JOURNAL OF PURE AND APPLIED MICROBIOLOGY, April 2013. Vol. 7(Spl. Edn.), p. 105-110

One-Pot Synthesis of Ag Nanoparticle / Graphene Composites using Sodium Citrate as Reducing Agent

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(Received: 03 March 2013; accepted: 14 April 2013)

A simple, inexpensive, one-step chemical method to in situ synthesis of reduced graphene oxide (RGO) and Ag nanoparticle-reduced graphene oxide (Ag-RGO) nanocomposites was achieved by using sodium citrate as a reductant and stabilizer. The synthetic process was carried out in a one-pot reaction, which graphene oxide (GO) and silver nitrate were simultaneously reduced with sodium citrate as an environmental reducing agent only in aqueous solution. The obtained RGO and Ag-RGO nanocomposites were investigated by UV-vis spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, transmission electron microscopy and energy-dispersive X-ray spectroscopy. The results indicated that the RGO and Ag-RGO nanocomposites formed stable colloidal dispersions which the sodium citrate played an important role. In addition, it was found that such Ag-RGO nanocomposites exhibited good electrochemical activity towards a biomolecule and good catalytic activity toward the reduction of hydrogen peroxide.

Key words: One-pot reaction, Sodium citrate, Nanocomposites, Electrocatalysis

Since the discovery of graphene by Geim and co-workers in 2004(Novoselov *et al*., 2004), it has attracted an increasing attention in recent years. Graphene, a monolayer of carbon atoms arranged in a honeycomb network, has a unique two-dimensional (2D) structure and excellent mechanical, thermal and electrical properties (Geim *et al*., 2007; Allen *et al*., 2010; Balandin *et al*., 2008). Due to its properties, it had been found a range of applications, such as sensors (Tang *et al*., 2010; Robinson *et al*., 2008), nanocomposites (Rafiee *et al*., 2009; Kim *et al*., 2010), supercapacitors and hydrogen storage. Recently, graphene-based composite materials had stimulated intense research due to the intriguing properties inherited from the synergistic effects of their components in addition to the intrinsic properties from each component by combination of different nanomaterials. So various graphene-based nanocomposites with metal oxides or metals nanoparticles distributed onto the surface of graphene had fabricated by the assembly of graphene sheets in the presence of presynthesized nanoparticles or inorganic precursors (Liu *et al*., 2010). Because the catalytic, anti-bacterial and electrical properties of Ag nanoparticles (Ag NPS) (Yang *et al*., 2008; Cui *et al*., 2008), the Ag nanoparticles - reduced graphene oxide (Ag-RGO) nanocomposites had been proved to be a most promising material.

To date, some solutions to prepare Ag-RGO nanocomposites had been reported. Pasricha *et al*. reported a facile and novel synthesis of Ag-RGO nanocomposites through a two-step route (Pasricha *et al*., 2009). Zhang *et al*. demonstrated a

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facile one-pot method to prepare high-quality Ag-RGO nanocomposites by simultaneous reduction of graphene oxide and silver ions with poly(N-vinyl-2-pyrrolidone) as the reducing agent, which were used as an active surface-enhanced Raman spectroscopy (SERS) substrate for detection of 4-aminothio-phenol (4-ATP) in a liquid environment (Zhang *et al*., 2011). Li *et al*. synthesized the Ag-RGO heterostructures through a route consists of four steps, which resulted in the redshift of the Ag surface plasmon band (Li *et al*., 2010). Ag-RGO nanocomposites were also prepared by an in situ chemical synthesis approach, which could be used as graphene-based biomaterials (Shen *et al*., 2010). Tang *et al*. reported a rapid approach to prepare Ag-RGO nanocomposites using formaldehyde as the reducing agent (Tang *et al*., 2011). Shen *et al*. demonstrated a one-pot hydrothermal synthesis of Ag-RGO nanocomposites with ionic liquid (Shen *et al*., 2011). These existing methods had significant efforts and the obtained nanocomposires had some advantages. However, there are still some challenges and problems in the field of Ag-RGO nanocomposites:

(1) The reducing agent used in some methods is highly toxic and potentially explosive, such as hydrazine hydrate, sodium borohydride.
(2) The preparation process is relatively complex, such as time consuming, the need of some steps
(3) The resulting Ag-RGO nanocomposites is not suitable for applications requiring well-dispersed materials and the dispersibility needs to be improved.

In this paper, we proposed a solution to prepare Ag-RGO. The advantages of our method are as follows:

(1) We used sodium citrate as reducing agent, which was demonstrated an environmentally friendly reducing agent for the synthesis of RGO and Ag-RGO nanocomposites.
(2) The sodium citrate can simultaneously reduce silver nitrate and graphene oxide (GO) in a one-pot reaction, and Ag NPS were scattered well on the surface of reduced graphene oxide (RGO) sheets.
(3) The RGO and Ag-RGO materials can be well-dispersed and stable for weeks by use of sodium citrate as a reductant and stabilizer.
(4) The nanocomposites exhibited good electrochemical activity and could be the advanced materials for sensing and biosensing application.

EXPERIMENTAL

Preparation of GO

The graphite oxide was synthesized from natural graphite powder according to a modified Hummers method (Hummers *et al*., 1958; Kovtyukhova *et al*., 1999). Subsequently, exfoliation of graphite oxide into graphene oxide (GO) was achieved by ultrasonication of the dispersion using a Sonifier (Scientz-IID, 400 W, 60% amplitude) for 30 min. The obtained brown dispersion was then subjected to 30 min of centrifugation at 3,000 r.p.m. to remove any unexfoliated graphite oxide. Finally, the homogeneous brown GO dispersion (about 5.0 mg/mL) was obtained.

Preparation of RGO

In a typical procedure for chemical conversion of graphite oxide to graphene, the resulting homogeneous GO dispersion(5.0 mL) was mixed with 20.0 mL of water, and 30 mg of sodium citrate was added to the aqueous dispersion of GO with constant stirring. The mixture was then stirred for 3 h in a water bath (98°C). The brown solution changed to a dark color, indicating the completion of the chemical reduction to graphene. The resulting graphene was collected by centrifugation and washed with the deionized water three times. After the re-suspension into the deionized water, the samples were stable for several weeks without any aggregation. The dispersion was used for further characterization in this work.

Preparation of Ag-RGO

The Ag-RGO hybrid materials were prepared in a one-pot reaction. Typically, 30 mg of sodium citrate was added to the GO aqueous dispersion (0.1 mg/mL, 25mL) with constant stirring for 2.5 h in a water bath (98!). After that, 20ìL of $AgNO_3$ solution (0.5mol/L) was added to the above solution with constant stirring for 0.5 h, which resulted in a color change of the solution from brown to blue. Finally, the resulting homogeneous dispersion was centrifuged and washed with deionized water for three times.

Electrocatalytic experiments

The glassy carbon electrodes (GCE, 3 mm in diameter) was carefully polished subsequently by 0.3 and 0.05ìm alumina powder respectively to a mirror finish, and then sonicated successively in ethanol and deionized water for several times. To prepare GO, RGO and Ag-RGO modified GCE electrodes, 5μL of GO, RGO or Ag-RGO nanocomposites was dropped on the surface of a GCE, and then the electrodes were left to dry in an oven desiccator and stored at 37°C.

RESULTS AND DISCUSSION

The UV-vis spectra of (a) GO, (b) RGO, and (c) Ag-RGO hybrid materials were displayed in Fig. 1. The UV-vis spectrum of GO (Fig. 1 (a)) showed an absorption peak at 232 nm and 300nm, which is consistent with the previous report (Li *et al*., 2010). After formation of RGO through the sodium citrate reduction, the peak of RGO (Fig. 1 (b)) redshifted from 232 nm to 259 nm and the shoulder peak at about 300 nm disappeared, suggesting that the electronic conjugation within grapheme sheets was restored after the reaction. When the Ag NPs were decorated onto the graphene, the absorption peaks of Ag-RGO nanocomposites were observed at 259nm and 410 nm (Fig. 1 (c)), which was corresponding to the absorption of graphene and Ag NPs (Kumar *et al*., 2003). In addition, the reduction of GO and the forming of Ag NPs were also confirmed by the color change of solution before and after reaction (from brown to dark and blue, as shown in the inset in Fig. 1) showed the relatively decreased peak intensity contrast with GO (Fig. 2 (b)), which confirmed the remove of the oxygenated groups. The peaks of Ag-RGO nanocomposites were clearly observed, which the peak of Ag 3d was expected from Ag atom; the peak of Na come from sodium citrate, and the peak of C1s was attributed to graphene sheets (Fig. 2 (c)). Though the sample consisted mainly of carbon, an insignificant amount of oxygen was appeared probably due to the presence of some unreduced oxygen functional groups on the graphene surface, which played a key role in the linkage of nanopaticals (Goncalves *et al*., 2009). In addition, the Ag3d $_{5/2}$ peak appeared at a binding energy of 368.2eV and the Ag3d $_{3/2}$ peak appeared at 374.2eV (Fig. 2 (d)), which confirmed that the Ag was present (Kumar *et al*., 2003).

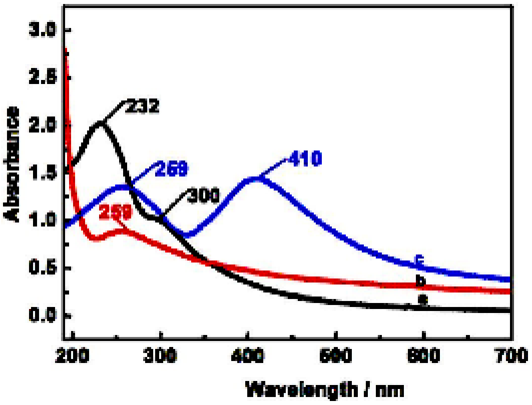

Fig. 1. UV-Vis absorption spectra of (a) GO, (b) RGO, and (c) Ag-RGO hybrid; insets: a photograph of GO (left), RGO (middle) and Ag-RGO (right) composite solutions

The transmission electron microscopy (TEM) images of nanoconpositeswas showed in Fig. 3 (a). It was clearly seen that Ag NPs were attached to the graphene surface and scattered well on the nanosheets. This result was further supported by scanning electron microsopy (SEM). It can be seen that the closely stacked layered structure of the graphene sheets, which can very easily and clearly see the edges, wrinkles, foldings, and ripples. In addition, Ag NPs homogeneously and densely attached to the surface of graphene nanosheets. The corresponding energy-dispersive X-ray (EDX) spectroscopy (Fig. 3 (c)) of Ag-RGO nanocomposites showed the peaks corresponding to C and Ag elements, confirming the existence of Ag NPs on the surface of graphene nanosheets and this was consistent with the XPS spectra. All these observations provided clear evidence to support the formation of Ag-RGO nanocomposites. Because cyclic voltammograms of the ferrocyanide system were a valuable and convenient tool to monitor the characteristics of a modified electrod, the good electrocatalytical activity of Ag-RGO nanocomposites was constructed for biosensing $K_3Fe(CN)_6$. The cyclic voltammograms of the bare electrode (Fig. 4 a), GO/GCE (Fig. 4 b), RGO/GCE (Fig. 4 c) and Au-RGO/GCE (Fig. 4 d) in 5.0 mmol/L $K_3Fe(CN)_6$ in 0.5 mol/L KCl solution were displayed in Fig. 4. A couple of well-defined redox peaks with the reduction and oxidation peak potentials were observed at the four electrodes. However, the peak currents had a clearly change. Due to the weak conductivity of GO, the redox behavior measured at GO/GCE exhibited a weak peak current at a potential scan rate of 50 mV/s. After GO was reduced by sodium citrate, the peak current distinctively increased relative to the GO/GCE electrode, which indicated that RGO had a good conductivity due to the restoration of a π-conjugated network and a high surface area lead to the increase of the electroactive surface area. In addition, the GCE modified with Ag-RGO had increase current signal compared with the RGO/GCE, which should be ascribed to the increase of area of Ag NPs anchored onto the graphene sheets. The above results showed that Ag-RGO can be expected to serve as candidate for further utilization of electrochemical sensing.

The nature of the oxidation process was found to be diffusion controlled, as proved by the linear plots of the peak current (I p) versus square

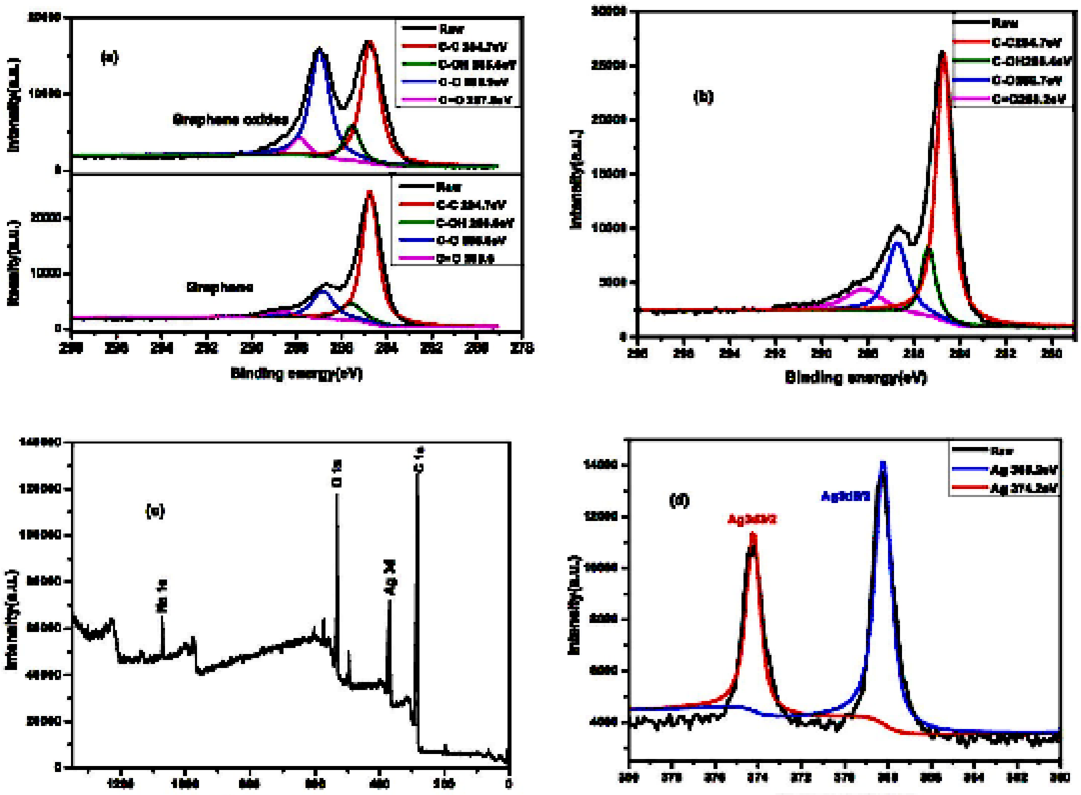

Fig. 2. C 1s XPS spectra of (a) GO and RGO, (b) Ag-RGO; XPS spectra of the Ag-RGO nanonanocomposites (c), and the Ag 3d doublet (d)

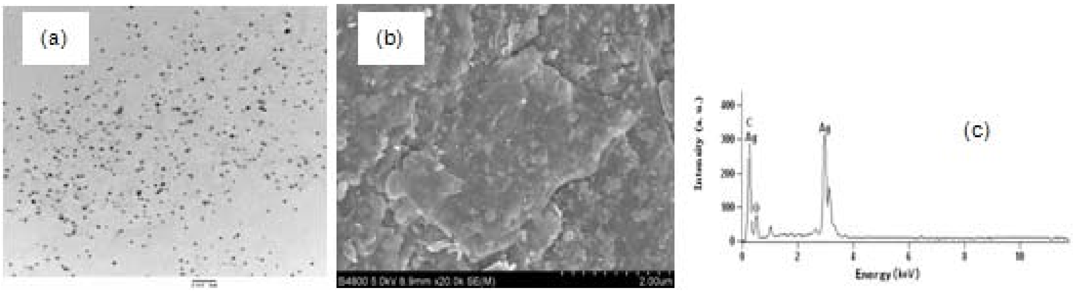

Fig. 3 (a) TEM image, (b) SEM image and (c) EDX analysis of Ag-RGO nanocomposites

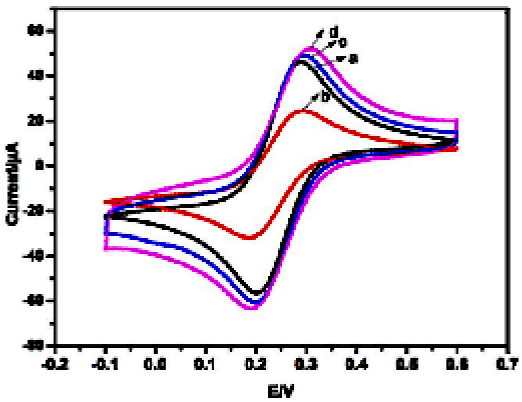

Fig. 4. Cyclic voltammograms of (a) bare, (b) GO, (c) RGO and (d) Ag-RGO electrodes in N2 saturated 0.5 mol/L KCl solution containing 5.0 mmol/L $K_3Fe(CN)_6$

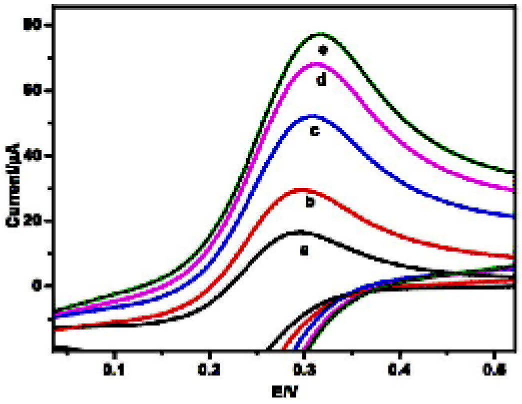

Fig. 5. Cyclic voltammograms of Ag-RGO modified GCE electrode with various scan rate: (a) 10, (b) 20, (c) 50, (d) 80, and (e) 100 mV/s; Inset: plots of peak current (I p) against square root of the scan rates ($v^{1/2}$)

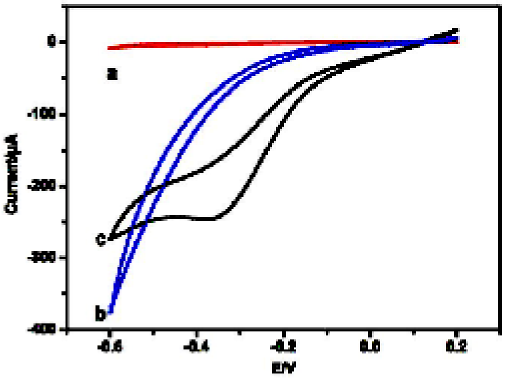

Fig. 6. Cyclic voltammograms of (a) GO, (b) RGO, (c) Ag-RGO electrodes in N2 saturated phosphate buffer (0.01 M, pH 7.0) containning 5 m M H_2O_2

root of the scan rate ($v^{1/2}$). The cyclic voltammograms of Ag-RGO/GCE in N2 saturated 0.5 mol/L KCl solution containing 5.0 mmol/L $K_3Fe(CN)_6$ at various scan rates were shown in Fig. 5. With the rising of scan rate, the anodic currents increased and the peak potential shifted positively. When I p values were plotted against $v^{1/2}$, a nice linear relationship was obtained (Fig. 5 inset). This behavior suggested that the regression equation was $I_p=8.7584v^{1/2}-10.044$, and the correlation coefficient (R^2) of the linear curve was 0.9998. All of this indicated that the oxidation process was controlled by diffusion, and Ag-RGO nanocomposites exhibited a high catalytic activity. The cyclic voltammograms of different modified electrodes in the presence of H_2O_2 were shown in Fig. 6. Similarly, Ag-RGO also showed an excellent reduction activity towards H_2O_2. As shown in curve c, an obviously catalytic current appeared for the Ag-RGO electrode and the peak potentials appeared at 0.35 V. The responses of H_2O_2 for the bare GO/GCE and RGO/GCE were obviously weak and even disregarded (Fig. 6(b) and (c)). This demonstrated that Ag-RGO/GCE possessed the relatively remarkable catalytic ability to H_2O_2, and the catalytic current mainly resulted from the Ag NPs on the electrocatalytic reduction of H_2O_2. The above results showed that Ag-RGO was one of the electroactive materials towards reduction of H_2O_2.

CONCLUSIONS

In summary, a facile one-pot method to high-quality Ag-RGO nanocomposites had been demonstrated, using sodium citrate a reducing agent. The method was simple and the reducing agent was environmentally friendly. The Au NPs can be scattered well on the nanosheets and the RGO and Ag-RGO dispersions can be stable for weeks. Moreover, the resulting Ag-RGO electrode had much better electrocatalytical activity towards reduction towards $K_3Fe(CN)_6$ and H_2O_2 than GO or RGO, which indicated that Ag-RGO hold great promise for the routing sensing and biosensing application in the future.

ACKNOWLEDGEMENTS

This work was financed by the National Natural Science Foundation of China

(No.21172171, No.21106101) and Natural Science Foundation of Tianjin (No.11JCZDJC22300, No.12JCZDJC 29500).

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