

INVESTIGATING THE IMPACT OF SYNTHESIS PROCEDURES ON ELECTROCHEMICAL PROPERTIES OF rGO-CeO₂ NANOCOMPOSITE

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Abstract

rGO-CeO₂ nanocomposite has been employed and significantly improved electrochemical sensors in terms of facility, sensitivity, and accuracy. Additionally, since synthesis procedures play an important role in the structure and properties of nanomaterials, it is necessary to investigate the effect of synthesis procedures to maximize the electrochemical performance of the sensor using rGO-CeO₂. In this study, two different approaches, namely *in situ* and *ex situ* methods, were used to synthesize GO-CeO₂, then GO-CeO₂ was reduced by hydrazine to form the final product rGO-CeO₂. Subsequently, the morphology and elemental analysis/mapping of these nanocomposites were examined by Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy, respectively. Afterwards, the nanocomposites were drop-casted on the surface of glassy carbon electrodes, and the electrochemical properties were evaluated by Cyclic Voltammetry and Electrochemical Impedance Spectroscopy in the presence of ferrocyanide/ferricyanide redox probe. The results indicated that CeO₂ nanoparticles were evenly distributed on the surface of wrinkled rGO sheets; also, in comparison to bare glassy carbon electrode, electrodes modified with the nanocomposites from both approaches reported lower charge transfer resistance and peak-to-peak separation, indicating enhanced electron transfer and electrical conductivity, and the electrode modified with rGO-CeO₂ from *in situ* approach having better improvement than the one with rGO-CeO₂ from *ex situ* approach.

Keywords: Reduced graphene oxide, nanoceria, nanocomposite, electrochemical properties

1. INTRODUCTION

Nanomaterials have been extensively incorporated into electrochemical sensors for multiple applications, for instance, working as labels for biomolecules, enhancing electron transfer, and catalyzing reactions. Consequently, this has led to considerable improvement for this type of sensor regarding facility, sensitivity, and accuracy [1]. Various classes of nanomaterials have been deployed, and among those, carbon-based nanomaterials, particularly reduced graphene oxide (rGO) has attracted considerable interest thanks to its appealing characteristics, consisting of large surface area, outstanding electrical and thermal conductivity, and high possibility of surface modifications. The latest characteristic is significantly important since it enables the incorporation of rGO with different groups of nanomaterials to form rGO-based nanocomposites. In comparison to pristine rGO, rGO-based nanocomposites are superior in terms of (1) overcoming the restacking and aggregation nature of rGO sheet, thus preventing the reduction in active surface area, and (2) combining the outstanding attributes of each pristine material to achieve a synergistic effect [2]. To combine with rGO, metal and metal oxide nanoparticles are frequently employed, and one outstanding example of this class of nanomaterials is nanoceria. CeO₂ is beneficial for electrochemical detection systems since this nanoparticle is affordable, non-toxic, biocompatible, has high surface area, and is capable of improving electron transfer [3,

4]. The integration of rGO and CeO₂ results in the formation of rGO-CeO₂ nanocomposite that has been noticed and applied to the electrochemical detection of multiple analytes, for example, neurotransmitter [5] and insecticide [6].

Although nanomaterials can greatly improve the performance of a sensor, the degree of enhancement is dependent on the characteristics, including size and morphology, of such nanomaterials [7]. Furthermore, synthesis procedures play an important role in the control of size and morphology [8], thus controlling the electrochemical properties of the product. Hence, to maximize the performance of an electrochemical determination, it is necessary to investigate the influence of synthesis procedures on the electrochemical properties of rGO-based nanocomposite. Herein, this study aims to evaluate how synthesis procedures impact the morphological characteristics and electrochemical performance of rGO-CeO₂ nanocomposites. More specifically, in terms of synthesis procedures, the loading of CeO₂ into graphene oxide (GO) sheets were implemented by two different approaches: *in situ* and *ex situ*. *In situ* approach refers to the formation and growth of CeO₂ from its precursors in the presence of GO; by contrast, *ex situ* method demonstrates the mechanical combination of as-synthesized CeO₂ and GO sheets [9]. Subsequently, GO-CeO₂ from both approaches were treated with hydrazine for the reduction of GO sheets to form rGO-CeO₂. Furthermore, to fulfill the ultimate goal of this study, three main objectives are proposed as follows: (1) Synthesis of rGO-CeO₂ by *in situ* and *ex situ* approaches; (2) Characterization of rGO-CeO₂ by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX); and (3) Examination of the rGO-CeO₂-modified electrode by Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS).

2. MATERIALS AND METHODS

2.1 Materials

For the synthesis of nanomaterials, Graphite flakes, Potassium permanganate (KMnO₄), Sulfuric acid (H₂SO₄), Hydrogen peroxide (H₂O₂), Cerium(III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O), Hydrazine monohydrate (N₂H₄·H₂O) were analytical grade and purchased from Merck KGaA (Darmstadt, Germany). Aqueous solution of ammonia (NH₃) with analytical grade quality was purchased from Lachner (Neratovice, Czech Republic). To clean the electrode surface, ethanol absolute (Penta, Prague, Czech Republic), four polishing suspensions (Electron Microscopy Sciences, Hatfield, PA, USA) of 0.5-micron diamond suspension, and alumina slurry with three different sizes of 1 μm, 0.3 μm, and 0.05 μm were employed. To prepare the working solution for electrochemical measurements, Potassium chloride (KCl), Potassium hexacyanoferrate(II) trihydrate (K₄Fe(CN)₆·3H₂O), and Potassium hexacyanoferrate(III) (K₃Fe(CN)₆) were analytical grade and purchased from Merck KGaA (Darmstadt, Germany). Lastly, ultrapure water (18.2 MΩ·cm) was deployed during the course of this study.

2.2 Synthesis of rGO-CeO₂ by *in situ* and *ex situ* approaches

GO was prepared as a precursor for the preparation of rGO-CeO₂ based on the simplified Tour's method [10]. Afterwards, rGO-CeO₂ synthesized by *in situ* and *ex situ* approaches were conducted as follows.

Ex situ approach: This approach was derived from an earlier study [11]. Briefly, Ce(NO₃)₃·6H₂O was dissolved in ultrapure water, and the pH was adjusted to 10 by the addition of aqueous solution of NH₃. Subsequently, this solution was mixed with a suspension of GO in ultrapure water and the mixture was ultrasonicated for 20 minutes. Afterwards, the mixture was heated to 90 °C prior to the addition of N₂H₄·H₂O dropwise and kept under reflux for one hour at the same temperature. Finally, the obtained product was washed 3 times with ultrapure water and denoted as rGO-CeO₂-1.

In situ approach: In comparison to *ex situ* approach, the only difference in this approach was that the solution of Ce(NO₃)₃ was mixed with the suspension of GO prior to the addition of aqueous solution of NH₃. Afterwards,

the mixture was sonicated and treated with $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, and the final product was washed in the same manner as aforementioned. From this approach, the nanocomposite was denoted as rGO-CeO₂-2.

2.3 Characterization of rGO-CeO₂ by SEM and EDX

SEM and EDX analysis were conducted by TESCAN MIRA3 XMU SEM coupled with Oxford Instruments EDX. The images from the SEM were obtained at resolution mode, accelerating voltage of 5kV, In-Beam secondary electron detector, and working distance of 3.0 mm. In terms of EDX analysis, the conditions of accelerating voltage and working distance were changed to 15kV and 15.0 mm, respectively; and the time for mapping was set to 20 minutes.

2.4 Evaluation of electrochemical properties of rGO-CeO₂ by CV and EIS

Before the modification of glassy carbon electrodes (GCE) by rGO-CeO₂, GCE were polished on polishing pads with 0.5-micron diamond suspension, and alumina slurry with three different sizes of 1 μm , 0.3 μm , and 0.05 μm , respectively, following by sonication in ethanol absolute and ultrapure water. Afterwards, GCE were left to be dried at room temperature. Subsequently, 5 μl of 1mg/ml suspension of either rGO-CeO₂-1 or rGO-CeO₂-2 was drop-casted to the surface of GCE and allowed to be dried at room temperature.

Autolab PGSTAT302N was employed for all electrochemical measurements. A three-electrode system was set up, consisting of a platinum electrode as counter electrode, Ag/AgCl 1.0 mol/l KCl as reference electrode, and GCE as working electrode. The working solution containing 5mM of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox probe and 0.1M KCl electrolyte was used for both CV and EIS. Afterwards, EIS was implemented to compare the charge transfer resistance of bare GCE to GCE modified with nanocomposites. EIS was conducted at these conditions: frequency range from 0.1 to 10 kHz with an amplitude of 10 mV, and applied voltage of 0.2 V. Also, CV was employed to assess the electrochemical performance of bare and modified GCE, and CV was performed within the potential range of -0.4 V to 0.9 V and scan rate of 0.05 V/s.

3. RESULTS AND DISCUSSION

3.1 Physicochemical properties of rGO-CeO₂ nanocomposites

As aforementioned, rGO-CeO₂ nanocomposites were synthesized by two different approaches, and the difference between these two approaches lies in the anchoring of either precursors of nanoceria or pre-synthesized nanoceria to the surface of GO. In the *ex situ* approach, CeO₂ nanoparticles were formed due to the addition of aqueous solution of NH_3 to precipitate Ce^{3+} ions (precipitation method). It is notable that this synthesis was implemented under ultrasonication. Acoustic cavitation in ultrasound irradiation generated cavitation bubbles and hot spots, with the former operated as nucleation sites and the latter provided sufficient energy for the formation of CeO₂ nuclei. Thanks to the adsorption of cavitation bubbles to the surface of CeO₂ nuclei, the interfacial free energy between the nuclei and the reacting solution was lower, thus avoiding the agglomeration of nanoparticles [11, 12]. Afterwards, CeO₂ nanoparticles were loaded onto GO, and CeO₂ is expected to distribute evenly on the surface of GO as well as rGO. For the *in situ* approach, at the beginning, Ce^{3+} ions were loaded onto the surface of GO, and upon the addition of aqueous solution of NH_3 for the precipitation method under ultrasound, two phenomena occurred. The first one was heterogeneous nucleation in which CeO₂ nuclei was generated on a foreign body as GO, and in liquid phase, these nuclei formed with ease due to the presence of GO as a stable nucleating surface [13]. The second phenomenon was due to the acoustic cavitation as aforementioned; thereby CeO₂ from this approach is expected to be decorated evenly on the surface of GO and then rGO. As can be seen in **Figure 1**, in both approaches, no agglomeration of CeO₂ nanoparticles was observed as expected, and the formation of wrinkled rGO sheet indicated successful reduction of GO to rGO by hydrazine.

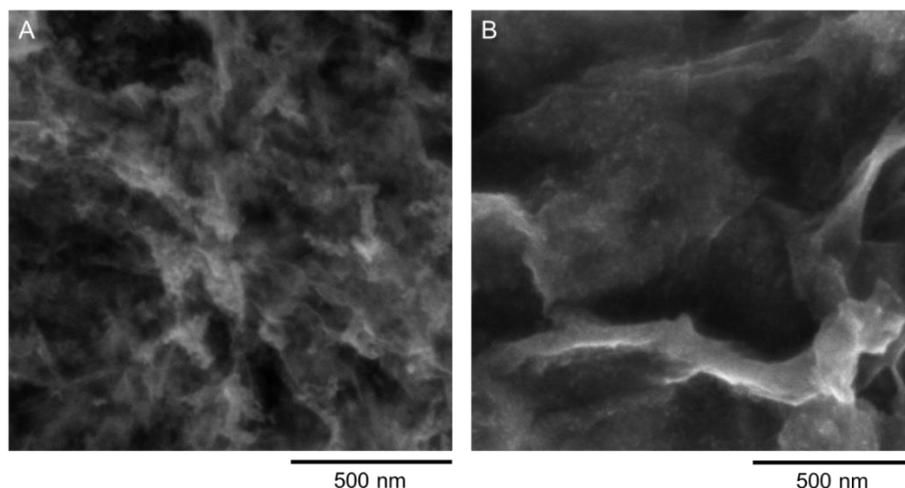


Figure 1 SEM images of rGO-CeO₂-1 (A) and rGO-CeO₂-2 (B) nanocomposites

The findings from EDX can demonstrate the elemental composition and mapping of each element from these nanocomposites. As can be seen from **Figure 2**, in each nanocomposite, three elements were detected, including carbon, oxygen, and cerium. Moreover, the elemental mapping further confirmed the uniform distribution of CeO₂ nanoparticles on rGO sheets, which is in good agreement with the results from SEM.

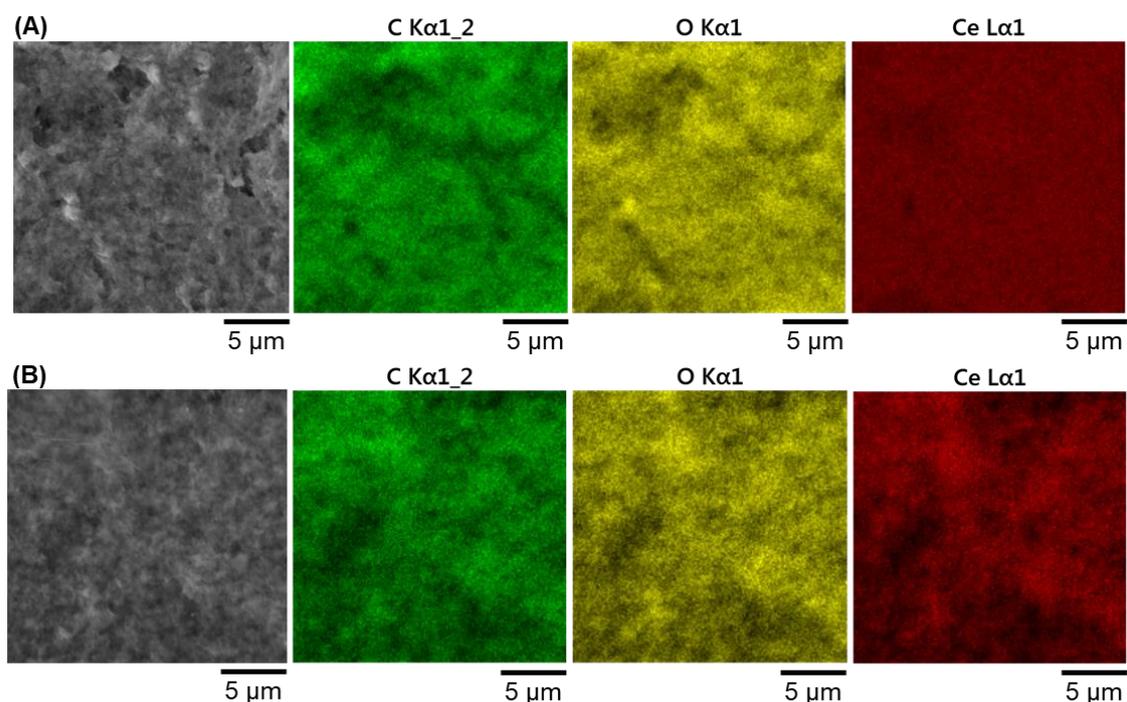


Figure 2 EDX analysis of rGO-CeO₂-1 (A) and rGO-CeO₂-2 (B) (green, yellow, and red maps correspond to carbon, oxygen, and cerium, respectively)

3.2 Electrochemical properties of rGO-CeO₂-modified GCE

EIS is a powerful method to study the charge transfer resistance of electrodes at the electrode-solution interface. Conventionally, EIS spectrum demonstrates a linear part at low frequency, which is attributed to the Warburg impedance for mass transport (diffusion) of redox species to the electrode interface. More importantly, EIS spectrum displays a semi-circle at high frequency, which is correlated with heterogeneous electron transfer process of redox species. The diameter of this semi-circle can be utilized to calculate the value of charge

transfer resistance (R_{ct}) [14]. From **Figure 3A**, the diameters of the semi-circle of modified GCE were significantly lower than that of bare GCE. More specifically, R_{ct} values of bare GCE, GCE/rGO-CeO₂-1, and GCE/rGO-CeO₂-2 were estimated as 132.65 Ω , 18.11 Ω , and 8.75 Ω , respectively. This implied an enhanced electron transfer and improved electrical conductivity due to the modification of bare GCE with rGO-CeO₂, and the impact of rGO-CeO₂-2 was slightly better than that of rGO-CeO₂-1.

CV was conducted to assess the electroanalytical performance of bare and modified GCE. As can be seen from **Figure 3B**, larger maximum current values were observed in the case of modified electrodes in both anodic and cathodic directions of potential scan. In addition, the peak-to-peak separation values for bare GCE, GCE/rGO-CeO₂-1, and GCE/rGO-CeO₂-2 were 134.28 mV, 107.42 mV, and 95.22 mV, respectively. Hence, faster electron transfer kinetics were observed thanks to the addition of rGO-CeO₂, with rGO-CeO₂-2 having higher improvement than rGO-CeO₂-1.

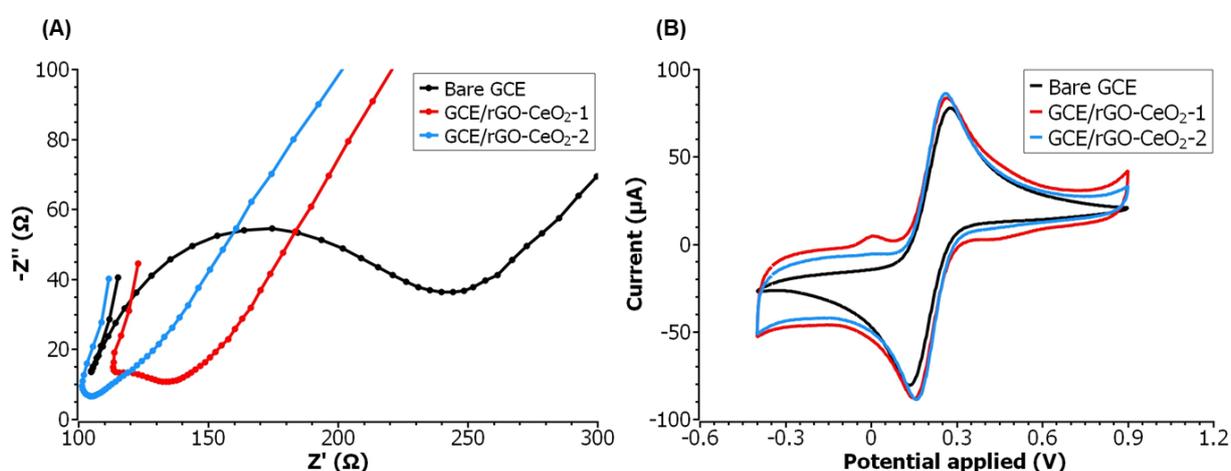


Figure 3 Nyquist plot (A) and cyclic voltammogram (B) of rGO-CeO₂-modified GCE

From both analyses implemented by CV and EIS, the electrochemical properties of modified GCE were superior in comparison to those of bare GCE, indicating the potential of this kind of nanocomposite within the discipline of electrochemical sensors. Moreover, better performance was recorded in the case of rGO-CeO₂ synthesized by *in situ* approach (rGO-CeO₂-2). This can be explained by the degree of uniform distribution of CeO₂ nanoparticles on rGO sheets. Although nanocomposites from both approaches illustrated good anchoring of CeO₂ on the surface of rGO from SEM and EDX results, the *ex situ* approach is more prone to non-uniform coverage of nanocereria by graphene sheets [15], thereby resulting in more agglomeration of nanocereria as well as less active surface area for electrochemical processes.

4. CONCLUSION

In conclusion, this study has demonstrated the impact of synthesis approaches, namely *in situ* and *ex situ* approaches, on the characteristics of rGO-CeO₂ nanocomposites. Firstly, based on the findings of SEM and EDX, rGO-CeO₂ from both approaches exhibited uniform distribution of CeO₂ nanoparticles on the surface of wrinkled rGO sheets. Secondly, from electrochemical measurements by CV and EIS methods, rGO-CeO₂ from both methods proved their capacities to enhance electron transfer and electrical conductivity, and this improvement is important for electrochemical detection of analytes (e.g., vitamin, neurotransmitter, and biogenic amine) in complicated real samples with many interferences. Lastly, the rGO-CeO₂ from *in situ* approach exhibited better electrochemical properties, which can be explained by the nature of this approach to form more uniform decoration of nanocereria on the surface of rGO, leading to less agglomeration of CeO₂ nanoparticles and in turn larger active surface area for electrochemical processes.

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