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Keywords

oxide, efficient, nonenzymatic, h₂o₂, biosensor, reduced, graphene, decorated, one, nanoparticles, ag, synthesis, green, pot

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One-pot green synthesis of Ag nanoparticles-decorated reduced graphene oxide for efficient nonenzymatic H₂O₂ biosensor

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Abstract

Ag nanoparticles (AgNP) with an average size of 12 nm are successfully decorated on the reduced graphene oxide (rGO) sheets through a simple one-pot hydrothermal method using gallic acid as the reducing agent. This AgNP/rGO hybrid has been successfully applied in the catalytic performance toward the reduction of H₂O₂. The nonenzymatic sensor demonstrates a linear relationship in a wide concentration range of 0.05-5 mM (R=0.999), and a high sensitivity of 255 $\mu\text{Acm}^{-2}\text{mM}^{-1}$ to the detection of H₂O₂.

Keywords: Ag nanoparticles; green synthesis; reduced graphene oxide; nonenzymatic; sensor

1. Introduction

Silver is a well-known noble metal with high catalytic activity, remarkable optical properties, and excellent antibacterial activity [1]. Surfactants are usually introduced in the synthesis process for small Ag nanoparticles (AgNP) in order to avoid the conglomeration and large size of Ag particles, which could significantly depress its activity and stability [2]. However, the residual surfactant can also seriously deactivate the as-prepared catalyst. Therefore, the better method to prepare AgNP is on

supporting materials, such as conducting polymers [3], carbon materials [4], mesoporous silica [5], and fiberglass [6], *et al.* Recently, graphene, as an ideal supporting material for the AgNP with large surface area and high electrical conductivity, has received significant attention. Byeong-Su K *et al* reported a green approach to synthesis of AgNP onto the surface of graphene oxide functionalized with mussel-inspired dopamine [7]. Won B K *et al* obtained uniformly dispersed AgNP on reduced graphene oxide by adding NaBH₄ as reducing agent [8]. Pruneanu *et al* synthesized AgNP on few-layers graphene by radio frequency catalytic chemical vapor deposition [9]. Most developed methods still involved multi-steps and require strong reducing agents. It is still a challenging to develop a simple facile approach to effectively prepare AgNP decorated graphene hybrid with quality control.

In this work, we report an environmental friendly one-pot hydrothermal route to produce Ag nanoparticles decorated reduced graphene oxide hybrid (AgNP/rGO) using gallic acid (GA) as a reducing agent, which could be found in tea leaves, sumac, and other plants. The fabrication process is illustrated in Figure 1a. Firstly, Ag⁺ ion was easily coordinated with negatively charged oxygen-containing functional groups on GO sheets. Followed by the hydrothermal process, AgNP/rGO hybrid is obtained with the presence of GA. The as-prepared AgNP/rGO hybrid exhibits enhanced electrocatalytic performance toward H₂O₂ reduction and has been successfully applied for H₂O₂ detection.

2. Experimental

All the reagents are of analytical purity grade and have been received from commercial sources. GO was synthesized by the modified Hummers method [10]. The resulting GO solution was ultrasound for 1 h, centrifuged to wipe off the unexploited graphite, and diluted in distilled water at a

concentration of 2.5 mg/mL. 1 mL of 50 mM AgNO₃ solution and 60 uL of 0.2 M ammonia solution were dissolved into 30 mL distilled water for further use. 2 mL of GO was dispersed into the foregoing solution. The mixtures were added 6 mL of 5 mg/mL gallic acid solution and stirred for 20 min at room temperature then transfer in a Teflon liner of 40 mL capacity, and then the liner was sealed in a stainless steel autoclave. The autoclave was maintained at 190 °C for 5 h and then allowed to cool to room temperature by cool-water. Dark brown-colored precipitate was filtered off, washed with distilled water and absolute ethanol several times, and then dispersed in water for further use. Reduced graphene oxide without adding silver salt was prepared by the same procedure for comparison.

The morphology and structure of the prepared samples were characterized by transmission electron microscopy (TEM, JEOL-2010, voltage of 200 kV) and X-ray diffraction (XRD, D8-advanced, Bruker, 40 kV, 20mA, Cu K α radiation). The atomic composition of AgNP/rGO was detected by X-ray photoelectron spectroscopy (XPS, Perkin Elmer, Al K α radiation). Raman spectroscopy was performed using a Jobin-Yvon HR800 Raman system.

All electrochemical experiments were performed on a CHI720 electrochemical workstation. Cyclic voltammetry (CV) and chronoamperometry (CA) testing were carried out using a three-electrode cell, including a glassy carbon electrode (GCE) as the working electrode, an Ag/AgCl electrode as the reference electrode, and a platinum wire electrode as the counter electrode. For the working electrodes preparation, required amount of samples was ultrasonically dispersed in 0.081% Nafion solution to obtain a 2 mg/mL uniform ink. Then 10 μ L of the ink was dropped on the GCE and dried in the air before the electrochemical tests.

3. Results and Discussion

The TEM images of the GO and AgNP/rGO are shown in Figure 1 (b, c). Figure 1b indicates that the as-prepared GO is of a flake-like shape with slight wrinkles on the surfaces. From Figure 1c, it clearly shows that the rGO sheet has been decorated with Ag nanoparticles with an average diameter of 12 nm. The existence of C, O and Ag elements is further confirmed by EDS (Figure 1d). Si peak originates from the substrate. The corresponding particle size distribution is shown in Figure 1e, revealing AgNP with an average size of 12.29 ± 0.12 nm dispersed on the rGO sheets.

The XRD was performed to investigate the phase structure of GO, rGO and AgNP/rGO (Figure 2a). The as-synthesized GO displays a typical characteristic (002) peak at 10.8° . After the hydrothermal process, the diffraction peak (002) shifts to a higher angle at about 24° , which is ascribed to the reduction of GO sheets and restacking into an ordered crystalline structure. While the diffraction peaks of the AgNP/rGO are in good agreement with the standard Ag (JCPDS card: 04-0783) [11] except for the broad (002) peak at approximately 25° , which can be indexed as disordered stacked graphitic sheets [12]. No peaks from other phase have been detected, indicating that the product is of high purity.

The comparison of Raman spectra of GO, rGO and AgNP/rGO are shown in Figure 2b. It is noted that GO exhibits a G band at 1603 cm^{-1} , while the corresponding band of rGO and AgNP/rGO are 1591 and 1590 cm^{-1} , respectively. The red shifts of G band of rGO and AgNP/rGO can be attributed to the recovery of the hexagonal network of carbon in the rGO [13]. The chemical states of elements in AgNP/rGO were further characterized by XPS measurements (Figure 2c) corresponding to the characteristic peaks of C1s, O1s and Ag3d. The XPS spectrum for Ag3d shown in Figure 2d exhibits two major peaks with binding energies at 368.2 and 374.3 eV , corresponding to Ag $3d_{5/2}$ and Ag $3d_{3/2}$, respectively, with a spin-energy separation of 6 eV , suggesting the formation of metallic

silver [14]. The C1s XPS spectrum of GO (Figure 2e) could be deconvoluted into four peaks arising from C-C/C=C (284.6 eV) in the aromatic rings, C-O (286.4 eV) of epoxy and alkoxy, C=O (287.8 eV) and O-C=O (289.3 eV) groups, respectively [15]. For AgNP/rGO (Figure 2f), the intensity of oxygenated groups decreased significantly, illuminating that GO was reduced to rGO during the hydrothermal process. The C/O ratio of AgNP/rGO is 11.2, four times higher than that (2.6) of GO. This result is in a good agreement with the results of Raman spectroscopy [15].

To assess the electrocatalytic performance of the as-prepared AgNP/rGO hybrid to H_2O_2 , a nonenzymatic sensor was constructed. Figure 3a shows the CV curves of bare GCE, GO, rGO, and AgNP/rGO modified GCEs toward the electrocatalytic reduction of H_2O_2 in a nitrogen saturated 0.2 M pH 6.9 phosphate buffer solution (PBS). As shown in Figure 3a, AgNP/rGO exhibits a notable catalytic reduction current peak at -0.43 V vs Ag/AgCl, while it exhibits no electrochemical response in the absence of H_2O_2 , indicating the catalytic H_2O_2 reduction. In contrast, bare GCE, GO/GCE and rGO/GCE exhibited very poor activity to the reduction of H_2O_2 under identical conditions. All these observations reveal that AgNP/rGO exhibits notable catalytic activity for H_2O_2 reduction. Figure 3b presents a typical steady response with successive addition of H_2O_2 at -0.43 V. As is shown in the low concentration range (the insert of Figure 3b), a quick amperometric response is observed within 5 s at 96% steady state current. This kind of H_2O_2 biosensor exhibits a linear relationship in a range from 0.05 to 5 mM ($R=0.999$) with a high sensitivity of $255 \mu\text{Acm}^{-2}\text{mM}^{-1}$. In addition, the detection limit is calculated to be about 0.01 mM at the signal-to noise ratio of 3. The relative standard deviation (RSD) of the current response to 1 mM H_2O_2 is 2.4% for 6 successive measurements. Typical interferences using uric acid (UA), ascorbic acid (AA), dopamine (DA), and glucose (Glu) were chosen to test the selectivity, in which no apparent interferences were observed (Figure 3d). It

could be concluded that this AgNP/rGO hybrid had the great potential to be employed as biosensors with high sensitivity and stability.

Conclusion

In summary, AgNPs with an average size of 12 nm have been successfully decorated onto the rGO sheets through a simple one-pot hydrothermal method using gallic acid as the reducing agent. The as-synthesized AgNP/rGO hybrid displays an excellent electrocatalytic activity toward H₂O₂ reduction, with a promising response.

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References

- [1] Xiaoyan L, Feifeng W, Qinrong Q, Xingpin L, Liren X, Qinghua C. Mater Lett 2012; 66: 370-373
- [2] Majid D, Ali KZ, Muhamad MR, Huang NM, Mohammad H. Mater Lett 2012; 66: 117-120.
- [3] Uzeyir D, Murat K, Atilla C, Murvet V. Electrochim Acta 2012; 85: 220-227.
- [4] Yi C, Tao W, Ding Z, Qianyi C, Changshan Z, Shuqing S, et al. J Phys Chem 2012; 116: 17698-17704.
- [5] Panuphong P, Nagahiro S, Osamu T. Mater Lett 2011; 65: 1037-1040.
- [6] Gordon N, Xuan L, Sharifeh M, Eric M, James E. Mater Lett 2011; 65: 1191-1193.
- [7] Eun KJ, Eunyong S, Eunhee L, Wonoh L, Moon-Kwang U, Byeong-Su K. ChemComm 2013; 49: 3392-3394.
- [8] Eun JL, Sung MC, Min HS, Youngmin K, Seonhwa L, Won BK. Electrochem Comm 2013; 28:100-103.

- 135 [9]Stela P, Florina P, Alexandru RB, Maria C, Fumiya W, Enkeleda D, et al. *Electrochim Acta* 2013; 89: 246-252.
- 136 [10]Hummers WS, Offeman RE. *J. Am. Chem. Soc.* 1958; 80:1339.
- 137 [11]Panbo L, Ying H, Lei W. *Mater Lett* 2013; 97: 173-175.
- 138 [12]Kazuma G, Tara K, Eiji J, Aki Y, Hideki H, Takahiro O, et al. *Carbon* 2011; 49: 1118-1125.
- 139 [13]Yupeng Z, Delong L, Xiaojian T, Bin Z, Xuefeng R, Huijun L, et al. *Carbon* 2013; 54: 143-148.
- 140 [14]Xiao YQ, Yong L, Wen L, Guo HC, Abdullah MA, Abdulrahman OAY, et al. *Electrochim Acta* 2012; 79: 46-51.
- 141 [15]Yanyuan W, Hanming D, Yongkui S. *Nanoscale* 2011; 3: 4411-447.

Figure 1. (a) A schematic for preparation of AgNP/rGO hybrid; (b, c) TEM images of the GO and AgNP/rGO; (d) EDS spectra and (e) particle size distribution histograms of AgNP/rGO.

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150 Figure 2. (a) XRD patterns and (b) Raman spectra of GO, rGO and AgNP/rGO; (c) XPS survey

151 spectra of GO and AgNP/rGO. (d) Ag3d XPS of AgNP/rGO, (e, f) C1s XPS of GO and AgNP/rGO.

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Figure 3 (a) CV curves of bare GCE, GO, rGO and AgNP/rGO modified GCEs in 0.2 M PBS N₂ saturated solution in the presence or absence of 1 mM H₂O₂; (b) Steady-state response of the AgNP/rGO to successive injection of H₂O₂ into 0.2 M PBS N₂ saturated solution; (c) The calibration curve of the reduction currents versus the concentrations of H₂O₂; (d) Current-time curve for the AgNP/rGO exposed to H₂O₂ (0.5 mM), UA, AA, DA (0.1 mM), and Glu (2 mM).