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 MΩ 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

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 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% H\(_2\)O\(_2\):98% H\(_2\)SO\(_4\) (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 Kα (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

![FTIR spectrum of carbon-coated Ag NPs](image)

**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 3d₃/₂ and Br 3d₅/₂, with binding energies ~68.75 and ~67.75 eV, respectively.

![XPS spectrum of Br 3d](image)

**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.

![XPS spectrum of O 1s](image)

**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.

![UV/Vis spectra](image)

**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:

\[
EF = \frac{I_{\text{SERS}} / N_{\text{SERS}}}{I_{\text{NR}} / N_{\text{NR}}}
\]

where \(I_{\text{SERS}}\) denotes the SERS intensity of the \(v_{8a}\) band of 4-MBA adsorbed on the carbon-coated Ag NPs using 632.8 nm radiation as the excitation source, \(I_{\text{NR}}\) denotes the normal Raman scattering intensity of the same band of dry 4-MBA powder, and \(N_{\text{SERS}}\) and \(N_{\text{NR}}\) 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 (~2 \(\mu\)m in diameter) and the penetration depth (~2 \(\mu\)m) of the focused beam. Since the density of 4-MBA was 1.5 gcm\(^{-3}\) and its molecular weight was 154.19 gmol\(^{-1}\), the number of 4-MBA molecules effectively excited by the laser beam was calculated to be \(3.68 \times 10^{10}\) (i.e., \(6.11 \times 10^{-14}\))
mol). On the other hand, the bonding density of 4-MBA molecules in a self-assembled monolayer is ~0.5 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 × 10\(^{-17}\) 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 \(\nu_{8a}\) aromatic-ring vibration bands at ~1584 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 ~1 × 10\(^4\).