J., Sun, X., ... Duan, X. (2012). Ternary ordered mesoporous hierarchical Ni–Co–O nanorods/ Co_3O_4 micro sheet/Ni foam supercapacitive electrodes have been constructed using a facile and cost-effective strategy. The unique architecture results in excellent electrochemical performance.
5. Mazloun-Ardakani, M., Sabaghian, F., Yavari, M., Ebady, A., & Sahraie, N. (2019). The $\alpha\text{-Fe}_2\text{O}_3@ \text{CeO}_2$ core-shell heterostructure was used as an advanced material for electrodes in supercapacitors. Due to the close contact between $\alpha\text{-Fe}_2\text{O}_3$ core nanoparticles and CeO_2 shells, the obtained electrochemical results could function in an excellent manner. The core-shell structured $\alpha\text{-Fe}_2\text{O}_3@ \text{CeO}_2$ sample demonstrated lower band gap energy (2.1 eV) in comparison to the pure

- α -Fe₂O₃ (2.23 eV) and CeO₂ (2.85 eV) samples, leading to the perfect electrochemical and capacitance activity, 152949.
6. Jeyaranjan, A., Sakthivel, T. S., Molinari, M., Sayle, D. C., & Seal, S. (2018). To determine the effect of morphology on charge storage capacity, three different morphologies, nanorods, cubes, and particles are synthesized by a one-step hydrothermal process. Electrochemical evaluation through cyclic voltammetry and galvanostatic charge–discharge techniques reveal specific capacitance to be strongly dependent on the nanostructure morphology. The highest specific capacitance in nanorods is 162.47 F g⁻¹.
 7. Cardenas Flechas, L. J., Raba Paéz, A. M., & Rincon Joya, M. (2020). The synthesis of undoped cobalt oxide and cobalt oxide with 4%nickel doping is studied in samples obtained through hydrothermal technique. After the final heat treatment at 300°C, X-ray diffraction analysis indicated the formation of cobalt spinel oxide with a complete replacement of nickel in the lattice. An average crystallite size of ~42 nm and ~31nm was found, as well as a particle size of ~ 20 nm and ~30 nm for Co₃O₄ and Co₃-xNi_xO₄, respectively. The energy band gap was found through UV-Vi's spectroscopy in two different regions. The SEM results indicated the formation of nanostructures with semi-cubic shapes and irregular rods.
 8. Cui, J., Zhang, X., Tong, L., Luo, J., Wang, Y., Zhang, Y. Wu, Y. (2015). Supercapacitors based on the as-prepared mesoporous Co₃O₄ /CeO₂ hybrid NWAs exhibit excellent pseudocapacitive performance with a capacitance of 4.98 F·cm⁻² at 10 mA·cm⁻² (1037.5 F·g⁻¹ at 2.08 A·g⁻¹) and only a small capacitance loss of 5 .6% after 5000 charge/discharge cycles. The remarkable pseudocapacitance and superior stability suggest that the mesoporous Co₃O₄ /CeO₂ hybrid NWAs are promising candidates for supercapacitor applications.
 9. Hu, Y., Shi, T., Ni, J., Jin, H., Zhu, M., Li, Y., & Bai, Q. (2012). Designs and fabricates CeO₂ nanoparticles on a large scale by hydrolysis and oxidation of cerium carbide. The electrochemical supercapacitor behavior of CeO₂ nanoparticles was investigated.
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11. Manibalan, G., Murugadoss, G., Thangamuthu, R., Kumar, M. R., & Kumar, R. M. (2019). CeO₂-SnO₂ nanocomposites were synthesized by a simple chemical precipitation method. HR-TEM results revealed the formation of nanocomposite in a spherical shape with less than 10 nm size and highly homogeneous. X-ray photoelectron spectroscopy confirmed the chemical composition and different ionization states of Ce3p/ Ce4p, Sn4p, and O1s. Functional groups of nanocomposites were identified using FT-IR spectroscopy. FT-RAMAN spectra were used to identify the Raman shift, which supported the formation of the nanocomposite. Thermal stability and phase changes of CeO₂-SnO₂ nanocomposite were characterized by TG and DTA. The paramagnetic property of the nanocomposite at room temperature was studied by the EPR technique.
12. Padmanathan, N., & Selladurai, S. (2014). hydrothermally synthesized CeO₂ of two different shapes with large exposed surfaces and porous microstructures. Based on its shape and porous nature the CeO₂ can be used as an electrode for supercapacitors. As the supercapacitor electrode, the CeO₂ nano hexagons and CeO₂/C nanorods exhibited a maximum specific capacitance of 381 F/g and 400 F g⁻¹ respectively at the constant current density of 20 A/g. These CeO₂ nanostructures have shown excellent rate capability and long-term stability as well.
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Chapter – 3

Aim and Scope

- Cerium-based metal oxides are attracted much due to their Astonishing application in supercapacitors.
- CeO_2 and $\text{CeO}_2/\text{Co}_3\text{O}_4$ nanocomposites are prepared and studied based on crystal size, morphology, and structural constitution.
- Heterostructures of CeO_2 and $\text{CeO}_2/\text{Co}_3\text{O}_4$ nanocomposite materials will be synthesized using a facile hydrothermal route.
- Studies on the structural property and Crystallite size are characterized using X-ray Diffraction [XRD].
- Studies on particle size, morphology and structure are characterized using Scanning Electron Microscope [SEM], and High-Resolution Transmission Electron Microscope [HR-TEM].
- Studies on chemical composition and oxidation state are characterized using X-ray Photoelectron Spectroscopy [XPS].
- Electrochemical characterization are carried out using Cyclic Voltametric studies [cv] and, Galvanostatic Charge-discharge test [GCD].

CHAPTER – 4

Chapter - 4 deals with the details of the synthesis and characterization techniques used for the prepared metal oxide nanomaterials targeted in this project. The facile hydrothermal method have been used for the synthesis of various nanomaterials explored in this project. The synthesized nanomaterials were examined by a variety of techniques in terms of the morphological, structural, compositional, and electrical properties Moreover, the prepared nanomaterials were used for various applications such as Supercapacitor applications. In a word, this chapter provides all the detailed procedures for the synthesis, characterizations, and applications of targeted nanomaterials in this project.

Chapter – 4

MATERIALS AND METHOD

4.1 INTRODUCTION

In this work, CeO₂ nanomaterials and CeO₂/Co₃O₄ nanocomposites are prepared via a hydrothermal route. The synthesized CeO₂ and CeO₂/Co₃O₄ nanomaterials were extensively characterized in terms of their morphological, structure, and electrochemical properties. To examine the structural properties, the prepared nanomaterials and nanocomposite materials were characterized by an XRD pattern. Studies on particle size, morphology, and structure were characterized by using Scanning Electron Microscope [SEM], and High-Resolution Transmission Electron Microscope [HR-TEM]. The chemical composition and oxidation states of prepared nanomaterials were investigated by XPS. The Electrochemical studies were characterized by Cyclic Voltametric studies [CV], Galvanostatic Charge-discharge test [GCD]. Finally, the synthesized nanomaterials were used for supercapacitor applications.

4.2 SYNTHESIS TECHNIQUES OF NANOPARTICLES

Research in nanotechnology has recently been devoted to developing several steadfast ways to synthesize nanoparticles by controlling their sizes, shapes, and chemical compositions. Primarily the nanoparticle synthesized methods are classified into two approaches, they are, top-down and bottom-up approaches. Here Figure 4.1 shows the top-down and bottom –up approaches [27].

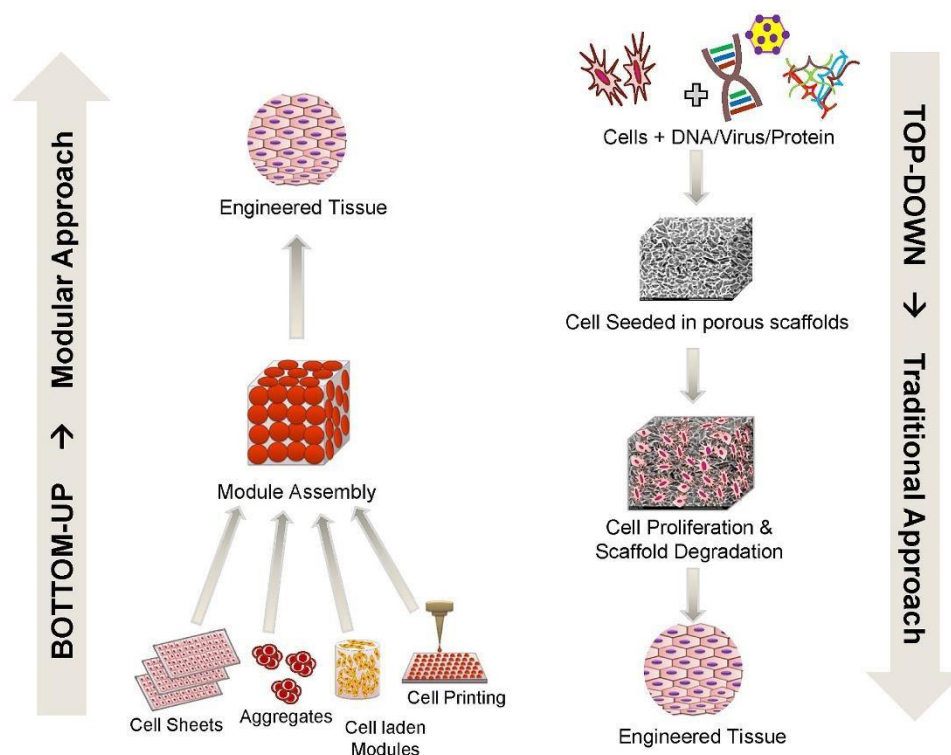


Fig 4.1: Top-Down and Bottom-up Approaches

A) TOP-DOWN APPROACH

In the top-down approach, bulk particles are broken up into smaller and smaller particles through processes such as milling, crushing, etc. Nanoparticles are formed as a result of these processes. Though this approach has a negative impact on the surface structure due to crystallographic injury during the nanostructure formation.

B) BOTTOM-UP APPROACH

The bottom-up approach includes chemical and biological processes such as sol-gel, laser pyrolysis, plasma spraying process, aerosol-based process, green synthesis method, and so on. where the formation of nanoparticles begins at the basic atomic or molecular levels, i.e., the nanostructures are formed by the addition of atom to atom, molecule to molecule, or cluster to cluster method. The bottom-up strategy is far superior to the top-down approach for producing nanostructured materials with

homogeneous structures and distributions. Various techniques that are used to synthesize nanomaterials are shown in Fig.4.2 [28]

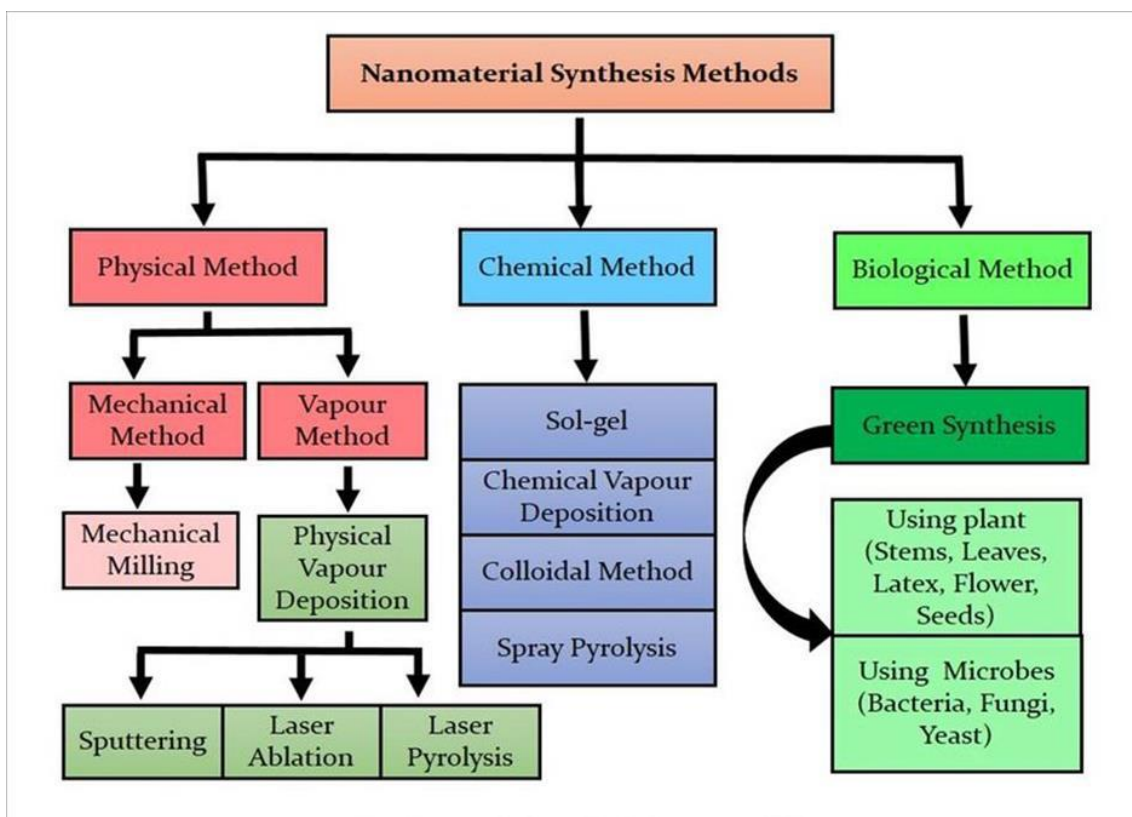


Fig 4.2: Synthesis techniques of nanoparticles

4.2.1 Sol-Gel Technique

Sol-gel is a chemical technique, it is displayed in Fig.4.3 [29]. That uses gelation, precipitation, and calcination to create nanoparticles. In general, the gel is made up of stabilized sols, which are frequently colloidal aggregates of tiny metal oxy- hydroxy particles in an aqueous solvent. However, in the presence of some capping agents, this aggregation can be broken apart. Controlled hydrolysis and condensation play a pivotal role during system gelation. The relative rates of hydrolysis and condensation are affected by physical and chemical factors such as temperature, pH, metal ion precursor solution concentration, and so on. The change in pH value has a significant impact on the surface properties of the synthesized material, which arise owing to changes in gel porosity. Metal alkoxides are used as precursors in an organic solvent, as customary in the creation of nanostructures. In addition to alkoxide, chelate

can be used as a precursor capable of stabilizing metal cations. Chelating is most useful in the manufacture of multicomponent gels [28].

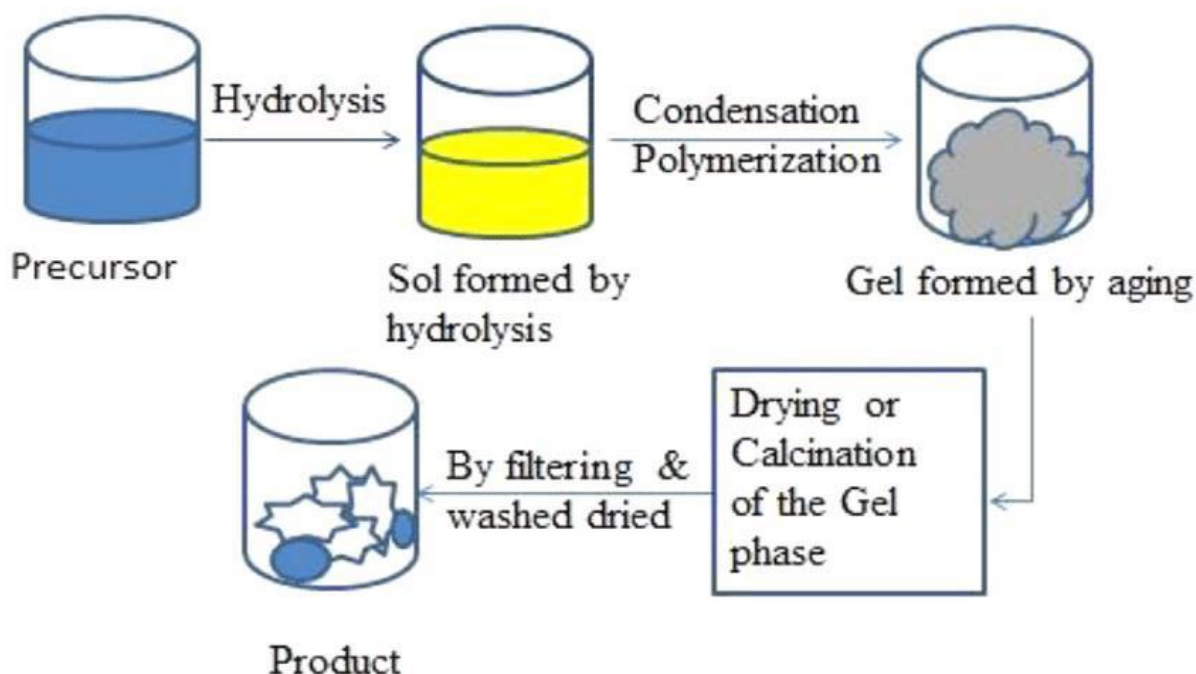


Fig 4.3. shows Sol-Gel Technique

4.2.2 Hydrothermal Synthesis

The hydrothermal technique is one of the common place methods for the synthesis of chemical reactions at a sealed autoclave reactor having an aqueous solvent or mineralizer below high strain and high temperature [30]. It is a solution-based reaction approach [31]. Advantages of the hydrothermal synthesis method include the ability to synthesize crystals of substances that are unstable near the melting point, and the ability to synthesize large crystals of high quality. A disadvantage is the high cost of the equipment and the inability to monitor crystal growth [32]. Morphological, structural, and optical properties of the synthesized products were examined. Lastly, the prepared nanomaterials can be used for wide range of applications like photovoltaic, photocatalytic, sensing applications. The outline of the autoclave reactor is shown in Fig 4.4 [33].

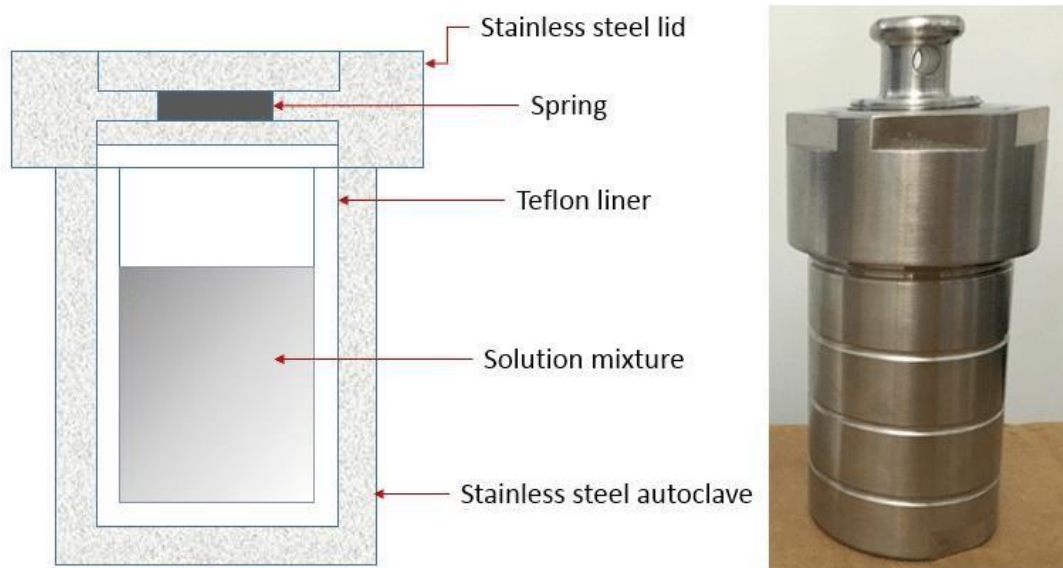


Fig.4.4: shows the structure of the hydrothermal reactor

4.3 MATERIALS

All chemicals were purchased in analytical grade and used without further purification. $\text{Ce}(\text{NO}_3)_3$ and $\text{Co}(\text{NO}_3)_3$ were purchased from Sigma Aldrich. Sodium hydroxide (NaOH), and polyvinylpyrrolidone (PVP) were obtained from Nice Chemical Company and were used as precursors. Ethanol and acetone were purchased from Sisco Research Laboratories Pvt. Ltd. (SRL). All the glassware used in this work was acid washed. Ultrapure water was used for dilution and sample preparation.

4.4 EXPERIMENTAL PROCEDURE

CeO_2 and $\text{CeO}_2/\text{Co}_3\text{O}_4$ composite were synthesized by a facile hydrothermal route.

4.4.1 Synthesis of CeO_2

Cerium oxide nanoparticles were synthesized by a facile hydrothermal route. As displayed Fig.4.5. Cerium Nitrate ($\text{Ce}(\text{NO}_3)_3$) in (50ml) of D.I. water was used as precursors for Ce and to reduce agglomeration 2 g of polyvinylpyrrolidone (PVP) is added to above solution. The reaction was stirred for 10 minutes. Later, 3 g of Sodium

hydroxide (NaOH) was thoroughly dissolved in 50 ml of D.I. water and added to the above solution. After that, the reaction was stirred for 2 hours. The resultant product was washed thoroughly with deionized water for removal of reaction residues followed by washing acetone. The prepared nanoparticles were formed and dried in an air oven for 12 hours 120⁰ C. Finally the prepared cerium oxide was grinded and packed.

4.4.2 Synthesis of CeO₂/Co₃O₄

In order to prepare CeO₂/Co₃O₄ nanocomposite. As displayed in Fig. 4.6. Cerium Nitrate (Ce(NO₃)) in (50ml) of D.I. water was used as precursors and to reduce agglomeration add 2g of polyvinylpyrrolidone (PVP) was added to the above solution. The reaction was stirred for 10 minutes. After that 5g of Cobalt nitrate (Co(NO₃)) was added to the above solution and allowed to stirrer for 5 minutes. Later, 3g of Sodium hydroxide (NaOH) was thoroughly dissolved in 50 ml of D.I. water and added to the above solution. After which, the reaction was stirred for 2 hours. The resultant product was washed thoroughly with deionized water for removal of reaction residues followed by washing of product with acetone. Later, the nanoparticles were formed and dried in an air oven for 12 hours at 120⁰ C. Finally the prepared sample was grinded and packed.

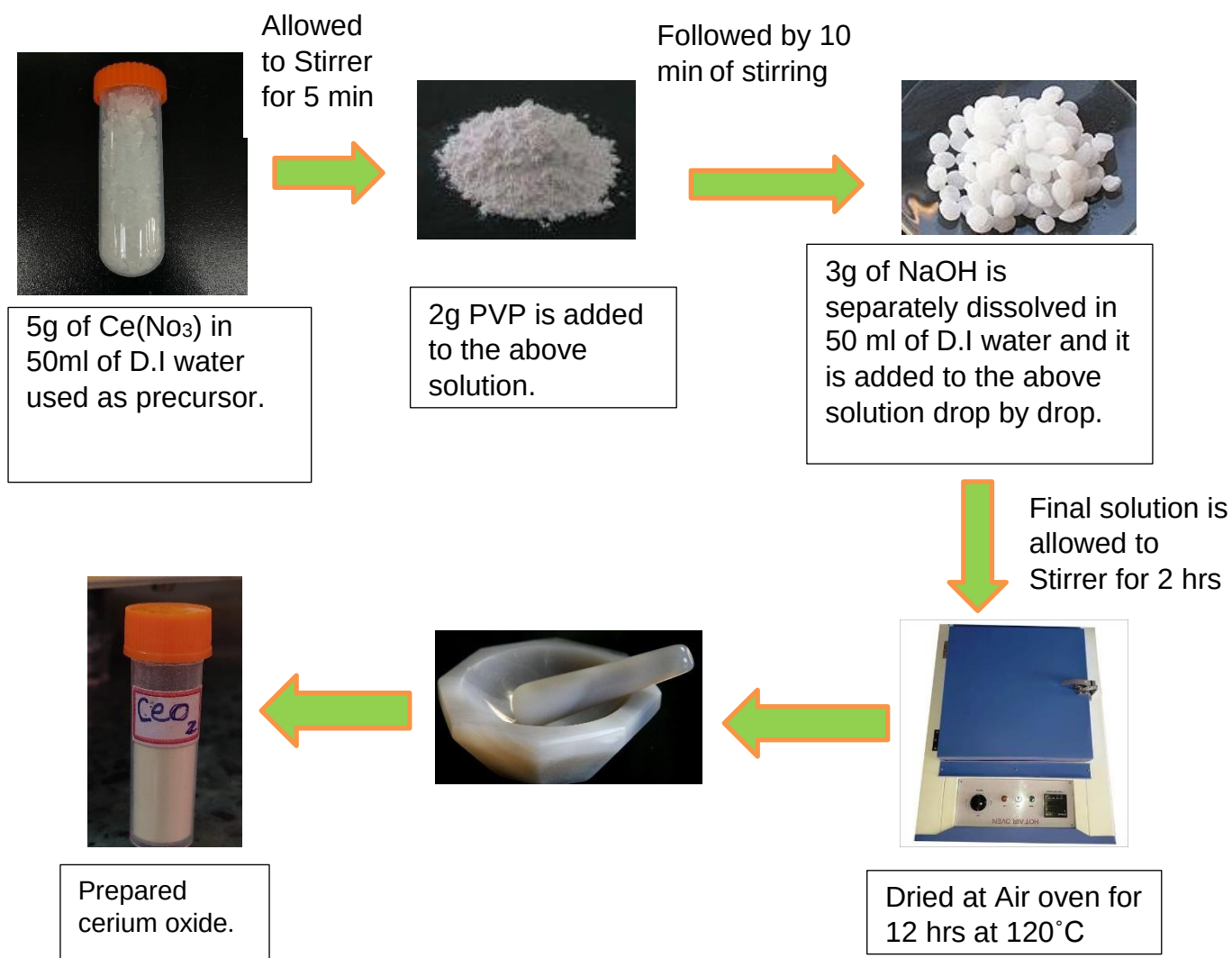


Fig: 4.5 shows the synthesis process of cerium oxide.

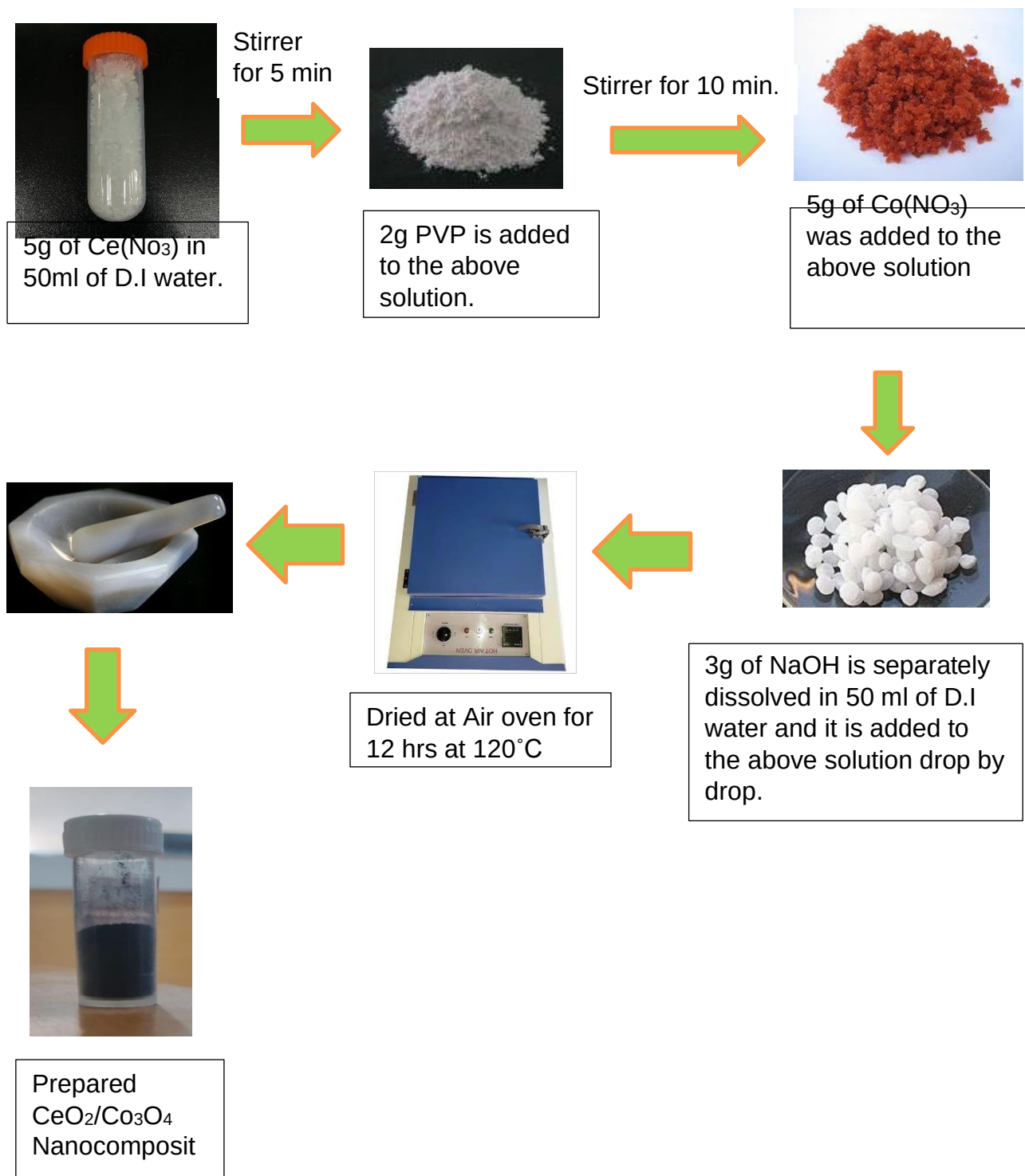


Fig: 4.6 shows the synthesis process of $\text{CeO}_2/\text{Co}_3\text{O}_4$ Nanocomposite

4.5 FABRICATION OF ELECTRODE

The electrochemical behaviour of the prepared samples was carried out using SP-300 electrochemical workstation in three cell electrode system. The electrochemical performances were exhibited using cyclic voltammetry (CV), Galvanostatic Charging Discharging (GCD) and Electrochemical Impedance Spectroscopy (EIS) analysis with 3 M KOH electrolyte. The prepared SiO₂ nanocomposites were used as active materials for working electrode. Platinum wires and saturated calomel electrode (SCE) were taken as a counter and reference electrode respectively and a desired concentration of the sample was mixed with polyvinylidene fluoride (PVDF) which used as a binder and carbon black (super P) which used as conducting materials in 80:10:10 weight percentage, respectively. The electrode fabrication method has followed two steps: In the first step, a piece of Nickel Foam (NF) was immersed into diluted HCL solution for 10 mins after that, it was cleaned with deionized (DI) water and then the foam was sonicated using ethanol solution for 5 min to remove the outer layer of NiO from the NF surface. Subsequently, the cleaned NF was dried in an oven at 60 °C and then measured the weight of the bare NF. The next step was to make a slurry, an N-methyl-2-pyrrolidone (NMP) was used as a solvent for the above mixer and grinded well and coated on NF. Next, the coated NF was dried at 100 °C for 4 h to the solvent present on the surface of coated NF. Then the modified electrode was again weighed to measure the weight difference between the empty NF and coated NF. The calculated mass loading of the catalyst was 2 mg. The specific capacitance for the prepared electrode was calculated by the following formula.

$$C_s = \frac{I \Delta t}{m \Delta v}$$

Where C_s represents the specific capacitance (F/g). I denote the current density (A g⁻¹), Δt is the discharge time (s), Δv represents the potential window (V) and m denotes the mass (g) of the active materials. Finally, the specific capacitance of the modified electrode was determined using CV and GCD data from the electrochemical workstation [34]. The electrode preparation was depicted in Fig.4.6 [35]

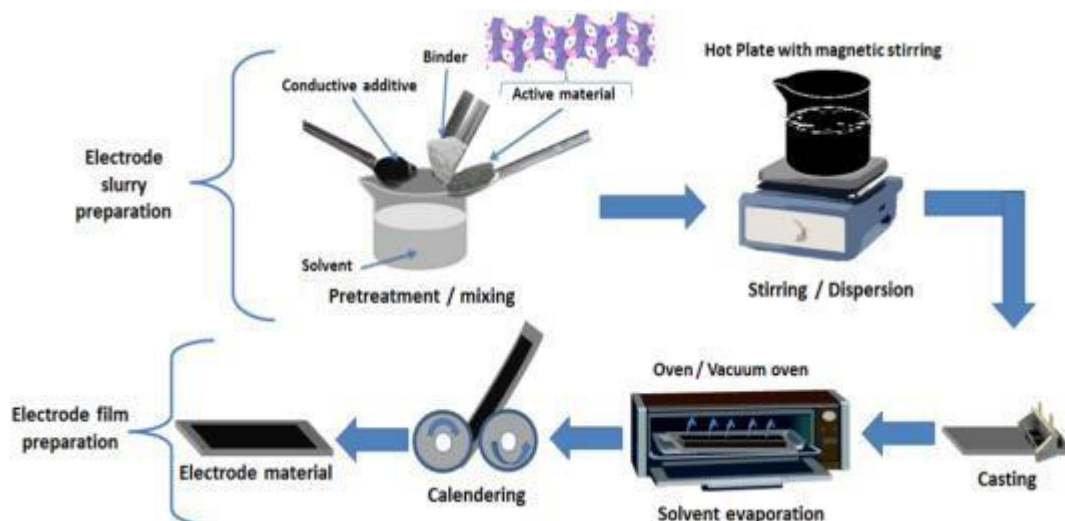


Fig: 4.7 displays the electrode preparation

4.6 CHARACTERIZATION OF PREPARED METAL OXIDE NANOMATERIALS

The prepared metal oxide nanomaterials presented in this project were characterized in detail in terms of their size, structural, morphological, and compositional properties. The structural properties were examined by XRD. A scanning Electron Microscope and High- Resolution Transmission Electron Microscope were used to identify the images with sufficient quality of nanoparticle size. XPS was used to look into the chemical composition and oxidation states of produced nanomaterials. Galvanostatic Charge-discharge Tests (GCD) and Cyclic Voltammetric research (CV) were used to characterize the electrochemical properties.

4.6.1 X-Ray Diffraction

The atomic planes of a crystal cause X-rays from an incident beam to interfere with one another as they leave. The phenomenon is called X-ray diffraction. In order to determine the crystal structure of a material, X-ray diffraction is used. The XRD pattern obtained from a crystal sample depends on the shapes and sizes of the basic unit cells of the crystal [36-40]. A crystal lattice is a three-dimensional arrangement of atoms arranged in a parallel plane separated by a distance (d). It is very important to determine the structure of a material after its synthesis. In order to determine the crystal structure of a material, XRD is the most commonly used technique because a material's properties are greatly influenced by its crystal structure. In the solid specimens, the standard database (JCPDS database) is used to identify the variety of crystalline phases. It can simultaneously characterize both the precursor and end products with a detailed nanoparticle behavior, it is one of the advantages of X-ray diffraction [41]. X-ray diffraction is used to determine the crystallinity and phase purity of inorganic materials. X-ray diffraction works based on Bragg's law. In XRD diffraction occurs only when Bragg's law is satisfied condition for constructive interference from planes with spacing d [42].

$$n\lambda = 2d \sin \theta$$

Where d indicates the distance between the variable and the atomic layers. The variable λ specifies the incident x-ray beam's wavelength and n as an integer, known as, the path difference, and order of the reflection in terms of wavelength, between waves scattered by adjacent planes of atoms [43]. A monochromatic beam of X-ray is allowed to the incident on a sample, and the detector detects the reflected X-rays [44]. Fig.4.8 shows the working principle of XRD [45]. The crystalline structure of the synthesized material was evaluated by using Debey – Scherrer equation

$$D = K\lambda / \beta \cos\theta$$

Where D represents the average crystalline size, λ indicates the wavelength of the incident ray and, β is the Full Width Half Maximum (FWHM) of the peak. K is the coefficient of the particle shape, θ is the angle of the diffraction peak.

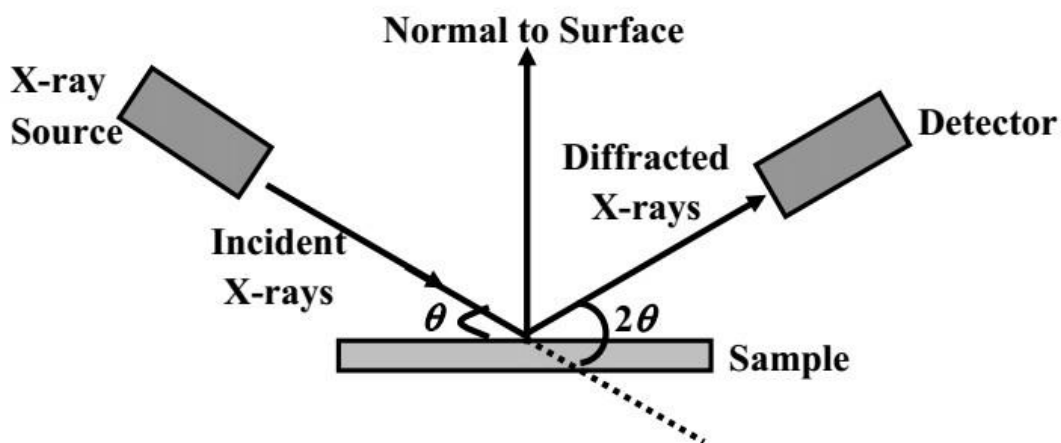


Fig 4.8 Working of XRD

4.6.2 Scanning Electron Microscope

A scanning electron microscope (SEM) is a type of electron microscope. By scanning the surface of a sample with a focused beam of electrons, it produces images. In the sample, the electrons interact with atoms and produce various signals which generate information about the morphology and composition of the sample. Scanning electron microscope is one of the most widely used instrumental methods for the examination and analysis of micro and nanoparticle imaging characterization of solid objects due to its resolution of 10 nm, that is, 100 Å. For the purpose of determining the composition or orientation of certain crystals or features, this device may also be used in conjunction with other related energy-dispersive X-ray microanalysis techniques. A high depth of field in SEM micrographs produces a distinctive three-dimensional look that is helpful for comprehending the surface structure of a sample. To fit on the specimen stage, SEM samples must be small enough. They may also require additional processing to enhance their electrical conductivity and stabilize them so they can endure the high vacuum conditions and the high energy electron beam.

The basic principle is, a source, typically a tungsten filament or field emission gun generates electron beams which is displayed in Fig 4.9 [46]. One or two condenser lenses were focused on the electron beam which has an energy range from 0.2 keV to 40 keV and it is accelerated through a high voltage. Then the surface of the specimen is scanned by the beam. From the specimen, electrons are ejected by the action of the scanning beam and collected by a suitably positioned detector. In the electron column, the beam passes through the pairs of scanning coils or pairs of deflector plates. The electron loses its energy when the primary electron beam interacts with the sample. By elastic scattering, the energy exchange beam and the sample result in the reflection of high-energy electrons. The specimen can also be detected and used to create images of the distribution of specimen current which is absorbed by the beam current. The advantages of SEM are, it gives detailed 3d and topographical imaging and versatile information and works very fast. Most SEM samples require minimal preparation actions [47].

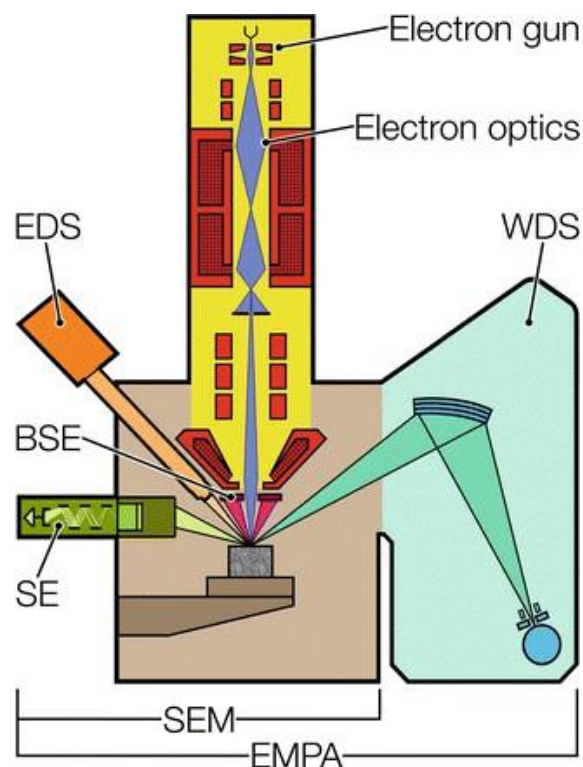


Fig.4.9. shows the SEM image and the working mechanism of the SEM

4.6.3 High-Resolution Transmission Electron Microscope (HRTEM)

High-Resolution Transmission Electron Microscope is a specialized transmission electron microscope. It allows direct imaging of the sample's atomic structure. It is a powerful tool to study the properties of materials on the atomic scale, such as metals, nanoparticles, semiconductors, and sp^2 -bonded carbon. It is also used to refer to scanning transmission electron microscopy in high resolution and phase contrast transmission electron microscopy. By using this HRTEM a clear crystallographic structure of samples can be obtained in atomic scale range. Tungsten electron guns are mostly used in HRTEM. The accelerating voltage range of the HRTEM is higher than the scanning electron microscope. To obtain an increment in image resolution the high voltages are utilized. The setup of HRTEM is given in Fig.4.10 [48]

The basic principle of HRTEM is, electromagnetic fields deflect the beam of electrons which is similar to the deflection of light by glass lenses. The electron beam was focused by the condenser lens on a section, in this section many of the electrons interact with the atoms and follow their path, others merely transverse the specimen without interacting. The objective lens received many electrons resulting in forming an enhanced image which is then projected through another magnifying lens. Usually, the image which is obtained by the HRTEM were in black and white, because of the adjustment between the electrons that knock the electron and the fluorescent screen which are confined in the tube of the microscope. The micrograph is composed of the electron lucent and electron dense which is called light and dark areas respectively. The sample is located between the objective lens and the pole pieces and its thickness must be less than a few hundred nanometres. The projector lens system and objective lens achieved 10^6 or higher magnification. We obtain the TEM- transmission electron microscope images with energy dispersive spectra and their corresponding area electron diffraction pattern [49].

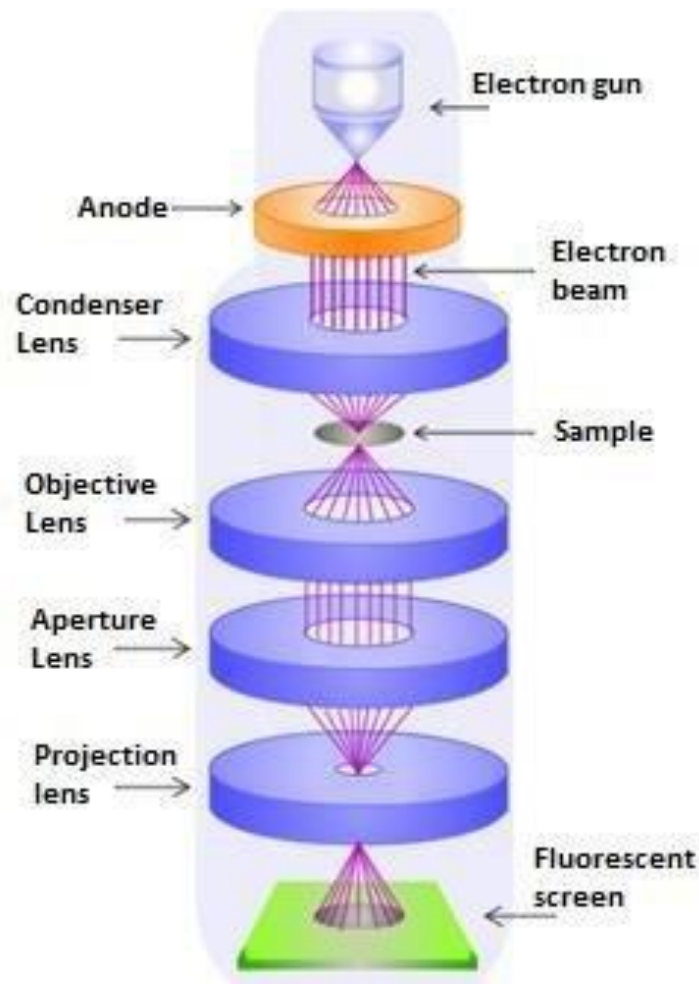


Fig.4.10 shows the working mechanism of TEM

(a) Selected Area Electron Diffraction (SAED)

Inside a TEM instrument selected area electron diffraction operates as a diffraction technique, it helps to give details of crystal defect and structure in the sample. It is also called a crystallographic experimental technique. Due to its area, it stands in unique ie) with very few hundred nanometers in size to be examined. But in XRD, the sample is examined in an area of several centimeters in size.

Based on the diffraction produced by the electrons scattered by the lattice, the sample of the phase and the crystal structure are understandable. It is simple to determine whether something is a single crystal, amorphous, or polycrystalline once it has been operated in a diffraction pattern. Each atom in the Selected Area Electron Diffraction pattern is dependent on the planes of the lattice of a certain miller index inside a single crystal. All chances are that the atom will be revealed by the Selected Area Electron Diffraction pattern. Each ring in the Selected Area Electron Diffraction

matches with a particular group of lattice planes if the sample is essentially polycrystalline.

(b) Energy Dispersive X-Ray Analysis (EDX)

The sample's elemental composition has been looked into using EDX. It is used in conjunction with TEM and SEM to examine the sample's surface. Some of the sample electrons are impacted when the bombardment electrons make contact with them. By changing electrons on the sample, which produces an X-Ray, it is possible to analyse the elemental makeup and examine the properties of the material.

It gives information about the elementary composition of each separate point or plots the lateral circulation of elements from the image of the area. Depending upon the X-Rays received EDX spectrum relates to the energy levels of the majority of X-Rays captured. The obtained original peak to an atom is constant with a single element. In the EDX spectrum, the intensity peak is directly proportional to the chemical composition of the specimen, if the peak is higher in the spectrum the concentration will be more [50]. The working mechanism of EDAX shown in Fig.4.11 [51].

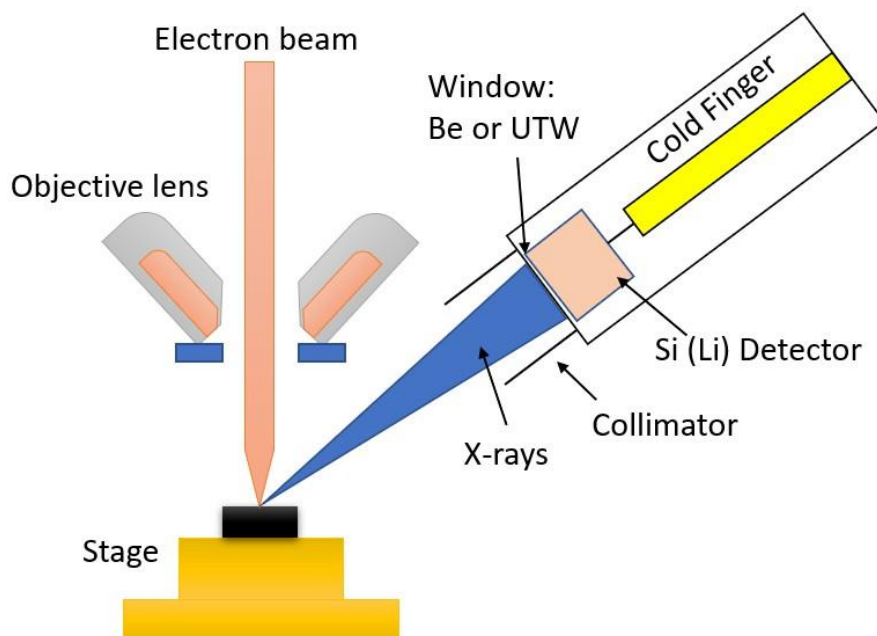


Fig.4.11 shows the working mechanism of EDAX

4.6.4 X-Ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy is a frequently used technique in the areas of chemistry, material science, and, chemical engineering in examining surface chemistry, bonding structure composition of surfaces, and interfaces. The effect of chemical shift is the backbone of the XPS technique, which refers to the changes in estimated binding energies of core-level electrons due to the response of an atom to the chemical environment. The monochromatic X-Ray sample is exposed to radiation as a result of photoelectron emission, with the elements inside the sample volume analyzing the photoelectrons' energies.

The binding energy is displayed against the number of electrons in the XPS graph. The electrons released by the specimen are measured in the 1-10 nm range. The electrons on the upper surface of the material will break when the X-Ray beam is irradiated from the sample. Based on the work function and binding energy, the material can be predicted. The comparative kinetic energy of the released electrons from the material will be noted utilizing an energy electron diagnosis, resulting in the modified XPS data.

Every element has its own unique binding energy values that are associated with each atomic core orbital, and each element has its own unique photoelectron spectrum peaks that coincide with the kinetic energy solved by the energy of the photon and their associated binding energies. The appearance of peaks at the correct energies confirms the presence of a specific substance in the sample. The specimen's absorption was connected to the peak intensity; quantitative surface composition analysis is also possible. Double tape is used to absorb the powdered samples into a steal holder. The electron cannon reduces the charge's property [52]. Fig.4.12 shows the working mechanism of XPS [53]

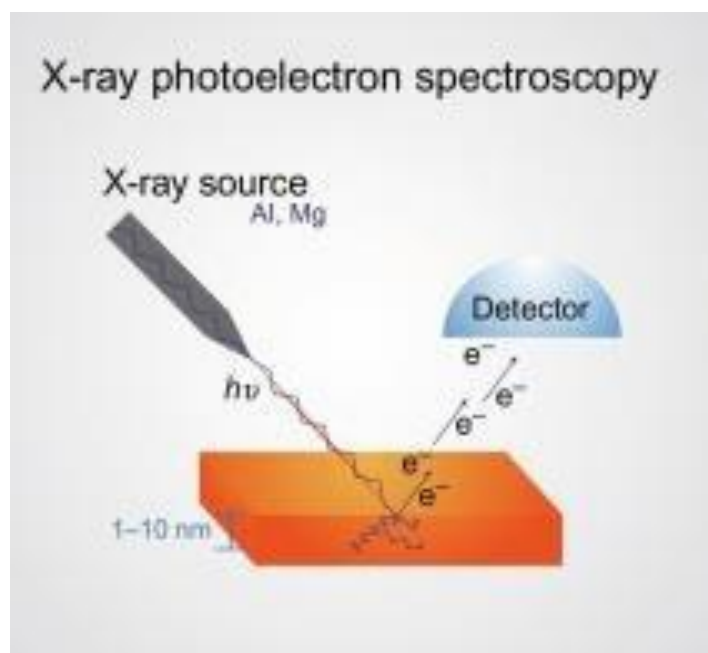


Fig 4.12 shows the working mechanism of XPS

4.6.5 Electrochemical characterization

Electrochemical studies are used to test the electrochemical performance of electrode materials and gain insightful information about electrode performance. In a 3-electrode system, any electrode material can be tested as the active electrode. This is very common for half-cell testing. A three-electrode system consists of three main components, which are as follows,

- A working electrode
- A counter electrode
- A Reference electrode

The reference electrode potential is held stable over a narrow potential range to report the potential of the working electrode. Platinum is also commonly used as the counter electrode. It plays an important role in conducting current through the working electrode and prevents the reference electrode from conducting current. This changes the potential of the reference electrode. Much better practical performance with

respect to the active materials is observed in the (full-cell) two-electrode system compared to the half-cell. This works just like a practical supercapacitor containing a positive and negative electrode. The electrodes are assembled with active materials in a full-cell system. In general, one electrode is suitable for practical two-electrode cell capacitors, but to examine the materials, consider the results shown by the three-electrode system.

Some of the well-known electrochemical techniques are described here to study the electrochemical performance of supercapacitor electrode materials.

A) Cyclic Voltammetry (CV)

This is done to qualitatively study the electrochemical reactions of electrode materials. It can be seen that the potential applied to the working electrode decreases linearly with time from the open circuit potential to the set potential. The potential then bounces back to the alternative collective potential in a similar fashion. Both sample rate and cycle are controlled in this analysis. A protocol for evaluating the electrochemical properties of electrode materials is to maintain the redox potential without exceeding the potential window of CV.

Among other things, this technique proposes a rapid spotting of the redox potential of the corresponding electroactive materials, together providing a practical analysis of the media during redox processes. Here, solution elements are electrolyzed (oxidized or reduced) by contact with the corresponding electrode surfaces. In addition, the surface is appropriately biased positively or negatively to force electron transfer. When the electrode surface is initiated by a specific voltage in relation to the reference half cell, such as calomel or Ag/AgCl, then the electrode voltage is modified to a higher (or) lower voltage at a specific rate before it is brought to the earliest voltage at the same narrow rate. The electrode circuit observes a significant amount of current, when the surface of the electrode reaches adequately positive or negative this evokes the solution species to acquire the electrons from the surface (or) to return the electrons to the surface. The cyclic voltammetry results are expressed as a curve in a graphical term.

Moreover, the charging current does not appear to be voltage-dependent. This changes the sign of the associated current if the applied potential is negative. However, in resistive systems, we observe that the current is potentially dependent. The slope graph shows an increasing slope when the resistance of the system is determined to be maximum. This changes the shape from a rectangle to a parallelogram. For Faraday systems, the CV results show deviations from the rectangle due to redox peaks, confirming the presence of redox species in the system.

B) Galvanostatic Charge- discharge analysis (GCD)

Galvanostatic charge-discharge analysis is the most proven method for determining the specific capacity/capacity of active materials. During analysis, the value of the relevant current flow in the cell is changed instantly from zero to some finite value. The charging and discharging process of the working electrode takes place over a set voltage range and is recorded over time. Meanwhile, positive and negative constant currents flow across the working electrode. If the working electrode exhibits ideal capacitive behavior, the GCD is expected to exhibit a triangular charge- discharge curve. In this work, GCD analysis is performed at different current densities.

C) Electrochemical Impedance Spectroscopy (EIS)

The impedance of an electrochemical system can be determined by EIS. In an electrochemical system, by applying an alternating potential of varying frequencies, we study its contribution to an associated current signal that functions as a function of sinusoidal frequency. Impedance, which is the result of dividing potential by current, is considered a complex number. Electrochemical impedance is analyzed using a Nyquist plot with the real part on the x-axis and the imaginary part on the y-axis. at this job. Electrochemical impedance is performed from 0.01 Hz to 100 kHz with an amplitude of 5 Mv [54].

CHAPTER- 5

RESULT AND DISCUSSION

Chapter 5 describes the main results and discussion of the project. This chapter is divided into several sections and each section describes the synthesis, detailed characterizations, and particular application of metal oxide nanomaterial.

Section 5.1 describes X-Ray diffraction of the CeO_2 and Co_3O_4 crystalline structure, characterization, and applications of nanoparticles grown via facile and Hydrothermal methods using commonly used laboratory chemicals.

Section 5.2 demonstrates the FESEM images and their characterization based on CeO_2 and $\text{CeO}_2/\text{Co}_3\text{O}_4$ nanomaterials.

Section 5.3. Demonstrates the characterization of HRTEM for $\text{CeO}_2/\text{Co}_3\text{O}_4$ nanocomposite in this chapter.

Section 5.4 exemplifies the X-ray photoelectron spectroscopy activity of the $\text{CeO}_2/\text{Co}_3\text{O}_4$ nanocomposite.

Section 5.5 shows the Electrochemical characterizations of CeO_2 and $\text{CeO}_2/\text{Co}_3\text{O}_4$ nanocomposite.

CHAPTER- 5

RESULT AND DISCUSSION

In this project, we have done an investigation on CeO_2 and $\text{CeO}_2/\text{Co}_3\text{O}_4$ nanocomposite using the facile hydrothermal method and observed a crystallite structure and surface morphology of our synthesized samples using X-Ray diffraction, FE-SEM, HR-TEM, XPS followed by that Electrochemical characterization are carried out for supercapacitor application. Fig 5.1 displays the image of prepared sample of CeO_2 as black in pale yellow color which confirms the formation of CeO_2 and Fig 5.2 represents the image of $\text{CeO}_2/\text{Co}_3\text{O}_4$ nanocomposite which is black in color which confirms the formation of $\text{CeO}_2/\text{Co}_3\text{O}_4$ nanocomposite.

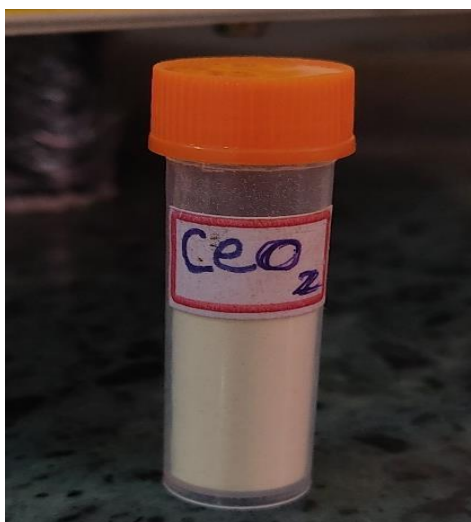


Fig 5.1: prepared CeO_2 nanoparticle



Fig.5.2. $\text{CeO}_2/\text{Co}_3\text{O}_4$ nanocomposite.

5.1 X-Ray Diffraction:

The XRD pattern of hydrothermally synthesized CeO_2 is depicted in Fig.1. All the diffracted peaks of the XRD patterns are precisely indexed to the face-centered cubic CeO_2 phase [55]. The peaks Fig.5.3 indexed at $2\theta = 28.8, 33.07, 47.71, 56.36, 77.0$ corresponds to (1 1 1) (2 0 0) (2 2 0) (3 1 1) and (3 3 1) planes of CeO_2 [56, 57]. And the diffracted peaks of the XRD patterns are in accord with the JCPDS card number (81-0792) [56, 58]. Fig.5.3 carried out the XRD pattern of as-prepared $\text{CeO}_2 / \text{Co}_3\text{O}_4$ nanocomposite. The XRD pattern apparently shows that all diffraction peaks fit a polycrystalline phase of Co_3O_4 which exactly matches with the JCPDS card No.42-1467. [59]. The following XRD pattern indexed at $19.30^\circ, 38.46^\circ$, and 44.88° corresponds to the (1 1 1), (3 1 1), and (4 0 0) planes of nanostructured face center cubic type Co_3O_4 [60]. The obtained diffraction peaks of both samples are involved to calculate the crystal size using the Debye – Scherrer [61] using equation (1) and the average crystal size is found to be a 19 nm for CeO_2 and 21 nm for $\text{CeO}_2 / \text{Co}_3\text{O}_4$ nanocomposite.

$$\tau_c = \frac{K\lambda}{\Delta 2\theta} \quad \text{----- (1)}$$

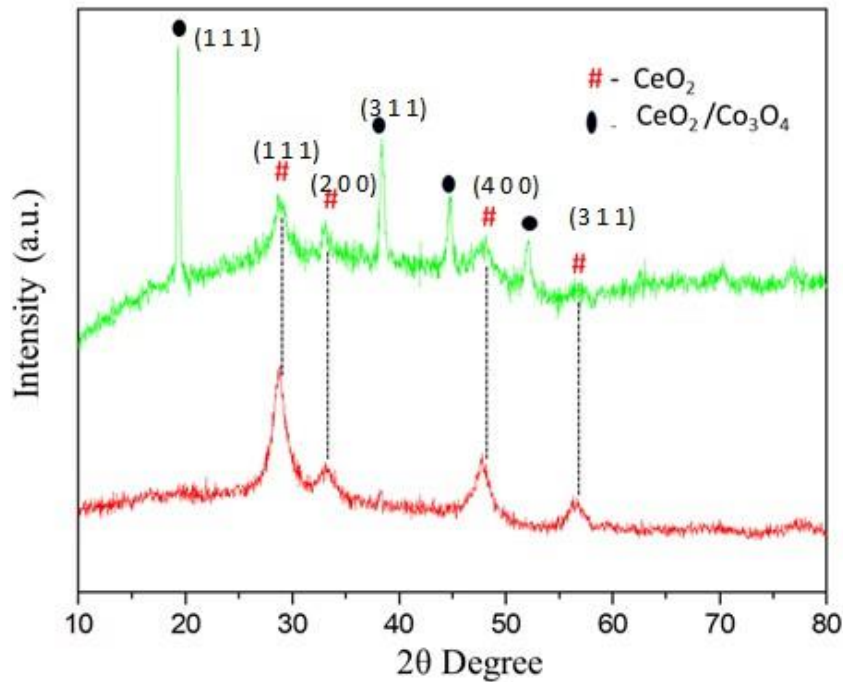


Fig.5.3: Shows the XRD pattern of CeO_2 and $\text{CeO}_2 / \text{Co}_3\text{O}_4$

5.2 Field Emission Scanning Electron Microscope:

Fig.5.4 (a-d) displays the FE-SEM images of CeO_2 prepared by the facile hydrothermal method, as seen in the figure, CeO_2 displays a nano sheet-like structure which is highly interconnected with one another, small particles of CeO_2 combine with one another and results in forming a sheet-like morphology. which aids in the pathway for fast ion insertion and redox reactions. Its corresponding Elemental mapping spectrum in Fig.5.5 clearly shows the presence of Cerium and oxygen. Fig.5.6 (a-d) displays the FE-SEM images of the $\text{CeO}_2 / \text{Co}_3\text{O}_4$ nanocomposite. As shown in the image the nanocomposite material displays a Heterostructure combination of sheet and sphere-like nanoparticle structure. The presence of Sphere like structure on the sheet confirms the formation of Co_3O_4 in CeO_2 as nanocomposite Fig.5.7 Displays the Elemental mapping of $\text{CeO}_2 / \text{Co}_3\text{O}_4$ nanocomposite, which confirms the presence of Ce, O and Co in the prepared sample.

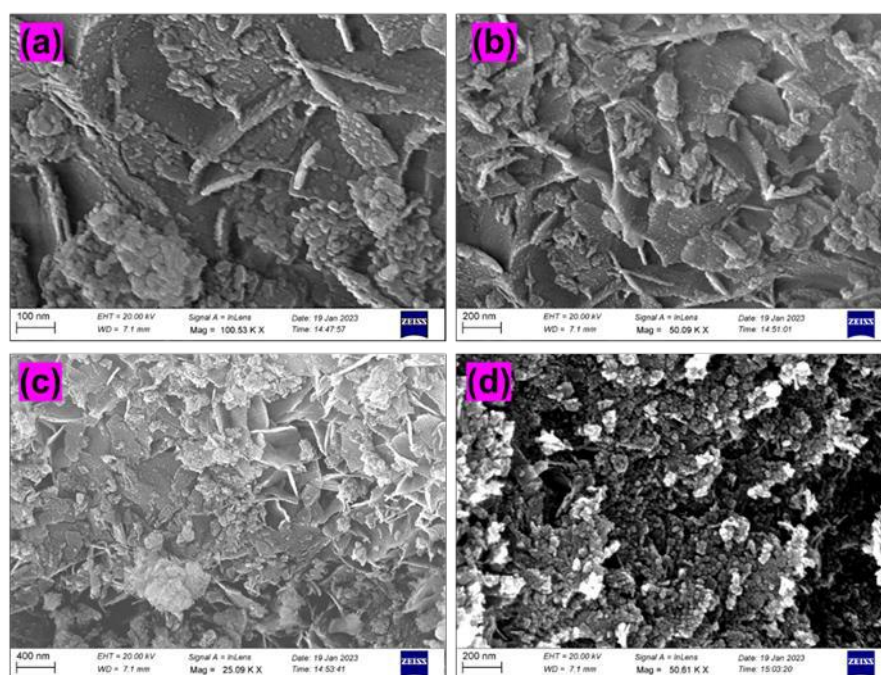


Fig.5.4 (a-d) displays FESEM images of CeO_2 sample.

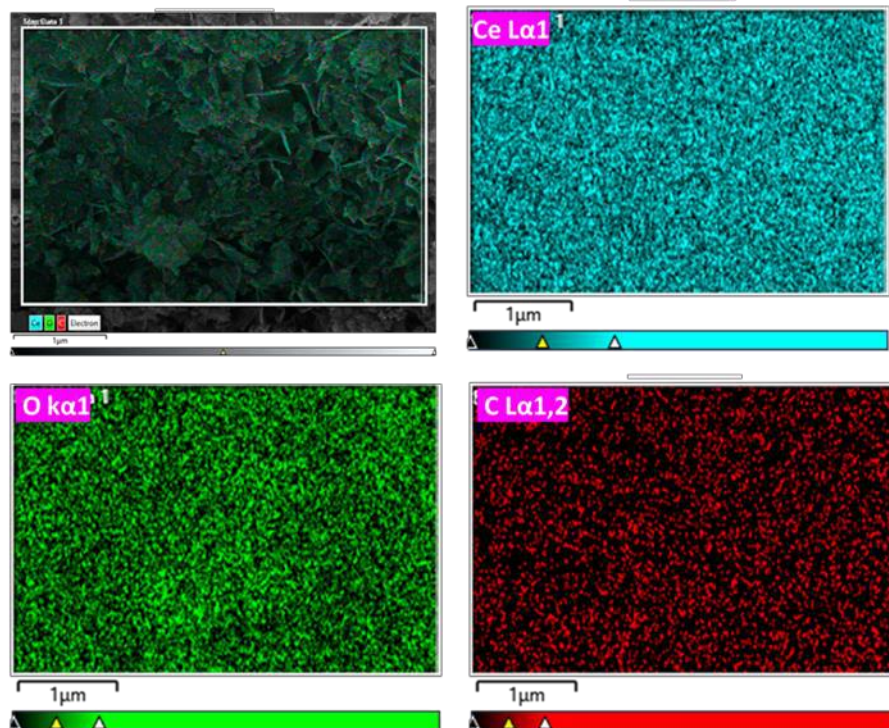


Fig.5.5 shows the Elemental mapping of CeO_2 sample.

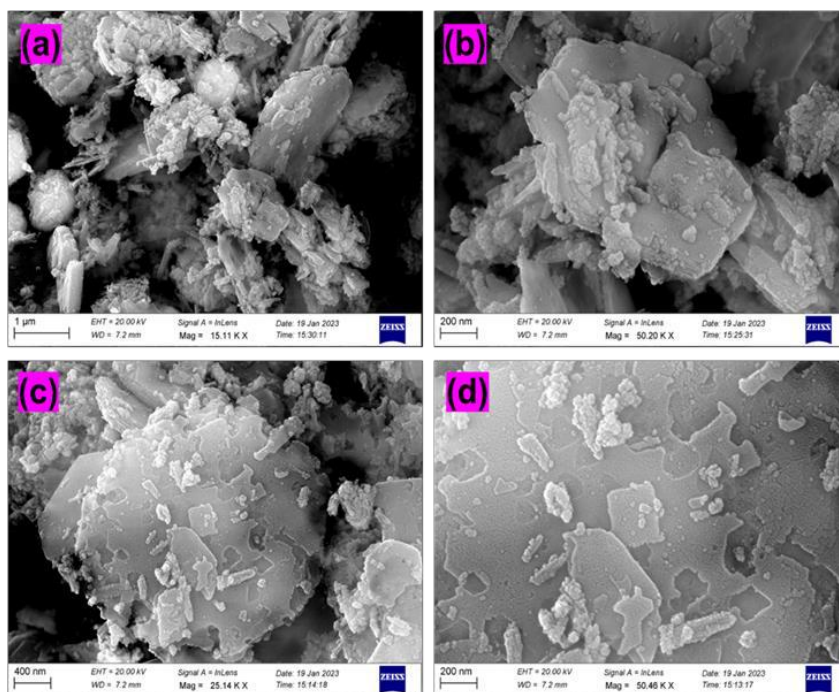


Fig.5.6 (a-d) displays the FE-SEM images of $\text{CeO}_2 / \text{Co}_3\text{O}_4$ nanocomposite

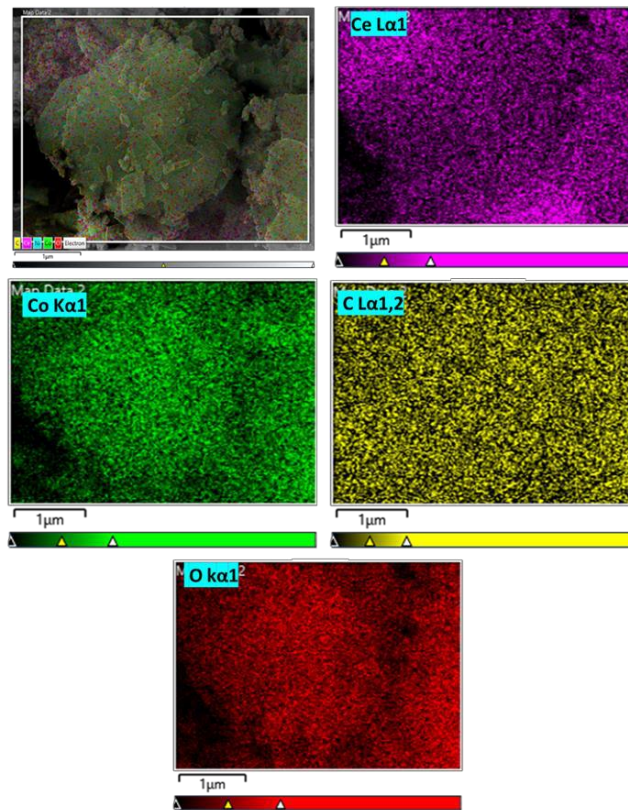


Fig.5.7 Elemental Mapping of CeO₂ / Co₃O₄ nanocomposite

5.3 Transmission Electron Microscope:

The morphology of the as-prepared CeO₂ / Co₃O₄ nanocomposite Hetero – Structure was examined by a High-resolution Transmission electron microscope as displayed in Fig.4 at different magnifications. Fig.5.8 (a-b) shows lower magnification HR-TEM images of CeO₂ / Co₃O₄ nanocomposite, which dispose of the sheet-like structure of CeO₂ and has a tiny nanoparticle of Co₃O₄ attached to it. It can be clearly seen that the heterostructure of CeO₂ / Co₃O₄ nanocomposite nanoparticles owns well-distributed size and good dispersion. The high magnification HR-TEM images in Fig.5.8 (c - h) shows the crystal lattice of the Heterostructure with fine resolution. The measured lattice spacing of $2d = 0.313$ nm correlate with the d spacing data and $d_{(111)}$ miller planes of heterostructure CeO₂ nanosheet, followed by the lattice planes of $2d = 0.262$ nm, is related to the d spacing of $d_{(311)}$ miller plane of heterostructure Co₃O₄ nanoparticles. Their corresponding Selected area diffraction pattern (SAED) is presented in the inset of Fig.5.8(i), which revealed the polycrystalline nature of the prepared CeO₂ / Co₃O₄ nanocomposite. The plane (111) exactly matches the CeO₂

cubic phase and the plane (311) plane correlate with the cubic face structure of Co_3O_4 nanoparticles. The unique heterostructure of the prepared CeO_2 / Co_3O_4 nanocomposite make it as a suitable candidate for energy storage applications.

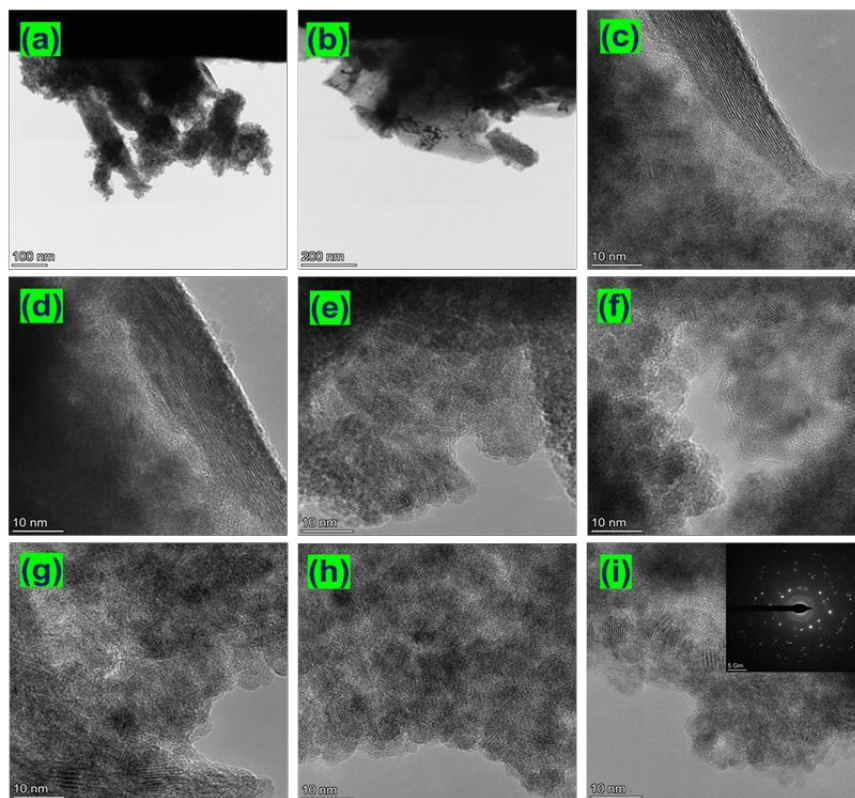


Fig.5.8 High resolution Transmission electron microscope images. Fig.5.8 (a-c) lower magnification of CeO_2 / Co_3O_4 . Fig.5.8 (d-i) HRTEM images at high magnification of CeO_2 / Co_3O_4 nanoparticle decorated with sheet-like structure. Insert of Fig.5.8 (i) displays the SAED pattern.

5.4 X-Ray Photoelectron Spectroscopy

The chemical bonding states of the sample is examined by XPS analysis as seen in Fig.5.9 the figure shows Ce species is evidently detected in the $\text{Co}_3\text{O}_4 / \text{CeO}_2$ nanocomposite. The O 1s spectrum in Fig.5.9 exhibits three peaks centered at 529.4 eV, 530.3 eV and 530.9 eV, respectively. The two peaks centered at 529.4 eV and 530.9 eV are consistent with oxygen species in Co_3O_4 and adsorbed OH- species on the surface of the samples. The oxygen peak at 530.3 eV is described to the oxygen bonded to cerium in CeO_2 . In addition, the oxidation states of Co and Ce are determined by Co 2p and Ce 3d XPS spectra. The Co 2p spectrum presents two main Co 2p_{3/2} and Co 2p_{1/2} peaks at 779.2 eV and 794.3 eV together with two shake-up satellite peaks, which are fitted with the chemical bonding states of Co_3O_4 . The peaks centered at 881.6 eV, 888.5 eV, and 898.5 eV belong to Ce 3d_{5/2}, and peaks at 900.7 eV, 903.6 eV, 907.2 eV and 916.4 eV correspond to Ce 3d_{3/2}. Only the peak centered at 903.6 eV belongs to Ce³⁺, and the other peaks are ascribed to Ce⁴⁺. 27-29 40 XPS analysis is in agreement with the XRD pattern and HRTEM results shown in Fig.5.9 [19]

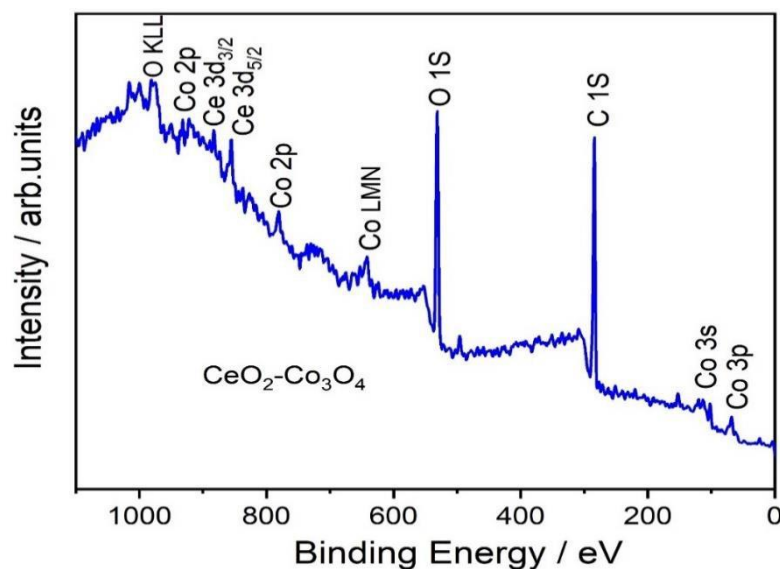


Fig 5.9: Displays the XPS analysis of $\text{CeO}_2 / \text{Co}_3\text{O}_4$

5.5 Electrochemical Characterization:

5.5.1 Cyclic Voltammetry Studies:

The Electrochemical performance of CeO₂ nanoparticles and CeO₂ / Co₃O₄ nanocomposite are evaluated using Cyclic voltammetry curves and Galvanostatic charge / Discharge (GCD) Analysis in a 3 M of KOH electrolyte solution. Fig.5.9 (a) and Fig.5.10 (a) display the Cyclic voltammetry curves of CeO₂ nanoparticles and CeO₂ / Co₃O₄ nanocomposite at diverse scan rates over a potential window of 0– 0.6 V (vs SCE). The shape of the CV curves of CeO₂ completely deviated from the regular pseudocapacitive Redox curves. The samples show up with a non-Faradaic charge storage behavior, in which the charges storage arises from the separation of polarized charge at the electrode/electrolyte interface which results in rectangular CV curves [62, 63]. The novel nano-sheet-like morphology aids in a faster ion adsorption process.

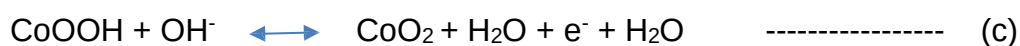
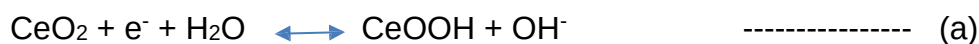
The absence of a faradaic process restricts the accessible surface area of active materials for ion adsorption providing a limited energy density, the charge storage behavior can be further confirmed by the linear symmetric response in GCD analysis [64] (Fig.5.9 (b)) for various current densities at 1 A/g, 2 A/g, 4 A/g, 6 A/g, 8 A/g, 10 A/g suggesting capacitive type charge storage type.

The Specific capacitance value can be calculated [29] from

$$C_s = \frac{I \Delta v}{m \Delta v} \quad \text{-----} \quad (2)$$

Holding on to the formula mentioned in equation (2) the specific capacitance values calculated for various current densities are as follows, 100 F/g, 56.66 F/g, 45.96 F/g, 32.98 F/g, and 25.43 F/g. As shown in cyclic voltammetric analysis (Fig. 5.10a) CeO₂ / Co₃O₄ nanocomposite with a Heterostructure offers a pseudocapacitive charge storage mechanism with visible oxidation and reduction peaks. In addition, when compared to the CeO₂ nanoparticles the increased area of the CV curves suggests the high specific capacitance of CeO₂ / Co₃O₄ nanocomposite which is closely associated with its heterostructure surface morphology which provides a large surface area, shorten ion conductive pathway to undergo fast faradaic redox reactions together with surface adsorption of ions resulting in enhanced electrochemical kinetics [65]. The pseudocapacitive performance is further validated by corresponding GCD curves by its apparent charge-discharge platforms originating from the faradaic redox

process. GCD curves (Fig.5.10b) for diverse current densities 1 A/g, 2 A/g, 4 A/g, 6A/g are analyzed which results from the conversion of multiple cobalt and cerium oxidation states. The chemical reactions [66] are as follows,



Hing to Equation (1) the specific capacitance calculated are 370 F/ g, 163 F/g, 64.5 F/g, 36.16 F/g, 22.3 F/g, 15.33 F/g. Moreover, the CeO_2 / Co_3O_4 nanocomposite exhibits high cyclic stability over 10000 charge-discharge cycles (Fig.5.10d) with a specific capacitance of 15.16 F/g at a maximum current density of 10 A/g .which confirms the structural stability of the composite material. The Remarkable specific capacitance is achieved by its novel heterostructure formed by nanosheet and nanoparticle surface morphology which aids in the promotion of high accessibility of electroactive sites. Electrochemical Impedance Spectroscopy measurements of CeO_2 nanoparticles and CeO_2 / Co_3O_4 nanocomposite Fig.5.9(c), Fig.5.10(c) are carried out in a three-electrode system. EIS Analysis is performed in a frequency range of 0.01 Hz to 10 KHz at a potentiostatic signal amplitude of 5 mV. The charge transfer resistance of CeO_2 / Co_3O_4 nanocomposite is small compared to CeO_2 nanoparticles, this is achieved by the addition of Co_3O_4 in CeO_2 as a composite electrode material to increment the Electronic Conductivity. Here, Co_3O_4 acts as an escalator which can increase the degree of electrochemical reaction between CeO_2 and electrolyte during consecutive faradaic redox reactions. In addition, CeO_2 is a highly active material that involves quick oxidation / Reduction leading to enhanced electrochemical performance. Table 1 displays the lots of specific capacitance values with the previously reported literature and our work.

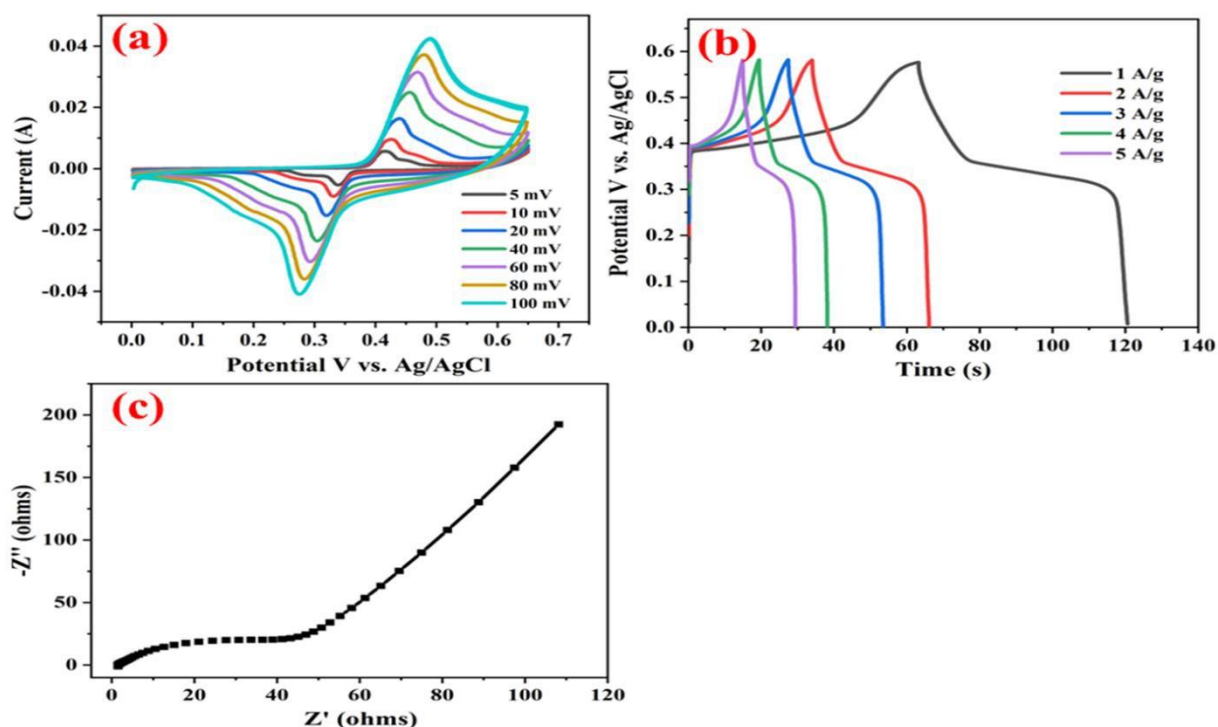


Fig.5.10 shows the Electrochemical Characterization Studies of CeO_2 nanoparticles. Fig. 5.10 (a) discloses the Cyclic Voltammetry curves, Fig.5.10 (b) shows the Galvanostatic Charge/ Discharge curves at various current density, Fig.5.10(c) represents the Electrochemical Impedance Spectroscopy measurements. The Cyclic Stability Test at a high current density of 6 A/ g is shown in Fig.5.10 (d)

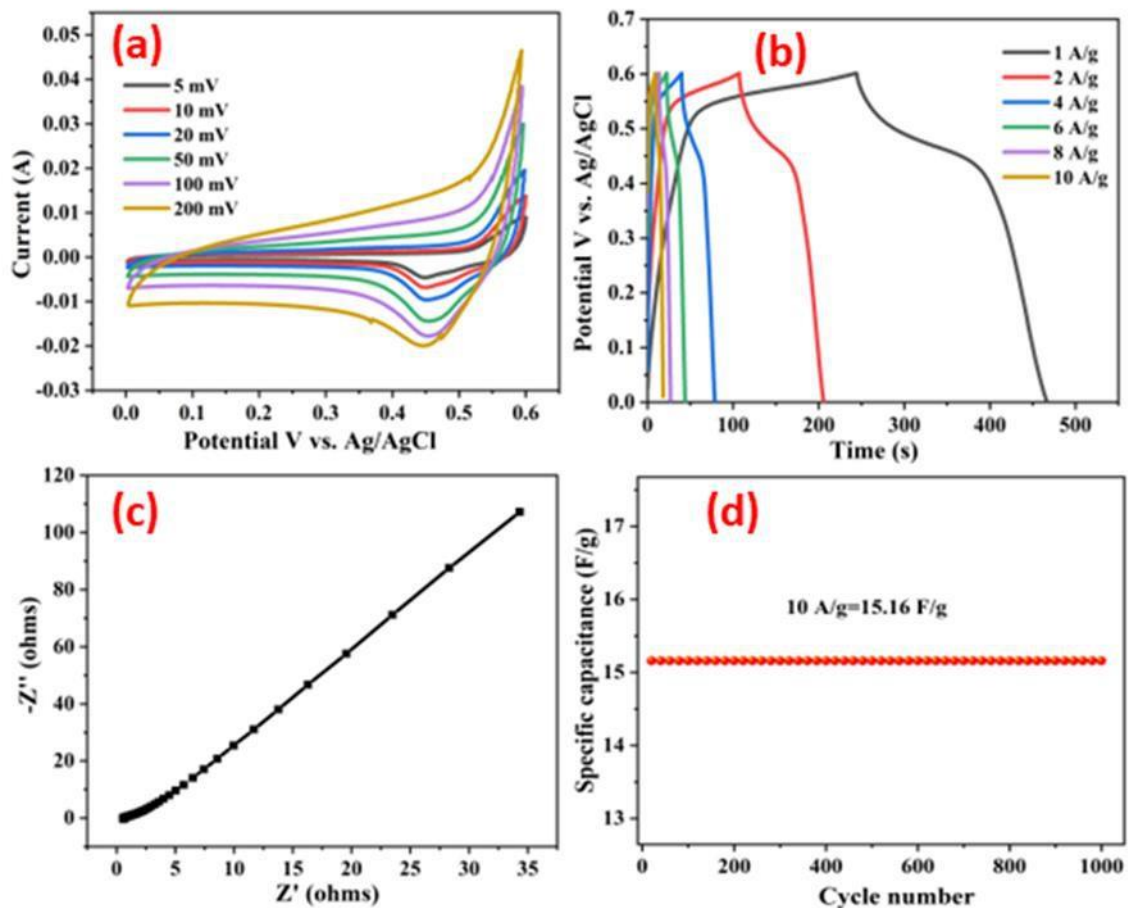


Fig.5.11 shows the Electrochemical Characterization Studies of $\text{CeO}_2 / \text{Co}_3\text{O}_4$ nanocomposite. Fig.5.11 (a) discloses the Cyclic Voltammetry curves, Fig.5.11 (b) shows the Galvanostatic Charge/ Discharge curves at various current density, Fig.5.11 (c) represents the Electrochemical Impedance Spectroscopy measurements. The Cyclic Stability Test at a high current density of 10 A/ g is shown in Fig.5.11 (d)

Electrode materials	Specific capacitance Fg ⁻¹	Current density Ag ⁻¹	Reference
CeO ₂	100	1	This work
CeO ₂ / Co ₃ O ₄	370	1	This work
CeO ₂	75	10m Vs ⁻¹	[67]
CeO ₂	57	1(5mVs ⁻¹)	[68]
CeO ₂	25	---	[69]
CeO ₂ /Fe ₂ O ₃	142.6	5mVs ⁻¹	[70]
CeO ₂ /Activated carbon	162	----	[71]
CeO ₂ /RGO	185	2	[72]
NiO-CeO ₂	305	1	[73]
MnO ₂ /CeO ₂	274.3	500 mAg ⁻¹	[74]

Table 1: Comparison of specific capacitance.

CHAPTER – 6

CONCLUSION

In recent years, numerous intensive research efforts in the field of nanotechnology have shown great potential. There have been significant improvements in the synthesis of desired inorganic nanomaterials and their several potential applications are presented by the scientists and reported in the literature. The development of nanomaterials helps us to move towards a bright and comfortable future. These materials offer more precise methods of addressing the several unsolved problems and needs of mankind. There are endless possibilities for improved devices, structures, and materials if understanding can be developed for assembly at small structures.

Nanotechnology has reached to the level of leading science with fundamental and research prospects in all basic cognitive sciences. An important lecture on nanotechnology is to bridge the gap between the atomic and molecular scale of fundamental sciences. overall conclusions of our work as presented in the previous chapter are presented here,

A brief introduction to metal oxide nanostructures, their various synthetic methods, and the properties of targeted metal oxides, i.e.) CeO_2 and $\text{CeO}_2/\text{Co}_3\text{O}_4$ have been presented in Chapter 1. In addition to this, Supercapacitor applications are also demonstrated in this chapter. Finally, chapter 1 describes the objective and importance of this project.

Chapter 2 contains the literature survey to which I have been referring from the beginning of the project. The aim and scope were discussed in Chapter 3.

The prepared metal oxide nanomaterials were mainly synthesized by facile hydrothermal route.

CHAPTER – 6

6.1 SUMMARY AND CONCLUSION

- ❖ Metal oxide-based materials are attracted in electrode materials for Supercapacitor application.
- ❖ Polyvinylpyrrolidone was used as a surfactant to reduce particle size.
- ❖ Herein, the CeO₂ nanocomposite was synthesized by the hydrothermal method at 120°C for 24 hours in an air oven.
- ❖ Crystallite structure and surface were confirmed by XRD. The size crystallite size was calculated by the Debye Scherrer formula the size was found that nanoparticles respectively.
- ❖ The FESEM microscopy demonstrated the synthesized CeO₂ sample was in a nanoscale region with a sheets-like structure that is highly interconnected with one another. The CeO₂ / Co₃O₄ nanocomposite was in Heterostructure with a combination of sheet and sphere-like nanoparticle structures.
- ❖ From, HRTEM analysis we have further confirmed the morphology of the prepared CeO₂ / Co₃O₄ nanocomposite. Heterostructure and confirmed the presence of CeO₂ / Co₃O₄ nanocomposite from the obtained SAED diffraction.
- ❖ From, XPS characterization we have studied the oxidation states of the prepared nanocomposite. It also provides the surface chemical composition and the corresponding valence state of CeO₂ / Co₃O₄ nanocomposites.
- ❖ Using Cyclic Voltammetry studies, we confirmed the presence of pseudocapacitive behavior of our CeO₂ and CeO₂ / Co₃O₄ nanocomposite samples.
- ❖ Using, Galvanostatic charge/ discharge analysis we have calculated the specific capacitance of our CeO₂ and CeO₂ / Co₃O₄ nanocomposite sample.
- ❖ When compared the stand alone CeO₂ material the CeO₂/Co₃O₄ nanocomposite, exhibits high specific capacitance of 370 F/g, which is attributed by its unique heterostructure surface morphology.

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