Surface-enhanced Raman scattering activities of carbon nanotubes decorated by silver nanoparticles

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1. Preparation steps of CNTs-Ag

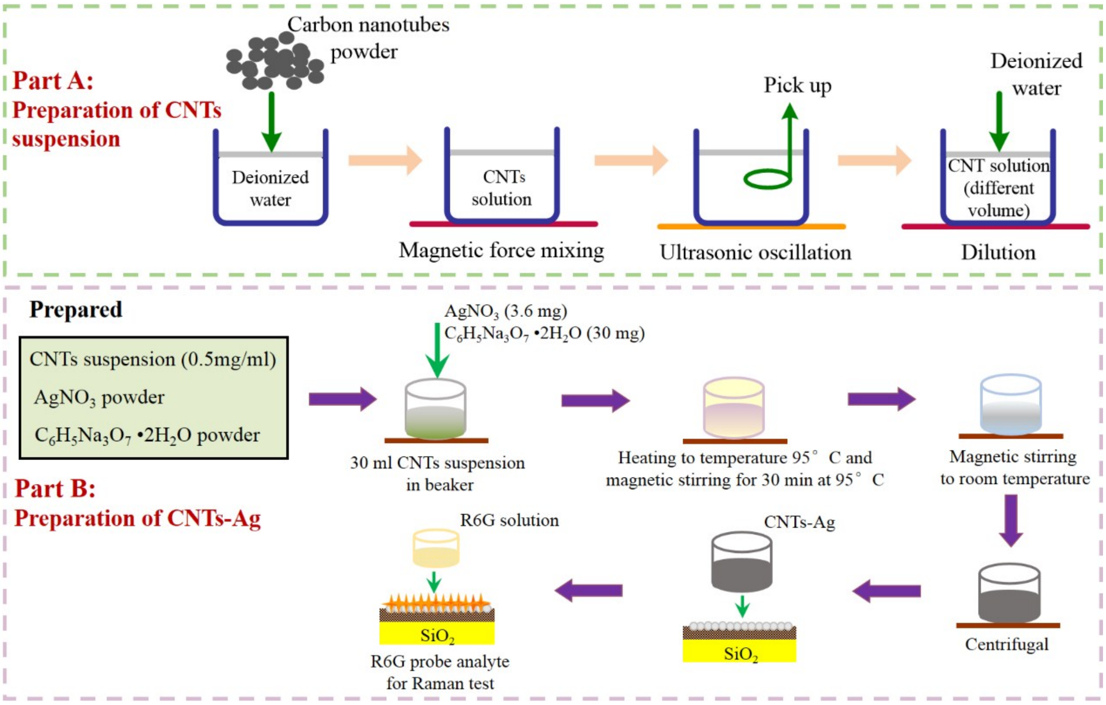

Fig.S1 CNTs suspension and CNTs-Ag composite preparation steps

The reported detection limits of R6G on different substrates by other researchers are shown in Table S1. In comparison with those measured on other substrates, our limit of detection (LOD) is lower, especial for the carbon nanotube composites structure. The reason could be: (1) carbon nanotube films help to detect organic molecules with high sensitivity; (2) the coverage of AgNPs on the CNTs is very high; (3) the gap of the prepared AgNPs is very small.

Table S1 Reported detection limits of R6G on different substrates

Researchers	SERS substrates	LODs
Zhou et al. [1]	Ag-SiNWs	10^{-14} M

Hsiao et al. [2]	Ag NWs-SPC	10^{-16} M
Sun et al. [3]	Ag-SACNT	10^{-6} M
Jiang et al. [4]	Au-CNT-Si	10^{-8} M
Sarkar et al. [5]	Ag-CNT-Si	10^{-12} M
Ou et al. [6]	Ag-Au	2×10^{-15} M
Ding et al. [7]	Ag-GO	10^{-7} M
Li et al. [8]	AgNPs-arrayed paper	10^{-11} M

2. Effect of different substrates

To compare the prepared CNTs-Ag sample, we fabricated Ag-sol and CNTs films samples, the preparation method of Ag-sol is the same with the AgNPs in CNTs-Ag sample. Fig. S2 shows the SERS spectra of R6G at a concentration of 10^{-7} M adsorbed on the three substrates. We can see that the Raman intensity collected on CNTs-Ag is larger than that collected on Ag-sol (pure Ag nanoparticles). For Raman peak position at 1362 and 1508 cm^{-1}, the Raman intensity collected on CNTs-Ag is about 13 fold than that collected on Ag-sol substrate. The reasons could be: (1) the enhancement induced by the coupling effect between CNTs and Ag nanoparticles is stronger than that of two silver nanoparticles, which results in greater Raman intensity; (2) the total surface area of the carbon nanotubes is about 1.5 times that of the planar [9], which indicates that the number of AgNPs adsorbed on CNTs is more than that of the planar substrate, which could also enhance the Raman intensity.

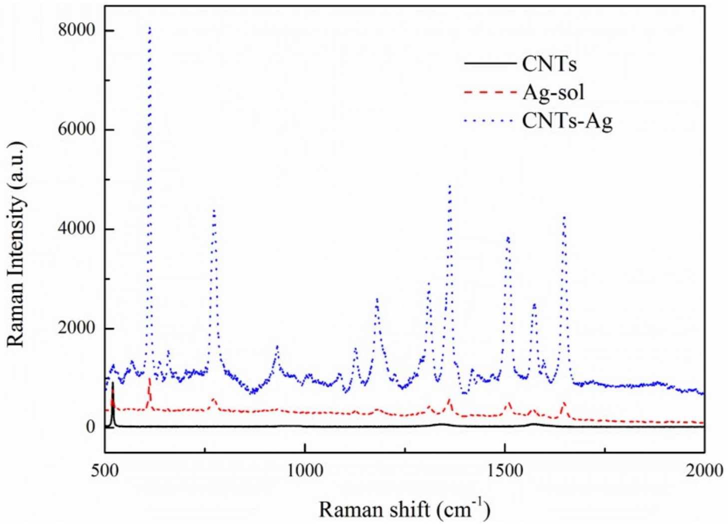

Fig. S2 SERS spectra of 10^{-7} M R6G on CNTs, Ag-sol and CNTs-Ag.

3. Stability of CNTs-Ag

To investigate the stability of CNTs-Ag, we selected a sample for Raman experiment, and compared with the freshly prepared substrate and the substrate stored in air for 8, 15, 22, 57, 65 days for SERS detection of R6G molecular, as shown in Fig. S3 (a). There is no shift in the major Raman peaks positions. The SERS intensity became weaker, but the characteristic Raman peaks of R6G were still distinguishable. The Raman intensity at 1362 and 1508 cm^{-1} versus exposure time is shown in Fig. S3 (b). With increasing exposure time in Raman peak at 1362 cm^{-1} dropped to 80.00%, 64.07%, 42.78%, 30.55%, and 15.12%, after 8 days', 15 days', 22 days', 57 days' and 65 days' aerobic exposure, respectively, compared with that of the fresh substrate. For Raman peak at 1508 cm^{-1}, Raman intensity dropped to 82.37%, 45.52%, 35.85%, 28.15%, and 16.30%, respectively. Similar observations were recorded for the other Raman peaks. The signals displayed no noticeable loss of the Raman peak features, but a sizable reduction in intensities. The reasons could be: Ag nanoparticles could be oxidized in air, which might cause individual silver nanoparticles to form a nanocluster after oxidation. The SEM images of fresh and oxidized sample are shown in Fig. S4 (a) and (b), the corresponding energy disperse spectroscopy (EDS) images are shown in Fig. S4 (c) and (d). As can be seen from the SEM images, after 65 days, the individual silver nanoparticles on freshly prepared sample re-united to form a nanocluster. Elements on CNTs-Ag surface include C, Si, Ag and O, where Ag content is 24.7 wt%, oxygen is 1.0 wt% for fresh sample. After 65-day exposure in ambient condition, Ag content is 16.0 wt%, oxygen is 12.1 wt%, and Ag/O atomic ratio of CNTs-Ag versus exposure time in ambient condition is 1.32. The reunion and oxidation of silver nanoparticles lead to the reduction of hot spots and the Raman intensity of the surface plasmon resonance.

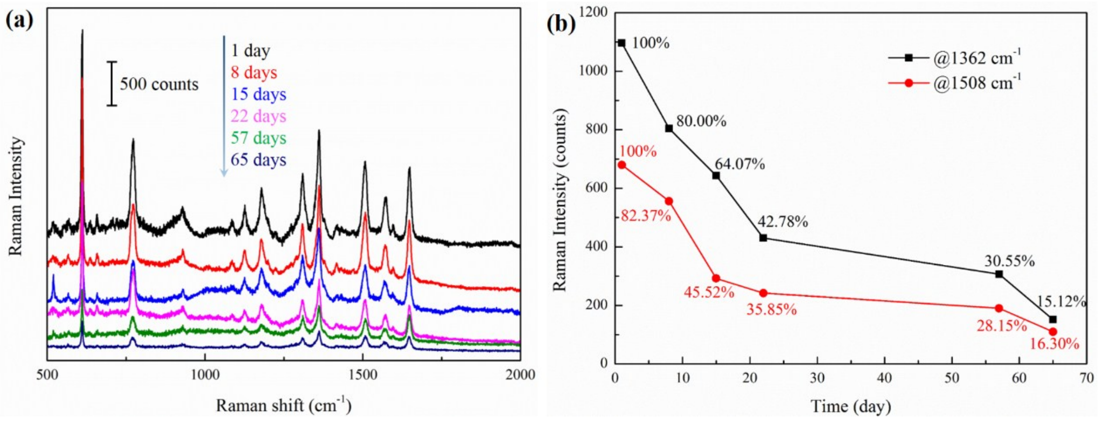

Fig. S3 SERS signals of R6G with 10^{-8} M (a) at different time points and (b) at 1362 and 1508 cm^{-1} long with exposure time.

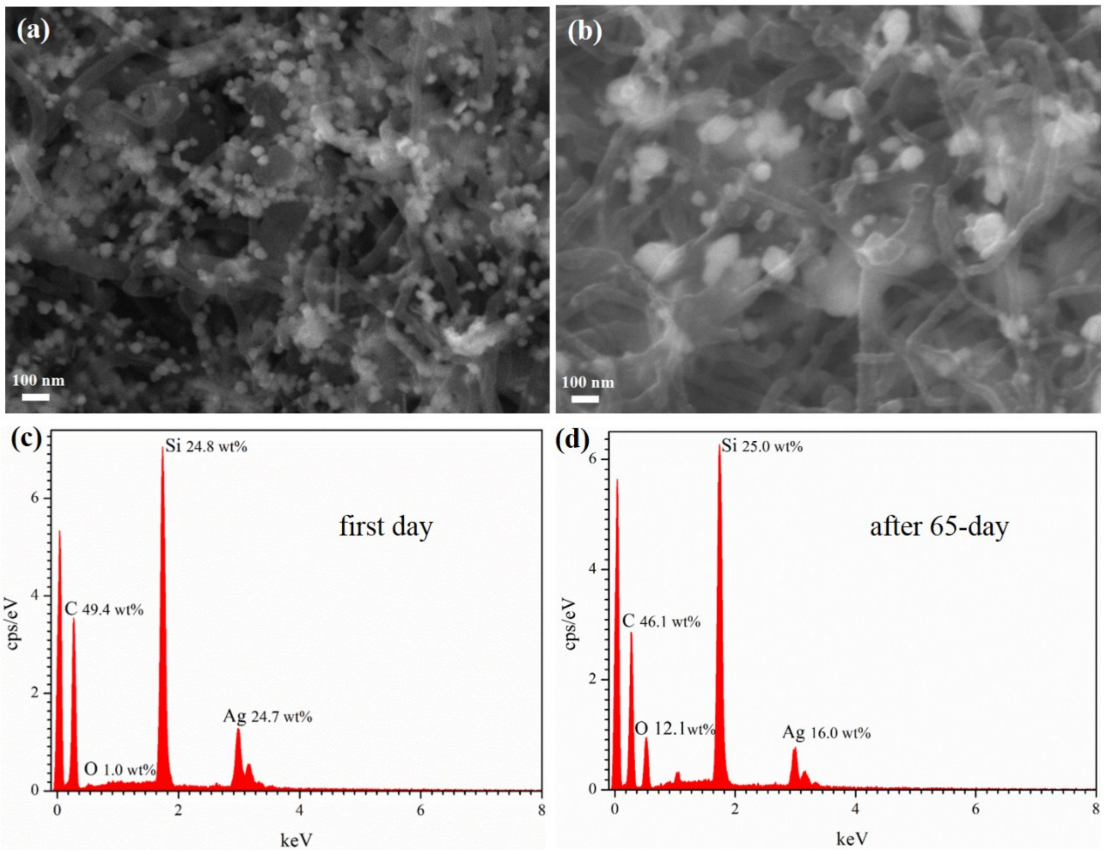

Fig. S4 SEM images of CNTs-Ag placed in the air for (a) one day and (b) 65-day, the corresponding ESD placed in the air for (c) one day and (d) 65-day.

4 Different loading amount of AgNPs

A. SEM for another two samples

SEM images and the corresponding size distribution of the AgNPs of sample 1 and sample 2 are shown in Fig. S5. From the SEM images, we can see that there is no essential change of the size of silver nanoparticles, and the gaps among Ag nanoparticles on CNTs gradually decrease as mass of CNTs suspension increases. The average size of Ag nanoparticles on the surface of CNTs for sample 1 and sample 2 is about 34.5 nm (±0.4 nm), 32.9 nm (±0.4 nm), respectively. The calculated number of Ag nanoparticles in an area of 1.2 μm^2 are 167, 278 for sample 1 and sample 2 respectively. The gaps among Ag nanoparticles on CNTs are 8.8 and 4.6 nm, respectively. The ratio of surface area of silver particles to the total covered area for sample 1 and sample 2 is about 53.9% and 61.3%, respectively.

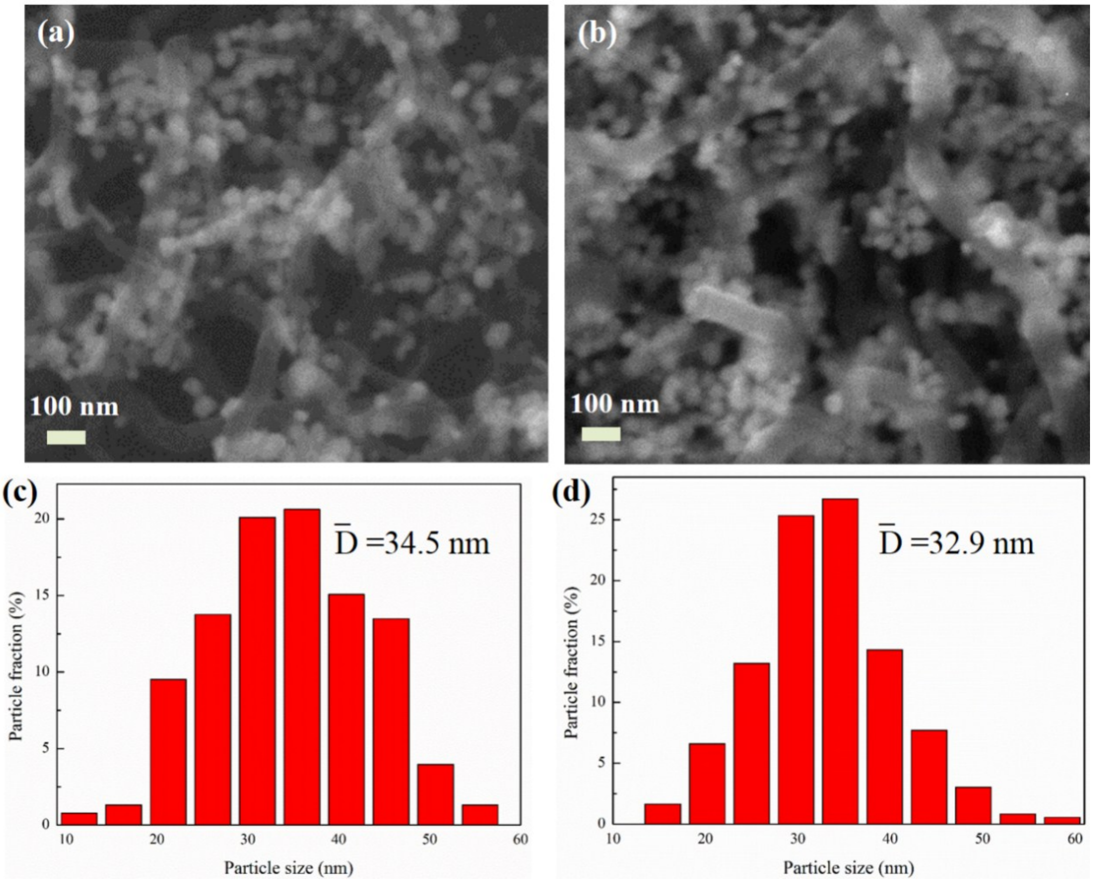

Fig. S5 SEM images of (a) sample 1 and (b) sample 2. The corresponding size distribution of AgNPs in (c) sample 1 and (d) sample 2.

B. Raman spectra for three samples

The Raman spectra of the prepared three samples are shown in Fig. S6. The Raman relative intensities of D peaks of the three samples are about 38, 78 and 153 counts, respectively. The Raman intensity of D and G peaks for sample 1 to sample 3 is increased, which is due to plasmon-induced E-field enhancement by increasing the number of AgNPs, indicating the SERS activity increased. In addition, the ratio I_D/I_G for three samples is about 1.02, 1.19 and 1.22 respectively, this difference arose because the presence of Ag nanoparticles caused change in the characteristics of the carbon wall [10]. The results obtained from Raman measurement imply that AgNPs on CNTs could provide electromagnetic enhancement to amplify SERS signal of CNTs.

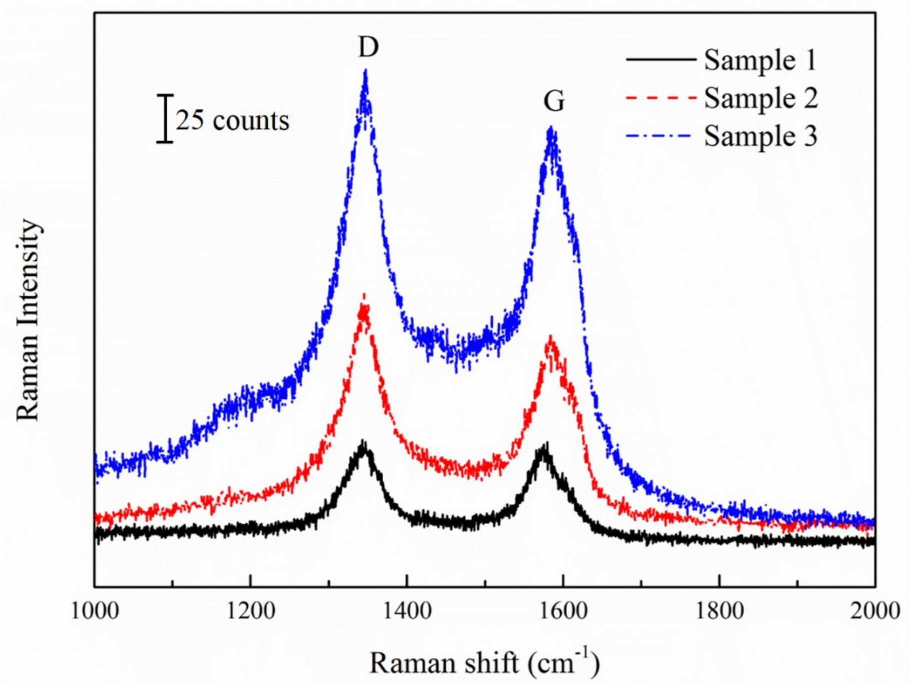

Fig. S6 Raman spectra of CNTs-Ag samples.

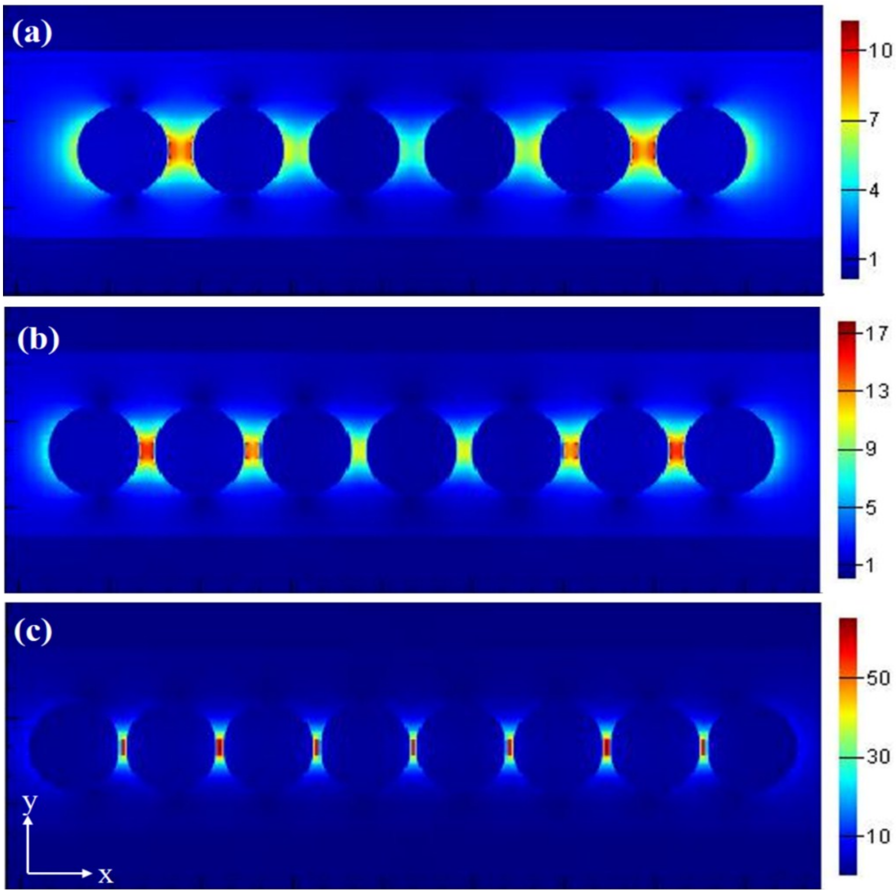

Fig.S7 Spatial distributions of the electric field intensity for the x-y planes with (a) CNTs-6-Ag, (b) CNTs-7-Ag and (c) CNTs-8-Ag.

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