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International Electronic Conference on Sensors and Applications
1 - 16 June 2014

www.mdpi.com/journal/sensors

Conference Proceedings Paper – Sensors and Applications

Preparation of *β*-Cyclodextrin Functionalized Reduced Graphene-Silver Nanocomposites: Application for Sensing of Nitrite

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Received: 19 March 2014 / Accepted: 19 April 2014 / Published: 1 June 2014

Abstract: *β*-cyclodextrin functionalized reduced graphene oxide-silver nanocomposites (*β*-CD/RGO/Ag) were successfully prepared using two step wet chemical method. The *β*-CD/RGO sheets were firstly synthesized via hydrazine reduction under 90 ℃. The Ag nanoparticles were loaded on the *β*-CD/RGO sheets by reduction of $AgNO_3$ with ammonia solution. The *β*-CD/RGO/Ag nanocomposites were well characterized by UV-vis spectroscopy, FTIR and SEM. The results confirmed that the *β*-CD was effectively covered on the RGO surface and the Ag nanoparticles with an average size of 80 nm were uniformly decorated on the *β*-CD/RGO sheets. The *β*-CD/RGO/Ag nanocomposites modified glassy carbon electrode was employed for selective determination of nitrite. Cyclic voltammetry measurements suggested that the *β*-CD/RGO/Ag exhibits an excellent electrochemical activity towards oxidation of nitrite due to the host-guest recognition and enrichment capability of *β*-CD as well as the outstanding electronic properties of RGO and Ag nanoparticles.

Keywords: Reduced graphene oxide; Silver nanocomposite; Sensor; Nitrite

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1. Introduction

Nitrite ion (NO_2^-) is a well-known widespread inorganic pollutant because it largely used as food preservatives and fertilizing agents as well as corrosion inhibitors [1,2]. However, excess uptake of

nitrite is harmful to human health, for example, it can react with hemoglobin and form methemoglobin which disable the transport oxygen function of blood [3]. Moreover, it potentially could cause gastric cancer [4]. Drinking water and consuming meat is two major pathways for people uptaking nitrite. For drinking water, industrial pollution and inadequate purification technique could lead to the excess nitrite. For consuming meat, study showed the nitrite in animal food not only toxic to the livestock, but also can pass through to the humans who consume the meat [5]. Therefore, develop a sensitive nitrite determination method is crucial for public health as well as the environmental protection.

Several techniques have been used for determining nitrite, such as chemiluminescence [6], capillary electrophoresis [7], chromatography [8] and electrochemical method [3,9-11]. Among these techniques, electrochemical approach has been found owing many advantages, including fast responses, low cost, and easy operation. However, the electrochemical method still facing the challenges of insufficient sensitivity and selectivity. In order to overcome these problems, electrode surface modification is a considerable method to make the traditional electrode suitable for specifically determining nitrite. In particular, silver (Ag) nanoparticles based electrochemical sensors have been developed for detecting nitrite due to their excellent conductivity and high specific surface area. For example, Ning et al. [3] demonstrated an electrochemical sensor based on the polyamidoamine dendrimer-stabilized silver nanoparticles to detection of nitrite. Rastogi and co-workers [11] developed a nitrite sensor by incorporating Ag nanoparticles into a copolymer of methyl methacrylate and 2-acrylamido-2-methylpropane sulfonic acid. Accordingly, Ag nanoparticle is a qualified candidate to modification of the electrode surface.

Graphene, a two-dimensional monolayer of graphite, has received tremendous attention since it was isolated in 2004 [12]. The graphene owing extraordinary mechanical strength, large specific surface area and high conductivity. Various electrochemical sensors have been developed for different analysis based on those properties. For example, Lu et al. [13] developed a hydrogen peroxide sensor based on PtAu bimetallic nanoparticles on graphene-carbon nanotube hybrid materials. Meanwhile, *β*-cyclodextrin (*β*-CD) is a cyclic oligosaccharide consisting of seven glucose units and being toroidal in shape with a hydrophobic inner cavity and a hydrophilic exterior. It has been reported for modification of electrode by its outstanding film-forming ability and special inclusion function, which can enable it interacts with various organic, inorganic and biological guest molecules into its cavities to form stable host–guest inclusion complexes [14]. Therefore, integration of *β*-CD with graphene and Ag nanoparticles might possess their unique properties together and service as a promising composite material for sensing nitrite. In the present work, we synthesized *β*-CD/RGO/Ag nanocomposites by a simple wet chemical method. The as-prepared *β*-CD/RGO/Ag nanocomposites exhibit an outstanding electrocatalytic performance for sensing nitrite.

2. Experimental

2.1 Materials

Poly(diallyl dimethyl ammonium chloride) (PDDA, 20 wt.%, Mw = 100 000-200 000 g/mol), hydrazine hydrate, ammonia solution and silver nitrate were purchased from Sigma-Aldrich. Graphene

oxide (GO) powder was purchased from JCNANO, INC. *β*-cyclodextrin (*β*-CD) was purchased from SANGHAIHUSHI. All other chemicals used were analytical grade reagents without further purification. Phosphate buffer solution (PBS) was prepared by mixing 0.2 M KH_2PO_4 and K_2HPO_4 solution to appropriate pH. Milli-Q water (18.2 MΩ cm) was used throughout the experiments.

2.2 Synthesis of β-CD/RGO/Ag nanocomposites.

In a typical synthesis of *β*-CD/RGO/Ag nanocomposites, 10 mg GO was firstly dispersed into 10 mL water by 1 h sonication. 1 mL PDDA and 0.5 g *β*-CD then successively added in to GO dispersion. After being vigorously stirred for 2 h, 500 μL ammonia and 300 μL hydrazine were added into the mixture solution. Then, the mixture was heated to 90 ℃ in a water bath and maintained for 4 h. Finally, a black precipitation was collected by centrifugation followed water washing cycles. Then, 1 mL *β*-CD/RGO dispersion (1 mg/mL) was mixed with 3 mL water and 1 mL $AgNO_3$ (5 mg/mL) for half hour stirring. 1 mL ammonia solution was then added into the mixture and keeps stirring for additional 1 h. The product was collected by centrifugation and washed three times to yields the *β*-CD/RGO/Ag nanocomposites.

2.3 Characterization

The surface functional groups present on the samples were characterized by Fourier transform infrared spectroscopy (FTIR, Nicolet iS5, Thermo Scientific, USA). The optical characterizations were obtained by UV-vis spectrophotometer in the wavelength range from 190 to 700 nm.

2.4 *Electrocatalytic activity towards detection of nitrite*

Prior to use, the glassy carbon electrode (GCE) was polished by 0.3 μm and 0.05 μm alumina slurry followed by rinsing with water, ethanol and water, in turn. Then, 5 μL of *β*-CD/RGO/Ag sample dispersion (0.5 mg/mL) was dropped onto the GCE and dried at room temperature. Before use, the modified electrode was rinsed with water to remove the loosely attached *β*-CD/RGO/Ag.

Electrochemical measurements were performed on a CHI430a electrochemical workstation (USA), using a three electrode system. A platinum wire was used as the auxiliary electrode and a Ag/AgCl (3M KCl) as the reference electrode.

3. Results and Discussion

3.1 Characterization of β-CD/RGO/Ag nanocomposites

The successful reduction of GO and surface functionalization of *β*-CD was confirmed by FTIR. Fig 1a shows the FTIR spectra of GO and *β*-CD/RGO nanocomposite. It can be observed that the GO spectrum presents typical peaks at 1730, 1620, 1398 and 1047 cm^{-1} which are assigned to the C═O stretching of COOH groups, C═O stretching vibration, C—OH stretching vibration and C—O vibrations from alkoxy groups, respectively. After chemical reduction, the intensity of these peaks becomes much less, indicating that the amount of oxygen-containing groups at the surface of GO was greatly reduced. Moreover, *β*-CD/RGO spectrum exhibits typical *β*-CD absorption peaks of C=C

conjugation at about 1633 cm^{-1}, CH_n stretching vibrations at 2925 cm^{-1}, O—H bending vibrations at 1140 cm^{-1} and the coupled C—O/C—C stretching at 1026 cm^{-1}, indicating the RGO sheets has been successfully functionalized by *β*-CD.

Fig 1b represents the UV-vis spectra of GO, *β*-CD/RGO and *β*-CD/RGO/Ag nanocomposites. It can be seen that the GO spectrum exhibits a characteristic absorption peak at 228 nm corresponding to the π→π* transition of aromatic C═C bonds. After chemical reduction, this peak shifts from 228 to 264 nm, further confirming the reduction of GO. Meanwhile, the absorbance of the entire visible range has a significant increase**.** For sample of *β*-CD/RGO/Ag nanocomposites, it can be observed a clear broad absorption peak centred at 380 nm, corresponding to the surface plasmon resonance absorption of Ag nanoparticles, indicating the formation of *β*-CD/RGO/Ag nanocomposites.

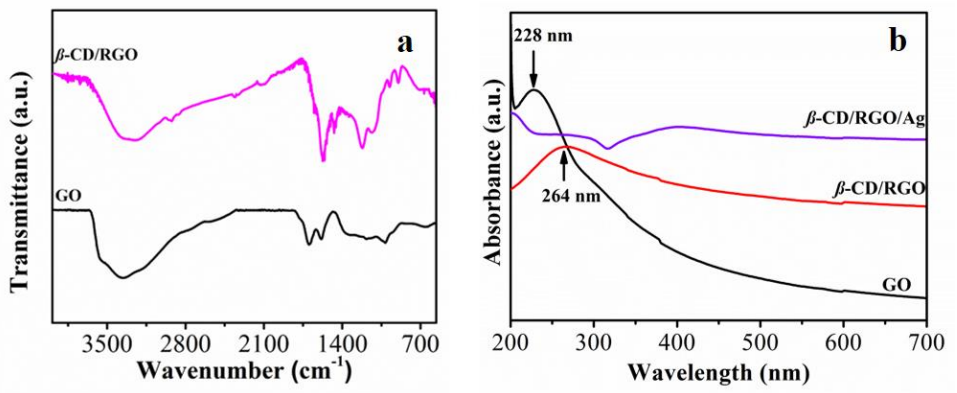

Fig 1. (a) FTIR spectra of GO and *β*-CD/RGO nanocomposites. (b) UV-vis spectra of GO, *β*-CD/RGO and *β*-CD/RGO/Ag nanocomposites.

For the purpose of examining the morphology of the *β*-CD/RGO/Ag nanocomposites, SEM characterization was conducted and the images are shown in Fig. 2. In comparison with the *β*-CD/RGO (Fig. 2a), the *β*-CD/RGO/Ag nanocomposites (Fig. 2b) show a uniform decoration of Ag nanoparticles on both sides of the *β*-CD/RGO sheets. The average size of Ag nanoparticle is 80 nm.

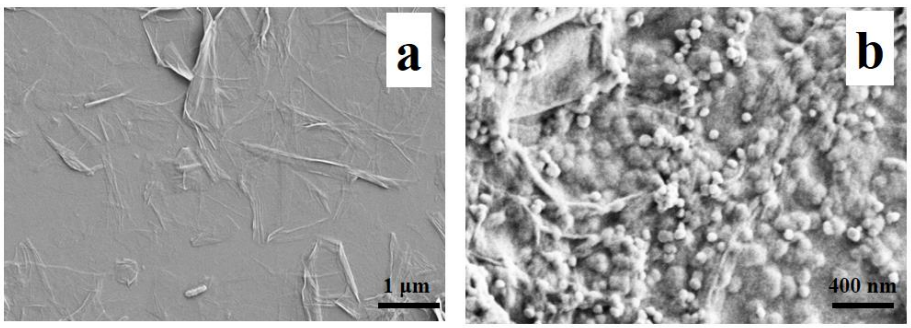

Fig 2. SEM images of (a) *β*-CD/RGO and (b) *β*-CD/RGO/Ag nanocomposite.

3.2 Electrochemical behaviour of nitrite on the β-CD/RGO/Ag modified electrode

Fig 3a compares the cyclic voltammograms (CVs) of bare, *β*-CD/RGO and *β*-CD/RGO/Ag modified GCE toward oxidation of nitrite. As shown in Fig 3a, no distinct current response of nitrite could observe on the bare electrode. At *β*-CD/RGO modified GCE, the CV profile shows a well-defined oxidation peak with peak potential at 0.85 V, indicating the *β*-CD/RGO modification exhibits a better direct electron transfer performance than bare electrode. Furthermore, the *β*-CD/RGO/Ag modified GCE shows a similar CV profile but with a much higher current response. The increase of current response reveals the *β*-CD/RGO sheets are an excellent platform for loading Ag nanoparticles, which not only increases the surface area of the modified electrode but also facilitates the electron transfer to the electrode. Fig 3b shows the typical amperometric responses of the *β*-CD/RGO/Ag modified GCE to the addition of nitrite. The responsive time is less than 8 s, which is due to the high electronic conductivity and good catalytic activity of *β*-CD/RGO/Ag. Meanwhile, the current responses of *β*-CD/RGO/Ag modified GCE show a linear relationship to the concentrations of nitrite. The inset Fig b presents the corresponding calibration curve. The linear regression equation can be obtained as I (μA) = 3.82 $C_{nitrite}$ (mM) + 0.4026 in a concentration range of 0.05 to 42.75 mM. In addition, the detection limit is calculated as 16.07 μM based on S/N = 3.

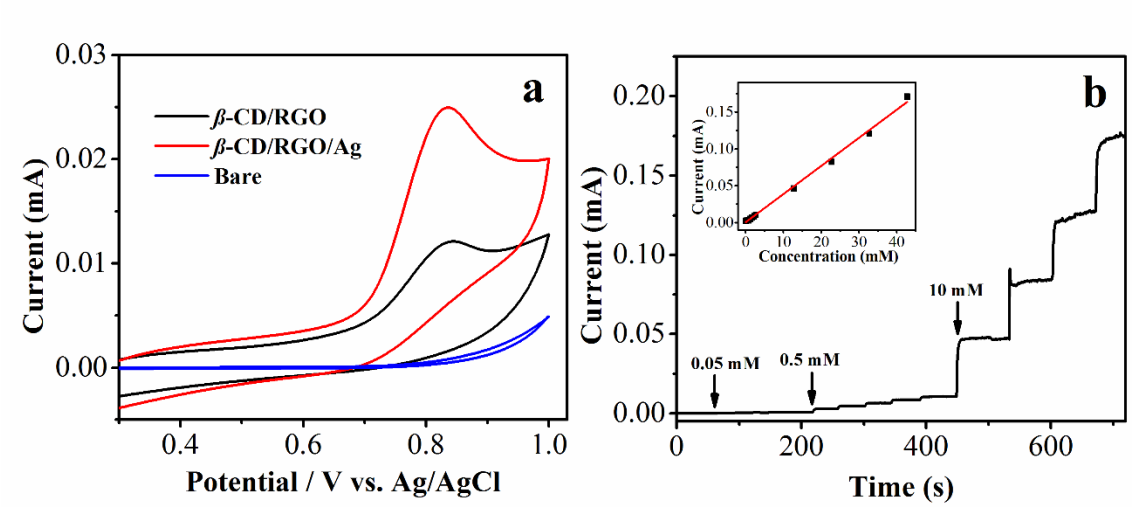

Fig 3. (a) Cyclic voltamograms of bare GCE, *β*-CD/RGO and *β*-CD/RGO/Ag modified GCE in PBS (pH 7) with 5.0 mM nitrite. Scan rate: 50 mV /s. (b) Amperometric response of the *β*-CD/RGO/Ag composite modified GCE for the successive addition of nitrite. Applied potential: ─0.85 V. Inset: Calibration curve at concentration range of 0.05-40 mM.

4. Conclusions

In summary, a novel *β*-CD/RGO/Ag nanocomposites were prepared via two steps wet chemical method. FTIR confirmed the reduction of GO and coating of *β*-CD on RGO sheets. SEM characterization showed the Ag nanoparticles with an average size of 80 nm were decorated on the *β*-CD/RGO sheets. The as-synthesized *β*-CD/RGO/Ag nanocomposites exhibit an excellent electrocatalytic activity towards oxidation of nitrite. The proposed nitrite sensor showed a linear response range from 0.05 to 40 mM and a low detection limit of 16.08 μM.

Acknowledgments

L Fu acknowledges the Swinburne University Postgraduate Research Award (SUPRA) for supporting this work.

Conflicts of Interest

The authors declare no conflict of interest

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