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Mesoporous CeO_2 nanoparticles modified Glassy carbon electrode for individual and simultaneous determination of Cu(II) and Hg(II): Application to environmental samples

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ABSTRACT

An electrochemical sensor based on the use of CeO_2 nanoparticles modified glassy carbon electrode (CeO_2/GCE) was prepared and applied for determination of Cu(II) and Hg(II) individually and simultaneously. The differential pulse anodic stripping voltammetry (DPASV) results indicates that the CeO_2 NPs based sensor exhibits good electroanalytical performance with two well-resolved voltammetric stripping peaks for Cu(II) and Hg(II). The proposed CeO_2 NPs based sensor shows a wide linear range from 10 to 350 μg/L and a lower detection limit (3σ) 2.9 for Cu(II) and 3.3 μg/L for Hg(II) under optimized conditions. The developed sensor was successfully applied for the quantification of Cu(II) and Hg(II) in real sample matrices, and satisfactory results were obtained.

1. Introduction

In recent years, environmental contamination including water, soil and air, by heavy metals has increased due to their extensive use in industry and agriculture sectors. Heavy metal ions contamination results serious threats to human health and the environment as they are not biodegradable and highly toxic to living organisms. As we know that Hg(II) ions are easily accumulated in the cell membrane and thereby causes severe diseases like Minamata disease, congnitive disorder and kidney damage [1,2]. On the other hand, Cu(II) is a vital microelement for plants, animals and humans but the deficiency and excessive intake of Cu(II) results bone abnormality/anemia [3], and Alzheimer's/Wilson's disease respectively [4,5]. Therefore, monitoring of Cu(II) and Hg(II) in real sample is very essential and urgent for the health and safety of living organisms. In this connection, simultaneous detection and quantification of Cu(II) and Hg(II) has attracted considerable research interest in recent years.

Electrochemical techniques have been regarded as efficient and economically feasible for the quantification of Cu(II) and Hg(II) compared to the conventional spectroscopic techniques such as atomic absorption spectroscopy (AAS), atomic emission spectroscopy (AES) and inductively coupled plasma mass spectrometry (ICPMS).

Several modifiers including functional organic molecules and noble metal nanoparticles [6–8] have been identified and successfully used for the electrochemical determination of Cu(II) and Hg(II). However, the sensitivity and selectivity of the modifiers depends upon the accumulation of Cu(II) and Hg(II), which in turn depends upon surface chemistry of the modifier. In this regard, zero dimensional nanomaterials are expected to play a significant role in the upcoming electrochemical sensors to demonstrate quantum size effects. Nano-sized CeO_2 has been considered as the most promising material due to its nontoxic, low-cost and reliability, besides their greater mechanical, thermal, electrical, and chemical inertness. Owing to these outstanding properties, nano-sized CeO_2 has been extensively used in supercapacitor [9] solar cell [10], fuel cell [11], battery [12], photocatalysis [13], CO oxidation [14,15], biomedical applications [16,17], Nox sensor, biosensors [18,19] and H_2O_2 sensor [20]. Additionally, the morphology of the CeO_2 also plays an important role in enhancing the catalytic activity. For instance, the CeO_2 nanorods and nanowires shows superior oxygen storage capacity and catalytic activity for CO oxidation compared to the CeO_2 nanoparticles [21].

However, CeO_2 has not been used for the detection of Cu(II) and Hg (II) in environmental samples. In contrast, the sensing performance of CeO_2 based sensors has dramatically improved when it is combined with graphene [6]. The addition of graphene into the cerium oxide not only makes the process tedious but also a very expensive and time

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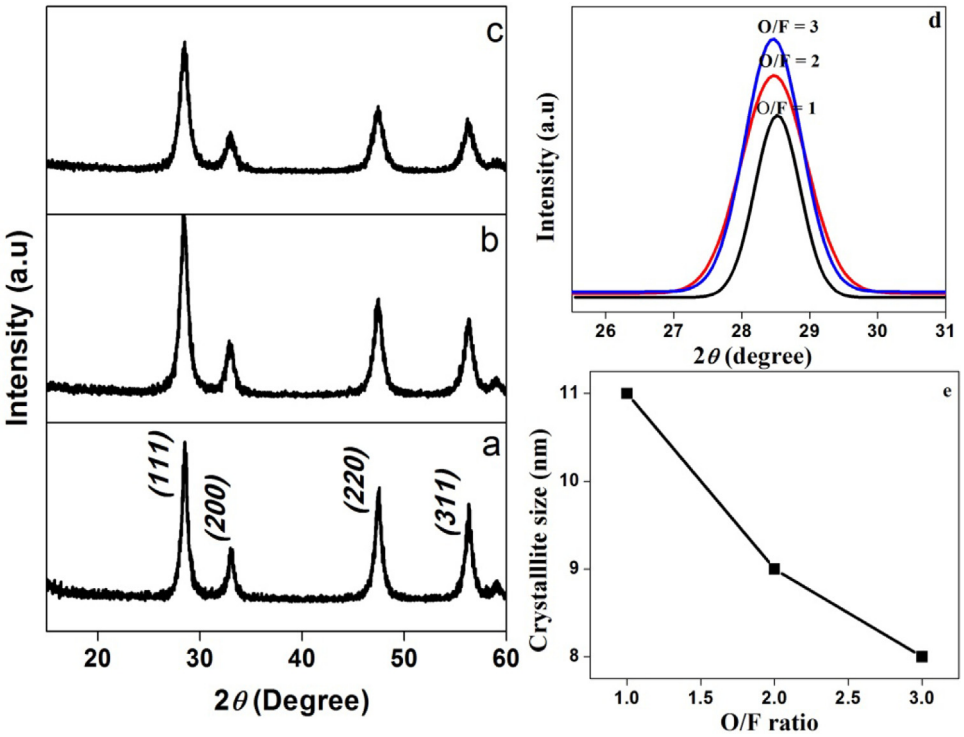

Fig. 1. Powder XRD patterns CeO_2 NPs prepared with O/F ratio (a) 1, (b) 2, (c) 3, (d) FWHM of (*111*) plane and (e) Crystallite size.

consuming in terms several days. Additionally, metal doped ceria nanoparticles have been widely considered to promote the active oxygen content on CeO_2 NPs surface by changing surface composition and thereby enhances the catalytic activity [22]. Thus, doping is considered as an effective avenue to enhance the properties of CeO_2 NPs in order to improve the structural properties for various applications [23–25].

Alternatively, reduction of crystallite size of CeO_2 to an appropriate size is an effective avenue to modify surface states, energy levels and transport performance of carriers thereby enhances the electrochemical properties in terms of sensitivity and selectivity. In this connection, a green and fast solution route has been proposed wherein the size of the CeO_2 NPs could be controlled to 8–11 nm. The electrocatalytic activity of CeO_2 NPs and application towards individual and simultaneous quantification of Cu(II) and Hg(II) from real samples have been evaluated. The proposed CeO_2 NPs modified GCE exhibits two well-resolved voltammetric peaks for Cu(II) and Hg(II). The key feature of the proposed sensor is wide linear range, low detection limit and direct electron transfer without any mediators in the determination of Cu(II) and Hg(II) individually as well as simultaneously.

2. Experimental

2.1. CeO_2 nanoparticles preparation

Cerium nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$, 99.9% purity) and sucrose ($C_{12}H_{22}O_{11}$, 99.9% purity) were used without further purification. The synthesis of CeO_2 NPs have been carried out according to our previous literature [26] In a typical synthesis, ($Ce(NO_3)_3{\cdot}6H_2O$ (3.0 g) was dissolved in minimum quantity of water (~7 mL). To this, sucrose (0.7 g) was added and stirred for 10 min to get homogeneous solution. The 3.0 g cerium nitrate and 0.7 g sucrose corresponds oxidizer to fuel (O/F) ratio 1 [27]. The resultant mixture was placed in a preheated muffle furnace maintained at 450 ± °C. Initially, the solution boils and water evaporates followed by frothing and it occupies whole beaker. Then, the froth undergoes smoldering type combustion wherein ultra-light CeO_2 NPs were formed along with the liberation of gaseous products such as water, carbon dioxide and nitrogen. Finally, the beaker was removed from the furnace and allowed to cool to room temperature naturally. The obtained powder was crushed and stored for further studies. The same experimental procedure was followed for the preparation of CeO_2 NPs using O/F ratio of 2 and 3.

2.2. Characterization

The powder X-ray diffraction (XRD) technique and Fourier transform infrared spectrometer (FTIR) has been used to study the purity of the prepared CeO_2 NPs. The powder XRD measurements were carried out using PANalytical X'pert PRO X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation source (λ = 1.541 Å). The FTIR spectrum was recorded using Fourier transform infrared Nicolet spectrometer. BET surface area and Nitrogen adsorption–desorption measurements were carried out at 77 K using a Quantachrome Corporation NOVA 1000. Transmission electron microscope (TEM) bright field images of the CeO_2 NPs were taken using FEI Tecnai F-30 TEM.

2.3. Electrode modification

Firstly, the glassy carbon electrode (GCE) was polished with 1, 0.3 and 0.05 μm alumina particles to get a mirror like smooth surface followed by thorough washing with double distilled water using ultrasonic bath. Then, the electrode was rinsed with ethanol and subsequently dried at room temperature. Secondly, 10 mg of as-prepared CeO_2 NPs were dispersed in 10 mL of water using ultrasonic bath. Then, the 5 μL of dispersed CeO_2 NPs suspension was drop casted onto the GCE. Finally, the drop casted electrode was dried at room temperature.

2.4. Sample preparation

The water samples were collected using polyethylene bottles from polluted lake, unpolluted lake and tap water supplied for drinking purpose. The water samples were filtered using the Whatman filter paper to remove any suspended particulate matter. Then, 5 mL of this