Materials Science and Engineering C 38 (2014) 39–45

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

Preparation of novel silver nanoplates/graphene composite and their application in vanillin electrochemical detection

Linhong Huang [a,b,c], Keyu Hou [b,c], Xiao Jia [b,c], Haibo Pan [a,b,c,*], Min Du [a]

[a] Fujian Key Lab of Medical Instrument & Pharmaceutical Technology, Yishan Campus, Fuzhou University, Fuzhou, Fujian 350002, China
[b] Institute of Research for Functional Materials, Fuzhou University, Yishan Campus, Fuzhou University, Fuzhou, Fujian 350002, China
[c] College of Chemistry and Chemical Engineering, Qishan Campus, Fuzhou University, Fuzhou, Fujian 350108, China

ARTICLE INFO

Article history:
Received 15 November 2013
Received in revised form 4 January 2014
Accepted 21 January 2014
Available online 29 January 2014

Keywords:
Ag nanoplates
Graphene
Electrocatalysis
Vanillin

ABSTRACT

Hexagonal Ag nanoplates (NPs) were synthesized by polyvinylpyrrolidone (PVP) and trisodium citrate (TSC) which selectively absorbed to Ag (100) and Ag (111) surfaces, then were anchored to graphene (GN) to form novel Ag NPs/GN composite. The thickness of Ag NPs is ~4 nm and the length is 18–66 nm. Transmission electron microscopy (TEM) image shows that the plates are f-c-c crystals containing {111} facets on their two planar surfaces. Zeta potential indicated that the surface of Ag NPs/GN is negatively charged while vanillin is positively charged. Thus Ag NPs/GN modified on glass carbon electrodes (GCE) allowed abundant adsorption for vanillin and electron transfer between vanillin and Ag NPs/GN/GCE. Square wave voltammetry (SWV) results indicated that the over potential on Ag NPs/GN/GCE negatively shifts 52 mV than that on Ag NPs/GCE. Ag NPs/GN with enhanced surface area and good conductivity exhibited an excellent electrocatalytic activity toward the oxidation of vanillin. The corresponding linear range was estimated to be from 2 to 100 μM ($R^2 = 0.998$), and the detection limit is 3.32×10^{-7} M (S/N = 3). The as-prepared vanillin sensor exhibits good selectivity and potential application in practical vanillin determination.

1. Introduction

Colloidal noble-metals, especially of Pd, Ag, Au, and Pt, have been studied intensively because of their application in catalysis [1], surface-enhanced Raman scattering (SERS) [2] and sensors [3]. Silver, a comparatively inexpensive catalyst and conductive metal, has been developed to many interesting structures, such as spheres, cubes, polyhedrons, wires [4], plates [5,6], and dendrite, because of its strong shape-dependent chemical and physical properties [7,8]. Note that Ag nanoplates (Ag NPs) have been researched owing to their fascinating catalytic and optical properties, large specific surface and effective/geometric area [9,10]. So the Ag NPs are expected to be synthesized and used as electrochemical sensing materials. The facet-specific capping has emerged as a facile route to the synthesis of Ag NPs, such as citrate and polyvinylpyrrolidone (PVP) which selectively bind to Ag (111) and Ag (100) surfaces, respectively. Further, the growth rate of silver atoms is distinct along the different facets to promote the plate structure forming [11]. In this field, the research on morphology control about Ag plates is well considered, but reports about composite based on the Ag NPs and their application are quite few.

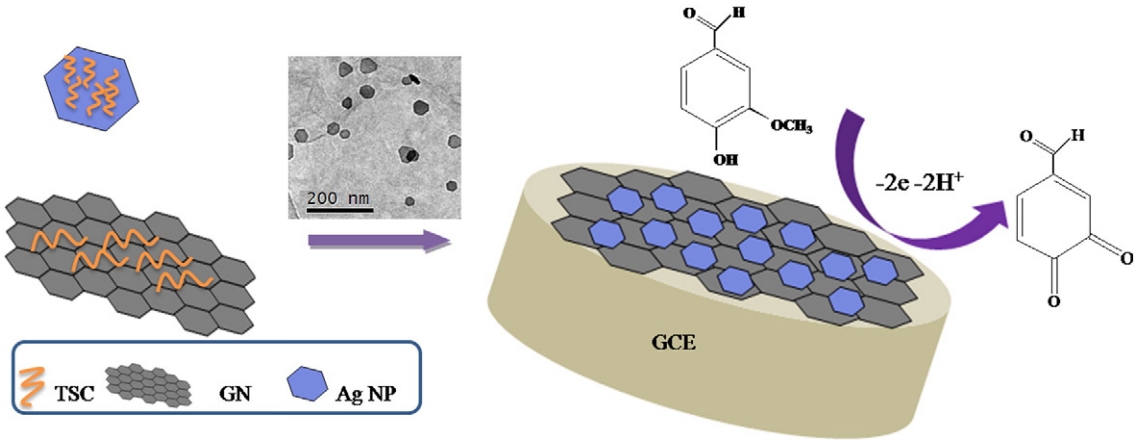
Graphene (GN) with high electron mobility (~200,000 $cm^2\ V\ s^{-1}$) [12] and high specific surface area (2600 $m^2\ g^{-1}$) [13] provides an avenue for fabricating electrochemical devices because it can facilitate electron transfer between electro-active species and electrodes [14,15]. The negatively charged graphene can attach free metal ions and oxygen groups at GO would act as crystal growth sites for the formation of composite. The oxygen-containing groups on graphene oxide (GO) would not only load metal ions but also afford targets for further covalent functionalization of GO [16,17]. The GN composite with the second component in layers can prevent the stacking of single-layer GN caused by π–π strong interaction [18,19]. Among various GN composites, Wang et al. indicated that the oxygen functional GO adsorbs trisodium citrate (TSC) on Ag triangle plates to drive the morphology modification [20]. In this work, GN with good conductivity will be added into pure Ag NPs to improve the electrical and catalytic performance.

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is widely used as flavor in milk powder, confectionery, beverages, food and perfumery [21]. However, excess vanillin is ingested into the human body, causing headaches and nausea and affecting liver or kidney functions. The maximum usage of vanillin is 7 mg/100 g (FAO/WHO 1992) while in the infant food vanillin is forbidden [22]. Hence, the determination of vanillin contents plays an important role in food fields. Several methods for determining vanillin have been researched including UV spectrophotometer [23], molecular imprinting [22], and electro-analysis [24,25]. However, electrochemical sensor based on nano-materials can be used for efficient detecting vanillin which contains electro-active groups.

In this work, we present the application of Ag NPs/GN/GCE to detect vanillin by square wave voltammetry (SWV). By controlling the

* Corresponding author at: College of Chemistry and Chemical Engineering, Qishan Campus, Fuzhou University, Fuzhou, Fujian 350108, China. Tel.: +86 591 83759450/22866127; fax: +86 591 22866127.
E-mail address: hbpan@fzu.edu.cn (H. Pan).

0928-4931/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.msec.2014.01.037



Scheme 1. The assembly process of Ag NPs/GN/GCE used in the detection of vanillin.

proportion of PVP and TSC, nano-scale hexagonal Ag NPs were synthesized and first anchored to GN through TSC. The Ag NPs/GN with enhanced surface area and good conductivity can lower over potential and increase peak current in electrochemical detection. Furthermore, we obtain the optimal condition for vanillin electro-oxidation and the analysis of vanillin in a real sample, biscuit. The sensor to vanillin exhibits high sensitivity, rapid response and good selectivity.

2. Experimental

2.1. Reagents

Natural graphite (FP, 99.95% pure), silver nitrate ($AgNO_3$), TSC (≥99%), sodium borohydride ($NaBH_4$, ≥99%), PVP (average Mw ~111) and vanillin were obtained from Sinopharm Chemical Regent Co., Ltd. Hydrogen peroxide (H_2O_2, 30 wt.%) was purchased from Tianjin Chemical Co., Ltd. All chemicals were used as received and without any further purification.

2.2. Apparatus

UV–vis spectra were recorded with a spectrophotometer (Perkin-Elmer Lambda 900 USA). The morphologies of samples were observed by AFM (Agilent 5500 USA). High-resolution transmission electron microscope (HRTEM) image was obtained using Tecnai G2 F20 S-TWIN, 200 kV (FEI Company, USA). Zeta-potential value measurement was performed on Zeta Sizer 3000 Laser Particle Size and Zeta Potential Tester (Malvern Corporation, UK), and deionized water was used as a dispersant here. Electrochemical experiments were performed with a CHI660D electrochemical workstation (CH Instrument Company, Shanghai, China) with a conventional three-electrode cell. A Pt wire and a Ag/AgCl electrode were used as the auxiliary electrode and reference electrode, respectively. Glass carbon electrode (8 mm diameter) loading different materials was used as working electrode. The surface of GCE was polished with 0.3 and 0.05 μm alumina slurries, ultrasonicated in water and ethanol, respectively. Then the bare GCE was dried under pure N_2. Finally, different materials were dropped on the surface of bare GCE, and dried under room temperature to form working electrode.

2.3. Preparation of Ag NPs/GN and the vanillin sensor

The synthesis of Ag NPs was referred to previous work [26]. Typically, 50 μL of $AgNO_3$ (0.05 M) was added into 24.15 mL deionized water followed by 0.5 mL of TSC (75 mM), 60 μL of H_2O_2 (30 wt.%), and 0.1 mL of PVP (17.5 mM) under vigorous stirring at room temperature. Then, 0.25 mL $NaBH_4$ (100 mM) was injected into the above solution. After the injection, the color of the solution immediately became light yellow and maintained 30 min, then the color of the solution changed into dark yellow and quickly tuned into red, green, and blue gradually.

GO was synthesized from natural graphite powder using the modified Hummers' method [27]. In brief, 1 g of graphite dispersed in 46 mL H_2SO_4 was slowly mixed with 1 g of $NaNO_3$ and 6 g $KMnO_4$ in an ice bath under strong stirring for 2 h. Then the mixture was transferred to a water bath and stirred for 2 h at 35 °C. The temperature was raised to 90 °C after the addition of 280 mL H_2O and kept at 90 °C for 1 h. The $KMnO_4$ was removed by the addition of 20 mL of H_2O_2. The light brown graphite oxide was purified by washing with 10 wt.% HCl and washed using warm water (30 °C) for several times. Exfoliation was accomplished by sonicating graphite oxide aqueous solution for 120 min and then centrifuged at 5000 rpm for 10 min to obtain GO solution. GO was reduced to GN by $NaBH_4$ in water bath for 1 h followed by addition of TSC. The composite was assembled by injecting Ag NPs into GN under vigorous stirring for 40 min at the ice bath. The route to construct vanillin sensor is illustrated in Scheme 1. The sufficient citrate ions in GN can act as complex sites and were purified by dialysis finally.

3. Results and discussion

3.1. Physicochemical characterization

Fig. 1 depicts the UV–vis absorption spectra of Ag NPs, GN, and Ag NPs/GN dispersed in water for reference. The as-prepared Ag NPs

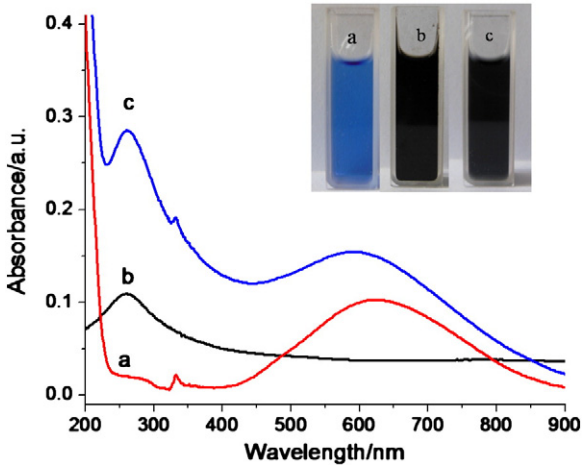


Fig. 1. UV–vis absorption spectra of (a) Ag NPs, (b) GN and (c) Ag NPs/GN. Inset: photographic images of Ag NPs, GN and Ag NPs/GN dispersed in H_2O.