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Preparation of highly sensitive Pt nanoparticles-carbon quantum dots/ionic liquid functionalized graphene oxide nanocomposites and application for H_2O_2 detection

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ABSTRACT

There is current interest in developing carbon nanomaterials, which are a novel kind of nanomaterial, for uses in electrochemical sensing and biosensors. We constructed a novel sensor based on a Pt nanoparticles-carbon quantum dots/ionic liquid functionalized graphene oxide (PtNPs-CDs/IL-GO) nanocomposite for detecting H_2O_2. We characterized the morphology and electrochemical performance of the modified electrode using scanning electron microscopy, transmission electron microscopy, Raman spectroscopy, and cyclic voltammetry, respectively. The unique chemical structure of PtNPs-CDs/IL-GO greatly accelerated the catalysis of H_2O_2 and provided plenty of active sites for electrochemical redox reactions. Electrochemical experiments demonstrated that the PtNPs-CDs/IL-GO sensor had high selectivity, a wide linear range from 1 to 900 μM, and a low detection limit of 0.1 μM with respect to the reduction of H_2O_2. These characteristics indicate good electrical conductivity and high electrocatalytic activity. This simple and effective method has potential applications in chemical sensors and electrochemical catalysis.

1. Introduction

Graphene is a promising carbon material because of its large surface area, fast electron transfer [1], and exceptional thermal, chemical, and mechanical properties [2]. It is a novel kind of two-dimensional material with honeycomb crystal lattices that are based on a form like the benzene six-membered ring [3]. Graphene oxide (GO) has a single atomic layer structure that can be stretched laterally [4]. GO has a large number of polar oxygen groups, which causes both high chemical activity and hydrophilic activity between the layers of GO [5]. During the preparation of GO, the introduction of oxygen-containing groups destroys the π-conjugated structure of natural graphene, weakening electroconductivity but retaining the function of GO as an electron receptor [6–8]. Additionally, the increased hydrophilicity facilitates electrochemical modification, which enables GO to act as a carrier material for nanoparticles [9,10]. GO can be modified in situ on an electrode and, as such, can be directly used in electrochemical applications [11]. Thus, the surface modification of GO has become a focus of research. Of the various ways that GO has been functionalized for different applications, ionic liquid functionalized GO (IL-GO) has particular advantages, such as strong electrical conductivity, a large specific surface area, good dispersibility, and stability [12,13]. Because of superior solubility and surface charge, the IL-GO prepared by Niu and coworkers, showed good dispersibility and long-term stability in various solvents [14]. In addition, electrochemical sensors and biosensors based on the direct electron transfer of IL-GO with respect to various redox enzymes and their use in detecting various types of compounds, such as glucose [15], nitrite [16], and NADH [17], have been reported extensively in the literature.

Carbon quantum dots (CDs) are novel carbon nanostructures that are less than 10 nm in dimension and were first discovered in 2004 [18] during the purification of single-walled carbon nano-

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tubes using electrophoresis. Since then they have attracted a great deal of interest because of their novel, unique, and benign nature. CDs have enormous potential in luminescence, catalysis, and sensors because of their superior electronic properties as electron donors and acceptors [19]. In the past few years, CDs have had promising applications in various fields [20], such as catalysis [21], electronic [22] and photo-catalysis [23], sensors [24], bioimaging [25], optoelectronics, and surface-enhanced Raman scattering because of their optical properties. In particular, CDs have promising uses in fluorescence emissions and other exclusive characters [26]. Therefore, wide attention has been focused on the structure, establishment, and use of CDs as remarkable materials for sensors and electrocatalytic preparations.

In recent years, researchers have prepared a series of CDs that have similar structures and compositions using a variety of methods or materials. The CDs were thus modified via deposition or coating methods [27] to fabricate biosensors, for instance, combined with metal particles, metal compounds, and organic polymers. So far, there are several research groups that have prepared CDs-metal nanocomposites to improve catalytic performance because of the outstanding electrocatalytic activity that noble metals exhibit [28,29]. Pt nanoparticles (PtNPs) are an excellent electrocatalyst material and have been widely used for detecting H_2O_2 because of how PtNPs promote the evolution of H_2O_2 and reduce the H_2O_2 overvoltage and thus easily avoid anodic interfering substances like uric acid (UA) and ascorbic acid (AA) [30]. The superior performance of PtNPs, such as good catalytic activity, high electron transfer efficiency, and good optical properties, make them potentially applicable in catalysts, fuel cells [31], and biosensors. In recent years, decorating PtNPs on nanomaterials, such as Au and graphene, has been reported to enhance electrocatalytic activity and to provide more active sites for attaching the substrate [32]. GO can be used as Pt nanocomposite support material because of its high specific surface area, adjustable surface functional groups, good conductivity, and good compatibility with a Pt precursor solution [33]. In addition, the surface functional groups of carbon materials, especially oxygen-containing functional groups, play an important role in improving the catalytic activity of PtNPs [34]. The synergy between CDs and GO causes PtNPs to stick on the support material and to improve the stability of PtNPs.

In this study, a PtNPs-CDs/IL-GO nanohybrid was prepared to modify the glassy carbon electrode (GCE) for the electrochemical determination of H_2O_2. Subsequently, scanning electron microscopy (SEM) and other methods were used to investigate the structure of the obtained PtNPs-CDs/IL-GO/GCE, and cyclic voltammetry (CV) was used to evaluate the electrochemical behavior of the modified electrode. The prepared sensor has outstanding performance in the determination of H_2O_2 with high sensitivity, a wide linear range, and a low detection limit.

2. Experimental

2.1. Chemicals and reagents

GO was purchased from Nanjing XFNano Materials Technology Co., Ltd. (Nanjing, China). $H_2PtCl_6{\cdot}6H_2O$, ethylenediamine, 1-methylimidazole, and 2-bromoethylamine hydrobromide were obtained from Sigma (Shanghai, China). Dopamine (DA), glucose, UA, AA, potassium ferricyanide, sodium citrate, and H_2O_2 were obtained from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). All reagents were analytical grade and were used as received. Nanopure deionized and distilled water (DDW, 18.2 $M\Omega\,cm^{-1}$) was used in all of the experiments.

2.2. Apparatus

Electrochemical studies were performed on a CHI660D electrochemical system (Chenhua Instruments, Shanghai, China) equipped with a personal computer for data storage and processing. The measuring unit was a conventional three-electrode system with a GCE as the working electrode, an Ag/AgCl/KCl (saturated) electrode as the reference electrode, and a platinum wire as the counter electrode. SEM was performed on an S-4800 electron microscope (Hitachi, Ltd., Japan). Transmission electron microscopy (TEM) was performed on a JEM-2100F electron microscope (JEOL, Ltd., Japan) at 300 kV. The UV–vis absorption spectra (UV–vis) was recorded using a Thermo Scientific NanoDrop 2000/2000C spectrophotometer. All experiments were conducted at room temperature.

2.3. Synthesis of IL-GO, CDs, and the PtNPs-CDs/IL-GO nanocomposite

IL-GO was synthesized by an epoxide ring-opening reaction between GO and the 1-(3-aminopropyl)-3-methylimidazolium bromide (IL-NH_2), according to the method described in our previous report [35]. 5 mg of GO reacted salt effect with 10 mg of IL-NH_2 and 10 mg of NaOH were added to the mixture and ultrasonicated for 10 min. The mixture was then subjected to an oil bath reflux for 24 h at 80 °C. The resulting substance was centrifuged three times and dried to obtain IL-GO.

CDs were prepared according to Xu's method [36], and the process was as follows: 25 mL of sodium citrate solution (0.1 M) and ethylenediamine (300 μL) were loaded into a 50 mL Teflon-lined stainless steel autoclave that was kept at 180 °C for 6 h. The product was used after filtering with a cylinder membrane filter (0.22 μm).

To prepare the PtNPs-CDs/IL-GO nanohybrid, 10 μL of CDs (1 $mg\,mL^{-1}$), 500 μL of IL-GO, and 40 μL of $H_2PtCl_6{\cdot}6H_2O$ solution (17 mM) were mixed and then 2.2 mg of $NaBH_4$ was added. The mixture was successively ultrasonicated for 10 min and centrifuged three times.

2.4. Fabrication of the modified electrode

Before modification, the GCE was polished to be mirror-like using aluminite powder, washed with DDW, and subjected to an ultrasonic bath successively in DDW and ethanol three times. The GCE was then dried at room temperature. To modify the electrode, 5 μL of the obtained PtNPs-CDs/IL-GO nanocomposite was dropped on the cleaned GCE surface and dried in air before the next process to obtain the PtNPs-CDs/IL-GO/GCE. CV at a scan rate of 0.1 $V\,s^{-1}$ was used to characterize the different modified electrodes in a 1.0 M $K_3Fe(CN)_6$ solution containing 0.1 M KCl. Finally, the amperometry signals were recorded at a constant potential (−0.08 V).

3. Results and discussion

3.1. Characterizations of the CDs

To study the apparent characteristic and optical behavior of the CDs, TEM and UV–vis were applied in detail. TEM was performed to determine the size of the nanoparticles. Fig. S1A shows the TEM images of the CDs and confirms that the CDs were definitely sized spheres with sizes ranging from 5 to 10 nm in diameter. As shown in Fig. S1B, the solution of CDs had a strong UV–vis absorption peak at 343 nm, which may arise from the π-π^* transition of the nanocarbon particles and from the excitation energy sink of the surface states. A maximum fluorescent emission wavelength was at 462 nm.

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