Supporting Information

Facile synthesis of core-shell-satellite Ag/C/Ag nanocomposites using carbon nanodots as reductant and their SERS properties

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Experimental section

Chemicals: Silver nitrate (AgNO₃, 98%), crystal violet (99%), polyvinylpyrrolidone (PVP K-30, 99%), hydrogen peroxide (30%), ethanol (99.7%), sodium citrate (99%) and sulphuric acid (98%) were purchased from Sinopharm Chem. Reagent Co., Ltd (Shanghai, China). The grass was obtained from the ground of Jiangsu University and wash by water for further use. The water used was double-distilled after a deionized exchange.

Synthesis of Ag/C: Carbon nanodots (CDs) were prepared according to the method reported previously,¹ and the details are described as follows. Firstly, grass (2 g) was added into 10 mL of water. Then the mixture was transferred into a 25 mL Teflon-sealed autoclave and heated at 180 °C for 3 h. A brown solution containing CDs was collected through centrifugation at 10000 rpm for 10 min. The CDs solution thus obtained was diluted to fixed volume (25 mL) for further use. The typical preparation of Ag/C composite nanoparticles was as follows: 0.1g of PVP was dissolved in 10 mL of water. Then, 5 mL of AgNO₃ aqueous solution (0.01 M) was put into the PVP solution using a pipette and stirred for 5 min. A 10mL portion of as-prepared CDs solution was dropped into the above mixed solution during the stirring process. After stirring for another 20 min, the reaction solution was transformed to a 50 mL Teflon-sealed autoclave and maintained at 180 °C for 4 h. After the reaction was completed, the solution was cooled in air to room temperature. The brown precipitates were collected by centrifugation at the speed of 8000 rpm, and then washed with deionized water and ethanol for 3 times, respectively. Finally, the
sample was dispersed in ethanol for further characterization.

**Synthesis of Ag/C/Ag:** In a typical synthesis, the preparation of reaction solution was same to that of the Ag/C synthesis. After the hydrothermal treatment at the same condition, the solution was put into a beaker and sealed. The solution was then irradiated with a high-intensity ultrasonic horn (Kunshan Co., China, KQ2200-DB; Ti-horn, 20 KHz, 60 W cm⁻²) for 30 min at constant 30 °C, and then washed with deionized water and ethanol for 3 times, respectively. Finally, the bright brown Ag/C/Ag samples was stored in ethanol for further use.

**Synthesis of pure Ag nanoparticles:** According to Turkevich’s method,² 20 mL of AgNO₃ aqueous solution (0.001 M) was put into a round-bottom flask and heated to boiling; then, 0.5 mL of aqueous solution of sodium citrate (1% by weight) was added under magnetic stirring. After reaction for 40 minutes, a grayish yellow suspension was obtained.

**Characterization:** Purity and crystallization of the samples were characterized by powder X-ray diffraction on a D/max-γA X-ray spectrometer (Rigaku, Japan) at 40 kV and 200 mA with monochromatic Cu Kα (λ=1.5418 Å) radiation. Transmission electron microscopy (TEM) and high transmission electron microscopy (HRTEM) images were taken on a TECNAI12 TEM instrument (Philips). The normal TEM and HRTEM samples were prepared by dropping the solution onto a copper grid with polyvinyl formal support film and dried in air, respectively. UV-vis diffuse reflectance spectra of the samples were measured by using an UV-2401 (Shimadzu) UV-vis spectrophotometer. The samples were also analysed by Fourier transform infrared
(FT-IR) spectra which were performed with KBr wafer technique. All Raman spectra were carried out at room temperature using a DXR Raman microscope with 514.5 nm excitation source from an Ar ion laser. To avoid laser-induced heating, the laser power was kept at 0.5 mW. The thermogravimetric analysis (TGA) was obtained using an integrated thermal analyzer (STA 449C) under nitrogen atmosphere at the heating rate of 10 K/min.

**Preparation of SRES-active substrates:** The solid samples for SERS measurements were prepared through the following procedures. First, silicon wafer was cleaned by sequential ultrasonication in acetone, ethanol, deionized water for 10 min in each medium and then treated with H₂SO₄ (98%)/H₂O₂ (30%) (3:1, v/v) at room temperature for 4 h to generate a hydrophilic surface. After repeated rinsing with Milli-Q ultrapure water, the clean silicon wafer was dried by blowing N₂. Then, 50 μL of pure Ag particles, as-prepared Ag/C and Ag/C/Ag nanoparticle suspensions with the same concentration (0.45 mg L⁻¹) were drop-cast onto the silicon substrates followed by evaporation of water at 60 °C. The probe molecule (CV) was adsorbed onto the as-fabricated SERS substrates by immersing the SERS substrates in 1 mL of the CV aqueous solution with different concentration (from 10⁻¹⁰ to 10⁻⁶ M) for 1 h. Lastly, the substrates were then thoroughly washed with Milli-Q ultrapure water and subsequently dried with N₂.

CV is a tri-p-dimethylaminophenyl carbonium ion with three rings symmetrically arrayed around a central carbonium atom. The high symmetry of CV can provide a relative rigorous test of the SERS theory. Therefore, we used CV dye to test the
different SERS effects on various substrates. The as-fabricated pure Ag, Ag/C and Ag/C/Ag films on Si wafers, referred to as Ag/Si, Ag/C/Si and Ag/C/Ag/Si, were used as SERS substrates for detecting CV molecules (Scheme. S1). The probe molecule (CV) was adsorbed onto the as-fabricated SERS substrates by immersing the SERS substrates in 1 mL of the CV aqueous solution with the same concentration \(10^5\) M. As a control, free CV molecule on Si wafer was prepared by doping 50 μL of \(10^3\) M CV aqueous solution onto the Si wafer. The substrates were then thoroughly washed with Milli-Q ultrapure water and subsequently dried with N\(_2\).

Herein, we focus attention on the comparation of SERS activities of Ag/C/Si and Ag/C/Ag/Si substrates. The enhancement factors (EF) were calculated by using the following equation:\(^4\)

\[
EF = \frac{I_{SERS}}{I_O} \times \frac{C_O}{C_{SERS}}
\]

where \(I_{SERS}\) and \(C_{SERS}\) are intensity of the band and concentration of the adsorbed molecules for SERS, respectively, \(I_O\) and \(C_O\) are the intensity of the band and concentration of free CV molecules.
Fig. S1 TEM images of Ag/C nanocomposites synthesized under different hydrothermal temperatures for 4 h: (a) 120 °C; (b) 140 °C.

Fig. S2 TEM images of Ag/C nanocomposites synthesized under 180 °C for 4 h in the absence of PVP.
Fig. S3 FTIR spectra of as-synthesized CDs (balck line) and Ag/C (red line).

In addition, as can be seen in Fig. S3, the obtained Ag/C exhibited characteristic absorption N-H stretching vibrations at 2970 cm\(^{-1}\), C-H stretching vibrations at 2917 cm\(^{-1}\), 2850 cm\(^{-1}\) and C-H bending vibrations at 1085-1050 cm\(^{-1}\).\(^5\) It indicates that part of PVP had incorporated into the CDs shell and closely absorbed on the surface of Ag nanoparticles.\(^6\) And the thermogravimetric analysis was acquired to further quantify the amount of PVP left in the carbon shell of the Ag/C composites. It is reported that the decomposition temperature of pure PVP is around 400 °C.\(^7,8\) So it can be observed in the TG curve of as-prepared Ag/C composites (Fig. S4) that the weight loss from 401 °C to 591 °C, which is assigned to the PVP left in the product, is estimated to be 1.22%. And the weight loss (1.19%) from 247 °C to 401 °C is attributed to decomposition of the carbon shell.
Fig. S4 TG curve of as-prepared Ag/C composites.

Fig. S5 TEM images of pure Ag nanoparticles.
Scheme. S1 Schematic illustration for the detection of CV molecules by as-fabricated Ag/C/Si and Ag/C/Ag/Si substrates.

Reference

1 S. Liu, J. Q. Tian, L. Wang, Y. W. Zhang, A. M. Asiri, A. O. Al-Youbi and X. P. Sun, 


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