

Facile assembly and properties of polystyrene microsphere/reduced graphene oxide/Ag composite

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ABSTRACT

A ternary assembly consisting of reduced graphene oxide (RGO), Ag nanoparticles, and polystyrene (PS) microsphere was prepared in aqueous solution by an electrostatic assembly combined with one-step reduction process. The composition and structure of the assembly (PS microsphere/RGO/Ag) were characterized by powder X-ray diffraction, transmission electron microscope, scanning electron microscope, X-ray photoelectron spectroscopy, and Raman spectroscopy. The interactions among RGO, Ag nanoparticles, and PS microsphere were investigated by surface enhanced Raman scattering spectroscopy. The results showed that there existed strong interactions among RGO, Ag nanoparticles, and PS microsphere. Importantly, the assembly showed high heat stability and good dispersion in water.

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1. Introduction

Graphene, a new ideal two-dimensional monolayer honeycomb carbon nanostructure, has attracted great attention due to its extraordinary electrical, thermal, mechanical, and chemical properties endowed with its unique structure [1]. For these specific properties, graphene has potential applications in sensors, catalysis, energy storage, supercapacitors, water purification, and splitting [2–7].

The functionalization of graphene has been considered to be important for improving its solubility, self-assembly properties, and device applications [8]. Using the π - π interactions between graphene and aromatic organic molecule is one of the effective methods generating attractive new properties absent in pristine graphene [9]. Attempts to use blends of functionalized graphene and poly(3-hexylthiophene) as an active layer in the polymer solar cell resulted in a power conversion efficiency of 1.4% [10]. Incorporation of graphene sheets into TiO₂ nanoparticle films used as photoanodes in dye-sensitized solar cells gave five times the power conversion efficiency than that obtained with TiO₂ nanoparticle films without carbon sheets [11]. Using the solution-based ultrasonic co-assembly method, Wu and co-workers fabricated the reduced graphene oxide-MnO₂ hollow sphere hybrid electrode materials, which can be used as high-performance electrochemical capacitors [12].

Ag nanoparticles and their composites have wide usages as the catalyst, antimicrobial, and surface enhanced Raman scattering

spectroscopy (SERS) substrate [13–15]. By means of formaldehyde as the reducing agent, poly(N-vinyl-2-pyrrolidone) as the surface modifier, and the hybridization of GO, Tang et al. demonstrate a rapid and efficient method for growth of silver nanocrystals on RGO [16]. Ag/AgBr/GO and Ag/AgCl/GO hybrid nanomaterials with well-defined morphologies are also assembled via a water/oil medium at room temperature [17]. Compared with the corresponding bare Ag/AgX nanospecies, the Ag/AgX/GO hybrid nanocomposites display enhanced photocatalytic performance.

However, unless stabilized by other substances, chemically converted graphene sheets are easy to form irreversible agglomerates through π - π stacking and van der Waals interactions owing to their hydrophobic nature [8]. Occurrence of aggregation is unfavorable for graphene sheets because most of their unique properties are only associated with individual sheet. In addition, the dispersion of metallic Ag on the surface of a semiconductor is also vital to its activity [18]. It is found that dispersion of graphene can be improved by the attachment of some stabilizers, adding extra polymer solution, emulsion rapid precipitation in the solvent-free condition, and freeze-drying [19–23]. Depositing Ag nanoparticles or RGO onto the surfaces of colloid particles, such as PS sphere, silica, and titanium dioxide are also effective ways to improve the dispersion of RGO and Ag [24–27]. Among them, PS sphere is one of the most common colloid particles due to their uniform size and various surface chemical performances. Siiman and Burshteyn have synthesized PS/Ag composites with the help of amino dextran-coated PS by taking advantage of the interactions between amine group and Ag nanoparticle [28]. Cheng and Zhang et al. have fabricated PS/Ag composite microspheres with the help of poly(styrene/acrylic acid) by

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the interactions between carboxyl group and Ag nanoparticle [29,30]. Hu et al. have immobilized separated Ag nanoparticles onto the PS microsphere surfaces by adsorbing Sn^{2+} ions [13]. Li et al. propose a facile method to obtain the polystyrene/graphene nanosheet composite particles [22].

Herein, combining the advantages of RGO with Ag nanoparticles, the PS microsphere/RGO/Ag assembly is prepared by using a straightforward and non-medium assembly process. In it, without using any other protective agents, RGO and Ag nanoparticles are assembled onto the surface of PS microspheres in order. Furthermore, the interactions among RGO, Ag nanoparticles, and PS microsphere, and the stability of the PS microsphere/RGO/Ag assembly are investigated.

2. Experimental details

2.1. Materials

PS microspheres (average diameter 1 μm) were purchased from Henghui Yangzhou Chemical Co. Graphite powder with an average size of 30 μm and purity of >95% was obtained from Shanghai Chemical Reagent Co. The other reagents (A.R.) came from Shanghai Chemical Reagent Co. and were used as received. Deionized water was used as solvent throughout the experiments.

2.2. Preparation of PS microsphere/RGO/Ag assembly

The graphite oxide (GO) was prepared by a modified Hummers method [31]. The simple strategy used to prepare the PS microsphere/RGO/Ag assembly is shown in Scheme 1.

In a typical procedure, 5 mL of 5% (w/v) PS microsphere aqueous dispersion was added in the 2.5 mL of 1 mg mL^{-1} GO aqueous solution and stirred overnight at room temperature. The solid obtained by centrifugation was washed with ethanol and water for three times, respectively. Then, it was re-dispersed into 5 mL of deionized water, and 2 mL of 1 mg mL^{-1} silver nitrate aqueous solution was added into it and stirred for 4 h. After that, 2 mL of 0.1 mol L^{-1} NaBH_4 aqueous solution was added slowly into the mixture under vigorous stirring. The mixture was sequentially stirred at 90 $^\circ\text{C}$ for 5 h under N_2 atmosphere before cooling to ambient temperature. The solid obtained by centrifugation was washed thoroughly with water. Under similar conditions, PS microsphere/Ag, RGO/Ag, and RGO were also prepared.

2.3. Characterization

The powder X-ray diffraction analysis (XRD) was made on a PANalytical Xpert Pro MRD X-ray diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.154056 \text{ nm}$) (Netherlands). The morphology of the sample was characterized on a JEM-1400 transmission electron microscope (TEM) (Japan) and FEI Magellan 400 XHR scanning electron microscope (SEM) (USA). X-ray photoelectron spectroscopy analyses (XPS) were carried out on a Thermo ESCALAB 250 X-RAY photoelectron spectrometer with a monochromated X-ray source ($\text{Al K}\alpha h\nu = 1486.6 \text{ eV}$) (USA). The energy scale of the spectrometer was calibrated using $\text{Au } 4f_{7/2}$, $\text{Cu } 2p_{3/2}$, and $\text{Ag } 3d_{5/2}$ peak positions. Raman spectra were measured by the Thermo Scientific

DXR Raman microscope with a 532 nm DPSS laser and a 50 \times objective (NA = 0.42) (USA). The spot is 1.1 μm . The incident laser power is 1 mW and the exposure time is 3 s to avoid laser-induced thermal effects or damage. The thermo-gravimetric and differential thermal analyzers (TG-DTA) were recorded on a PerkinElmer Pyris Diamond TG/DTA instrument (USA). The heating rate was 10 $^\circ\text{C}$ per minute under N_2 atmosphere.

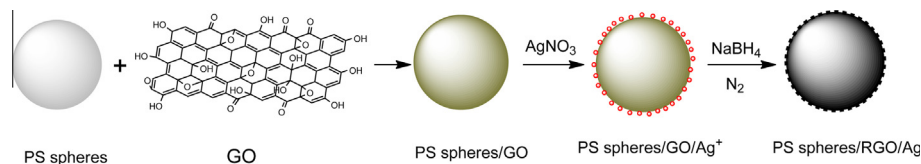
2.4. SERS measurement of PS microsphere/RGO/Ag assembly

Ten micro liter of 1 mg mL^{-1} PS microsphere/RGO/Ag suspension was mixed with 10 μL of $1 \times 10^{-5} \text{ mol L}^{-1}$ crystal violet aqueous solution. Then, 10 μL of the suspension was dropped on the Si substrate to form the SERS substrate of the PS microsphere/RGO/Ag. The substrates consisting of PS microsphere/Ag, RGO/Ag, or RGO were also prepared under the same conditions, respectively. The enhancement factor (EF) was calculated by the intensity ratio of Raman peaks of the test substrate to pure crystal violet on the Si substrate.

3. Results and discussion

The assembly strategy of PS microsphere/RGO/Ag has been schematically depicted in Scheme 1. In this approach, GO-coated PS microspheres are facilely prepared first by the hydrophobic interaction and π - π interaction between GO and PS microsphere. Because of the hydroxyl groups linked on the periphery of GO sheets, the surface of GO-coated PS microspheres possesses a certain amount of negative charges. It is favorable to adsorbing Ag^+ onto the surface of PS microsphere/GO by the electrostatic interaction. After the NaBH_4 solution is added, the GO and Ag^+ are reduced simultaneously and co-loaded on the surface of PS microspheres. Subsequently, an assembly consisting of PS microspheres, RGO, and Ag are achieved. The ordered assembling of RGO and Ag on the surface of PS microspheres is important for the electron transfer in the assembly.

The morphology of the as-prepared sample is observed by TEM and SEM. As shown in Fig. 1a–c, there exists a thin layer of RGO on the surface of PS microspheres, and some nanoparticles are stucked on the RGO, though partly convolution of RGO sheets on the PS microspheres lead to some aggregated Ag nanoparticles. The size of nanoparticles is ranging from 20 to 50 nm. Moreover, no isolated nanoparticles and RGO sheets are found outside of the spheres. SEM image of PS microsphere/RGO/Ag assembly is taken to further demonstrate the surface morphology of the composites. As shown in Fig. 1d, the generated Ag nanoparticles onto the surface of the spheres are sparse. As we can see in Scheme 1, the interaction between Ag^+ and GO plays an important role in the growth of Ag nanocrystals [32]. So the distribution of Ag nanocrystals like Fig. 1a–d maybe attribute to the reduced and non-uniform hydroxyl groups linked on the periphery of GO sheets after reduction [13]. For comparison, in the absent of PS microspheres, the reduction of both GO and Ag^+ will lead to decreasing of contents of the oxygen-containing groups and weakening of the interaction of the silver with RGO. So Ag nanoparticles and RGO sheets aggregate seriously (Fig. 1e), which is unprofitable for exhibiting the unique properties of RGO sheets and Ag nanoparticles. The results of TEM and SEM are consistent with the design of Scheme 1.



Scheme 1. Assembly scheme of PS microsphere/RGO/Ag.

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