Fabrication of Gd$_2$O$_3$ Nanosheet-Modified Glassy Carbon Electrode for Nonenzymatic Highly Selective Electrochemical Detection of Vitamin B2

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ABSTRACT: A novel Gd$_2$O$_3$ nanosheet was synthesized by the template-free chemical coprecipitation method. Interestingly, upon calcination at 600 °C, nanoparticles were transformed into a nanosheet, as observed from field emission scanning electron microscopy (FESEM) images. An increase in the calcination temperature to 600 °C increases the particle size to 50 nm, which results in aggregation. A sheetlike Gd$_2$O$_3$ exhibits superparamagnetism from 300 K. The highly selective nonenzymatic sensing of riboflavin (RF) was studied using a modified glassy carbon electrode with Gd$_2$O$_3$ nanosheets, and its various applications were made possible by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The redox behavior of the RF was determined. The newly fabricated sensor showed high sensitivity, stability, and reproducibility and was also tested with a commercial vitamin B2 tablet and a milk powder sample.

INTRODUCTION

The changes in the particle size and morphology of various transition-metal oxides, which influence the properties of nanoparticles, are a great challenge in research. In recent decades, gadolinium oxide (Gd$_2$O$_3$) has received much attention because of its excellent optical and paramagnetic magnetic properties compared to those of rare-earth oxides and its potential applications in magnetic-luminescence dual-mode probe materials. The dual-mode probe is used in many ways, which overcomes the deficiencies of the one-mode probe, such as low biological penetration, low sensitivity, and hard to real-time imaging.

Various strategies are used to prepare nanostructured Gd$_2$O$_3$ materials through different chemical methods. Chemical coprecipitation is a simple and cost-effective method for the preparation of nanosized materials with best morphology and increased physical properties. This method produces materials with better properties for industrial applications.

Meanwhile, riboflavin (RF) is an important vitamin for human nutrition that appears in various food products. In our body, RF is converted into two active coenzymes, flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD). RF is absorbed by RF receptors, which are expressed as both soluble and membrane-bound isoforms. Multiple-acyl-CoA dehydrogenation deficiency, an autosomal recessive disorder, responds well to treatment with RF. The complex formation with RF and ultraviolet-A treatment increases gene mutations 7 times higher than that with UV radiation exposure alone. From the problems can be caused by the effect of RF concentrations in urine. Therefore, the RF concentration level was measured to treat the diseases. Different electrochemical techniques are used to determine the effect of RF. Among these techniques, electrochemical processing has received considerable attention due to its high sensitivity, selectivity, low cost, high sensitivity, long-term reliability, reproducibility, and convenience.

Recently, electrochemically pretreated glassy carbon electrode (GCE) is used to determine riboflavin concentration by voltammetric methods. Cr-doped SnO$_2$ for riboflavin sensing has been reported in the literature. Govindan et al. investigated the microwave-assisted synthesis of Ce-doped SnS$_2$ nanoflowers for enhanced vitamin B2 sensing. Madhuvilakku et al. reported the flowerlike structure of Fe$_3$O$_4$-anchored RGO nanocomposites for the electrochemical detection to measure riboflavin concentration.

In the present work, the size dependence of Gd$_2$O$_3$ crystallites on their physicochemical properties is well defined. Gd$_2$O$_3$ nanosheets prepared by the coprecipitation method were calcined at the crystallization temperature. Calcination temperature is a key factor to control the magnetic and
biosensing behaviors of Gd$_2$O$_3$ nanosheets. In addition, the RF values are determined by the differential pulse voltammetry (DPV) method.

**RESULTS AND DISCUSSION**

**Structural Analysis.** The phase and the crystalline nature of Gd$_2$O$_3$ nanoparticles were measured by the X-ray diffraction method. The X-ray diffraction pattern of the as-synthesized Gd(OH)$_3$ is shown in Figure 1A (a). Diffraction peaks are observed in the hexagonal phase with $2\theta$ values of 30.01, 41.14, and 50.78, in agreement with the literature. After calcination, the revealed cubic phase of Gd$_2$O$_3$ is confirmed by the X-ray diffraction (XRD) pattern shown in Figure 1b, and this phase is well matched with JCPDS card no 11-0608. The crystallite size and strain of Gd$_2$O$_3$ nanoparticles were estimated using the Debye–Scherrer formula.

The average crystallite size of Gd$_2$O$_3$ NPs is found to be $\sim$30 nm, and increasing crystalline size from 30 to 42 nm with an increase of calcination temperature indicates the improvement of crystallinity and phase purity of the calcinated sample. An increase in the calcination temperature regulates the atomic migration and induces the coalescence of atoms, thereby leading to the formation of large crystals. The larger crystallite size indicates the good crystalline nature of the nanoparticles. An increase in the purity of Gd$_2$O$_3$ reduces the defect rate of dislocations of the nanomaterial matrix.

**FTIR Analysis.** The FTIR spectra of the as-synthesized and calcined Gd$_2$O$_3$ NPs are shown in Figure 1B. The O$\cdots$H asymmetric stretching band observed at 3457 cm$^{-1}$ is attributed to the adsorbed water, and the C$\cdots$H stretching band is found at 2927 cm$^{-1}$. The strong OH bending vibration band shows splitting at 2347 cm$^{-1}$, which is attributed to the mixed gadolinium oxide and hydroxide. The Gd$\cdots$O stretching band at 564 cm$^{-1}$ can be assigned to Gd$_2$O$_3$, which also confirms the formation of the material.

**Morphological Analysis.** The FESEM images of the Gd$_2$O$_3$ nanoparticles as prepared and calcined at 600 °C are shown in Figure 2. Figure 2a,b shows that the as-prepared Gd(OH)$_3$ nanoparticles exhibit microsphere-like structures with a high degree of agglomeration. Figure 2c,d shows uniform-sized sheet-shaped Gd$_2$O$_3$ nanoparticles. It is noted from the chemical synthesis process that the particles are
agglomerated by increasing the calcination temperature, and finally, nanoparticles with larger dimensions are formed.\textsuperscript{23,24} This modification of morphology and crystallites changes is good aggregated with diffraction peaks are high intense and peaks are narrow by subjecting the sample for calcinations temperature.

**Photoluminescence Studies.** Figure 3\textsuperscript{a,b} shows the photoluminescence spectra of as-prepared Gd(OH)\textsubscript{3} nanoparticles and Gd\textsubscript{2}O\textsubscript{3} nanosheets, respectively, and excitation wavelength at 350 nm. The PL spectra of Gd\textsubscript{2}O\textsubscript{3} nanoparticles show emission peaks at 407, 420, 459, 486, and 518 nm. The blue emission is around 459 nm, and the green emission is around 515 nm. The strong blue emission at 407–486 nm is attributed to various types of surface defects of Schottky and Frenkel types. The oxygen vacancies and the interstitial and surface defects in the metal oxide systems can be attributed to the modified photoluminescence response.\textsuperscript{25–27}

The green emission peaks range between 515 and 540 nm, due to the stark-level transition from the G band charge transfer state of the Gd\textsuperscript{3+} ion. The nanostructure phase and the enhanced oxygen vacancy of the prepared sample at 600 °C calcination exhibit increased intensity of emission peaks.

**Raman Analysis.** Raman spectroscopy is used to determine the formation of the desired phase and the presence of impurities and structural defects, etc. Le Luyer et al. investigated both monoclinic and cubic phases for Gd\textsubscript{2}O\textsubscript{3} theoretically and experimentally by Raman spectroscopy,\textsuperscript{28} and Zarembowitch et al. reported the monoclinic B-type form experimentally.\textsuperscript{29}

Figure 4 shows the cubic Gd\textsubscript{2}O\textsubscript{3} by micro-Raman spectrometry. A 514.5 nm incident radiation from an argon laser was used in the experiment. The Raman bands are located in the region between 100 and 600 cm\textsuperscript{-1}. The Raman-active modes are 4E\textsubscript{g}, 4A\textsubscript{u}, 14F\textsubscript{g}, 5E\textsubscript{u}, 5A\textsubscript{u}, and 16F.\textsuperscript{30} All of the grade (g) modes are Raman-active, whereas the E\textsubscript{g} and A\textsubscript{u} modes are Raman-inactive and the F\textsubscript{g} mode is infrared-active.\textsuperscript{30} However, the Raman-active modes for the cubic phase are found to be 159, 259, 358, 438, and 561 cm\textsuperscript{-1}. The strongest Raman peaks are observed at 159 and 358 cm\textsuperscript{-1}. There is no formation of impurity phase rather than the Gd\textsubscript{2}O\textsubscript{3} nanoparticles.

**X-ray Photoelectron Spectroscopy (XPS) Studies.** The elemental composition of materials can be identified by XPS and is found to be effective to determine the characteristics (valence) of the constituent atoms (ions) by displaying binding energies. The Gd 3d high-resolution XPS spectra consist of a Gd 3d spin–orbit doublet located at 1222.6 and 1198.2 eV, which is attributed to the Gd 3d\textsubscript{5/2} and Gd 3d\textsubscript{3/2} oxidation states, and three satellite peaks 1232.3, 1238.7, and 1243 eV are found for Gd 3d\textsubscript{5/2}, as shown in Figure 5a. This indicates that the Gd ions in the NPs contain +3 oxidation states observed in the form of Gd\textsubscript{3}O\textsubscript{4}.

The O 1s oxidation states of Gd\textsubscript{2}O\textsubscript{3} NPs are shown in Figure 5b. The O 1s peak located at 533 eV, as shown in the high-resolution O 1s XPS spectrum, is attributed to Gd–O species, further indicating the existence of Gd\textsubscript{2}O\textsubscript{3}. In the calcinated samples, a small shift was observed in the binding energy value of the sharp peak (532.8 eV) and, at the same time, an additional shoulder peak was observed at 531.1 eV.\textsuperscript{31,32} This shoulder peak is attributed to the residual oxygen groups like –OH, C=O, and = O/C–O, due to the coordination of oxygen in Gd–O–Gd.

**Magnetic Behavior.** Figure 6 displays magnetization (M) as a function of applied magnetic field for the Gd(OH)\textsubscript{3} and calcinated Gd\textsubscript{2}O\textsubscript{3}. These samples show paramagnetism at room temperature. The Gd(OH)\textsubscript{3} and calcinated Gd\textsubscript{2}O\textsubscript{3} samples do not reach the saturation value when a magnetic field strength of 20 000 Oe was applied. The magnetic field M of the Gd(OH)\textsubscript{3} sample is lower than that of calcinated Gd\textsubscript{2}O\textsubscript{3} when the applied field is 20 000 Oe. The magnetization is increased with increasing calcination temperature, which may need more energy for the formation of nucleation particles and can be provided by the higher temperature. Higher energy can alter the local environment of the Gd\textsuperscript{3+} state, which is reflected in the luminescence, leading to an improved order–order degree.\textsuperscript{33,34} On the other hand, the higher annealing temperature results in the removal of residual carbon and the reduction of the nonmagnetic component.

**Nonenzymatic Electrochemical Detection of Vitamin B2 (riboflavin) at Gd\textsubscript{2}O\textsubscript{3} Nanosheet-Modified Glassy Carbon Electrode.** To study the electrochemical behavior of Gd(OH)\textsubscript{3} and Gd\textsubscript{2}O\textsubscript{3}-fabricated electrodes through the riboflavin (RF) oxidation, we investigated the fabricated electrode using cyclic voltammetry (CV) in the absence (solid line) and presence (dotted line) of 0.1 mM RF solution in 0.1 M phosphate-buffered saline (PBS, pH 7.4) at a scan rate 50 mV s\textsuperscript{-1} in the potential window −0.6 to 0.2 V, as shown in Figure 7A. It is clearly seen in Figure 7A (curve b) that Gd(OH)\textsubscript{3}-modified GCE does not display any oxidation peak on RF, suggesting that the kinetics are slow due to the weak adsorption of RF. However, the excellent redox peak shown in Figure 7A (curve d) indicates an enhancement of the RF oxidation current (1.18 μA) for the Gd\textsubscript{2}O\textsubscript{3}-modified GCE compared to Gd(OH)\textsubscript{3} (0.89 μA). Liu et al. and Anacia Grace
et al. calculated the number of electron transfers occurring in this electrochemical reaction using the following formula:

\[ i_p = \frac{nFQ}{4p} \nu \frac{R}{T} \]

where \( n \) is the number of electrons transferred, \( F \) is the Faraday constant (96,500 C mol\(^{-1}\)), \( Q \) is the electric quantity (C), \( R \) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), \( T \) is the temperature (298 K), and \( \nu \) is the scan rate (V s\(^{-1}\)). From this equation, the \( n \) value is calculated to be 1.91 e\(^{-}\), which is approximately two electrons. This result indicates the two-electron two-proton oxidation/reduction reaction in the electrocatalysis reversible reduction of RF at the Gd\(_2\)O\(_3\)-modified electrode.

**Effect of Scan Rate.** The kinetics of electrode reaction in the presence of 0.1 mM RF in 0.1 PBS is investigated using CV by measuring the effect of scan rate (Figure 7B). Cyclic Voltammogram of Gd\(_2\)O\(_3\)-GCE was performed in PBS (pH 7.4) containing 0.1 mM of RF with effect of scan rate. The PBS (pH 7.4) containing 0.1 mM of RF was saturated with nitrogen gas to remove the dissolved oxygen evaluation. The anodic and cathodic (redox) peaks current were increased with the increasing scan rate (10 to 100 mV/S) that confirm the diffusion controlled reaction.

**Effect of Riboflavin Concentration by DPV.** Figure 8 shows highly sensitive differential pulse voltammetry (DPV) curves, which are widely investigated for the sensitivity of the Gd\(_2\)O\(_3\)-GCE-fabricated electrode through riboflavin detec-
tion. It exhibits the DPV behavior at different concentrations of RF sensing ranging from 0.1 to 550 μM at the Gd2O3−GCE-modified electrode. The well-defined and stable oxidation current is increased with increasing concentration of RF. This result indicates that the Gd2O3−GCE-modified electrode has good electrocatalytic activity toward RF sensing. A plot of peak current vs concentration displays three linear ranges, 0.1−100, 100−400, and 400−550 μM, with correlation coefficients of 0.902, 0.98, and 0.58, respectively. The detection limit is found to be 10 nM.

Stability and Reproducibility of the Gd2O3 Electrode. Different pretreatment processes can be followed to achieve faster electron transfer rates and more reproducible results. These results increase in the surface and other functional groups, which can then catalyze the oxidation/reduction of the analyte.

As even 100 repeated continuous electrochemical cycles in 0.1 mM RF solution (Figure 9A) do not modify the film stability and do not cause leaching of the adsorbed RF, it can be concluded that RF strongly oxidizes the modified electrode surface.\(^{37,38}\) Moreover, the contact of the modified electrode with air does not cause loss of electroactivity. The strong binding is believed to be due to the P−P interaction of the aromatic ring, as well as the NH group of RF with Gd2O3 nanosheets deposited on the modified electrode. Figure 9B clearly shows that after the fifth cycle, the peak current is decreased dramatically compared to the first cycle. These results indicate that the material is falling off from the electrode. Gd2O3 shows higher stability compared to the Gd(OH)3-modified electrode. Hence, only the Gd2O3−modified electrode was used for sensing application. To ascertain the reproducibility of the results, different GCEs were modified with Gd2O3, and their response toward the oxidation of 0.1 μM RF was tested (Figure 9C). With the measurements of 10 independent electrodes obtained, the peak current showed a relative standard deviation of 3.75%, confirming the high reproducibility of the results. The fabricated RF sensor performance was comparable to the early literature values. The comparative data suggest that the present sensor has good sensitivity over some reported RF sensors, the possible reason being the high surface area and good electrocatalytic activity of Gd2O3.

Selectivity Analysis. The Gd2O3 behavior toward RF sensing was investigated using the DPV technique in the presence of potential interferences like uric acid, dopamine, epinephrine, serotonin, biotin, etc. (Figure 10). These potential interferences were 0.5 mM each.

Figure 9. (A) Stability of GCE-Gd2O3− and (B) GCE-Gd(OH)3-modified electrodes for 100 cycles in the presence of 0.1 mM RF at a scan rate of 50 mV s\(^{-1}\). (C) Reproducibility of RF for 10 times.

Figure 10. DPV response of GCE-Gd2O3 for 0.5 mM RF in the presence of 0.5 mM interferences; UA: uric acid, DA: dopamine, EP: epinephrine, ST: serotonin, BT: biotin.
interferences are added at a specific concentration (0.5 mM). No signal interference is observed for these molecules, which confirms the high selectivity of the sensor toward RF. Potential interferences like dopamine (DA), epinephrin (EP), biotin (BT), serotonin (ST), and uric acid (UA) were highly active on the bare glassy carbon electrode surface during Gd2O3 fabrication. However, these results indicate that the newly fabricated sensor is highly selective, stable, reproducible, and practically usable.

**Determination of RF in Real Samples.** The modified electrode for the determination of RF was verified through the analysis of real samples. The determination of RF was applied in a modified Gd2O3 electrode in tablet (Figure 11A) and milk powder (Figure 11B) samples using the DPV technique. The milk powder sample and the RF tablet were fabricated before the sensor calculation as follows: starting, the milk powder was weighed and then dissolved in PBS in pH 7.4. Figure 11A shows the similar concentrations of commercially obtained RF (0.5 mm, curve b) and vitamin B2 tablet (obtained from medical shops in our region). Both samples are similar oxidizers with well-defined oxidation peak current and potential. This result indicates a 100.9% recovery of RF in the tablet sample compared to the commercial sample. A similar experiment was conducted for the detection of RF in milk powder (Figure 11B).

**CONCLUSIONS**

The structural, morphological, magnetic behavior and the highly selective nonenzymatic sensing of riboflavin (RF) were investigated using Gd2O3 prepared by the template-free coprecipitation method. XRD spectra indicated that the as-synthesized Gd(OH)3 and calcinated Gd2O3 exhibit monoclinic and cubic crystal phases. The surface morphology was investigated by FESEM analysis. Increased crystallinity and modification of specific morphology were used to control the magnetic and biosensing behavior of the Gd2O3 nanosheets. The voltammetric behavior of the Gd2O3 nanosheets has been investigated using RF, and also the measurement of RF in the buffer solution by an analytical method in real samples was investigated. The Gd2O3-enhanced catalytic behavior of the redox of RF was used for the determination. The DPV technique with optimized experimental conditions was used for the determination of RF in buffer solution. Gd2O3-GCE was utilized to detect RF, and the obtained results showed good sensitivity, stability, selectivity, and reproducibility. Furthermore, the proposed sensor effectively interacts with and without any additives or DNA, leading to the sensitive detection of different concentrations of RF. All of these advantageous features can lead to applications in medical, food, and other areas.

**EXPERIMENTAL MATERIALS**

Gadolinium(III) nitrate hexahydrate [Gd (NO3)3·6H2O] and dopamine were procured from Sigma Chemicals (Madrid, Spain). Propylene carbonate, ascorbic acid, riboflavin, epinephrin, biotin, serotonin, magnesium chloride, uric acid, potassium chloride, glucose, sodium chloride, sucrose, calcium chloride, fructose, sodium dihydrogen phosphate, sodium monohydrogen phosphate, and sodium hydroxide (NaOH) pellets were procured from Thermo Fisher Scientific, India. All other solvents and chemicals are of analytic pure grade. Double-distilled (DD) water was used throughout the process. Phosphate buffer (PB, 0.1 M) with pH 7.4 was used for the preparation of CPZ standards and electrochemical measurements.

**Synthesis of Gd2O3 Nanosheets by Coprecipitation Method.** Gd (NO3)3·6H2O (0.05 M) was dissolved in DD water, and 1 M NaOH solution was added into the Gd (NO3)3·6H2O solution dropwise. The mixed solution was kept at 80 °C and stirred for 3 h to obtain light green precipitate powders. After that, the obtained precipitate was washed several times using DD water and ethanol to remove unreacted components. Finally, the product was dried at 120 °C for 1 h. The obtained sample was annealed at 600 °C for 2 h, and then the Gd2O3 nanoparticles were collected and used for further studies.

**Fabrication of Gd2O3 Nanosheet-Modified Glassy Carbon Electrode (Gd2O3-GCE).** The schematic representation of the steps involved during the design of Gd2O3-modified GC electrode is shown in Scheme 1. Prior to the electrochemical measurements, the GC electrode was polished with alumina powder of size 0.05 and 0.3 μm on a smooth polishing cloth to obtain a mirrorlike surface, followed by sonication in...
ethanol, and then it was washed using double-distilled water. Gd₂O₃ (5 mg) was dispersed in 1 mL of DD water to obtain a proper dispersion of the Gd₂O₃ sample and sonicated for 15 min. Subsequently, 6 μL of the resultant dispersion of Gd₂O₃ NPs was subjected to physical entrapment on the GC electrode by a facile drop-casting method to obtain a film. After drop-casting, the electrode was allowed to dry overnight at 50 °C. Finally, the electrode was washed with 0.1 PBS (pH 7.4) and used for further analysis. The electrode thus obtained is denoted GC/Gd₂O₃.

Materials Characterization. The structural properties of the samples were analyzed by a powder X-ray diffractometer (XRD) (PANalytical X’Pert Pro) using Cu Kα radiation (wavelength: 1.5418 Å). The pattern was recorded in the 2θ range of 10–80° with a step size of 0.05 at an ambient temperature. The functional groups of the prepared samples were identified by Fourier transform infrared (FT-IR) spectroscopy (Thermo Nicolet 380), and the spectra were recorded in the range of 400–4000 cm⁻¹ with a resolution of 2 cm⁻¹. The morphology of the samples was studied using an FEI QUANTA 250 scanning electron microscope (SEM). A Cary Eclipse photoluminescence (PL) spectrometer was used to analyze the luminescence properties using a Xe lamp with an excitation wavelength of 325 nm at room temperature. X-ray photoelectron spectroscopy (Carl Zeiss) was carried out in ultrahigh vacuum with Al Kα line (1486.6 eV) as an exciting source to analyze the surface chemical composition of the synthesized samples. Raman spectra were recorded using a micro-Raman spectrometer (Acton Spectra Pro 2500i, Princeton Instruments, Acton Optics & Coatings) using a Ar laser source with a wavelength of 514.5 nm. The magnetic measurement was carried out using a vibrating sample magnetometer (Lake Shore Model-7404). Electrochemical experiments such as CV and DPV were carried out using the CHI 440B electrochemical analyzer/workstation (CH Instruments). A conventional three-electrode system consisting of a glassy carbon working electrode (3 mm diameter), a platinum wire (1 mm diameter and 2 cm long) counter electrode, and Ag/AgCl reference electrode was used.

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Notes
The authors declare no competing financial interest.

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