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Full Length Article

Graphene oxide-wrapped flower-like sliver particles for surface-enhanced Raman spectroscopy and their applications in polychlorinated biphenyls detection

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ABSTRACT

Graphene oxide (GO) serving as an ultrathin, seamless and passivated shell has been intensively investigated in shell-isolated surface-enhanced Raman scattering (shell-isolated SERS) research field. Here we report a novel and effective SERS platform based on GO wrapped flower-like Ag microparticles (Ag@GO). GO layers were efficiently enclosed around cysteamine functionalized Ag particles by electrostatic interactions. The morphology of flower-like Ag microparticles could be optimized by varying the reaction conditions such as growth temperature and the amount of reagents. The prepared Ag@GO SERS-active substrates exhibited much higher stability wherein the SERS intensities of Ag@GO hybrids were only decreased by 16 ± 5% after 50 days exposure under ambient condition, comparing with a 69 ± 10% decrease for bare Ag particles. Furthermore, the SERS sensitivity of rhodamine 6G (R6G) on Ag@GO hybrids was improved 3.5 times due to the chemical enhancement from transparent GO shell. The excellent reproducibility with average intensity variations less than 5% was also achieved. Most importantly, eliminating an extra surface modification steps, Ag@GO composite substrates demonstrated a high enrichment capability and remarkable SERS response toward polychlorinated biphenyls (PCBs), which have weak affinity on noble metal surface. Specifically, GO wrapped Ag particle hybrid could offer spectroscopic identification of two PCB congeners in mixed solution, showing promising potential for practical applications of single-particle SERS-based sensing and on-site monitoring in environment.

1. Introduction

Surface-enhanced Raman scattering (SERS) as an ultrasensitive and nondestructive technique has aroused extensive research in chemical and biochemical analysis [1–4]. The SERS performance is critically dependent on the morphologies and structures of substrates in nanometer-scale. Therefore, fabrication of effective SERS substrates is desired for improving the SERS activity and realizing the widespread real-world applications. Noble metals (Au, Ag, Cu), especially Ag nanostructures have been demonstrated to be ideal SESR substrates due to their unique plasmonic properties in visible and near-infrared spectral regions. Thus, considerable efforts have been made to design and fabricate varieties of Ag SERS substrates. Ag ordered arrays have been successfully developed as SERS-active substrates for trace analysis [5–7]. Core-shell nanoparticles (Au@Ag) with tunable plasmonic properties have been demonstrated to possess high SERS activity for detection of pesticide thiram [8]. Three dimensional (3D) Ag nanostructure with high density of hot spots and large surface for target molecules loading has also exhibited outstanding SERS performance [9,10], even with attomolar (10^{-18} M) sensitivity [11]. Ag micro-hemispheres with sub–10 nm gap [12], and hierarchical flower-like Ag particles with highly roughened surface [13–16], which were visible under optical microscope and could concentrate intense field on single particles, have been shown to possess excellent sensitivity and reproducibility. Unfortunately, sensitivity, reproducibility and stability have been hardly achieved at the same time. In addition, bad biocompatibility of Ag nanostructures and their lower adsorption capacity for aromatic compounds also hinder their widespread applications.

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Graphene, a single-atom thick sheet of carbon atoms arranged in an ideal two dimensional (2D) honeycomb crystal lattice, exhibits extraordinary electrical performance and Raman scattering properties. Graphene oxide (GO), the oxidized graphene sheet, also possesses outstanding physicochemical properties as well as other advantages due to the presence of defeats and functional oxygen-containing groups on its surface. Graphene/graphene derivatives-noble metal nanocomposites have become a hot research topic in fields of biosensor applications, electronic sensors, supercapacitor and fluorescence based sensors [17–20]. Especially, these nanohybrid materials have been explored as unique SERS platforms [21,22]. Graphene as a sheath coating on nanoparticles could effectively prevent metal-molecules direct interactions and thus acquire enhanced Raman activity and reproducibility [23]. The GO-supported noble metal nanostructures with tunable local surface plasmon resonance (LSPR) have been successfully fabricated to achieve an optimized SERS detection sensitivity [24]. The graphene/graphene derivatives-involved sandwich nanostructures were developed to serve as efficient SERS substrates with extremely high sensitivity, as well as for selective pesticide monitoring due to multi-dimensional plasmonic coupling [25,26]. However, these approaches assembling graphene/graphene derivative layers on metal nanoparticles or decorating metal nanoparticles on graphene-based sheets could not thoroughly avoid direct metal-molecule interaction, which would weaken SERS reproducibility. Recently, it has been reported that enclosing metal nanoparticles with an ultrathin, seamless and passivated graphene/GO film could successfully prevent metal-molecule contact and undesirable SERS signal variations [27–30].

In this work, we report a novel and excellent SERS-active substrate based on GO-wrapped flower-like Ag particles (Ag@GO). The cysteamine functionalized flower-like Ag particles were seamlessly enclosed by GO layers via electrostatic interaction. The maximum SERS enhancement could be achieved by controlling the synthetic conditions such as reaction temperature and amount of reagents. Compared with bare Ag particles, the as-prepared Ag@GO composite substrates exhibited higher stability after exposure to ambient conditions over a long time, because of the protection of inert GO shell. The sensitive SERS detection of rhodamine 6G (R6G) on Ag@GO substrate was achieved as low as 10^{-13} M, due to the combination of electromagnetic (EM) enhancement from the highly rough surface of Ag particles and chemical enhancement generated by charge transfer between GO and target molecules. The detection limit of R6G on bare Ag particles was only 10^{-10} M. Particularly, the composite substrates without any surface modifications demonstrated excellent SERS response for aromatic compounds with weak affinity on noble metal surface. Furthermore, the Ag@GO hybrids also could provide selective detection for polychlorinated biphenyls compounds (PCBs, a kind of persistent organic environmental pollutants), suggesting the potential applications in SERS-based biological and chemical monitoring.

2. Experimental section

2.1. Synthesis of flower-like Ag particles

The flower-like Ag particles were synthesized by a previously reported method with some modifications [30]. $AgNO_3$ aqueous solution with various volumes (0.1, 0.2 and 0.3 mL, 1 M) and Polyvinyl pyrrolidone (PVP) aqueous solution (2 mL, 1 M) were added into 10 mL ultrapure water under vigorous stirring. Then, 0.2 mL of 1 M ascorbic acid (AA) aqueous solution was injected quickly into the mixture under vigorous stirring for 15 min at different temperatures (0 °C, 25 °C, and 50 °C). The resulting samples were centrifuged (2000 rpm for 5 min) and washed with ultrapure water. Finally, the as-synthesized flower-like Ag particles were dispersed in 12 mL ultrapure water for subsequent experiments.

Table 1
Summary of bare Ag micro-particles and Ag@GO hybrids prepared from different synthetic conditions.

Sample I	Sample II	$AgNO_3$/mL	Temperature/°C
Ag-1	Ag@GO-1	0.3	0
Ag-2	Ag@GO-2	0.3	25
Ag-3	Ag@GO-3	0.3	50
Ag-4	Ag@GO-4	0.2	0
Ag-5	Ag@GO-5	0.1	0

2.2. Fabrication of Ag@GO composite

Graphene oxide was prepared according to the modified Hummers method [31]. Then the graphene oxide was dispersed in water and sonicated for 3 h to obtain 0.01 mg/mL GO aqueous solution. To prepare Ag@GO hybrid, 1 mL as-prepared Ag particle dispersion was added into 9 mL ultrapure water under stirring, followed by the addition of 50 μL cysteamine with different concentrations (5 mM, 15 mM, and 30 mM). After stirring for 1 min, 15 mL of GO aqueous solution was added into the mixture and mildly stirred for another 1 h at room temperature. Finally, the resulting products were centrifuged (8000 rpm for 15 min) and re-dispersed in 5 mL Milli-Q ultrapure water.

2.3. Characterization

Morphological features and structures of Ag and Ag@GO microstructures were characterized by scanning electron microscope (SEM, Tescan MIRA 3LMH), transmission electron microscope (TEM, JEOL-2100F TEM) and X-ray diffraction (XRD Siemens D500). SERS spectra were collected with a model confocal microscopy Raman spectrometer (Renishaw inVia). A 785 nm laser with 5 mW power was used for SERS excitation according to plasmonic resonant wavelength of Ag and Ag@GO hibrids (Fig. S1). The integral time was 10 s and the samples were detected using a 100 × objective lens. For the detection of R6G, 20 μL of the Ag@GO aqueous suspension was mixed with 20 μL of different concentrations of R6G, and sonicated for 30 min to reach the adsorption equilibrium. Then, 20 μL of the solution was dropped on a Si wafer and dried for SERS detection. PCBs were also detected using the same method.

3. Results and discussion

3.1. Synthesis and characterization of Ag@GO hybrids

It is generally recognized that the EM field enhancement originating from the excitation of surface plasmons on metal surfaces contributes dominantly to the Raman enhancement. Therefore, the design and facile synthesis of noble metals with particular nanostructures and controllable morphologies are especially important. Here, the morphologies of Ag cores were tuned by varying the reaction temperatures and reagent concentrations. All the details of as-synthesized bare Ag particles prepared from different synthetic conditions were summarized in Table 1. Fig. 1a–c shows the SEM images of bare Ag particles obtained at different reaction temperatures, 0 °C, 25 °C and 50 °C in fixed concentration of $AgNO_3$ aqueous solution (0.3 mL, 1 M). It is apparently observed that the reaction temperature can greatly affect the morphologies. When the reaction temperature was 0 °C, flower-like Ag particles with average diameter of 700–900 nm were formed and possessed many random nanosheet protrusions on the surface (Fig. 1a). At 25 °C, the size and stack density of sheet-like petals decreased clearly (Fig. 1b).