Journal of Hazardous Materials 197 (2011) 320–326

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Synthesis of Au nanoparticles decorated graphene oxide nanosheets: Noncovalent functionalization by TWEEN 20 in situ reduction of aqueous chloroaurate ions for hydrazine detection and catalytic reduction of 4-nitrophenol

Wenbo Lu[a], Rui Ning[a,b], Xiaoyun Qin[a], Yingwei Zhang[a], Guohui Chang[a], Sen Liu[a], Yonglan Luo[a], Xuping Sun[a,*]

[a] State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, Jilin, China
[b] Graduate School of the Chinese Academy of Sciences, Beijing 100039, China

ARTICLE INFO

Article history:
Received 15 August 2011
Received in revised form
23 September 2011
Accepted 23 September 2011
Available online 1 October 2011

Keywords:
TWEEN 20
Graphene oxide
Au nanoparticle
4-Nitrophenol
Hydrazine detection

ABSTRACT

In this paper, we develop a cost-effective and simple route for the synthesis of Au nanoparticles (AuNPs) decorated graphene oxide (GO) nanosheets using polyoxyethylene sorbitol anhydride monolaurate (TWEEN 20) as a stabilizing agent for GO as well as a reducing and immobilizing agent for AuNPs. The AuNPs assemble on the surface of TWEEN-functionalized GO by the in situ reduction of $HAuCl_4$ aqueous solution. The morphologies of these composites were characterized by atomic force microscopy (AFM) and transmission electron microscopy (TEM). It is found that the resultant AuNPs decorated GO nanosheets (AuNPs/TWEEN/GO) exhibit remarkable catalytic performance for hydrazine oxidation. This hydrazine sensor has a fast amperometric response time of less than 3 s. The linear range is estimated to be from 5 μM to 3 mM ($r = 0.999$), and the detection limit is estimated to be 78 nM at a signal-to-noise ratio of 3. The AuNPs/TWEEN/GO composites also exhibit good catalytic activity toward 4-nitrophenol (4-NP) reduction and the GO supports also enhance the catalytic activity via a synergistic effect.

1. Introduction

Graphene, a free-standing two-dimensional crystal with a single layer structure, has become one of the hottest of topics in the fields of physics, chemistry, nanotechnology and materials science [1–4]. Graphene-based nanocomposites have stimulated intense research over past decades because of their new optical, electronic, mechanical, and catalytic properties [4–7]. Particularly, due to the large surface area and above mentioned properties, graphene oxide (GO) has been an attractive choice as the substrate for nanocomposites [8–11]. Among them, Au nanoparticles (AuNPs)/GO nanocomposites have attracted immense attention [12,13]. It is well-documented that AuNPs play a key role in electrocatalytic reactions and AuNPs modified electrodes exhibit higher electrocatalytic activities for the detection of some small molecules such as hydrazine [14], H_2O_2 [15], and nitric oxide [16] than other traditional modified electrodes. Meanwhile, AuNPs also show a good catalytic activity for reduction of 4-nitrophenol (4-NP) [17]. More recently, many efforts have been devoted to the design of AuNPs supported on GO sheets. For example, Pham and coworkers have reported a method for immobilization of AuNPs on GO sheets by covalent bonding [18]. Zhou et al. have prepared AuNPs/GO composites obtained by immersing the Ag nanoparticles/GO composites in the $HAuCl_4$ solution [9]. However, all the above-mentioned methods suffer from more or less drawbacks, such as the prior GO functionalization [18] and the multiple-step preparation process [9]. Accordingly, the development of new preparation strategy overcoming all the shortcomings is highly desired.

Hydrazine is extensively used in chemistry industry, aerospace industry and pharmaceutical field, including catalysts, fuel cell, rocket fuels, high-energy propellant, missile systems, herbicide and pesticide [19–23]. It is a neurotoxin, and hence produces mutagenic and carcinogenic effects causing damage to kidneys, lungs, liver, respiratory tract infection and long-term effects on the central nervous system [20,21]. Due to the above reasons, it is highly desirable to fabricate a sensitive analytical tool for the effective detection of hydrazine. Water pollution by phenol and phenolic compounds is of tremendous public concern. Nitrophenols and their derivatives, which result from the production processes of pesticides, insecticides, synthetic dyes and herbicides, are some of the most refractory pollutants that occur in industrial wastewaters [24–26]. The United

---

* Corresponding author. Tel.: +86 431 85262065; fax: +86 431 85262065.
E-mail address: sunxp@ciac.jl.cn (X. Sun).

0304-3894/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2011.09.092

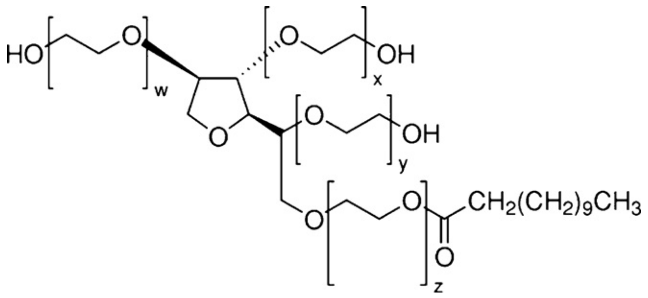

Fig. 1. The chemical structure of TWEEN 20.

States Environmental Protection Agency lists nitrophenols among the top 114 organic pollutants [25]. Because of the aforesaid reasons, this study for catalytic reduction of 4-nitrophenol becomes more fascinating from the point of pollution abatement.

Polyoxyethylene sorbitol anhydride monolaurate (TWEEN 20), a commercially available and innoxious chemical with aliphatic ester chains, is composed of three chemical sections (as shown in Fig. 1): aliphatic ester chains that can prevent nonspecific binding of biomolecules, an aliphatic chain that can easily be adsorbed on a hydrophobic surface by noncovalent interaction, and three-terminal hydroxyl groups that are hydrophilic and can be chemically modified for further applications. Although Park et al. have fabricated a strong TWEEN 20 dispersion of chemically reduced GO composites [27], the synthesis and applications of nanoparticle-decorated TWEEN/GO composites have not been reported. In this paper, we report on our recent finding that AuNPs can be in situ reduced and immobilized on TWEEN 20-functionalized GO through a cost-effective strategy with the use of TWEEN 20 as a stabilizing agent for GO [27] as well as a reducing and immobilizing agent for Au nanoparticles. Scheme 1 illustrates the noncovalent functionalization of GO by TWEEN 20 and the subsequent in situ synthesis of AuNPs on TWEEN/GO. It was found that the resultant AuNPs decorated TWEEN/GO (AuNPs/TWEEN/GO) composites exhibit notable catalytic performance toward hydrazine oxidation. Meanwhile, the AuNPs/TWEEN/GO composites exhibit good activity in catalyzing the reduction of 4-nitrophenol (4-NP) by $NaBH_4$ and the GO support has a synergistic effect to enhance the catalytic activity of AuNP catalysts.

2. Experimental

2.1. Materials

TWEEN 20, $HAuCl_4$, NaH_2PO_4, Na_2HPO_4, graphite, chitosan and H_2O_2 (30 wt%) were purchased from Aladin Ltd. (Shanghai, China). $KMnO_4$, $NaNO_3$, ammonium hydroxide ($NH_3{\cdot}H_2O$) (28 wt% in water), H_2SO_4, ethanol were purchased from Shanghai Chemical Factory (Shanghai, China). All chemicals were used as received without further purification. The water used throughout all experiments was purified through a Millipore system. Phosphate buffer saline (PBS) was prepared by mixing stock solutions of NaH_2PO_4 and Na_2HPO_4 and a fresh solution of H_2O_2 was prepared daily.

2.2. Instruments

Atomic force microscopy (AFM) was conducted with a SPI3800N microscope (Seiko Instruments, Inc.). UV–vis spectra were collected on a UV5800 modal spectrophotometer. Transmission electron microscopy (TEM) measurements were made on a HITACHI H-8100 EM (Hitachi, Tokyo, Japan) with an accelerating applied potential of 200 kV. The sample for TEM characterization was prepared by placing a drop of the dispersion on carbon-coated copper grid and dried at room temperature. Electrochemical measurements are performed with a CHI 660D electrochemical analyzer (CH Instruments, Inc., Shanghai). A conventional three-electrode cell is used, including a GCE (geometric area = $0.07\ cm^2$) as the working electrode, a Ag/AgCl (3 M KCl) electrode as the reference electrode, and platinum foil as the counter electrode. All potentials given in this work are referred to the Ag/AgCl electrode. All the experiments are carried out at ambient temperature.

2.3. Preparation of GO

GO was prepared from natural graphite powder through a modified Hummers method [28]. In a typical synthesis, 1 g of graphite was added into 23 mL of 98% H_2SO_4, followed by stirring at room temperature over a 24 h period. After that, 100 mg of $NaNO_3$ was introduced into the mixture and stirred for 30 min. Subsequently, the mixture was kept below 5 °C by ice bath, and 3 g of $KMnO_4$ was slowly added into the mixture. After being heated to 35–40 °C, the mixture was stirred for another 30 min. After that, 46 mL of water was added into above mixture during a period of 25 min. Finally, 140 mL of water and 10 mL of 30% H_2O_2 were added into the mixture to stop the reaction. After the unexploited graphite in the resulting mixture was removed by centrifugation, as-synthesized GO was dispersed into individual sheets in distilled water at a concentration of 0.5 mg/mL with the aid of ultrasound for further use.

2.4. Synthesis of AuNPs/TWEEN/GO composites

In a typical synthesis, 400 μL of TWEEN 20 (0.4 g/mL) solution was added into 1 mL of GO (0.6 mg/mL) aqueous solution, and then the mixture was sonicated for 30 min. Next, the mixture was centrifuged and the precipitates were redispersed in 0.5 mL of water. After that, 40 μL of 24.3 mM $HAuCl_4$ and 12 μL of 1 M NaOH aqueous solution were added into the previous solution under relatively mild shaking. The color of the resulting solution changed to dark-red after 5 s at room temperature.

2.5. Synthesis of TWEEN 20 stabilized AuNPs

As a control experiment, TWEEN 20 stabilized AuNPs (AuNPs/TWEEN) were also synthesized in the same way as synthesis of AuNPs/TWEEN/GO composites by mixing 40 μL of $HAuCl_4$ aqueous solution (24.3 mM) and 100 μL of TWEEN 20 (0.4 g/mL), and then 12 μL of 1 M NaOH aqueous solution was added into the mixture under relatively mild shaking. The color of the solution changed to dark-red after 3 s at ambient temperature. Finally, the mixture was diluted to 552 μL with water.

2.6. Electrocatalytic and optical experiments

The modified electrodes were prepared by a simple casting method. Prior to the surface coating, the GCE was polished with 1.0 and 0.3 μm alumina powder, respectively, and rinsed with doubly distilled water, followed by sonication in ethanol solution and doubly distilled water successively. Then, the electrode was allowed to dry in a stream of nitrogen. For the cyclic voltammetry experiment, 100 μL of AuNPs/TWEEN/GO composites was dropped on the surface of pretreated GCE and left to dry at room temperature. For current time experiment, 2 μL of chitosan (0.3%) was additionally cast on the surface of the above modified GCE and dried before electrochemical experiments. For the catalytic reduction of 4-nitrophenol (4-NP), freshly prepared aqueous solution of $NaBH_4$ (1.0 mL, 0.16 M) was mixed with 4-NP aqueous solution (1.0 mL, 7 mM) in the quartz cell (1.5 cm path length), leading a color change from light yellow to yellow-green. Then, the catalysts were added