

**ILJS-24- 103 (SPECIAL EDITION)****Fabrication of Novel Electrodes from Graphene oxide, Cerium oxide Nanoparticles, Acetylene black and their Composites****H. I. Adegoke, A. Ibrahim, A. Kareem and T. Ajide**

Department of Chemistry, University of Ilorin, P.M.B. 1515, Ilorin, Nigeria.

Abstract

In this study, novel electrodes were fabricated from graphene oxide, acetylene black and cerium oxide (CeO_2) nanoparticles. Graphene oxide (GO) was synthesized using Hummers method, cerium oxide (CeO_2) nanoparticle was synthesized using precipitation method. Acetylene black electrode (ABPE) was also prepared from acetylene black and solid paraffin. CeO_2 nanoparticles was dispersed into GO and a homogeneous CeO_2 -GO nanocomposite suspension was obtained by ultrasonic sonication. The prepared CeO_2 -GO nanocomposite was composited on the prepared ABPE to form CeO_2 -GO/ABPE. The prepared electrode was characterized using Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX). The electrochemical studies were conducted by cyclic voltammetry (CV) in a solution containing potassium ferrocyanide and potassium chloride as the supporting electrolyte. Specifically, for the bare ABPE, the anodic peak potential was -0.1253 V, cathodic peak potential was 0.4245 V, anodic peak current was $3.8407\text{E}-05 \text{ A/cm}^2$, and cathodic peak current was $4.2695\text{E}-05 \text{ A/cm}^2$. The CeO_2 -GO/ABPE electrode revealed anodic peak potential of 0.37628 V. The characterization results suggest the suitability of the electrodes to be potential candidates for the detection of heavy metals.

Keyword: Fabrication; Electrodes; Electrochemical techniques; Nanoparticles; Graphene oxide**1. Introduction**

In recent decades, a variety of electrochemical sensors have been developed and effectively applied across diverse fields, especially for environmental pollutant analysis, due to advancements in transducer and electrode fabrication techniques. These sensors are known for their high sensitivity, selectivity, and portability, making them suitable for real-time environmental monitoring (David et al., 2016). Given the importance of detecting pollutants accurately, considerable research has focused on enhancing electrochemical sensors with modified electrode materials to achieve greater sensitivity and specificity (Deng et al., 2014).

Historically, electrochemical analysis methods such as cyclic voltammetry (CV) and chronoamperometry (CA) were commonly used for analyte detection. However, these methods often demonstrated limitations in sensitivity and speed. As a result, techniques like differential pulse voltammetry (DPV) and square wave voltammetry (SWV) have become more prevalent due to their enhanced sensitivity, faster response times, and controlled over-oxidation (Goudarzi et al., 2016).

The efficiency and accuracy of electrochemical sensors are largely influenced by the electrode materials used in their construction. Graphene oxide (GO), cerium oxide (CeO_2) nanoparticles, and acetylene black are among the materials identified as highly promising for fabricating advanced electrodes, attributed to their

exceptional conductivity, stability, and electrochemical activity. Specifically, composite materials combining these elements offer an optimized surface area, catalytic activity, and electrical conductivity, which are ideal for pollutant detection in complex environmental samples.

In related research, a novel gold working electrode immobilized with a graphene oxide–cerium oxide (GO–CeO₂) nanocomposite was used for the detection of the pesticide chlorpyrifos (CLP) in a phosphate buffer (PBS) solution with a pH of 7.0. Graphene oxide (GO) was synthesized using a modified Hummer's method, while cerium oxide (CeO₂) nanoparticles were prepared using a coprecipitation technique. The GO–CeO₂ nanocomposite was synthesized *via* sonochemical methods (Khan *et al*, 2024)

In a similar study, hybrid alginate–polyacrylamide hydrogel was prepared *via* an *in situ* self-assembly of reduced graphene oxide–cerium oxide nanocomposite (rGO–CeO₂) and cytochrome *c* (Cyt *c*) and employed for electrochemical detection of reactive oxygen species, ROS. The hydrogel platform, on one hand, provided a very large electroactive surface coverage and effectively increased the reactivity of Cyt *c*, and also integrated the rGO–CeO₂ nanocomposite for enhancing electrochemical signals and structural stability. The formation of the rGO–CeO₂@Cyt *c* hydrogel was confirmed through various microscopic and spectroscopic techniques (Kumar *et al*, 2020)

In this study, we aim to synthesize graphene oxide sheets and cerium oxide nanoparticles using Hummers' method and a precipitation technique, respectively. These materials will then be incorporated onto an acetylene black paste electrode (designated as CeO₂-GO/ABPE) to enhance the electrode's electrochemical properties. The prepared composite electrode will undergo electrochemical characterization to evaluate its sensitivity and efficiency in pollutant detection, thus contributing to advancements in electrochemical sensing technology.

2. Materials and Methods

2.1 Chemicals and Reagents

The reagents used for this study include: Cerium sulphate tetrahydrate Ce (SO)₄.4H₂O, glycerol, hydrazine solution (80 wt. %), ammonia solution (25 wt %), hydrogen peroxide solution (30 wt. %), Acetylene black, graphite powder, potassium permanganate (KMnO₄), sodium nitrate (NaNO₃), sodium hydroxide (NaOH), sulphuric acid (H₂SO₄), hydrogen peroxide (H₂O₂), hydrochloric acid (HCl), solid paraffin, Deionized water and 2- Nitrophenol.

2.2 Synthesis of Materials

2.2.1 Synthesis of Graphene Oxide

Graphite was oxidized to graphene oxide using a modified Hummers method. A 0.5 g of graphite, 0.5 g of NaNO₃ and 23 ml of H₂SO₄ were stirred together in an ice bath, 3 g of KMnO₄ was slowly added to the mixture. The mixture was transferred to a 35 °C water bath and stirred for about 2 h to form a thick paste, 40 ml of water was then slowly added, the reaction solution was stirred for 30 min while the temperature was raised to 95 °C. A 100 ml of water was then added, followed by slow addition of 3 ml of H₂O₂ (30%). The resulting suspension was filtered, washed twice with 1 M HCl and deionized water, then vacuum-dried at 50 °C for 24 h to obtain graphene oxide, The graphene oxide was then dispersed in deionized water (0.5 mg mL⁻¹) and exfoliated to GO by ultrasonication for 2 h. It was then centrifuged at 6000 rpm for 30 minutes to remove the excess, unoxidized graphite and unexfoliated graphene oxide (Deng *et al.*, 2013).

2.2.2 Synthesis of CeO₂ nanoparticles

In a typical procedure Cerium (iv) oxide CeO₂ nanoparticles was synthesized via the precipitation procedure, taking cerium (IV) sulphate tetrahydrate as precursor material and an aqueous solution of sodium hydroxide as precipitating agent. In detail, 3 g of cerium salt was dispersed and dissolved in 60 mL of glycerol at 70 °C

under vigorous stirring, until the solution became clear. Initially, the dispersed powder in glycerol was yellow in color; then, the solution faded and became colorless, and finally a clear solution without dispersed particles was obtained. At this stage, the glycerol solution was cooled at room temperature; then, a 10 % hydrogen peroxide solution (10 mL) was added followed by dropping a sodium hydroxide solution (3 mol/L) until pH = 12. Afterwards, this solution was mixed with 60 mL of deionized water and maintained under vigorous stirring for 1h. The precipitate was washed several times with deionized water and then separated by centrifugation at 10,000 rpm until the pH of the supernatant becomes neutral. The resulting product was dried at 40 °C for 24 h under vacuum, calcined at 600 °C for 2 h in air, and allowed to cool at room temperature in an oven (Fifere et al., 2021).

2.2.3 Preparation of Acetylene black past Electrode (ABPE)

Acetylene black paste electrode (ABPE) was fabricated by mixing 3.0 g Acetylene black (AB) powder and 0.5 g solid paraffin thoroughly in a mortar and further heated at 80 °C to generate a homogeneous paste. A part of the paste was tightly packed into the cavity of a glass tube (inner diameter 3 mm), and an electrical contact was established between the copper wire and the end of the paste. (Deng *et al.*, 2013).

2.2.4 Preparation of CeO₂-GO/ABPE

A 1.0 mg mL⁻¹ GO dispersion was obtained by adding appropriate amount of graphite oxide into water and exfoliating to GO by ultrasonication for 2 h. A 1.0 mg of CeO₂ nanoparticles was dispersed into 1.0 mL GO dispersion and a homogeneous CeO₂-GO nanocomposite suspension was prepared by ultrasonic agitation for 20 min. Before coating, ABPE was polished on a polishing cloth with 0.3 μm alumina powder and then ultrasonic treatment was carried out successively in ethanol and ultrapure water. Then, 5.0 μL of the CeO₂-GO suspension was casted on the surface of ABPE and dried under an infrared lamp. After that, the CeO₂-GO/ABPE was put into 0.1 M phosphate buffer solution (PBS, pH 6.5), and was electrochemically reduced under a constant potential of - 1.2V for 120 s. The prepared electrode (denoted as nano-CeO₂/RGO/ABPE) was washed with water before use.

2.3 Characterization of the Prepared Materials

2.3.1 Voltammetric Measurement

For voltammetric measurements, the three-electrode system was immersed in a 10-ml electrochemical cell containing electrolyte solution (1.0 mM K₃[Fe (CN)₆] and 0.1 M KCl mixture) using a Potentiostat (Cortest 300CS model) in the Department of Chemistry, University of Ilorin, Ilorin, Nigeria. The cyclic voltammograms was recorded between 0.6 V and 1.2 V at a scan rate of 0.1Vs⁻¹ The second-order derivative linear sweep voltammograms was recorded in the potential range from 0.2 V to 1.2 V at a scan rate of 0.1 Vs⁻¹, after 120 s accumulation at the potential of 0.0 V under stirring and a 5 s rest. 1.0 M H₂SO₄ was used as the supporting electrolyte. Figure 2.1 below shows the electrochemical setup which contain the prepared GR/ABPE as working electrode, a reference electrode, that is: Ag/AgCl and a counter electrode, platinum mesh.

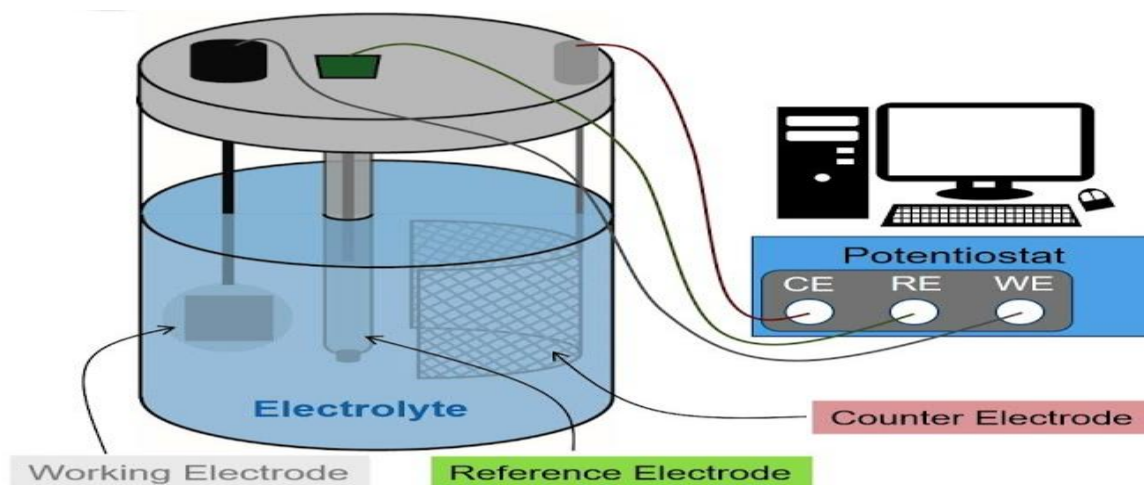


Figure 2.1: Electrode system containing a working electrode, reference and counter electrode

3. Result and Discussion

3.1 Fourier Transform Infrared Spectroscopy (FTIR) of CeO₂ Analysis

The infrared spectra of CeO₂ nanoparticles were recorded and represented in Figure 3.1a above. In the FTIR spectra of CeO₂ sample, the peak at 3300 cm⁻¹ corresponds to -OH stretching vibrations of the hydroxyl groups. The band at 1500 cm⁻¹ can be attributed to the interlayer stretching and bending vibration of molecular water. A peak noticed at 800 cm⁻¹ is attributed to the O-Ce-O bonding nature of ceria nanoparticles. The small bands obtained at 700, 615 and 545 cm⁻¹ correspond to Ce-O stretching mode. The spectrum of synthesized CeO₂ obtained is in conformity with the observation according to Farahmandjou *et al.*, 2016.

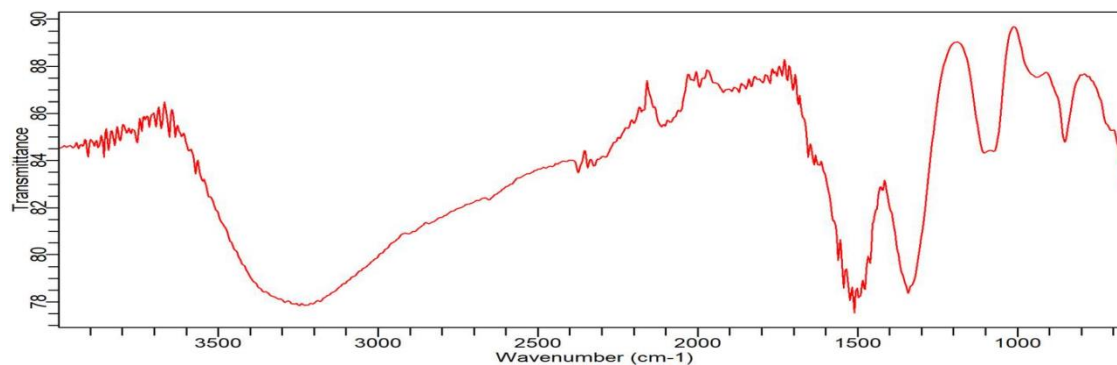


Figure 3.1a: FT-IR Spectrum of as-synthesized CeO₂ sample

3.2 Fourier Transform Infrared Spectroscopy (FTIR) of ABPE.

The infrared spectrum in figure 3.1b below, showed the peaks located at 2884 cm⁻¹ and 2999 cm⁻¹ were attributed to the asymmetric and symmetric vibrations of C-H and the peak at 1500 cm⁻¹ was ascribed to the vibration of C-C. Moreover, the broad resonance peak located at the range of 2900 to 3000 cm⁻¹ signified the presence of hydrophilic hydroxyl groups. The spectrum of ABPE compared to the report of Guo *et al.*, 2015, showed the stretching and bending peaks conforms with the prepared sample.

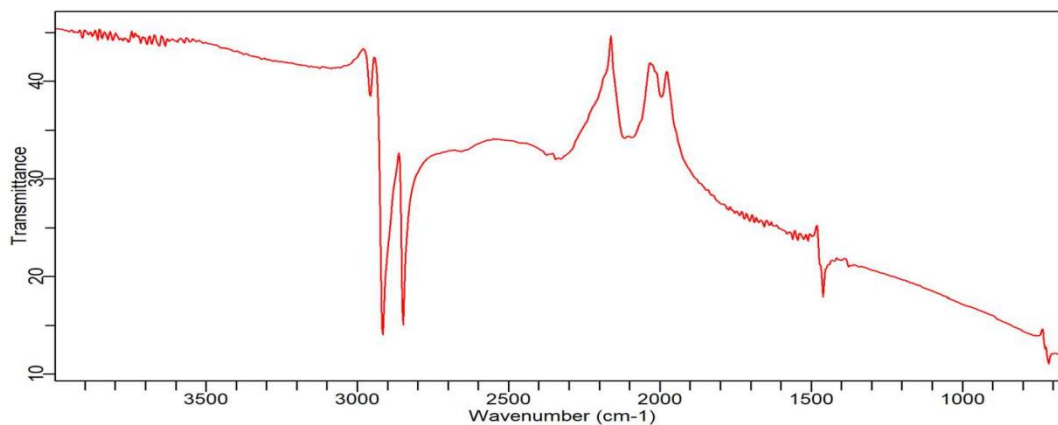


Figure 3.1b: FT-IR Spectrum of Prepared ABPE

3.3 Fourier Transform Infrared Spectroscopy (FTIR) of Graphene oxide

The broad peaks at 3500 cm^{-1} and 2500 cm^{-1} in the IR spectrum of GO in figure 3.1c below is due to the carboxyl O-H stretching mode. The absorption peaks corresponding to O-H stretching (a peak 3300 cm^{-1} and 3400 cm^{-1}) which is superimposed on the OH stretch of carboxylic acid, is due to the presence of absorbed water molecules and alcohol groups. The IR peaks corresponding to $3330, 2927\text{ cm}^{-1}$ and 2849 cm^{-1} are due the asymmetric and symmetric CH_2 stretching of GO respectively while the peak around 1619 cm^{-1} is attributed to C-C stretches from unoxidized graphitic domain. The peak at around 1720 cm^{-1} is attributed to C-O stretch of carboxyl group, 1224 cm^{-1} corresponds to C-O stretch of alcohol group, 1080 cm^{-1} is attributed to C-O stretching vibrations of C-O-C. The spectrum of GO shown by Roy *et al.*, 2013 revealed the stretching and bending peaks which is in conformity with the synthesized material.

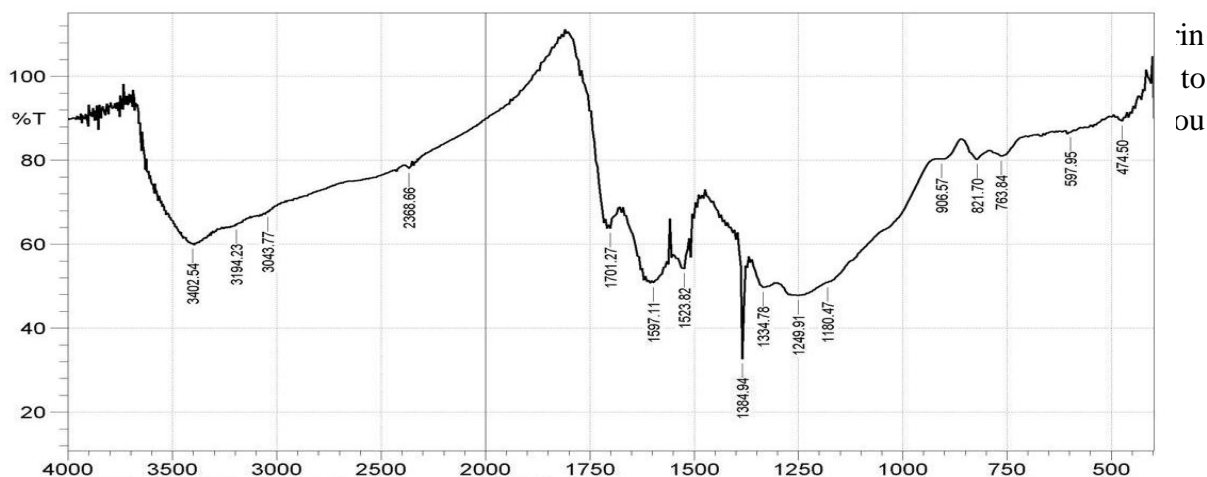


Figure3.1c: FT-IR spectrum of as-synthesized for Graphene oxide

3.4 Scanning Electron Microscopy (SEM)

The morphology of ABPE was also examined by a scanning electron microscope (SEM). The typical SEM image is shown in the figure 3.2a above. Surface topography for ABPE showed a granular surface with the granules isolated and clearly distinguished (Deng *et al.*, 2013).

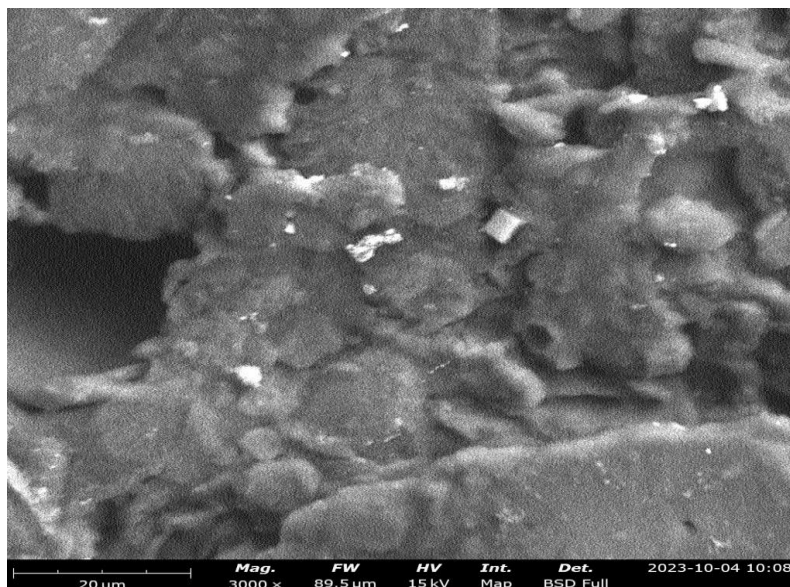


Figure 3.2a: SEM image for ABPE

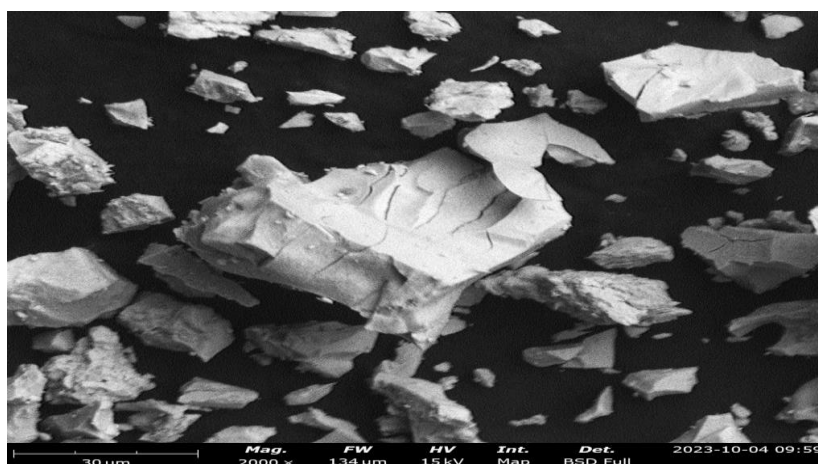


Figure 3.2b: SEM image for Cerium Oxide

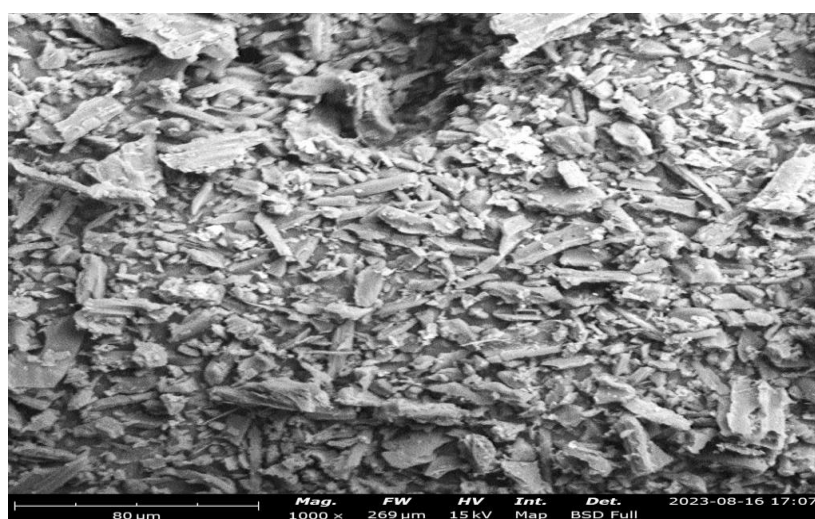


Figure 3.2c: SEM image for Graphene oxide

The image of graphene oxide indicates the existence of fewer stacks indicating that there has been exfoliation of the structure on graphite. The graphene nano sheets have a ripple surface, a smaller and uniform size of

particles and pore size, has a randomly arranged aggregate with a thin layer and is tightly linked to one another to form an irregular solid (Wei *et al.* 2020).

3.5 Energy Dispersive X-Ray Spectroscopy

Figure 3.3a below showed the EDX spectrum of CeO₂ nanoparticle which revealed the chemical composition of the sample. The chemical composition of the CeO₂ was found to be Ce = 37.22% and O = 60.84% which confirm the presence of CeO₂.

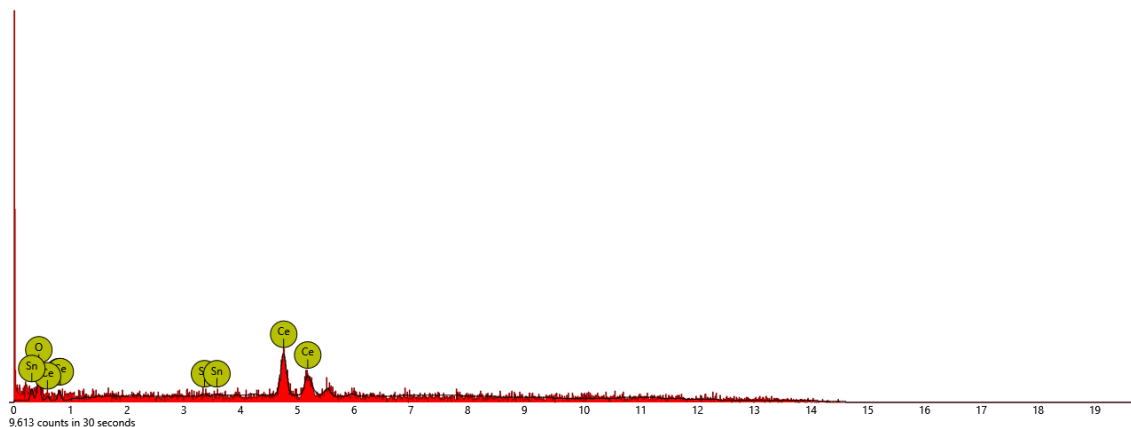


Figure 3.3a: EDX spectrum of cerium oxide

Table 3.1: Elemental Composition of Cerium Oxide

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
8	O	Oxygen	60.84	15.16
58	Ce	Cerium	37.22	81.26
50	Sn	Tin	1.94	3.58

Figure 3.3b below showed EDX spectrum of acetylene black paste electrode which revealed the chemical composition of the sample. The chemical composition of the electrode was found to be C = 47.09% and O = 45.57%.

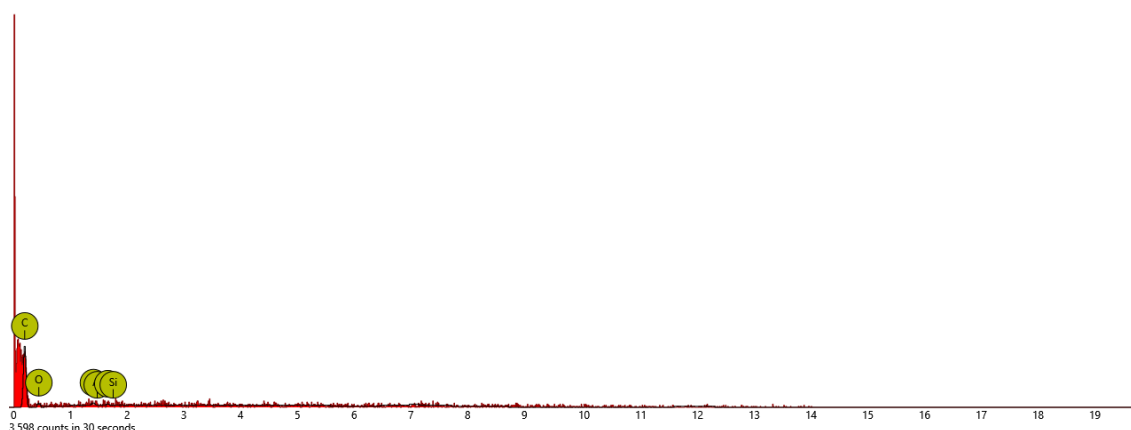


Figure 3.3b: EDX spectrum of ABPE

Table 3.2: Elemental Composition of ABPE

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	55.71	47.09
8	O	Oxygen	40.47	45.57
13	Al	Aluminium	2.65	5.03
14	Si	Silicon	1.17	2.31

Figure 3.3c showed EDX spectrum of GO which revealed the chemical composition of the sample. The chemical composition of the GO was found to be C = 15.24% and O = 84.76% which confirm the presence of GO.

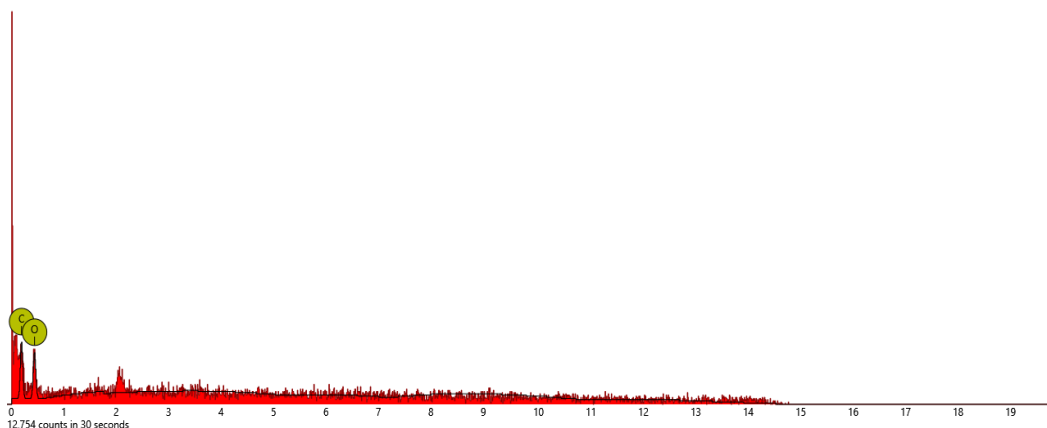


Figure 3.3c: EDX spectrum of Graphene Oxide (GO)

Table 3.3: Elemental Composition of GO

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
8	O	Oxygen	80.68	84.76
6	C	Carbon	19.32	15.24

3.6 Electrochemical Characterization

3.6.1 Cyclic Voltammetry

The $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple was used for the electrode characterization and the electrochemical response from $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple can reflect the conductivity of the electrode interface. The electrochemical behaviors of different modified electrodes were investigated in 1.0 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 0.1 M KCl mixture solution with cyclic voltammogram shown in Figure 3.4 (a and b) at a bare ABPE, a pair of symmetric quasireversible CV peaks appeared with cathodic peak potential (E_{pc}) of 0.4 V and anodic peak potential (E_{pa}) of - 0.1 V. The peak-to-peak separation (ΔE_p) was 500 mV. After GO was electrochemically reduced, the electrochemical behavior was dramatically improved with the ΔE_p , of the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ which was due to the high conductivity and the reactive edge defects of GR.

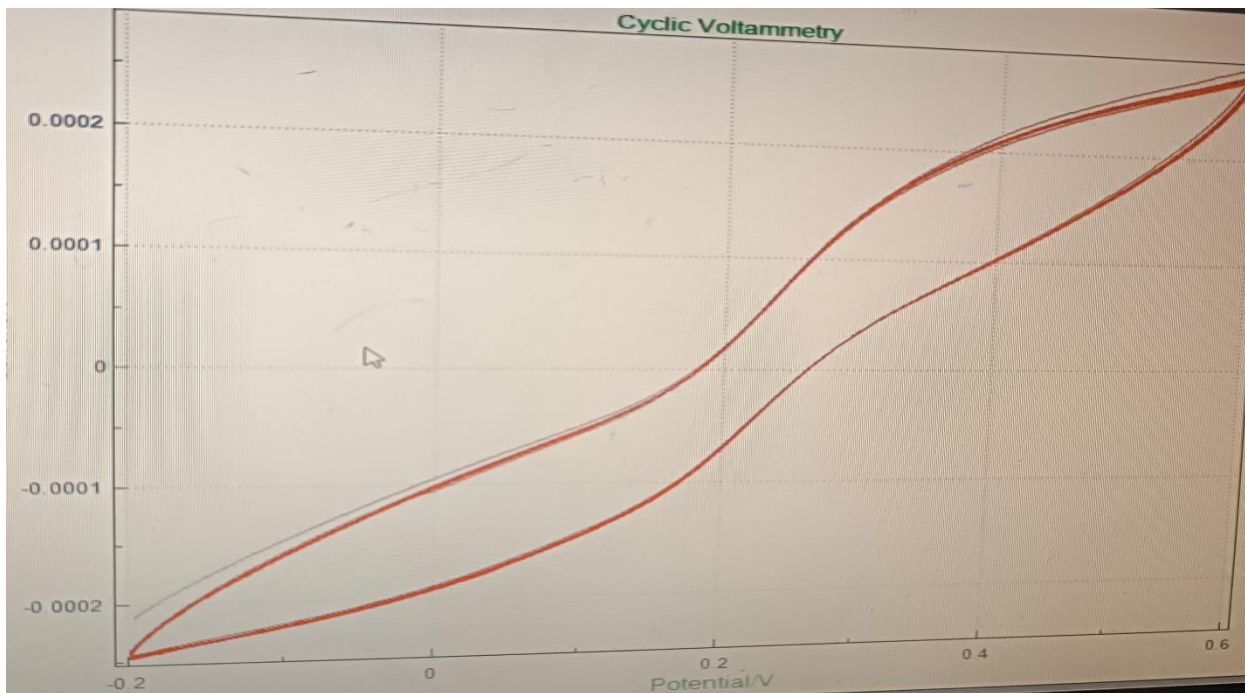


Figure 3.4a: cyclic voltammogram of ABPE

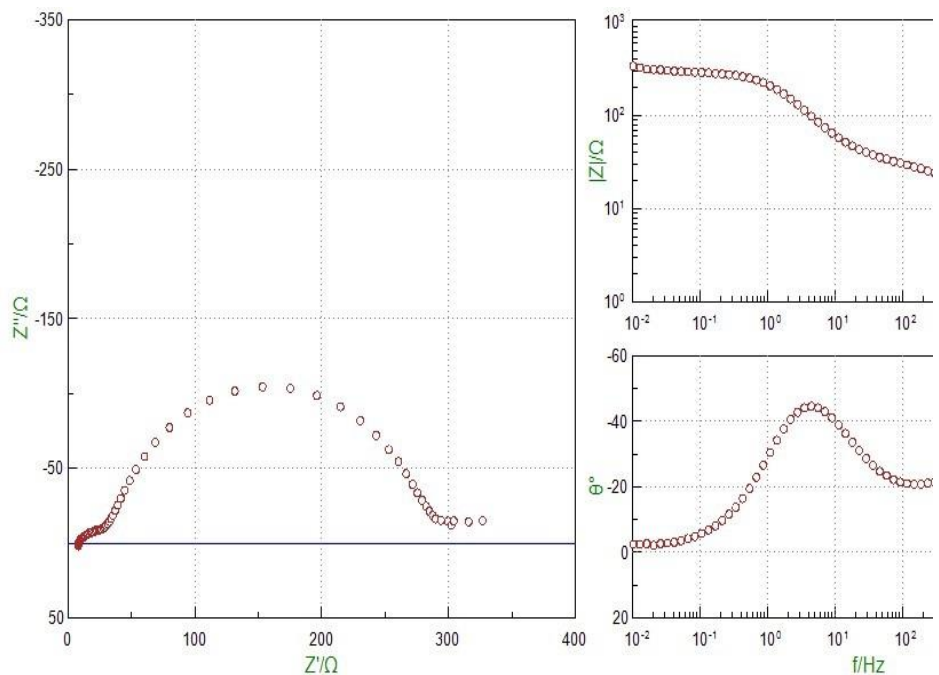


Figure 3.4c below showed the EIS curve of the prepared cerium (IV) oxide graphene oxide-acetylene black paste electrode (CeO₂-GO/ABPE). The large sinusoidal curve observed at the Bode and Nyquist curve confirm the high sensitivity and conductivity capacity of the modified electrode which in turn serve as a good sensor for the organic pollutant.

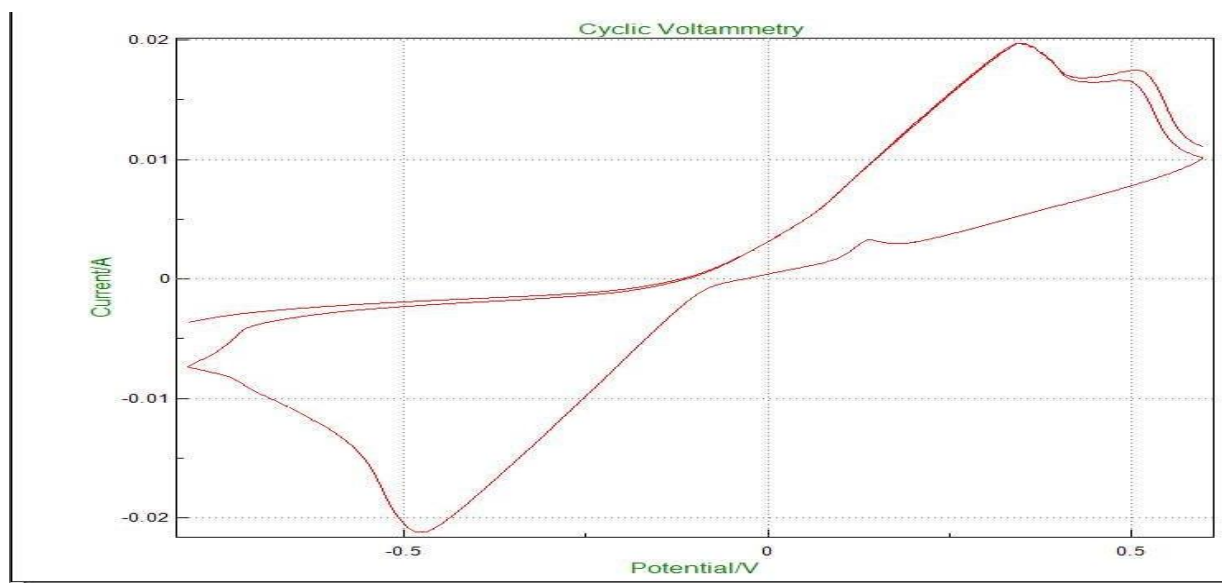


Figure 3.4c: EIS curve of the prepared cerium (IV) oxide graphene oxide-acetylene black paste electrode (CeO₂-GO/ABPE).

4. Conclusion

In this present work, a new modified electrode based on electrochemical reduction of exfoliated graphene oxide sheets on the surface of an acetylene black paste electrode (denoted as CeO₂-GO/ABPE) was introduced. Graphene oxide and cerium oxide were successfully synthesized via Hummers and precipitation method. The synthesized materials were characterized by subjecting them to several spectroscopic techniques such as FT-IR, SEM XRD, and EDS. The prepared electrodes were tested for electrochemical technique using cyclic voltammetry and electrochemical impedance spectroscopy (EIS). The modified electrode proved to be a promising one due to large surface area of acetylene black and high conductive property together with nano cerium oxide as catalyst for the electrochemical sensing.

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