

Synthesis, Characterization and Electrochemical Sensing Properties of CeO₂@SiO₂

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ABSTRACT

CeO₂@SiO₂ nanoparticles were synthesized by thermal decomposition method. The synthesized CeO₂@SiO₂ was characterised by X-ray diffraction, DRS-UV-Vis and FE-SEM. CeO₂@SiO₂ nanoparticles were used to modify the glassy carbon electrode (GCE) and the modified electrode was used to detect ranitidine by voltammetric techniques. The determination is based on electrochemical reduction of ranitidine using acetate buffer solution (pH 6). The modified electrodes exhibit better electro catalytic activity than the bare glassy carbon electrode (GCE).

Index Terms— Thermal decomposition, CeO₂@SiO₂, Electrochemical sensing, Ranitidine

1 INTRODUCTION

CeO₂ has been one of the scientifically most significant oxide materials being exploited in the research industry due to its well-known redox chemistry.[1] The redox and catalytic properties of CeO₂ are strongly influenced when it is combined with other transition metals or rare earth oxides.[2] Ceria (CeO₂) is ability to shift easily between reduced and oxidized states (Ce³⁺/Ce⁴⁺) and to accommodate variable levels of bulk and surface oxygen vacancies.[3] In 2002, Nishikawa et al. demonstrated high performance CeO₂ dielectrics because of their good interfacial properties on Si substrate.[4] Silica nanoparticles are very attractive material, due to their chemical inertness, corrosion resistance and mechanical and thermal stability. Ranitidine is an H₂ receptor antagonist commonly used in the treatment of duodenal and gastric ulceration associated with Helicobacter pylori infection, gastroesophageal reflux disease, conditions of elevated gastric acidity and the treatment of photogenic gastrointestinal hypersecretory condition such as the Zollinger-Ellison syndrome.[5] In this paper, we have synthesized the CeO₂@SiO₂ nanoparticles and it is characterized by various techniques. The synthesized CeO₂@SiO₂ nanoparticles were modified by the bare GCE and used to detect ranitidine by voltammetric techniques.

2 EXPERIMENTAL

2.1. MATERIALS

Ceric ammonium nitrate, Tetraethyl orthosilicate (TEOS) were purchased from Qualigens and Polyethylene glycol 600 from

Merck. Ammonium hydroxide, Ethanol and Double distilled water were used as solvents. All the solvents were employed of best grade available and were used without further purification.

CeO₂@SiO₂ nanoparticles were prepared by thermal decomposition method. Ceric ammonium nitrate (1.5 mmol) and 2 mL of PEG-600 was dissolved in 30 mL of double distilled water and stirred for 10 min. To the mixture, 10 mmol of tetraethyl orthosilicate was added dropwise and the pH was adjusted to 10 by the addition of ammonium hydroxide. The obtained precipitate was heated at 70 °C for 2 h. The resulted product was washed with water and ethanol several times. The obtained product was calcined at 750 °C for 2 h.

2.2. PREPARATION OF MODIFIED ELECTRODE

1mg of CeO₂@SiO₂ was dispersed in 3ml of ethanol by using ultra-sonication for 30min. The glassy carbon electrode was polished by alumina powder 0.5 micron and washed with double distilled water. The GCE was coated with one drop of the overhead suspension by drop coating method. Finally, the electrode was modified as CeO₂@SiO₂/GCE.

3 RESULTS AND DISCUSSIONS

Fig.1 shows the XRD pattern of CeO₂@SiO₂ was determined by Rich Siefert 3000 diffractometer with Cu-Kα1 radiation (λ = 1.5406Å). The observed XRD pattern compared and well matched with the standard JCPDS data (65-5923) confirms the formation of CeO₂ phase having cubic fluorite crystal structure. Four distinct peak observed at (28.5), (33.0), (47.4), (56.3) respectively, corresponding to the reflections of (111), (200), (220), (311) plane. No reflection peak of SiO₂ is observed in the pattern of CeO₂@SiO₂ and may be due to the formation of CeO₂ over the SiO₂. No other phase is observed.

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DRS UV-Vis spectrum of CeO₂@SiO₂ recorded using Perkin-Elmer 650 spectrophotometer. CeO₂ has a strong absorption band in the UV region 200 to 350 nm which is due to the band gap transition from valence band to the conduction band [6]. Fig.2 shows a strong absorption band at 312 nm can be attributed to the inter-band transitions. The direct band gap have been deduced from Tauc plot of (αhν)² versus hν were shown in Fig.2. The calculated direct band gap energies (E_g) of CeO₂@SiO₂ are 3.1eV which is similar to the results reported in the literature.[7]

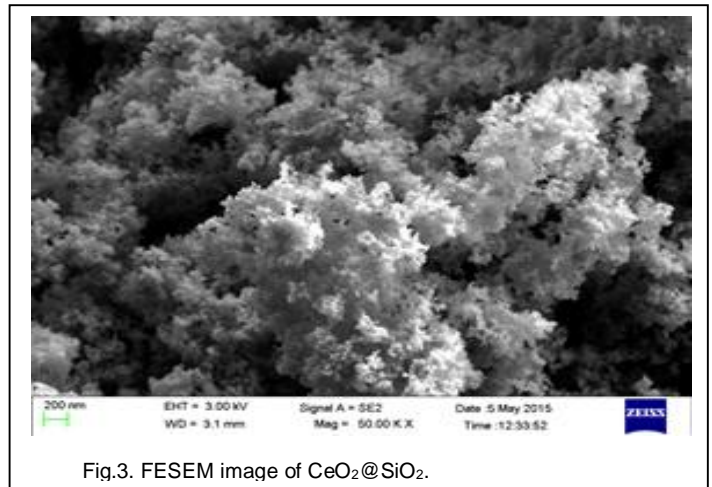
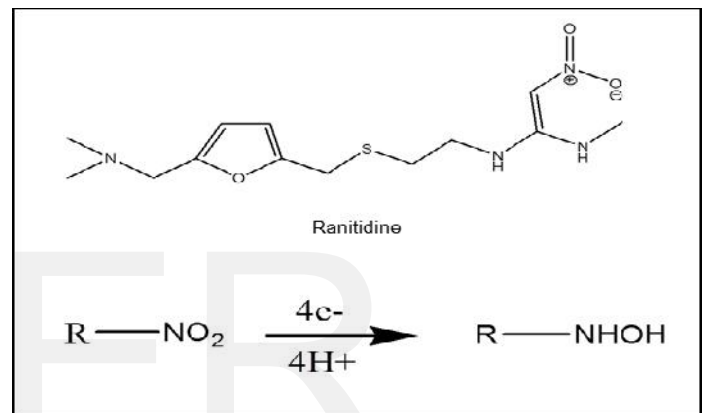


Fig.3. FESEM image of CeO₂@SiO₂.



3.1. ELECTROCHEMICAL PROPERTY

The electrochemical sensing experiments were carried out using a CHI 1103A electrochemical instrument in a conventional three electrode system using the bare and modified GCE as the working electrode. Platinum wire was used as the counter electrode and saturated calomel electrode (SCE) was used as the reference electrode. All the electrode was immersed in 8ml of 0.001M Phosphate Buffer solution containing 2 ml of ranitidine.

Fig.4 shows the cyclic voltammogram of bare and modified GCE in presence of 0.1 mM ranitidine in 0.1 M acetate buffer pH 6 at the scan rate of 50 mVs⁻¹. In the potential range of 1.5V to -1.5 V, a reduction peak at -0.91 V was observed at bare GCE in the presence of ranitidine but there is no oxidation peak occurs in the bare GCE. The modified CeO₂@SiO₂/GCE in presence of ranitidine reduction peaks at -0.95 V and the absence of oxidation peak in the 50 mVs⁻¹ were observed. The reduction of ranitidine is due to formation of N=O functional group to NH-OH.[5]

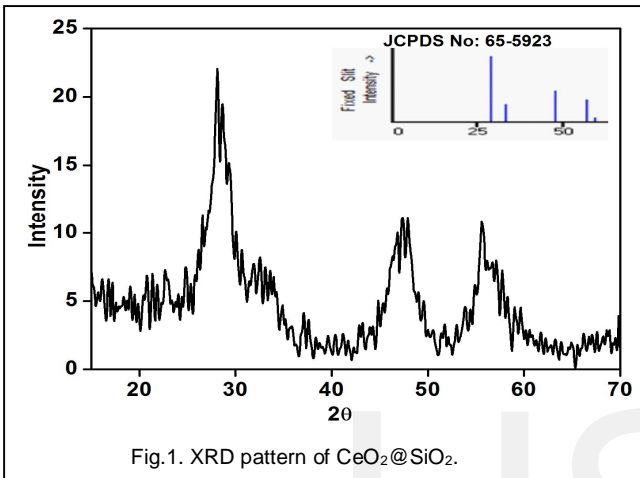


Fig.1. XRD pattern of CeO₂@SiO₂.

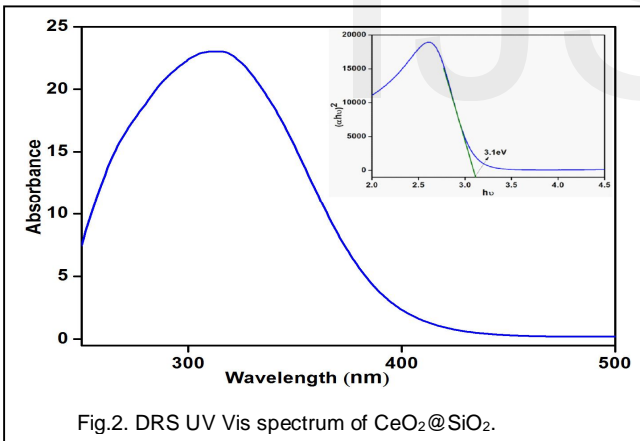


Fig.2. DRS UV Vis spectrum of CeO₂@SiO₂.

The morphology and the size of the sample were analysed by FE-SEM using a HITACHI SU6600 field emission-scanning electron microscopy. The FESEM image of CeO₂@SiO₂ was shown in Fig 3. The morphology of the CeO₂@SiO₂ is agglomerated spheres and the particle size is ~20 nm.

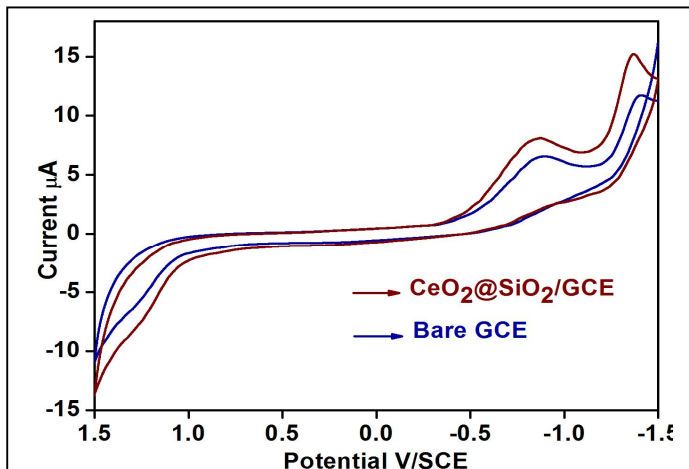


Fig.4. Cyclic voltammogram of bare and modified CeO₂@SiO₂ GCE in presence of 0.1 mM 4-Ranitidine in 0.1M PBS at the scan rate

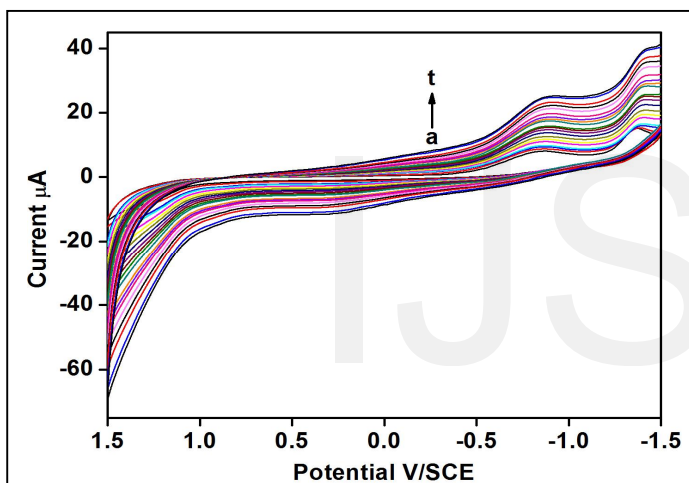


Fig.5. Cyclic voltammograms of the CeO₂@SiO₂/GCE in pH 6 at the different scan rate (a to t): 50-600 mVs⁻¹.

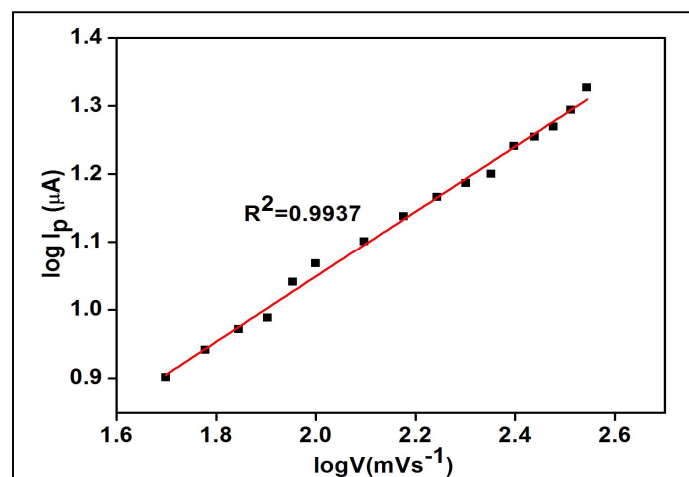


Fig.6. Double logarithm plots of scan rate vs current.

3.2. EFFECT OF SCAN RATE

Fig.5. shows the cyclic voltammograms of CeO₂@SiO₂/GCE in 0.1 mM Ranitidine at different scan rates (50-600 mVs⁻¹) at pH 6. From the Fig.5, it can be seen that the peak potentials and corresponding currents vary with change in scan rate value. The increasing scan rate leads to increase in peak current. It explains that scan rate directly proportional to the peak current. A linear relationship was obtained between scan rate and cathodic peak current. Fig.6. shows the double logarithmic plots of log(V) vs log(I_{pc}) shows a linear range from 50 to 600 mVs⁻¹. The linear relation was expressed with the following linear regression equation, I_{pc} = 0.4787 log v - 0.0917, (R² = 0.9937). From the slope value, we observed that the electrochemical reaction follows diffusion controlled process. The number of electron transfer was calculated using $i_p = nFQ_0v/4RT$, the calculated value is 4e⁻ for reduction process.

4 CONCLUSION

The CeO₂@SiO₂ nanoparticles were prepared by a thermal decomposition method. The synthesized CeO₂@SiO₂ was confirmed by XRD analysis. The modified CeO₂@SiO₂/GCE was successfully fabricated for the determination of Ranitidine. The electrochemical reaction follows the diffusion controlled process and four electron transfer in the reduction process. From the result, modified CeO₂@SiO₂/GCE shows the good sensitivity and it can be used for the determination of ranitidine.

5 ACKNOWLEDGMENT

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