



One-step synthesis of graphene–AuNPs by HMTA and the electrocatalytic application for O₂ and H₂O₂

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ABSTRACT

A green, one-step method for synthesis of graphene–Au nanoparticles (graphene–AuNPs) was introduced in this article, using an environmentally benign hexamethylenetetramine (HMTA) as reducing and stabilizing agent. HMTA slowly was hydrolyzed to generate aldehyde ammonia to reduce graphene oxides (GO) and hydrogen tetrachloroaurate (Au precursor). The structure and composition of the graphene–AuNPs nanocomposites were studied by means of ultraviolet visible (UV) absorption spectra, X-ray photoelectron spectroscopy (XPS) and Transmission electron microscopy (TEM). The AuNPs are well-dispersed on graphene nanosheets in narrow size range. The nanocomposites have excellent electrocatalytic properties for catalytic reduction of O₂ and H₂O₂.

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1. Introduction

Graphene, a two dimensional monoatomic thick building block of a carbon allotrope, has triggered extensive attention in electrochemical studies, due to its fascinating electronic and mechanical properties [1,2], since its discovery by Geim and co-workers in 2004 [3]. Because of its unique nanostructure and extraordinary properties, graphene is not only a basic building block for graphitic materials of all other dimensionalities [1], but also considered to be the thinnest and strongest materials [4]. However, pure graphene cannot remain good dispersibility as single-layer sheets in aqueous solution [5,6]. To overcome this problem, the functionalization of graphene has been considered to be an important method for expanding its application in recent years [7]. In addition, graphene-based nanocomposites have been received increased attention due to the synergistic contribution of two or more functional components and its many potential applications [8,9]. Up to now, a number of works have reported for graphene–metal nanocomposites, such as Au [10–17], Ag [16], Pt [17], and Pd [18] decorated graphene nanosheets.

As well known, Au nanoparticles (AuNPs) are one of the most intensively studied and applied metal nanoparticles in electrochemistry due to their extraordinarily physical and chemical

properties [19–21]. These unique properties allow them to provide major functions like electroanalysis and construct electrochemical sensors [22,23]. Herein, AuNPs are decorated on graphene nanosheets to enhance the electrocatalytic activity of the nanocomposites by improving their electrical conductivity. However, the electrocatalytic activity of graphene–AuNPs nanocomposites greatly depends on the size and dispersion of the AuNPs. Therefore, the method of synthesizing AuNPs in narrow size and good dispersion requires for further study. Different synthetic methods have been developed to prepare the desired AuNPs. One of the common methods is the reduction of hydrogen tetrachloroaurate (Au precursor) by sodium citrate [24]. AuNPs synthesized by such method are in big size. In the Brust method, AuNPs were reduced by sodium borohydride in the presence of alkylthiols [25], but the disadvantage of this method introduces the contamination of boride impurities. A few other one-step reduction processes were also developed to generate monodispersed AuNPs [26,27], for example, some amine-containing organic reagent can reduce Au precursor to AuNPs [28–30]. This method is limited to organic media.

Hexamethylenetetramine (HMTA), a heterocyclic organic compound with cage-like structure similar to adamantane as an environmentally friendly reagent, is widely applied in aqueous-phase synthesis. Owing to its inexpensiveness, commercial availability, high solubility in water and polar organic solvents, HMTA has been applied in a broad variety of fields [31]. It can serve as a reductant to prepare water-soluble metal nanoparticles [32], in which metal precursor is reduced in situ by the generated

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aldehyde ammonia from the hydrolysis of HMTA in water [32–34]. Recently, HMTA was also used as an effective reductant to prepare graphene nanosheets with highly stable aqueous colloidal dispersions [35]. So it is possible that HMTA can act as an effective reducer and stabilizer to simultaneously reduce the Au precursor and graphene oxides (GO) to produce the graphene–AuNPs nanocomposites under mild conditions.

In this paper, one-step method was firstly adopted to synthesize the graphene–AuNPs nanocomposites from GO and Au precursor with the help of HMTA. HMTA was able to ensure the homogeneous nucleation of AuNPs at the initial process by slowing the reaction rate. HMTA was slowly hydrolyzed to generate aldehyde ammonia, which could reduce Au precursor and GO to form well-dispersible AuNPs decorated graphene nanosheets. The attachment of AuNPs onto graphene not only prevents the restack of these sheets during the chemical reduction process, but also leads to the formation of a new class of graphene-based nanocomposites. The nanocomposites modified glassy carbon electrode (graphene–AuNPs/GCE) shows excellent electrocatalytic activity toward O_2 and H_2O_2 . The good electrocatalytic activity provides greatly importance to its potential application in chemical sensors and biosensors.

2. Experimental

2.1. Reagents and materials

Graphite powders (320 mesh) were of spectroscopic purity and purchased from Shanghai Chemicals, China. $H AuCl_4 \cdot 3H_2O$ was obtained from Aldrich. Hydrogen peroxide solution (30 wt% aqua) was purchased from Beijing Chemicals. Hexamethylenetetramine and sodium oleate were both purchased from Shanghai Chemical Reagent Company and used without further purification. Unless otherwise stated, reagents were of analytical grade and used as received. Aqueous solutions were prepared with double-distilled water from a Millipore system ($>18 M\Omega cm$).

2.2. Instruments

Ultraviolet visible (UV) absorption spectra were recorded by a Hitachi U-3900 spectrometer. Transmission electron microscopy (TEM) images were obtained using a Hitachi-600 transmission electron microscope operating at 100 kV. X-ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCALAB MK II X-ray photoelectron spectrometer. Cyclic voltammetry (CV) measurements were carried out using a conventional three-electrode system with a platinum wire as auxiliary electrode and an $Ag/AgCl$ (3 M KCl) as reference electrode in a CHI 660A Electrochemical Workstation (CHI, USA). The working electrodes were bare or modified (GCE, d: 3 mm). Before utilization, GCE was carefully polished to a mirror finish with 1.0, 0.3 and 0.05 nm alumina slurries successively, and rinsed with double-distilled water, followed by sonication in acetone and double-distilled water in succession, and finally dried in N_2 . The electrolyte solution used for CV experiment was 0.05 M phosphate buffer solution (PBS, pH 7.4), which was used in all electrochemical studies unless otherwise stated.

2.3. Synthesis of GO

GO was synthesized from natural graphite powder by a modified Hummers method [36,37]. The graphite powder (10 g) was put into an 80 °C solution of concentrated H_2SO_4 (15 mL), $K_2S_2O_8$ (5 g), and P_2O_5 (5 g). The mixture was kept at 80 °C for 4.5 h using a hotplate. Successively, the mixture was cooled to room temperature, and diluted with distilled water, filtered, and washed on the filter until the rinse water pH became neutral. The preoxidized graphite was dried in air at ambient temperature. The oxidized graphite powder

(10 g) was put into cold (0 °C) concentrated H_2SO_4 (230 mL). Then, $KMnO_4$ (30 g) was added gradually under stirring and the temperature of the mixture was kept to be below 20 °C by cooling. The mixture was then stirred at 35 °C for 2 h, and distilled with distilled water (460 mL). The temperature of the mixture increased to 98 °C and maintained for 15 min. The reaction was terminated by the addition of a large amount of distilled water (1.4 L) and 30% H_2O_2 solution (25 mL). The mixture was filtered and washed with 1:10 HCl solution (2.5 L) in order to remove metal ions. The GO dispersion was subjected to dialysis 3–4 days to completely remove metal ions and acids. Finally, the resulting purified GO powders were collected by centrifugation and air drying.

2.4. Synthesis of graphene and graphene–AuNPs nanocomposites

A general procedure for the preparation of graphene–AuNPs nanocomposites is described as follows. At first, 0.015 g $H AuCl_4 \cdot 3H_2O$ were dissolved in 1.25 mL of 0.1 M HCl solution and 0.0125 g sodium oleate were dissolved in 10.0 mL of double distilled water under stirring, respectively. Then the above two solutions were mixed to be a lemon solution. The resulting solution was dropwisely added to 10 mL GO in a 50 mL round-bottom flask. Next, 0.15 g HMTA were mixed under vigorous stirring for 10 min, and in this process, the pH of this mixture was adjusted to 13.0 with addition of 0.4 M KOH. Subsequently, the mixture was refluxed in an oil bath at 80 °C under stirring for 80 min over which the color of the solution gradually changed into amaranth. Finally, the resulting nanocomposites were centrifuged and collected for 12 min at 8000 rpm. HMTA could be hydrolyzed in aqueous solution generating ammonia and formaldehyde little by little, which reduces Au precursor to uniformly dispersed AuNPs decorating graphene nanosheets. In this procedure, in order to control the growth and size of the final produced AuNPs, sodium oleate was regarded as the surfactant. Uniform vesicle structures could be generated in aqueous systems. In this process, when water-soluble Au precursor was dispersed in the sodium oleate solution, many separated micro-reactors were formed for the synthesis of well-dispersed AuNPs. As a result, GO and Au precursor could be reduced to the narrow size and favorable dispersion of graphene–AuNPs nanocomposites. Scheme 1 shows the chemical structure of HMTA and the schematic of the process for preparing the graphene–AuNPs nanocomposites. The graphene was prepared according to a previous report [35].

2.5. Fabrication of graphene/GCE and graphene–AuNPs/GCE nanocomposites films

The GCEs were polished subsequently with 1.0, 0.3 and 0.05 μm alumina slurry, and then sonicated in water for several times. To prepare graphene and graphene–AuNPs modified GCE, an aliquot of 5 μL 2.5 mg mL^{-1} graphene and graphene–AuNPs aqueous solution was dropped onto the surface of GCE using a microsyringe, respectively. The dried films could be obtained after 10 h at 4 °C.

3. Results and discussion

3.1. Structure characterization

The UV absorption spectra, XPS and TEM studies were carried out to investigate the chemical and structural information of the as-prepared graphene–AuNPs nanocomposites. The UV absorption spectra of GO (black), the reduced GO (blue) and graphene–AuNPs aqueous solutions (red) were shown in Fig. S1. The UV absorption spectra of the GO dispersion reached an absorption peak at ca. 227 nm (curve a in Fig. S1). When the GO aqueous dispersion was reduced by HMTA, the absorption peak red shifts to 254 nm (curve

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