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Featured Letter

Freestanding silver dendrite/graphene oxide composite membranes as high-performance substrates for surface-enhanced Raman scattering

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ABSTRACT

Herein we report the facile synthesis of freestanding silver dendrite (AgD)/graphene oxide (GO) composite membranes, and demonstrate their use as an efficient and robust substrate with large-area uniformity and good reproducibility for surface-enhanced Raman scattering (SERS) applications. The as-prepared composite membranes exhibit excellent sensitivity for detecting rhodamine 6G and 5,5′-dithiobis-(2-nitrobenzoic acid). The results suggest that AgD/GO nanocomposite membrane holds great promise as a high-performance SERS substrate for plasmonic sensing applications.

1. Introduction

Surface-enhanced Raman scattering (SERS) has been an ultrasensitive and nondestructive spectroscopic technique for a variety of applications ranging from food safety control, environmental monitoring and assessment, forensic investigation, to medical diagnosis. [1–6] The SERS performance is critically determined by the morphologies and structures of noble metals such as Au, Ag and Cu etc. Therefore, controlled synthesis of SERS-active substrates with good sensitivity and reproducibility is highly needed. Among these material candidates, silver dendrites (AgDs), which is a special structure of silver metal with high surface area-to-volume ratios, have been proven to be a high-performance SERS substrate. Different approaches were employed to fabricate dendritic Ag structures, these include electrochemical deposition, galvanic replacement reaction, solvothermal or hydrothermal reaction etc.[7–12] On the other hand, due to the superior biocompatibility and chemical stability of graphene oxide (GO), utilization of freestanding paper-like or foil-like GO membrane has attracted tremendous attention in applications such as protective layers, chemical filters, components of electrical batteries or supercapacitors.[12] Considering the beneficial properties of both AgDs and GO for SERS, this flexible AgD/GO nanocomposite should be attractive for use as a SERS substrate. Here we report a facile method to synthesize AgD with a galvanic replacement reaction, followed by its deposition by spin-coating onto the flexible and mechanically strong GO membrane for SERS applications.

2. Experimental

A copper foil was first immersed in a solution of hydrochloric acid (1 M) to remove surface contamination, followed by thorough rinsing with distilled water. Then, the copper foil was immersed into a $AgNO_3$ solution (200 mM) for 20 s to conduct the replacement reaction. The as-synthesized AgDs were centrifuged and washed for 3 times and then spin-coated on the GO membrane, which was prepared by filtration of freshly-made GO (synthesized following the modified Hummer's method [13]) through a 0.22 μm membrane to form a freestanding film. The crystal structure of the AgD/GO composite membrane was examined by X-ray diffractometry (XRD, Rigaku SmartLab with Cu Kα radiation between 2θ angles from 5° to 60°). The morphology and structure of the samples were observed by field-emission scanning electron microscopy (FE-SEM, FEI Verios 460L). The mechanical properties of GO membranes were measured using an Instron tensile tester. Prior to the tensile test, the membranes were cut into 1 cm × 5 cm size and the thickness of each sample was measured and recorded. The FT-IR spectra were measured using a Nicolet iS5 FT-IR spectrometer. The SERS spectra were collected using a Horiba Raman Microscope with a 100 × objective lens, an integration time

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of 10 s, and a laser excitation at the wavelength of 532 nm, which had a power of approximately 1 mW on the sample surface.

3. Results and discussion

The GO membrane displays uniform and dark brown color under white light with good flexibility (Fig. 1A). The morphologies of the as-prepared GO membrane, AgDs and AgD/GO composite were further observed by SEM. The GO membrane exhibits a flat surface but some individual, well-defined GO wrinkles are still seen, which were induced during the filtration process. This also indicates a layered structure of the GO membrane (Fig. 1B). From the cross-sectional image (Fig. 1C), the thickness of the GO membrane was determined to be approximately 6.5 μm without any structural defects. For the AgDs, it is evident that all the AgDs consisted of long central stems up to ~3 μm length with numerous

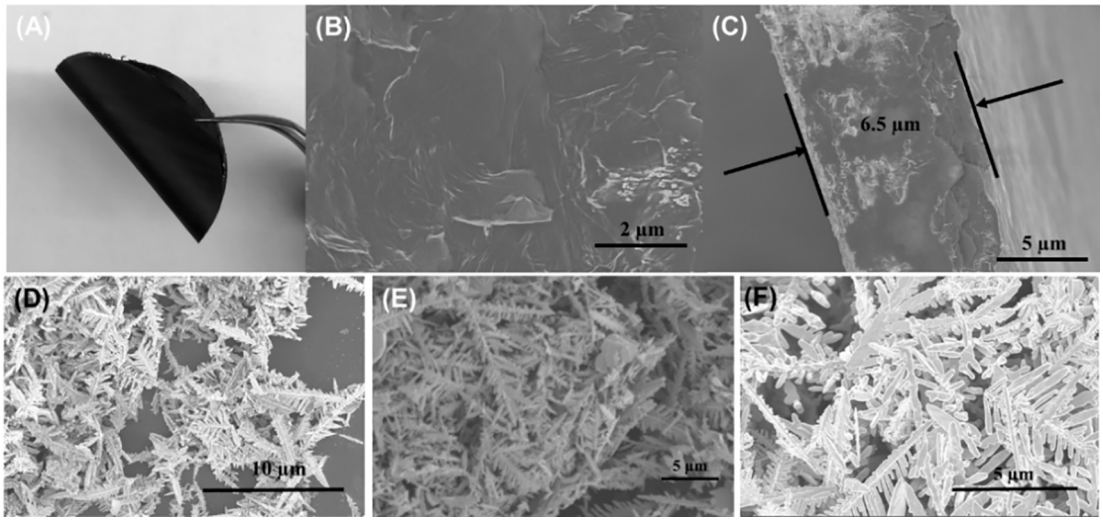

Fig. 1. (A) A picture of GO membrane; (B)-(C) Surface and cross-sectional SEM images of GO membrane; (D) SEM image of as-prepared AgDs; (E)-(F) SEM images of AgD/GO composite.

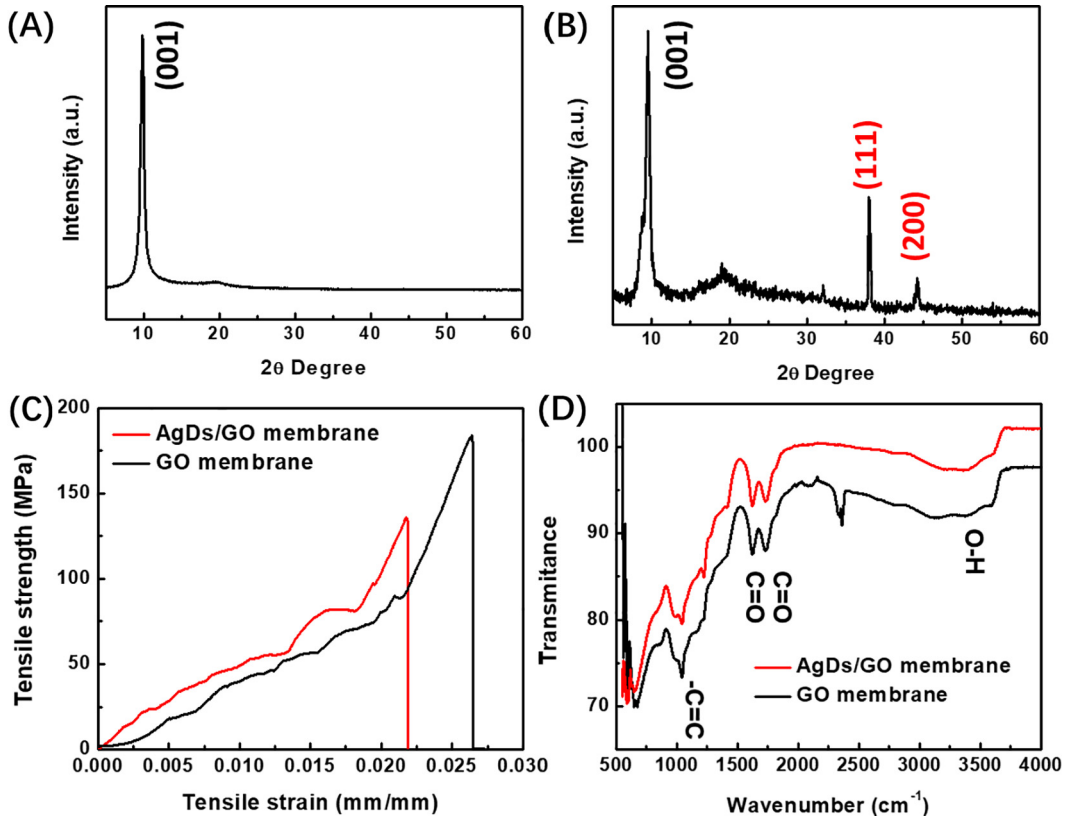

Fig. 2. XRD patterns of GO membrane (A) and AgD/GO composite membrane (B) ; (C) tensile test of GO membrane and Ags/GO composite membrane; FT-IR curves of GO membrane (C) and AgD/GO composite membrane (D).

secondary or tertiary branches uniformly grown along the central stems. The large area-to-volume ratio of this dendritic structure can provide numerous active SERS hot spots and also present a high concentration of edges and terraces, which makes the AgDs effective SERS substrates (Fig. 1D-F) [8]. After depositing the AgDs onto the GO membrane, the GO surface is fully covered and the oxygen-containing functional groups on the GO are beneficial in bonding the AgDs tightly onto the GO membrane surface, which helps to keep the structural integrity of the SERS substrate.

Fig. 2A-B present the XRD patterns of GO and AgD/GO composite, respectively. For pure GO membrane (Fig. 2A), a sharp peak is observed at $2\theta = 9.7°$. which can be ascribed to the (001) peak of GO. For the AgD/GO composite membrane (Fig. 2B), the (001) peak of GO is still detectable, indicating the thin layer of AgD deposited on the GO membrane. In addition, two more peaks located at 38.2° and 44.1° are observed, corresponding to the (111), (200) crystalline planes of face-centered cubic Ag.[1] Considering that as high-performance sensor substrate, the graphene oxide paper must be mechanically strong to ensure its durability, tensile test measurement was conducted on the graphene oxide paper. From Fig. 2C, it is seen that the curve shows an initial straightening region followed by a "linear region", which is consistent with results from others.[14] Finally, it can be determined that the GO paper shows a high tensile stress as 183.9 MPa with a tensile strain of 2.9%, demonstrating a stiff property of the GO membrane. Compared with the GO membrane, the AgDs/GO composite membrane exhibits similar tensile property. However, the tensile strength and tensile strain have decreased slightly, which can be ascribed to the relatively weaker bonding between the AgDs and GO compared with the GO/GO bonding (Fig. 2C). Furthermore, the functional groups on the GO membrane were also investigated. The FTIR spectra of pure GO membrane and AgDs/GO composite membrane showed approximately the same spectra with negligible difference (Fig. 2D). The presence of a large amount of oxygen-containing functional groups on the GO membrane helps in both anchoring the AgDs and preventing the AgDs from oxidation.

Rhodamine 6G (R6G) was used as the analyte molecule to evaluate the SERS performance of the GO/AgD flexible substrate. As shown in Fig. 3A, well-resolved peaks of R6G can be clearly seen in the spectra even when the concentration was decreased to 10^{-12} M. Meanwhile both the fluorescence background and the GO peaks were greatly suppressed in the SERS spectra. As the concentration of R6G decreased from millimolar to picomolar, key spectral features remain intact but the SERS intensity significantly decreased, probably due to the reduction of the regions of highly enhanced local electromagnetic field "SERS hot spots".[15] Compared with AgDs-based SERS substrates reported by others [14], a lower minimum concentration of R6G could be detected by this AgDs/GO composite membrane, demonstrating an enhanced sensitivity.

Another crucial parameter for the practical application of excellent SERS substrates is their stability over a period of time. In this work, the AgD/GO membrane was kept in ambient conditions for 20 days to test the long-term stability of AgD/GO, and 5,5-dithiobis-(2-nitrobenzoic acid) (DTNB) was used as another probe molecule to evaluate the SERS performance. As demonstrated in Fig. 3B,

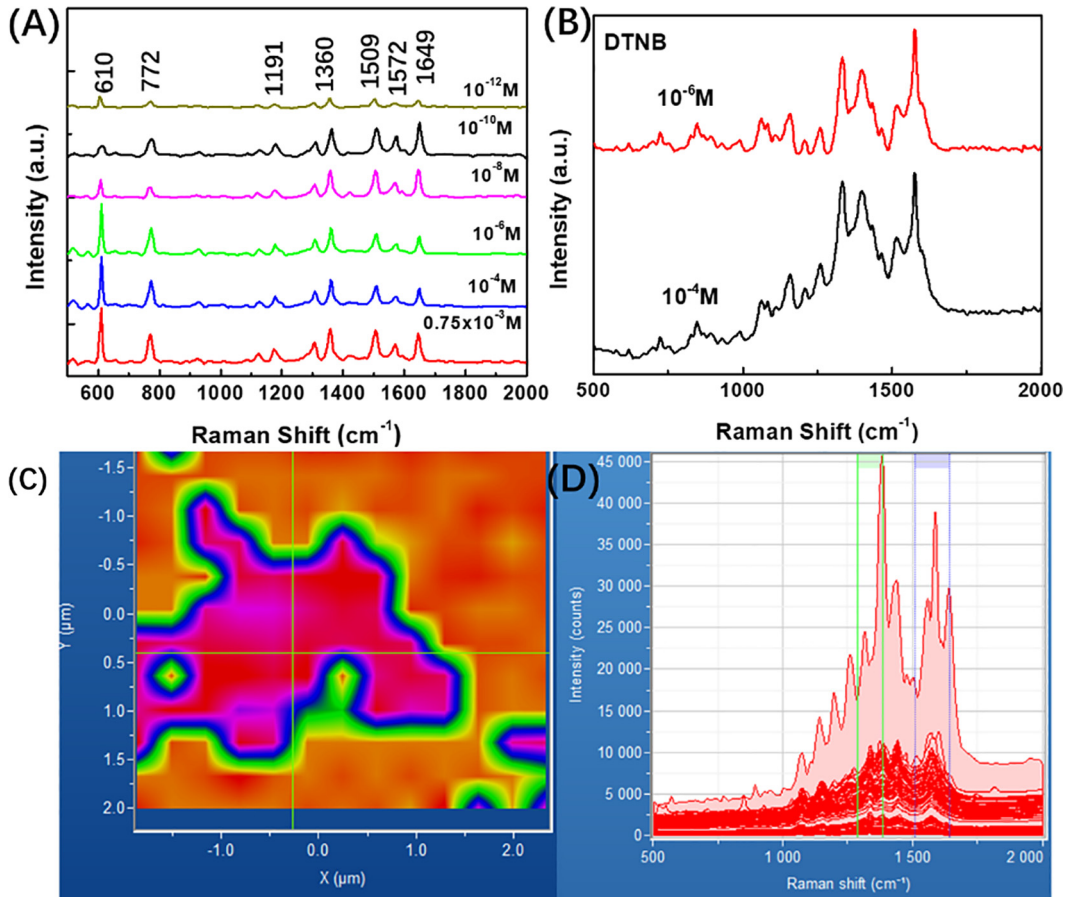

Fig. 3. (A) Raman spectra of R6G molecules on the AgD/GO composite membrane; (B) Raman spectra of DTNB molecules on the AgD/GO composite membrane prepared after 20 days; (C) Raman mapping pattern of DTNB molecules on the AgD/GO composite membrane; (D) Raman spectra of DTNB molecules on the AgD/GO composite membrane corresponding to (C).

the characteristic Raman peaks of DTNB are prominent, indicating good reproducibility and durability of the AgD/GO substrate. This long-term stability property can be attributed to the GO membrane, which could function as a protective substrate to prevent the AgDs from oxidation. Moreover, the Raman mapping was also conducted using DTNB as the analyte molecule (Fig. 3C). The SERS active hot spots (red color) are concentrated along the edge parts of the AgDs instead of the central part of AgDs, which indicates that the Raman enhancement mainly comes from the edge part of the AgDs, resulting from more disordered structures of fractals. Furthermore, it is evident that the SERS hot spots are uniformly distributed all over the AgDs (Fig. 3D). Two factors are believed to contribute to the superior SERS performance. The first one is the Ag dendritic nanostructures with a large surface-to-volume ratio, which provide numerous active hot spots. The other one is the chemical enhancement caused by the GO, which is induced by the π- π stacking and charge transfer from the lone-pairs of electrons on the oxygen-containing functional groups of GO membrane.[14,16,17] As a result, these two synergic effects work in tandem to make this AgD/GO composite membrane a highly sensitive, reproducible and stable SERS substrate.

4. Conclusion

We developed a facile approach to synthesize free-standing SERS-active substrates based on AgD/GO composite. The as-prepared AgD/GO membrane exhibits excellent SERS activity for detecting R6G and DTNB. Our results suggest that AgD/GO membrane holds great promise as a high-performance SERS substrate for plasmonic-based sensing applications.

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