

Preparation and Characterization of Ultrathin Carbon Shell Coated on Silver Core for Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy

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SUPPLEMENTAL INFORMATION

Materials and Sample Preparation. All chemicals used were of reagent grade, and were used without further purification. Highly pure water with a resistivity higher than 18.0 M Ω cm was used in all the preparations. Silver sols were prepared using the Lee–Meisel method,¹ i.e., AgNO₃ (0.0169 g, 0.1 mmol) was dissolved in 100 mL of H₂O and brought to a boil with vigorous stirring. To this, 2.6 mL of 1 wt% sodium citrate was quickly added under vigorous stirring. The mixture was kept boiling for 30 min and then cooled

¹ P. C. Lee and D. Meisel, *J. Phys. Chem.*, 1982, **86**, 3391.

² G. Socrates, *Infrared Characteristic Group Frequencies: Tables and Charts*, Second Edition, John Wiley & Sons, Chichester, 1994.

³ C. J. Orendorff, A. Gole, T. K. Sau and C. J. Murphy, *Anal. Chem.*, 2005, **77**, 3261.

under ambient conditions.

To modify Ag sols with 4-mercaptobenzoic acid (4-MBA), an ethanolic solution of 4-MBA (2 mL, 1 mmol L⁻¹) was added into 15 mL of the Ag sols under stirring for 24 h in order to allow the 4-MBA to completely reach adsorption equilibrium, followed by 5 min sonication in ethanol, rinsing with ethanol to remove excess reactants. After pH value of the mixture was adjusted by sodium hydroxide aqueous solution (20 wt%) to 9, Cetyltrimethyl ammonium bromide (CTAB) ethanol solution (21 mL, 1 mmol L⁻¹) was subsequently added into to the system, and then the whole mixture was stirred for 24 h. Thus, CTAB was fabricated onto the 4-MBA adsorbed on the Ag sols via electrostatic interaction. Carbonization was performed by adding concentrated sulfuric acid (50 mL) into the system under stirring and heating at 90 °C for 15 min. After a thorough washing with water, CTAB was alternately adsorbed on the carbon films formed in the previous step via hydrophobic interaction and carbonized by using concentrated sulfuric acid for 4 times. The products were collected by centrifugation and washed several times with water and ethanol, and then dried under vacuum at room temperature for 4 h.

A borosilicate cover glass (diameter = 12 mm, Deckglaser) was soaked in a piranha solution [30% H₂O₂:98% H₂SO₄ (1:3)] for 30 min and then sonicated in distilled water for 10 min, followed by rinsing with ethanol, and then finally dried in an oven at 70 °C for 20 min.

Characterization. Transmission electron microscopy (TEM) images were obtained using a Philips-FEI Tecnai F30 microscope. TEM samples were prepared by drying aqueous suspensions of the particles on carbon-coated TEM grids under ambient conditions. X-ray photoelectron spectroscopy (XPS) measurement was carried out with a Thermo VG

ESCALAB250 spectrometer with a monochromatic X-ray source of Al K α (1486.6 eV). Infrared spectrum of the sample was obtained using a Nicolet 5700 FT-IR spectrometer. X-ray powder diffraction (XRD) pattern of the carbon-coated Ag NPs was recorded with a D8ADVANCE powder diffractometer over a 2-theta range of 20–90° at an angular resolution of 0.02°. Ultraviolet/visible (UV/Vis) absorption spectra were obtained using a VARIAN Cary-5000 spectrophotometer. Raman measurements were performed with a Jobin Yvon LabRam HR 800 micro-Raman spectrometer equipped with a microscope (Panasonic Super DYNAMIC). Laser light at 632.8 nm was used as the excitation source.

FTIR spectrum. Fig. S1 shows the IR spectrum of the carbon-coated Ag nanoparticles (NPs). The characteristic IR peaks of alcohol appear at 3434, 2923, 2852, 1632, 1384, 1093, and 798 cm^{-1} . The peaks at 3434, 1632, 1384, 1093, and 798 cm^{-1} in Fig. S1 can be attributed to the O–H stretching vibration, in-plane O–H deformation vibration, C–H deformation vibration, C–O stretching vibration, and C–C skeletal stretching vibration of alcohol, respectively, while the bands at 2923 and 2852 cm^{-1} are due to the C–H stretching vibration of alcohol.²

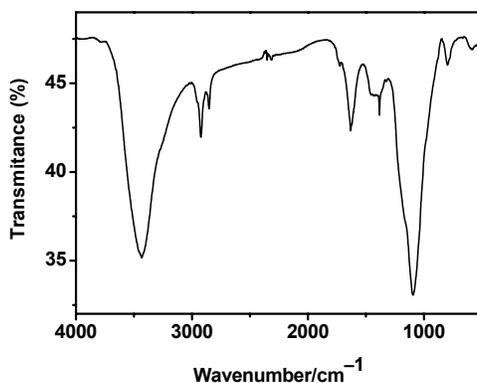


Fig. S1 IR spectrum of the carbon-coated Ag NPs.

XPS spectra. The XPS spectrum of Br 3d in Fig. S2 shows that the binding energy of Br 3d is 68.2 eV, and consists of two individual peaks Br 3d_{3/2} and Br 3d_{5/2}, with binding energies ~68.75 and ~67.75 eV, respectively.

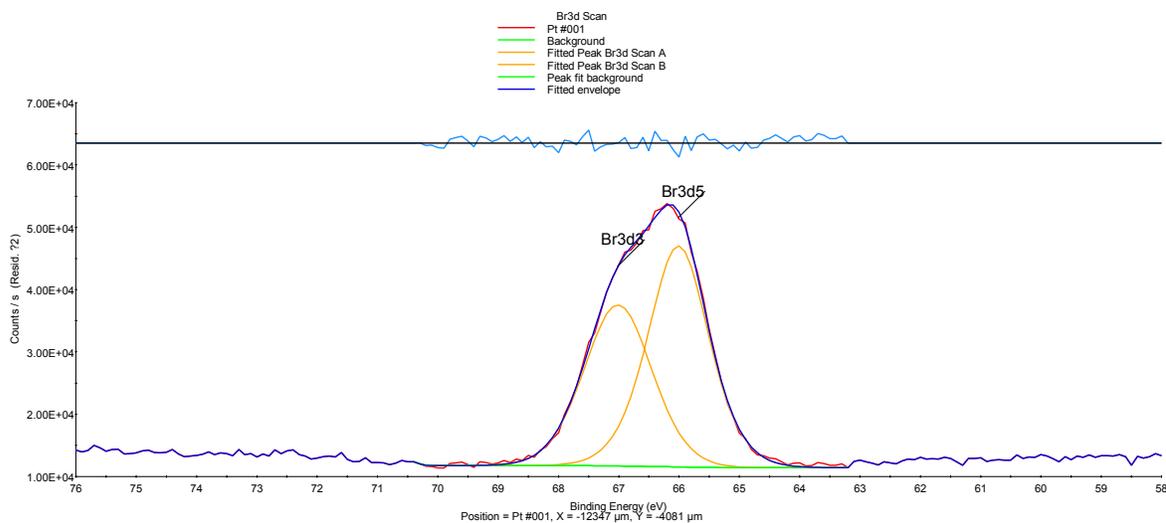


Fig. S2 XPS pattern of sample in Br 3d spectral region.

The XPS spectrum of O 1s in Fig. S3 shows that the binding energy of O 1s is 530.3 eV.

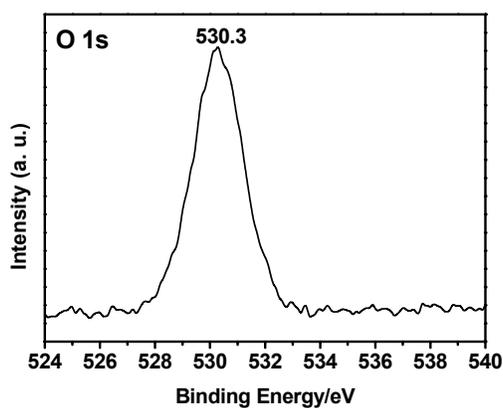


Fig. S3 XPS pattern of sample in O 1s spectral region.

UV/Vis spectra. Fig. S4 shows the UV/Vis spectra of silver colloids and the carbon-coated Ag NPs.

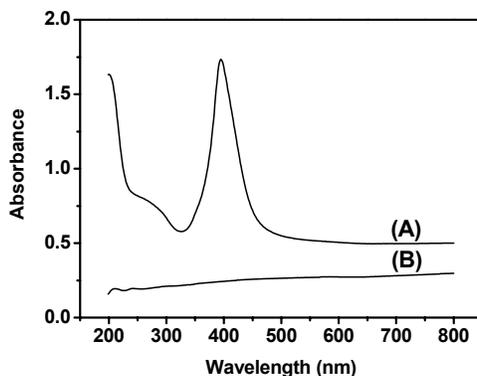


Fig. S4 UV/Vis spectra of (A) silver colloids and (B) the carbon-coated Ag NPs.

Enhancement factor. We attempted to estimate the SERS enhancement factor (EF) using the following equation:

$$EF = (I_{\text{SERS}} / N_{\text{SERS}}) / (I_{\text{NR}} / N_{\text{NR}}) \quad (1)$$

where I_{SERS} denotes the SERS intensity of the ν_{8a} band of 4-MBA adsorbed on the carbon-coated Ag NPs using 632.8 nm radiation as the excitation source, I_{NR} denotes the normal Raman scattering intensity of the same band of dry 4-MBA powder, and N_{SERS} and N_{NR} are the numbers of 4-MBA molecules effectively excited by the laser beam to obtain the corresponding SERS and NR spectra, respectively. We assumed that the sampling volume from which the NR spectrum of dry 4-MBA powder as shown in Fig. 3 (main text) was obtained was the product of the area of the laser spot ($\sim 2 \mu\text{m}$ in diameter) and the penetration depth ($\sim 2 \mu\text{m}$) of the focused beam. Since the density of 4-MBA was 1.5 g cm^{-3} and its molecular weight was $154.19 \text{ g mol}^{-1}$, the number of 4-MBA molecules effectively excited by the laser beam was calculated to be 3.68×10^{10} (i.e., 6.11×10^{-14}

mol). On the other hand, the bonding density of 4-MBA molecules in a self-assembled monolayer is $\sim 0.5 \text{ nmol cm}^{-2}$;³ therefore, the total number of molecules sampled in the SERS experiments using the carbon-coated Ag NPs as a substrate will be 9.45×10^6 (i.e., $1.57 \times 10^{-17} \text{ mol}$). In this estimation, we assumed that the SERS signals of 4-MBA adsorbed on the carbon-coated Ag NPs were from a monolayer. The intensity ratio of the ν_{8a} aromatic-ring vibration bands at $\sim 1584 \text{ cm}^{-1}$ in Fig. 3 (main text) was measured to be 2.6:1 and was taken using 632.8 nm excitation and normalized with respect to the absolute intensity from a silicon wafer. The EF, estimated using 4-MBA as the probing adsorbate, was $\sim 1 \times 10^4$.