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Fabrication of graphene oxide/Ag hybrids and their surface-enhanced Raman scattering characteristics

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ABSTRACT

A kind of surface-enhanced Raman scattering (SERS) substrate with high sensitivity was prepared via covalent assembly between silver nanoparticles (AgNPs) and graphene oxide (GO) sheets. With the high specific surface area, GO sheets can adsorb plenty of AgNPs; moreover, these adsorbed AgNPs formed some gathered state which can generate more hot spots of SERS. 4-Mercaptopyridine (4-MPY) was used to evaluate the SERS performance of the as-prepared substrate. The Raman enhancement factor (EF) of 4-MPY on the GO/AgNPs hybrids was up to 5.04×10^7, and the detection limit was estimated to be as low as 1 nM. The result showed that GO/AgNPs hybrids can produce stronger signals compared to silver colloids.

1. Introduction

Surface-enhanced Raman scattering (SERS) technique is one of the most powerful analytical tools for chemical and biological detection due to its high sensitivity and specificity [1–4]. When a molecule absorbs on the noble metal nanoparticle, SERS enhance the molecular Raman signal by many orders of magnitude owing to significant increase in the scatting cross-section. There are two SERS mechanisms that are generally accepted. Electromagnetic mechanism (EM) is based on the enhancement of the local electromagnetic field (the enhancement factor of 10^6–10^8); meanwhile, chemical mechanism (CM) is based on charge transfer between absorbed molecules and metal surface (the enhancement factor of 10^1–10^2) [5,6]. Noble metal nanostructures have excellent SERS activity, especially Au and Ag are conventional SERS substrates used for the ultra-sensitive detection [7–9].

Graphene, which is an ideal two-dimensional monolayer sheet of hexagonal carbon atoms, has received great attention because of its unique structure and exceptional physiochemical properties [10–14]. Recently, it has been reported that graphene was used as an SERS-active substrate for enhancement of Raman signals of absorbed molecules [11,15–19]. However, there are several issues that greatly limit the practical applications of graphene substrate, such as the aggregation of graphene in aqueous solution caused by the strong π–π stacking interaction between graphene sheets, the chemical inertia of graphene originated from defect-free structure, and little Raman enhancement factor. Graphene oxide (GO) is an exfoliation of graphite oxide, which has been widely applied in the fields of molecule enrichment and drug delivery [20–22]. Because GO contains hydroxyl and epoxy groups in the plane and carboxyl groups at the edge, it has good dispersibility in polar solvents and many reactive sites for decorating organic and inorganic species [15,23,24]. Considering that the noble metal nanostructures are excellent in SERS, decorating metal nanoparticles (NPs) on the surface of GO is an effective method for increasing their SERS activity [25] and preventing the aggregation of GO sheets. Two ordinary approaches including *in situ* reduction in metal cations and self-assembly of pre-synthesized metal NPs on GO have been explored to obtain such GO/metal NPs composites. Yang et al. reported the synthesis of GO/AgNPs hybrid SERS substrates using N,N-dimethylformamide as a reductant [26]. Huang et al. [27] and Ren et al. [16] assembled gold or silver NPs onto the GO surface though electrostatic adsorbing and π–π stacking methods. To reinforcing the link between metal NPs and GO, many GO/AgNPs structures were fabricated via covalent assembly between silver NPs and GO sheet [15]. However, most works were based on decorating the silver NPs onto single side of GO. The SERS activities of substrates largely depend on the quantity of Raman hot spots formed at the junction between neighboring AgNPs [28]. Therefore, raising the loading ratio of AgNPs on GO sheets is an effective strategy for heightening the SERS enhancement of substrate.

Herein, we developed a GO/AgNPs nanostructured SERS substrate with high activity and fine controllability. The GO sheets not only provide large surface area to richen target molecules, but also serve as anchor spots for the aggregation of silver NPs. Silver NPs decorated onto both sides of GO sheet through covalent interaction provided additional enhancement of Raman signals.

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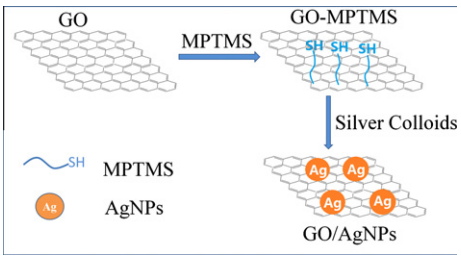

Scheme 1. Fabrication procedure of the GO/AgNPs hybrid composite.

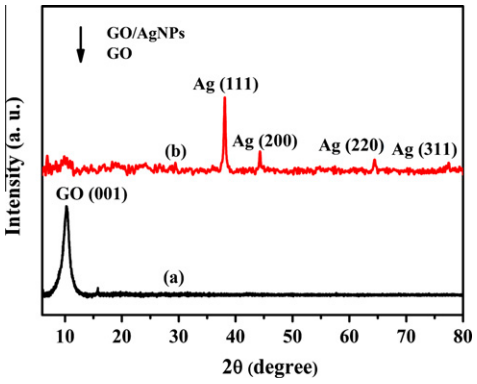

Fig. 1. XRD patterns of (a) GO and (b) GO/AgNPs hybrid composite.

The performance of the obtained GO/AgNPs hybrids was evaluated via 4-mercaptopyridine (4-MPY) as the probe molecule.

2. Experimental

2.1. Materials

Silver nitrate ($AgNO_3$, AR), sodium borohydride ($NaBH_4$, 96%), trisodium citrate ($Na_3C_6H_5O_7{\cdot}2H_2O$, AR), and ethanol (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). (3-Mercaptopropyl) trimethoxysilane (MPTMS, 95%) was purchased from Alfa Aesar. 4-Mercaptopyridine (4-MPY, 96%) was purchased from J&K. The sample of graphene oxide was provided by zhaoping Liu group (Ningbo Institute of Material Technology and Engineering, CAS). All chemicals were used as received without further purification. The water used throughout all experiments was deionized (DI) water form a Millipor-Q purification system (Millipore, USA) of resistivity 18.2 MΩ cm.

2.2. Preparation of silver colloid

Silver colloid was prepared based on the method of Lee and Meisel [29] with a little modification. In a typical procedure, 20 ml of 10^{-2} M $AgNO_3$ was first mixed with 80 ml of water and 20 ml of $Na_3C_6H_5O_7$ solution (1 wt.%). Then, 100 ml of 10^{-2} M freshly prepared $NaBH_4$ solution was added into the mixture under vigorous stirring. The reaction proceeds for 1 h at room temperature.

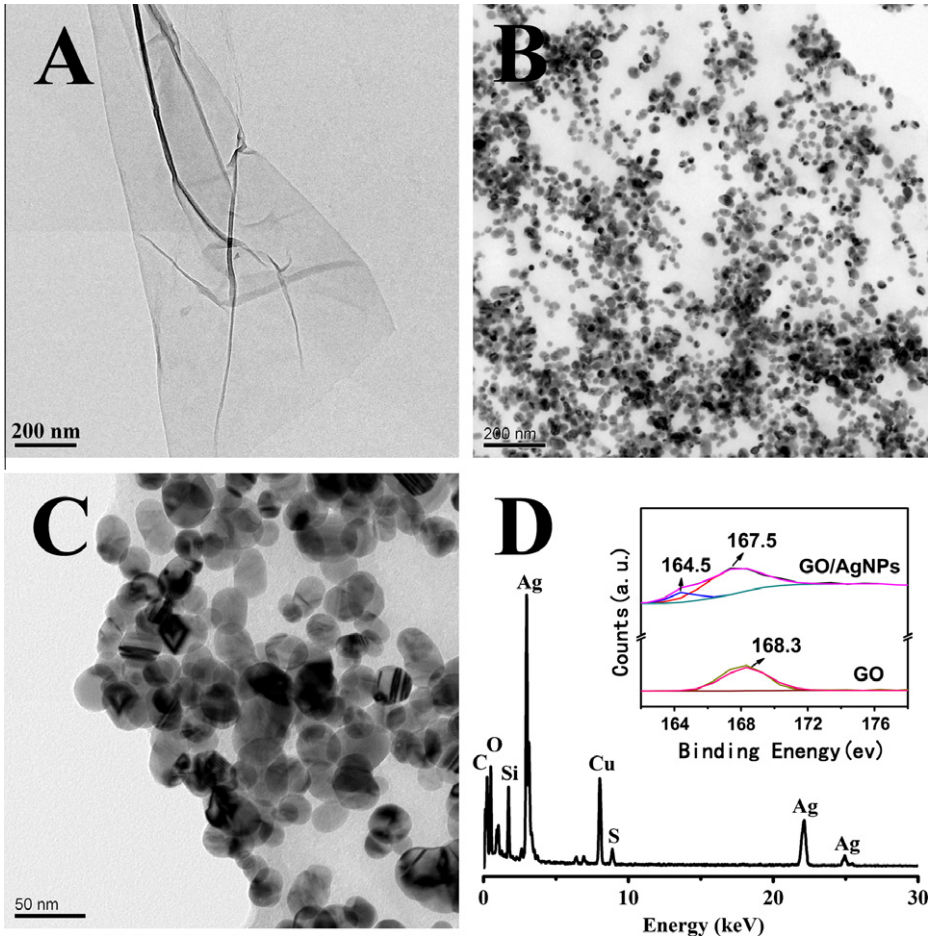

Fig. 2. TEM images of GO (A), GO/AgNPs (B) and (C), and EDX image of GO/AgNPs (D), inset: XPS result, the high-resolution S 2p peaks of GO and GO/AgNPs.