



Monodispersed graphene quantum dots encapsulated Ag nanoparticles for surface-enhanced Raman scattering

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ABSTRACT

We report our successful fabrication of graphene quantum dots shell-isolated Ag nanoparticles (Ag@GQDs NPs) which size was in the range of 40–80 nm. To the best of our knowledge, this is the first report to fabricate Ag@GQDs NPs of less than 100 nm in particle sizes, particularly with monodispersion characteristic and smooth surface. Transmission electron microscopy (TEM) images reveal that Ag NPs cores are completely encapsulated by 2–4 layers of GQDs. More importantly, Ag@GQDs NPs show a significantly higher Raman signal for the absorbed crystal violet molecules as compared to Ag NPs, suggesting that the Ag@GQDs NPs can act as a new type substrate for surface enhancement of Raman scattering (SERS) substrate.

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1. Introduction

In the last decades, many studies have utilized graphene (GN) and graphene oxide (GO) as the shell to fabricate core-shell structured particles [1]. These structured materials exhibit excellent properties such as electroconductivity, electrorheological property [2], photocatalytic activity [3], energy storage property [4] and SERS activity [5]. Thus, it has great potential applications such as lithium ion battery, photo degradation, sensors, bioimaging, photoacoustic imaging and so on [1]. Presently, graphene wrapped core-shell structures were usually fabricated by self-assembly method, and the size of these structures was in the range of tens of nanometers to several micrometers [6–8]. Since the size of graphene oxide is usually several hundred nanometers to several micrometers, large core particles (> 300 nm) are easy to form uniform and monodispersed core-shell structures [3,9,10] because the size of core is comparable to (or larger than) that of the GO nanosheet. But for nanoparticles with size smaller than 200 nm, the core-shell nanostructures were usually not monodispersed [4,6,11,12] because two or more nano-cores usually wrapped by a single GO sheet, which can be explained by the bridging action of GO sheets.

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In this work, we report our success in synthesizing silver-graphene quantum dots (GQDs) core-shell nanostructure (Ag@GQDs NPs). The GQDs shell wrapped on the surface of Ag NPs (around 60 nm) through electrostatic interaction between the amino groups of Ag-NH₂ NPs and carboxyl groups of GQDs. The Ag@GQDs NPs were well monodispersed and the thickness of the shell was about 2–4 layers of GQDs. Raman spectra of crystal violet molecules suggesting that it has great potential for SERS applications.

2. Experimental

The preparation process for Ag@GQDs NPs is illustrated in Fig. 1. GQDs were synthesized by hydrothermal method according to the method reported by Sun et al. [13]. Ag NPs were synthesized according to the method reported by Zhang et al. [14], followed by amination with 3-aminopropyltriethoxysilane (APTES) to obtain aminated Ag NPs (Ag-NH₂ NPs). Next, dispersion solutions of Ag-NH₂ NPs (1 mg/mL) and GQDs (0.005 mg/mL) were mixed and stirred for 24 h at room temperature. Finally, the mixture was centrifuged to obtain Ag@GQDs core-shell nanoparticles. The products were characterized by using transmission electron microscope (TEM, Hitachi H-7600) and atomic force microscope (AFM, Veeco, USA). Raman spectra were measured at ambient condition using a DXR Raman Microscope (Thermo Fisher) with a 532 nm laser and incident laser power of 0.1 mW.

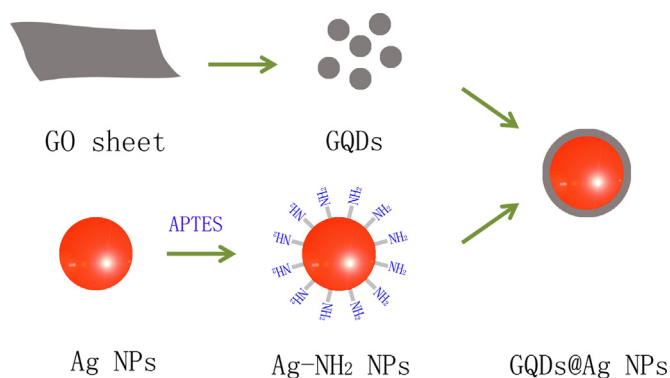


Fig. 1. Preparation process for the Ag@GQDs NPs.

3. Results and discussion

The TEM images and AFM images were quite typical and showed that GQDs were well dispersed (Fig. 2a and b). The size distributions (Fig. 2c) showed that most of GQDs were in the range of 5–11 nm, while the height distributions (Fig. 2d) showed that most of the GQDs were single layer. Fig. 3a is the TEM images of the Ag NPs. It shows that all Ag NPs show sphere-like morphologies and the average diameter is about 60 nm. The Ag@GQDs NPs were successfully prepared using the process shown in Fig. 1. As shown in the TEM images of Fig. 3b, it can be found that all Ag NPs were completely wrapped by GQDs. We found that the Ag@GQDs NPs were well monodispersed without any bridging action from GQDs (Fig. 3d). This is very different from that reported in other literatures [4,6,11,12,15], where the core nanoparticles were encapsulated by wrinkled large graphene oxide nanosheet. Additionally, from the TEM images of individual Ag@GQDs NPs (Fig. 3b), it is clear that Ag NPs are completely wrapped by multi-layer GQDs with a thickness of about 2–4 nm. Previous studies

found that the self-assembled GO layer by electrostatic force is composed of 2–4 GO nanosheets [16]; this suggested a 2–4 nm thickness of the GO layer.

It was suggested that GQDs have great potential for efficient SERS applications because it can reduce the substantial cost of SERS by using low-cost carbon materials instead of expensive noble metal substrates [17,18]. Herein, we explored the potential of Ag@GQDs NPs for SERS applications by taking crystal violet as model molecules. Ag NPs and Ag@GQDs NPs were drop-casted on SiO₂ substrate. Crystal violet molecules were absorbed on the surface of SiO₂, Ag NPs and Ag@GQDs NPs substrate by soaking the substrate in the crystal violet aqueous solutions with a concentration of 10^{−5} mol/L. As shown in Fig. 4, highly enhanced Raman peaks with good signal-to noise ratio are observed for crystal violet on both Ag NPs and Ag@GQDs NPs. All peaks occurred at 500–2000 cm^{−1} can be exclusively assigned to the crystal violet molecules [19]. However, the Ag@GQDs NPs show significantly higher signal than that of the Ag NPs, with an overall 14- to 57-fold enhancement for Ag@GQDs NPs (Table S1) was observed on the basis of the intensity of different Raman peaks, which was 6–8 times higher than that for Ag NPs. Our results showed much higher SERS activity than other literature [19], suggesting that the GQDs shell can contribute extra enhancement to the SERS signal.

4. Conclusion

In summary, we have fabricated Ag@GQDs NPs and investigated their potential applications for SERS. Unlike most of other graphene oxide-based core-shell nanostructures wherein the size of graphene oxide sheet was much higher than core particles and the core-shell nanostructures were usually not monodispersed, Ag@GQDs NPs was well monodispersed because the size of GQDs was much smaller than the Ag NPs. In addition,

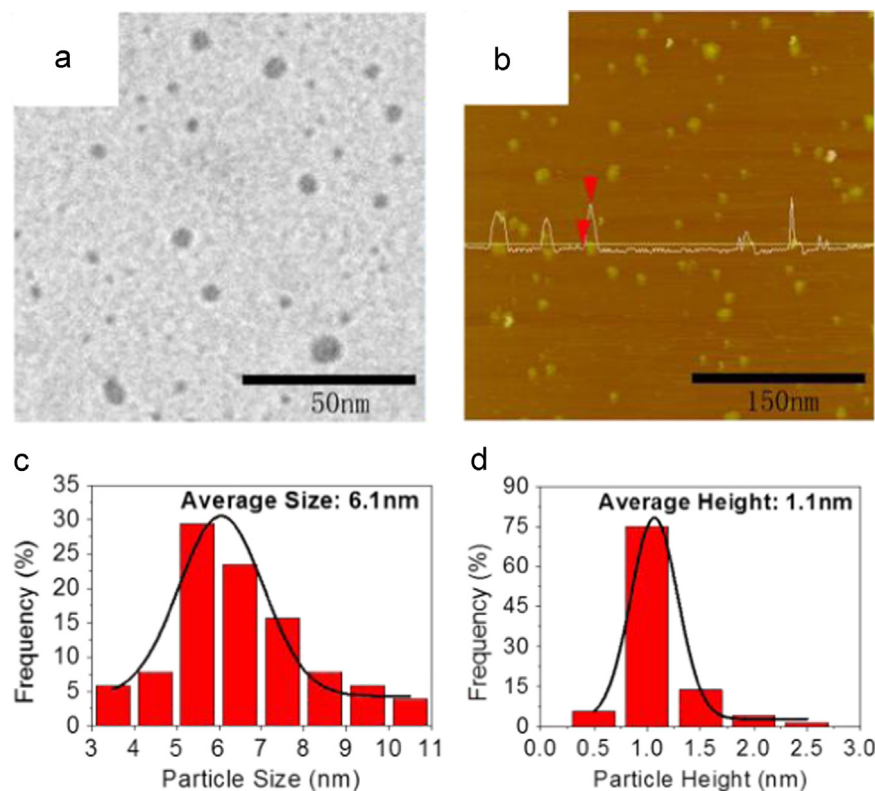


Fig. 2. TEM image of GQDs (a) and AFM image of GQDs (b), (c) and (d) are the size and height distributions of GQDs, respectively.

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