Chapter2

Materials and Instrumentation Methods

This chapter deliberates the complete description of materials and experimental methodologies for the synthesis of various materials Co-NTA, PdNPs, Co@NC, Co@Pdnps1, Co@Pdnps2, and Co@Pdnps3, Pdnps1, Pdnps2**.** This chapter provides a theoretical overview of instrumentation and experimental techniques used to characterize synthesized materials. Nanomaterials and nanocomposites are extensively characterized using X-ray Diffractometer (XRD), Scanning Electron Microscope (SEM), Transmission Electron Microscopy (TEM), Energy Dispersive Spectroscopy (EDX), and X-ray Photoelectron Spectroscopy (XPS).

Cyclic voltammetry (CV) is used for electrochemical characterization. Additionally, LSV, and Electrochemical Impedimetric Spectroscopy (EIS) are utilized for electrochemical OER application. Each technique is briefly discussed to provide background information.

2.1 Materials

Merck, India, provided potassium tetrachloropalladate (K_2PdCl_4), Pd-nanopowder(SRL), cobalt chloride hexahydrated ($CoCl_2.6H_2O$), and 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (EETMOS). Sigma Aldrich provided the nitrilotriacetic acid (NTA),3-Aminopropyltrimethoxysilane(3-APTMS) and SD Fine Chem Ltd, India provided the isopropanol. The formaldehyde, polyvinyl alcohol (PVA), and polyvinyl pyrrolidone (PVP), were acquired from Sigma Aldrich and used without additional purification (Bangalore, Karnataka, India). Merck supplied the potassium hydroxide (Bangalore, Karnataka, India). All of the studies were carried out with deionized water that had been double-distilled.

2.2 Synthesis

2.2.1 Synthesis of Co-NTA

0.002 mol$CoCl_2.6H_2O$ was dissolved in 15 mL deionized water and agitated for 20 minutes to form a homogeneous solution. 0.005 mol of NTA was distributed and swirled for 30 minutes in 15 mL of isopropyl alcohol. The NTA solution was added to the cobalt chloride solution and agitated for 30 minutes. The resultant mixture was transferred for 6 hours at 180°C in a Teflon-lined autoclave (50 mL capacity). It was essential to let the autoclave drop to ambient temperature. The pink precipitate was collected, washed with deionized water several times, and then centrifuged with ethanol at 8000 rpm for 10 minutes. In a hot air oven set to 60^0C, the recovered solid was dried for 6 hours (B Wang et al.,2019).

2.2.2 Synthesis of Co@NC

Co-NTA fine powder (100 mg) was placed in a crucible boat and pyrolyzed for 3 hours at 600°C in an N_2 environment. The tubular furnace was let to cool naturally at ambient temperature. Co@NC was used to represent the black powder that was collected (Y Bang et al.,2014).

2.2.3 Synthesis of Pdnps1

Palladium nanoparticles were made by a wet chemical reduction process using EETMOS, as reported earlier (P.C.Pandey et al 2018) and shown in video link https://youtu.be/Zl-QT574j8Q. First we prepared a methanolic solution of K_2PdCl_4 (10mM,1mL) and PVP(1%,1mL). Then, with a concentration range of 0.1- 4.32M, a methanolic solution of EETMOS was created. The solution of K_2PdCl_4 (80µL) and PVP (15µL) was added to the required concentration of EETMOS (15µL),stirred for 2 minutes, and incubated at 40^0C for 10-15minutes. The black colloidal solution was obtained.

2.2.4 Synthesis of Pdnps2

100µL of 10 mM of K_2PdCl_4 solution in methanol was premixed with 20µL of methanolic solution of 3-APTMS (0.5-4M) stirred for 2 minutes, followed by the addition of 100µL formaldehyde. The solution was kept under the microwave oven for incubation for till 80 seconds. The black colloidal solution was obtained (P.C.Pandey et al 2021).

2.2.5 Pdnps3-CAS No.7440-053.

2.2.6 Synthesis of CoPd-NTA1

0.1mM$CoCl_2.6H_2O$ was dissolved in 15 mL deionized water and agitated for 20 minutes to form a homogeneous solution. 0.005 mol of NTA was distributed and swirled for 30 minutes in 15 mL of isopropyl alcohol. The NTA solution was added to the cobalt chloride solution andpre synthesised Pdnps (2.5mM), there after agitated for 30 minutes. The resultant mixture was transferred for 6 hours at 180°C in a Teflon-lined autoclave (50 mL capacity). It was essential to let the autoclave drop to ambient temperature. The darkpink precipitate was collected, washed with deionized water several times, and then centrifuged with ethanol at 8000 rpm for 10 minutes. In a hot air oven set to 60^0C, the recovered solid was dried for 6 hours (P.C.Pandey et al.,2015).

2.2.7 Synthesis of CoPd-NTA2

2.5mM $CoCl_2.6H_2O$ was dissolved in 15 mL deionized water and agitated for 20 minutes to form a homogeneous solution. 0.005 mol of NTA was distributed and swirled for 30 minutes in 15 mL of isopropyl alcohol. The NTA solution was added to the cobalt chloride solution and pre synthesised Pdnps (0.1 mM), there after agitated for 30 minutes. The resultant mixture was transferred for 6 hours at 180°C in a Teflon-lined autoclave (50 mL capacity). It was essential to let the autoclave drop to ambient temperature. The dark pink precipitate was collected, washed with deionized water several times, and then centrifuged with ethanol at 8000 rpm for 10 minutes. In a hot air oven set to 60^0C, the recovered solid was dried for 6 hours (P.C.Pandey et al,. 2015).

2.2.8 Synthesis of CoPd@NC-1 and CoPd@NC-2

CoPd-NTA-1 and CoPd-NTA-2 fine powder (100 mg) were placed in a crucible boat and pyrolyzed for 3 hours at 700°C in an N_2 environment. The tubular furnace was let to cool naturally at ambient temperature. CoPd@NC-1 and CoPd@NC-2 were used to represent the black powder that was collected.

2.2.9 Fabrication of Co@Pdnps

The black powder of Co@NC (80 mg) and Pdnps1, Pdnps2, and commercial Pdnps3 was mixed thoroughly in to a mortar pestle and after that, it were placed in a crucible boat respectively and pyrolyzed for 3 hours at 700^0C in an N_2 environment. It was decided to let the furnace cool down to room temperature. Co@Pdnps1, Co@Pdnps2, and Co@Pdnps3 were the collected dark black powder names.

At high temperature Co@NC might be facilitated the interaction between Pdnps and functionalized Co@NC to make nanocomposite as evidence in tem image which is entirely differ from individual tem image.

2.3 Fabrication of nanocatalyst modified carbon cloth electrode

For the first 30 minutes, 5 mg of Co@Pdnps, CoPd@NC-1 and CoPd@NC-2 were ultrasonically distributed in a solution containing 10 µL of Nafion solution and 100µL of ethanol. Finally, the 5 mg catalyst was dripped onto a bare carbon cloth (CC)(1×2cm^2) and dried in the oven to achieve the same loading level (3.5 mg cm^{-2}) for CC-supported nanoarrays**.**

2.4 Characterizations

In this section, Various instrumental tools are utilized to characterize synthesized materials, including UV-Visible spectroscopy (UV-Vis), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffractometer (XRD), Scanning Electron Microscope (SEM), Energy Dispersive Spectroscopy (EDX), and X-ray Photoelectron Spectroscopy (XPS). Thermal properties of the synthesized material are determined using Thermogravimetric Analysis (TGA), while the surface properties are analyzed with a BET surface area analyzer. Wettability and water contact angles are assessed using a Contact angle instrument. Electrochemical measurements are conducted employing Linear Sweep Voltammetry (LSV), Cyclic Voltammetry (CV), and Electrochemical Impedance Spectroscopy (EIS). Each technique is briefly discussed for contextual understanding.

2.4.1 X-ray Diffraction (XRD)

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample (Ermrich Martin et al 2013). These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d \sin \theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacing allows identification of the mineral because each mineral has a set of unique d-spacing. Typically, this is achieved by comparison of d-spacing with standard reference patterns. All diffraction methods are based on generation of X-rays in an X-ray tube (Epp J et al 2016). These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays. The Rigaku Miniflex X-ray diffractometer is a tool used for XRD analysis, as shown in figure 2.1. Cu-Kα radiation (λ=1.5405Å) is commonly used. Calibration is done using silicon powder, and single crystal silicon is used as a standard for obtaining accurate values of 2θ for calculating the quasi-lattice parameter. XRD patterns are collected typically over a range of 10-80° in 2θ, with a step size of 3 °/min. (Hammond C et al,.2015 and Holder CF et al 2019)

Figure 2.1 XRD instrument image

2.4.2 Fourier transform infrared (FTIR) Spectroscopy

Infrared (IR) spectroscopy, specifically Fourier Transform Infrared (FT-IR) technique, is instrumental in obtaining the spectrum of solid, liquid, or gaseous materials through absorption or emission. By analyzing the spectrum within the range of 4000 to 400 cm^{-1}, various functional groups present in the material can be identified. This process involves mathematically transforming the raw data, known as the interferogram, into the actual spectrum using Fourier transform. Functional groups within molecules act as dipole moments, each corresponding to a specific vibrational energy. When molecules encounter wavelengths within the 4000-400 cm^{-1} range, they selectively absorb energies necessary for specific vibrations while transmitting others. Each functional group, defined by its unique set of atoms and bond strength, exhibits vibrations determined by parameters like reduced mass (μ) and bond spring constant (k), making their vibrational energy distinct and characteristic. Consequently, FT-IR spectroscopy not only aids in identifying functional groups but also provides insights into the surface chemistry of nanomaterials, as surface-bound functional groups exhibit different FT-IR patterns than their free counterparts. Our study utilizes a Thermo Scientific Nicolet spectrometer, specifically the 6700 FT-IR model, operating within the spectral range of 450-4000 cm^{-1}.

The key component of FT-IR spectroscopy, the Michelson interferometer, sets it apart from typical dispersive infrared spectroscopy. Unlike dispersive IR spectroscopy, where monochromatic lights sequentially illuminate the sample across the infrared wavelength range, non-dispersive FT-IR spectroscopy employs an interferometer to simultaneously expose the sample to multiple IR frequencies. In the Michelson interferometer setup, a beam source emitting diverse IR wavelengths is directed through a beam splitter. Half of these wavelengths encounter a fixed mirror, while the remaining wavelengths reach a moving mirror with constant velocity. Upon reflection and recombination, an interference pattern is generated based on the path difference between the beams, revealing constructive and destructive interference patterns. The resulting interferogram, representing the interference pattern, is then directed to a detector as the transmitted portion. To generate the complete spectrum, typically presented as percent transmittance versus wavenumber, the interferogram is compared to a reference sample, and Fourier transform is applied to convert the data.

2.4.3 Scanning Electron Microscopy (SEM)

An image is formed by a powerful scanning electron microscope (SEM), which utilizes electrons. Imaging of conductive samples at magnifications unachievable by traditional microscopes is enabled. While modern light microscopes achieve up to ~1,000Xmagnification, magnifications over 30,000X can be reached by typical SEM. Images are in black and white because light is not used in the imaging process by the SEM. Conductive samples are placed on the SEM's sample stage. The sample chamber is vacuumed, and the electron gun is aligned to the correct location by the user. A beam of high-energy electrons is emitted by the electron gun, passing through lenses and apertures before striking the sample. As electrons are continuously shot at the sample by the electron gun at a precise location, secondary electrons bounce off. These secondary electrons are detected by the detector (Goldstein JI et al 2017). The signal from the secondary electrons is amplified and displayed on the monitor as a 3D image, being sent there.

Electrons are emitted from a heated electron gun acting as a cathode and accelerated towards the anode, traveling in the same direction as the sample under the influence of a strong electric field. As the electron beam is focused, it passes through the objective lens, which is adjusted by the user to a specific position on the sample. Upon striking the conductive sample, several interactions occur. Initially, primary electrons penetrate the sample to a depth determined by their energy level. Subsequently, secondary and backscattered electrons are emitted from the sample surface. These emitted electrons are detected by either a secondary electron (SE) or backscattered electron (BS) detector. The detected signals are processed to generate an image of the sample on the screen.

In SE mode, the low-energy secondary electrons are attracted towards the positively biased detector front, and the signal intensity varies with the sample's surface angle, providing detailed topographical images. In contrast, BS mode detects electrons nearly opposite to the beam direction, and the intensity is proportional to the sample's atomic number, yielding less topographical but more compositional information. BS mode is less affected by sample charging, making it suitable for non-conductive samples.

Electrons are emitted from a heated tungsten filament or Lanthanum hexa Boride (LaB6) single crystals, accelerated by a voltage typically in the range of 20 V to 30 kV, and directed down an electron optical column consisting of magnetic lenses to produce a focused electron beam that strikes the specimen's surface. The position of the electron beam on the sample is controlled by scanning coils, allowing for scanning over the sample surface. Image formation in the Scanning Electron Microscope (SEM) relies on signals generated from interactions between the electron beam and the sample, specifically inelastic interactions (secondary electrons, SEs) and elastic interactions (backscattered electrons, BSEs).

BSEs provide information from deeper areas of the sample, offering both topographic and compositional details. SEs, on the other hand, originate from surface regions, providing information on topographic contrast and surface texture with good resolution. Most conductive nanomaterials can be directly observed by SEM by loading them on carbon tape. However, non-conductive samples, such as bioorganic nanomaterials, require metal coating (e.g., Gold, Silver, Platinum). In SEM instruments, backscattered and secondary electrons are utilized to construct an image. The SEM instrument used for characterization is depicted in figure 2.2

Figure 2.2 Schematic representation of SEM Instrument

2.4.4 Transmission Electron Microscopy (TEM)

TEM is the technique where an electron beam is transmitted through an ultra-thin specimen (100nm) which interacts with the specimen as the electron passes through it. The two important features of the TEM are its high lateral spatial resolution and its capability to provide both the image and the diffraction of the sample. This technique is used to obtain the full morphological, crystallographic, atomic structural, microanalytical (chemical composition, bonding), electronic structure, and coordination number from the samples.The TEM works with a high voltage electron beam to create the image, where the electron gun is placed at the top which produces the electron that travels through the vacuum tube. The electromagnetic lens is used to focus the fine beam of electrons that passes through the ultra-thin specimen. The transmitted electrons get hit on the fluorescent screen which is present at the bottom of the microscope. The image of the specimen with its assorted parts appears on the screen which is based on its density. The obtained image can be directly studied or also photographed (Inkson BJ et al 2016 and Walther T et al 2017). TEM analyzes morphological, crystallographic, and compositional information. HR-TEM was produced on the Cu grid using a Tecnai G2 (New Zealand). The HR TEM instrument is shown in figure 2.3.

Figure 2.3 depicts the image of TEM Instrument.

2.4.5 Energy dispersive X-ray spectroscopy (EDX)

This technique serves as a complementary tool to SEM, FE-SEM, and TEM, providing insight into the elemental composition of specimens through qualitative and quantitative analysis. By detecting elements and their relative percentages, it offers spectra displaying peak intensities corresponding to different elements, along with elemental mapping for each element present.

2.4.6 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive analytical technique.The technique is also recognized as Electron Spectroscopy for Chemical Analysis (ESCA). Quantitative atomic composition and chemistry are determined using X-Ray Photoelectron Spectroscopy. In XPS, a sample is irradiated with a primary beam containing photons and electrons, leading to the emission of secondary electrons from the substrate surface. These secondary electrons are then measured by a spectrometer. In this technique, X-rays are directed at the material surface, and the kinetic energy of the emitted electrons is analyzed. XPS is known for its surface sensitivity and its ability to determine the chemical and oxidation states of elements in a sample. Figure 2.4 shows the XPS instrument.

Figure 2.4 depicts the XPS instrument.

All elements except helium and hydrogen can be identified using XPS. XPS spectra are typically plotted as intensity (count/sec) versus binding energy (eV). A wide scan XPS spectrum, known as a survey spectrum, scans from 0 to 1200 eV binding energy. In this study, XPS was used for elemental analysis and to identify the oxidation state of synthesized nanomaterials and nanocomposites (Krishna DNG et al 2022 and Isaacs MA et al 2021).

2.4.7 Surface Area Analysis: Brunauer-Emmett-Teller (BET) Theory

The Brunauer-Emmett-Teller (BET) theory, proposed by Stephen Brunauer, Paul Hugh Emmett, and Edward Teller in 1938, provides a framework for analyzing multilayer adsorption. This technique involves the physical adsorption of gas molecules onto a solid surface, enabling the measurement of specific surface area of solid materials. The theory is particularly suited for systems involving multilayer adsorption, where gases such as N_2, Ar, and CO_2, serving as the adsorbates, are employed. Notably, N_2 is commonly utilized as the adsorbate in BET analysis, with measurements typically conducted at the boiling temperature of N_2 (77 K).

When determining surface area based on estimated values and sample characteristics, the choice of adsorbate gas is crucial. Typically, a monomolecular layer of a known gas is employed for this purpose. The adsorption of this gas is measured either volumetrically or through a continuous flow method. Subsequently, the BET surface area is evaluated using the Rouquerol transform, focusing on the linear segment of the BET plot. Before measurement, it's essential to prepare the sample adequately to remove any physically bonded contaminants from its surface. This preparation process is referred to as degassing, also known as outgassing. During degassing, the sample is subjected to elevated temperatures, adjusted according to its thermal properties, while being exposed to either a vacuum or a continuously flowing inert gas. The BET theory serves as an extension of Langmuir's theory of monolayer adsorption to accommodate multilayer adsorption. The BET equation, utilized for calculating specific surface area from N_2 adsorption-desorption isotherms, is expressed as follows:

$$\mathrm{P}/(P0-P) = 1/\ VmC + C-1/\ VmC\ (\ P\ P0\ ) \qquad \text{Eq. 2.1}$$

2.4.8 Electrochemical Measurement

Electrochemical experiments were conducted on Electrochemical workstation model CHI660B, TX, the USA, in an electrochemical cell equipped with a three-electrode cell with a working capacity of 3 mL. Co@NC/Co@Pdnps, CoPd@NC-1 and CoPd@NC-2 nanocatalyst was used to modify the CC with active working electrode of $1\times1\mathrm{cm}^2$), Ag/AgCl was used as the reference electrode, and Pt wire was used as the counter electrode. The following equation was used to calibrate the Ag/AgCl reference electrode to the reversible hydrogen electrode.

$$\mathbf{E(RHE) = 0.197+E\ (Ag/AgCl)\ +0.0591pH} \qquad \text{Eq. 2.2}$$

In a 1M KOH solution, all electrochemical analyses were performed. Nanoparticles were deposited on carbon cloth using a Nafion-based supporting polymer and dried at 45^0C. The electrode was sonicated before usage and then cleaned with deionized water and acetone afterward. The blank electrode's cyclic voltammogram was first recorded, followed by recording the subsequent voltammograms for the catalyst-modified electrode at variable scan rates. The current catalyst grew directly on carbon cloth as the working electrode without using non-conductive binders, effectively eliminating the effects of binders on the catalyst's electrochemical activity. Furthermore, during the experiment, all phenomena of the catalyst from the conductive substrate, such as strong gas escape under high current density, could be successfully startled, boosting the catalyst's endurance. EIS ere made using CHI 660B at appropriate polarization voltage between 1 Hz to 100 kHz frequency range. These measurements were performed using a three-electrode assembly to measure current potential. The working electrode is sensitive to the analyte's concentration and undergoes the electrochemical redox reaction. The counter electrode completes the electric circuit, while the reference electrode's potential is known with respect to the standard hydrogen electrode (0.00 V) and measures the potential of the working electrode relative to the reference electrode, independent of analyte concentration(Krishna DNG et al 2022).

Cyclic voltammetry (CV) is a versatile potentiodynamic electroanalytical technique used to investigate the electrochemical properties of electroactive species. The corresponding spectrum of a CV, plotted as current vs. voltage, reflects changes in current corresponding to varying voltage in the solution. CV typically uses microelectrodes in an unstirred solution, limiting the measured current by analyte diffusion at the electrode surface (Isaacs MA et al 2021).In a cyclic voltammetry experiment the potential applied between the reference electrode and working electrode increases in a linear fashion with time (scan rate (V/s)). Concomitantly, the current is measured between the working and counter (or auxiliary) electrode resulting in data that is plotted as current (i) vs. potential (E).

Electrochemical Impedance Spectroscopy (EIS) utilizes a small amplitude, alternating current (AC) signal to study the impedance characteristics of an electrochemical cell over a range of frequencies (Lisdat F et al 2008). This technique differs from direct current (DC) methods by enabling the study of inductive, capacitive, and diffusion processes within the electrochemical cell. EIS is valuable for studying interfacial properties related to bio-recognition events, making it useful in various biomedical diagnosis and sensing applications (Kashyap B et al 2022 and Lisdat F et al 2008).

2.5 Conclusions

In conclusion, the synthesis and instrumentation for the evaluation of the oxygen reduction reaction (ORR) play pivotal roles in advancing the development of efficient electrocatalysts for various applications, particularly in fuel cells and metal-air batteries. Through meticulous synthesis techniques, tailored catalysts can be engineered with enhanced catalytic activity, selectivity, and durability. The choice of instrumentation is critical for accurately probing the kinetics and mechanisms of the OER, allowing for the optimization of catalysts and electrode designs. Furthermore, advancements in characterization techniques, such as in-situ, offer deeper insights into the dynamic behavior of catalysts under realistic operating conditions. Continued research efforts in synthesis methodologies and instrumentation innovations are essential for overcoming existing challenges and unlocking the full potential of oxygen electrocatalysis in renewable energy technologies.