UtilitasMathematica

ISSN 0315-3681 Volume 122 (2), 2025

MORPHOLOGICAL, OPTICAL AND CYCLIC VOLTAMMETRY STUDIES ON HAFNIUM OXIDE NANOPARTICLES

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Abstract

Hafnium oxide nanoparticles were synthesized through the microwave-assisted chemical method. The as-prepared samples were calcined at 700 °C. The synthesized hafnium oxide nanoparticles were characterized by Scanning Electron Microscope with energy dispersive spectroscopy and UV-visible spectroscopy. The scanning electron micrographs of the materials showed uniform distribution of particles. Energy dispersive spectroscopy confirms the purity of the prepared sample. UV-Visible spectrum hafnium oxide nanoparticles showed the minimum absorption in the entire visible region. The energy bandgap of the synthesized hafnium oxide nanoparticles was determined through Tauc plot and found to be 5.65 eV. The cyclic voltagram of the hafnium oxide nanoparticles were studied through electrochemical impedance analyzer. The specific capacitance and energy density of hafnium oxide nanoparticles were determined.

Key words: Hafnium oxide, Microwave assisted, SEM, UV-Vis, Electrochemical

Introduction

The rapid advancement of nanotechnology has fostered the development of engineered nanoparticles with unique and tunable physicochemical properties. Hafnium oxide (HfO_2) nanoparticles have attracted widespread interest due to their combination of high chemical and thermal stability, wide band gap, elevated dielectric constant, and significant optical transparency across the UV–vis–NIR spectrum. These characteristics make HfO_2 nanoparticles promising for a wide range of applications, spanning microelectronics, optoelectronics, catalysis, biosensing, energy storage, and emerging biomedical uses such as radiotherapy enhancement and imaging [1-4].

Structurally, HfO_2 nanoparticles can be synthesized using a diverse array of techniques, including sol-gel, hydrothermal, laser ablation, and magnetron sputtering methods, each offering precise control over morphology, crystallinity, particle size, and surface chemistry. Morphological attributes, such as phase composition, particle size distribution, and surface area, play a decisive role in dictating the nanoparticles' functional characteristics. Comprehensive analyses using X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) have revealed that HfO_2 nanoparticles may exist in monoclinic, tetragonal, or hexagonal phases, with grain sizes tunable from the few-nanometer scale to several tens of nanometers; these nanostructures can also display core-shell architectures in air [5-11].

Optical properties of HfO_2 nanoparticles are central to their integration into cutting-edge devices. The wide band gap (~5.3–5.7 eV), high refractive index, and strong absorption across UV-Vis-NIR regions offer opportunities for developing efficient photonic components and coatings. Furthermore, engineered HfO_2 nanoparticles have demonstrated suitability as radiosensitizers and contrast agents in clinical imaging due to their high atomic number, mass attenuation coefficient, and physiological inertness, enabling targeted delivery and energy deposition for cancer therapy [12-13].

Electrochemical characterization, particularly through cyclic voltammetry (CV), provides critical insight into the redox activity, charge storage mechanisms, and electron transfer dynamics in HfO_2 nanoparticles. These properties form the basis for their application in next-generation capacitors, sensors, and electrocatalytic systems. Systematic studies coupling CV with detailed morphological and optical analyses are vital for optimizing performance and clarifying the structure–function relationships in these advanced materials [14-15].

Overall, the multifaceted nature of HfO_2 nanoparticles—their accessible synthesis, tunable morphology, impressive optical and dielectric properties, and robust electrochemical performance—drives ongoing research at the intersection of fundamental science and practical technology development. In this context, comprehensive morphological, optical, and cyclic voltammetry studies enable a deeper understanding and broader utilization of HfO_2 nanoparticles in diverse scientific and engineering disciplines.

Materials and Methods

AR grade hafnium chloride and urea were taken in different ratios of 1:3 and dissolved in 100 ml of ethylene glycol. The solution was stirred for one hour to reach homogeneity. Then the solutions were kept in a microwave oven and subjected to microwave irradiation (2.45 GHz and 800 W) until complete precipitation. The resulting colloidal precipitates were filtered and washed with deionized water and acetone to remove the organic contaminants. The obtained sample was dried in atmospheric air and calcined at 800ºC to remove the residual in the samples. Then the synthesized hafnium oxide nanoparticles were stored for the characterization studies.

Results and Discussion

The morphology and surface features of the samples were characterised using Scanning Electron Microscopy (SEM), a widely used imaging technique for nanomaterials. The SEM image, captured at a magnification of 10,000× and an accelerating voltage of 20 kV, reveals detailed surface characteristics of the synthesised hafnium oxide nanoparticles. Figure 1 represents the scanning electron microscopy images of hafnium oxide nanoparticles for the various magnification.

The observed particles mostly exhibit irregular shapes and agglomeration, with grain sizes ranging broadly across the sample. Some larger, brighter grains are present, potentially pointing toward localized regions of agglomeration or the presence of unreacted precursor or dopant-rich zones. Most grains are within the sub-micron domain, aligning with the expected nanostructured profile of hafnium oxide nanoparticles [9].

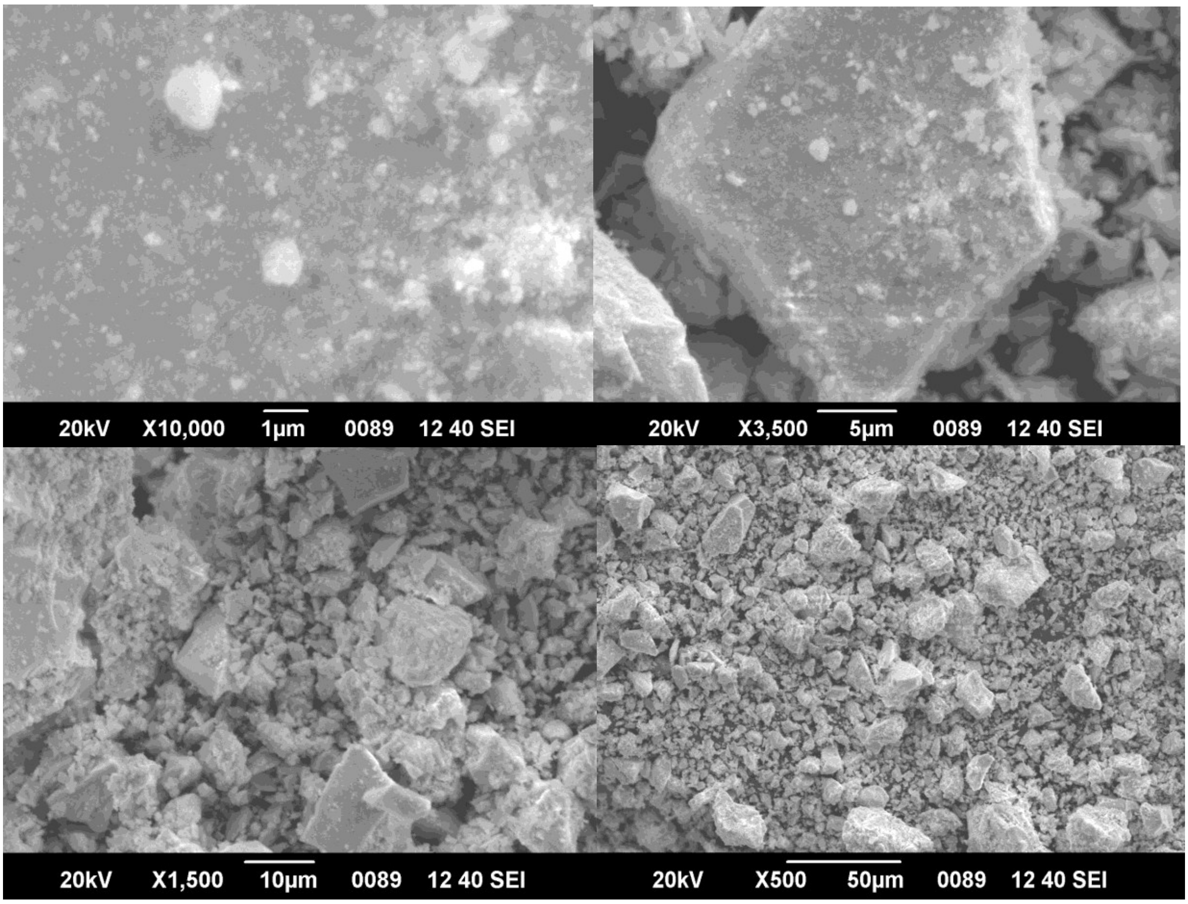

Figure 1: Scanning Electron Microscopy image of the hafnium oxide nanoparticles

Agglomeration is noted within the sample, a typical feature in oxide nanoparticles attributed to their elevated surface energy. Nevertheless, the microstructure appears relatively dense, and the rough texture of the surface may arise from accelerated nucleation rates during synthesis, possibly favoured by microwave-assisted methods. The absence of cracks, pores, or phase-segregated domains in the micrograph further suggests that the integration of dopants does not adversely affect the morphological stability of hafnium oxide nanoparticles.

Energy Dispersive X-ray Spectroscopy (EDS), when coupled with Scanning Electron Microscopy (SEM), represents a pivotal technique for the in-depth analysis of the elemental composition within nanomaterials, providing qualitative and quantitative insights into their chemical makeup. In the present investigation, EDS was performed on synthesized hafnium oxide (HfO_2) nanoparticles, as depicted in Figure 2. The resulting spectrum distinctly exhibits strong, well-defined peaks corresponding to both hafnium (Hf) and oxygen (O), substantiating the presence of these two elements as the primary constituents of the sample.

Notably, the absence of any extraneous peaks related to potential impurities or foreign elements underscores the chemical integrity and compositional purity of the synthesized nanoparticles. Such results are indicative of a successful synthesis approach, yielding hafnium oxide nanoparticles devoid of detectable contamination, which is critical for applications requiring high chemical purity. Furthermore, the stoichiometry inferred from the EDS profile suggests an appropriate Hf:O atomic ratio consistent with the expected formula of HfO_2, reflecting effective control during the synthesis process [10].

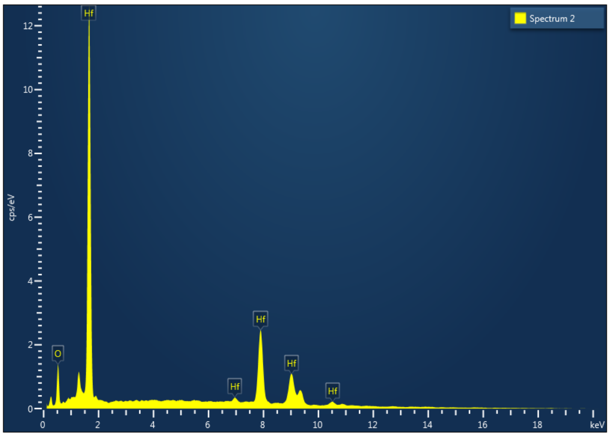

Figure 2: EDS spectra of hafnium oxide nanoparticles

The optical properties of the synthesized hafnium oxide (HfO_2) nanoparticles were examined using UV–Visible absorption spectroscopy over the wavelength range of 200–800 nm. The absorption spectrum is illustrated in Figure 3.

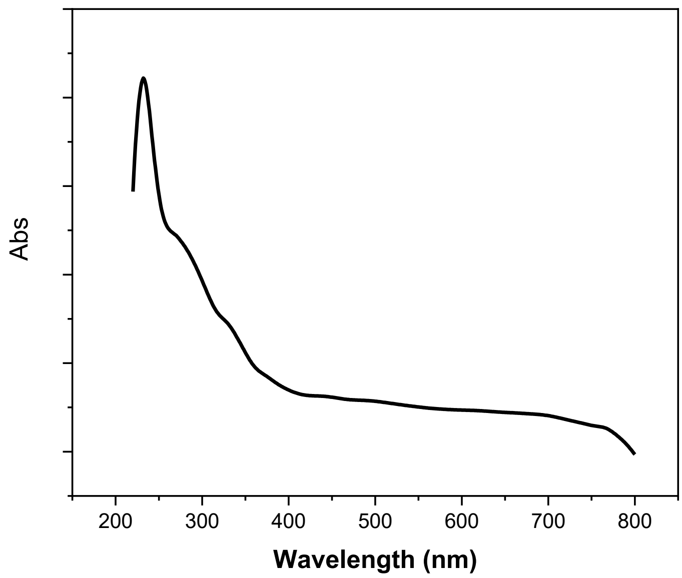

Figure 3: UV-Visible absorption spectrum of hafnium oxide nanoparticles

An intense absorption peak was detected near 262 nm, which corresponds to intrinsic band-to-band electronic transitions in hafnium oxide (HfO_2) nanoparticles. Alongside this, a broad absorption shoulder appeared around 371 nm, likely attributable to surface states, defect-related energy levels, or oxygen vacancies commonly found in nanostructured HfO_2 materials. These features are indicative of the complex electronic structure associated with such nanomaterials.

The pronounced absorption edge at 262 nm signifies the presence of a wide band gap in HfO_2, reinforcing its semiconducting character and underscoring its suitability for applications in dielectric and optoelectronic devices. Meanwhile, the additional shoulder at longer wavelengths suggests the existence of sub-bandgap energy levels, often caused by localized defects or a degree of lattice disorder within the crystal framework [16].

Optical band gap values for both pure and doped HfO_2 nanoparticles were derived through Tauc plot analysis, utilizing ultraviolet-visible (UV–Vis) absorption data. Figure 4 illustrate the Tauc plots for the sample.

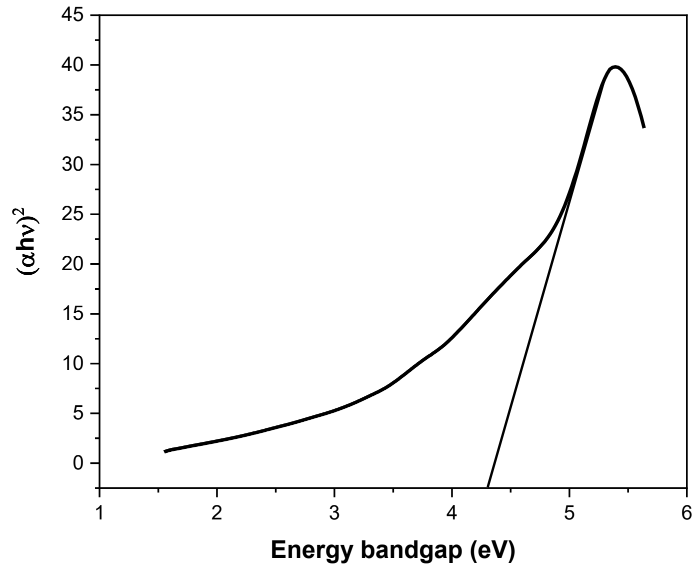

Figure 4: Tauc plot of hafnium oxide nanoparticles

The pure HfO_2 sample displayed a wide optical band gap of approximately 4.35 eV, which aligns with the known monoclinic structure and indicates a low density of defect states that could otherwise reduce the band gap.

The cyclic voltammetry (CV) technique provides vital information regarding the nature of the charge storage mechanism. This measurement was carried out in a conventional three-electrode setup using hafnium oxide nanoparticles as the working electrode, platinum wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. A 6 M KOH aqueous solution was employed as the electrolyte. Figure 5 represents the cyclic voltagram of the hafnium oxide nanoparticles.

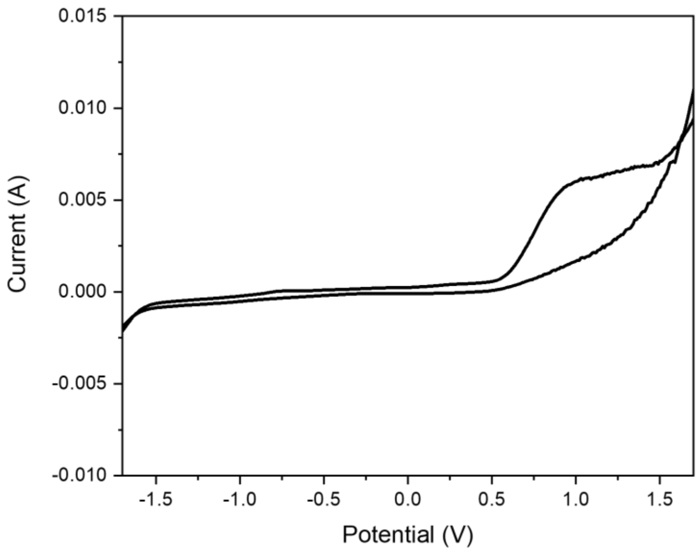

Figure 5: Cyclic voltagram of hafnium oxide nanoparticles

The cyclic voltammetry (CV) response displayed a nearly rectangular shape without distinct redox peaks, indicating ideal pseudocapacitive behaviour with fast surface-controlled charge storage. The specific capacitance calculated from the CV curve was 34 F g^{-1}**,** confirming efficient charge accumulation within the electrode material. Based on this, the energy density was determined using, yielding 272 J g^{-1}**.** This result highlights the electrode's ability to deliver high energy density while maintaining stable pseudocapacitive characteristics, making it a promising candidate for next-generation supercapacitor applications.

Conclusion

The synthesized hafnium oxide (HfO_2) nanoparticles exhibit irregular, agglomerated morphology with a dense microstructure, as revealed by SEM analysis. EDS confirms high chemical purity with no detectable contaminants, indicating successful synthesis. Optical studies show a sharp absorption peak at 262 nm and a shoulder at 371 nm, corresponding to intrinsic band-to-band transitions and defect-related states, respectively. The estimated optical band gap of 5.65 eV highlights the semiconducting nature of HfO_2. Electrochemical analysis via cyclic voltammetry demonstrates ideal pseudocapacitive behaviour with a specific capacitance of 34 F g^{-1} and an energy density of 272 J g^{-1}. These findings suggest that the microwave-assisted synthesis method yields high-quality HfO_2 nanoparticles with promising applications in optoelectronics, dielectrics, and energy storage devices. The combined morphological, compositional, optical, and electrochemical properties position HfO_2 as a versatile material for advanced technologies.

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