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Preparation and characterization of an ultrathin carbon shell coating a silver core for shell-isolated nanoparticle-enhanced Raman spectroscopy†

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A well-designed type of ultrathin carbon shell coating a silver core was prepared for the first time through an alternate adsorption and carbonization method. The obtained ultrathin carbon shell shows prominent advantages, including sufficient uniformity, better chemical stability than silica or alumina, biocompatibility, being free of pin-holes and low cost.

Since the discovery of surface-enhanced Raman scattering (SERS),[1] there have been extensive theoretical and experimental studies on this effect.[2] Although the theories explaining SERS are not definite and still evolving, the experimental research and development in recent years has demonstrated SERS to be a potential technique for trace analysis of a wide range of adsorbates, enabling the detection of even a single molecule.[3] However, SERS has noticeable disadvantages, namely that its applicability is limited to a few metal substrates, such as Au, Ag and Cu.[4] The invention of tip-enhanced Raman spectroscopy (TERS) led to a breakthrough in the substrate and surface generalities of SERS,[5] but the total Raman scattering signal from the tip area is rather weak, thus limiting TERS to molecules with high Raman cross-sections. Moreover, the instrument is expensive, making it impractical for many applications. Very recently, on the basis of TERS, Tian and Wang *et al.* exploited a promising approach named shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS), in which the Raman signal amplification is provided by gold nanoparticles (NPs) with an ultrathin silica or alumina shell. Thus, this approach simultaneously brings thousands of TERS tips to the substrate surface to obtain the jointly enhanced Raman signal, which removes the limitation of the adsorbed molecule generality.[6] The main virtue of SHINERS is its much higher detection sensitivity and its vast number of practical applications involving various materials with diverse morphologies.

It is well-known that SERS efficiency exponentially decreases with increasing distance between the adsorbed molecules and substrate surface. Therefore, to use SHINERS in routine applications, a key problem is the development of ultrathin shells with thickness of 1–2 nm. Moreover, the ultrathin shells should be chemically inert, free of pin-holes, reproducible, easy to control and inexpensive. In fact, various shells have been successfully coated onto coinage metal surfaces for SERS. Among these shell materials, silica is the most popular,[7] owing to its merits of biocompatibility, stability, and a weak Raman scattering. However, it is very difficult to prepare an ultrathin silica shell (<5 nm) with sufficient uniformity.[8] The sodium silicate solution method designed by Tian and Wang *et al.*,[6] as well as the reverse microemulsion method used by Ying *et al.*,[9] can prepare ultrathin silica shells, but they need careful control of the synthesis and processing parameters, such as the reaction time, temperature, pH, and concentration. An ultrathin alumina shell has been prepared by the atomic layer deposition technique,[6,10] but this always needs special equipment. Moving forward from this, it is highly desirable to improve the performance of these systems through exploiting novel fabrication methods and available materials.

In this communication, we report an alternate adsorption and carbonization method for the preparation of an ultrathin carbon shell that coats a silver core for SHINERS. In the first step, 4-mercaptobenzoic acid (4-MBA) was self-assembled onto Ag sol surfaces. We chose 4-MBA as a modification molecule because 4-MBA should adsorb favorably onto Ag by forming an Ag–S bond and the oxygen anions of the carboxyl group pendents, with respect to the Ag substrate, were presumed to connect with the nitrogen cation of cetyltrimethyl ammonium bromide (CTAB) *via* electrostatic interactions. Carbonization in concentrated sulfuric acid subsequently proceeded as the second step. Then, CTAB was alternately adsorbed on the carbon films formed in the second step *via* hydrophobic interactions and carbonized by using concentrated sulfuric acid 4 times. The procedure for the synthesis of the ultrathin carbon shell is depicted in Fig. 1a.

Transmission electron microscopy (TEM) was used to analyze the surface completeness and thickness of the ultrathin carbon shell; an example image is shown in Fig. 1b. The TEM image of the carbon-coated Ag suggests that a continuous carbon layer has been obtained and the shells of these NPs are extremely thin. The coated particles were seen to be essentially monodisperse and their sizes were 10–20 nm. A high-magnification

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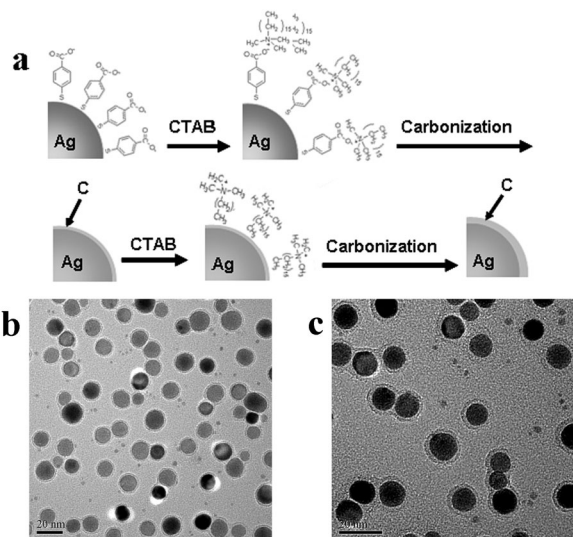
Fig. 1 (a) The proposed procedure of the synthesis of an ultrathin carbon shell coating an Ag core. (b) A TEM image of carbon-coated Ag NPs. (c) A high-magnification TEM image of carbon-coated Ag NPs.

Fig. 2 (a) XPS patterns of the carbon-coated Ag NPs in the C 1s, Ag 3d, and Br 3d spectral regions. (b) The XRD pattern of the sample.

TEM image of carbon-coated Ag NPs is shown in Fig. 1c, revealing a well-closed carbon ring with a compact wall that looks quite uniform in thickness, which is estimated to be 2 nm. It can also be seen from Fig. 1b and c that there is a dark region in the central part of every particle, with a size in the range 8–18 nm, which is the metal Ag core. We chose Ag as a core because Ag is, by far, the best enhancing substrate found to date. This results from its narrow, pronounced plasmon resonance.

The formation of the ultrathin carbon shell was confirmed by X-ray photoelectron spectroscopy (XPS) spectra. The characteristic XPS peak of graphitic carbon is known to appear at 284.6 eV;[11] hence, a strong XPS peak appears at 284.6 eV, as shown in Fig. 2a, ensuring the formation of the carbon shell on the Ag NPs. It is evident that the C1s peak is not a single peak, as a shoulder represents carbon present in alcohol groups (285.8 eV).[11] This is due to the fact that the carbon-coated Ag NPs were stored in an alcohol solvent. The Fourier transform IR (FTIR) spectrum of the carbon-coated Ag NPs (see Fig. S1, ESI†) supports the conclusion drawn from the XPS analysis. The characteristic IR peaks of alcohol appear at 3434, 2923, 2852, 1632, 1384, 1093, and 798 cm^{-1}. The Ag 3d spectrum of the carbon-coated Ag NPs consists of two individual peaks at 373.6 and 367.5 eV, which can be attributed to Ag 3d$_{3/2}$ and Ag 3d$_{5/2}$ binding energies, respectively.[12] A comparison of the relative areas of integrated intensity shows that carbon is the predominant component of the outer surfaces of the as-synthesized core-shell NPs, which accounts for 59.2 mol% of all of components. From the XPS peak area, the Ag content is calculated to be 9.8 mol%. The spectrum of Br 3d 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 of $\sim$68.75 and $\sim$67.75 eV, respectively. The calculated Br$^-$ surface content of the sample is 7.8 mol%. The O 1s peak at 530.3 eV results from the adsorbed oxygen,[13] which accounts for 23.2 mol% of all of the components
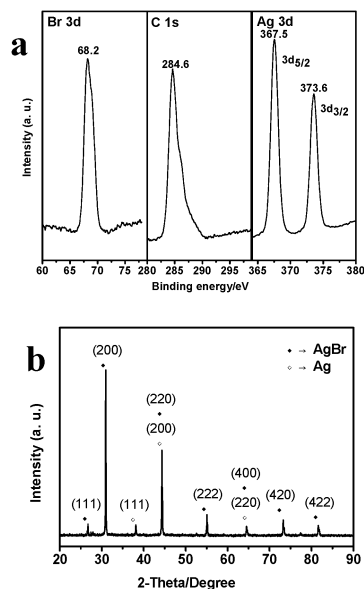
(see Fig. S2 and 3, ESI†). Trace AgBr results from the reaction of the Br$^-$ of CTAB with the Ag$^+$ adsorbed onto the Ag sol surfaces during the fabrication as CTAB moves towards the 4-MBA-functionalized Ag sols, thus, AgBr must exist in the internal layer of the shell. Despite trace AgBr existing in the shell, according to Liu et al.,[14] AgBr colloids themselves have SERS activity, and AgBr exists in the internal layer of the shell. Thus, it is believed that AgBr does not affect the applications of the as-synthesized core-shell NPs in SHINERS.

The formation of the ultrathin carbon shell was also confirmed by ultraviolet/visible (UV-Vis) spectra (see Fig. S4, ESI†). A plasmon absorption appears at about 394 nm for the silver colloids and this absorption vanishes for the carbon-coated Ag NPs. Therefore, it is presumed that the homogeneous carbon shell layer on the silver particles is formed without independent silver particles in the medium, which is consistent with the result obtained by TEM and XPS.

In order to further confirm the composition of the carbon-coated Ag NPs, X-ray powder diffraction (XRD) measurements were performed on a D8ADVANCE powder diffractometer over a 2θ range of 20–90° at an angular resolution of 0.02°. As shown in Fig. 2b, three distinct diffraction peaks were clearly observed at 2θ values of 38.14°, 44.34°, and 64.52° corresponding to the reflections of the {111}, {200}, and {220} crystal planes, respectively, of the cubic structure of metallic Ag. In addition, the XRD analysis also revealed five characteristic peaks for the {111}, {200}, {222}, {420}, and {422} crystal planes of the cubic structure of AgBr at 2θ = 26.74°, 30.96°, 55.06°, 73.26°, and 81.6°.[11] The characteristic peaks for the {220} and {400} planes of AgBr at 2θ = 44.46° and 64.60° possibly overlapped with those for the {200} and {220} planes of Ag at 2θ = 44.34° and 64.52°. Consequently, the XRD pattern shows the peaks for both AgBr and Ag. No characteristic peaks for carbon or silver oxide were observed from the phase analysis by XRD in Fig. 2b, indicating that the carbon coating the Ag NPs is amorphous and that the Ag cores have not been oxidated by concentrated sulfuric acid.
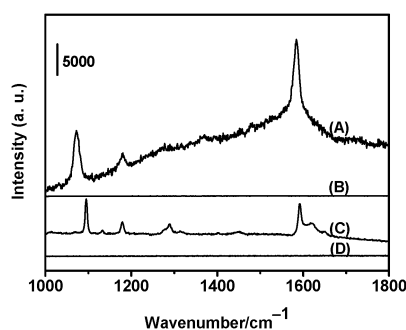
Fig. 3 Raman spectra of 4-MBA physisorbed on the carbon-coated Ag NPs (A) before and (B) after washing with ethanol, (C) dry 4-MBA powder and 4-MBA physisorbed on a borosilicate cover glass.

Consulting the TEM, XPS, UV-Vis, and XRD data, the ultrathin carbon shell should have been synthesized over the Ag NPs. Nonetheless, it is not evident whether the Ag NPs are fully covered by the carbon shells without any defects. If the sizes of the possible pin-holes were too small and beyond the practical resolution of the TEM instrument, it would be impossible to distinguish the holes in the TEM images. For this reason, we designed and conducted a SERS measurement. The carbon-coated Ag NPs were put into a 0.1 mmol L^{-1} ethanolic solution of 4-MBA for 24 h, followed by 5 min sonication in ethanol and thorough washing with ethanol. The sample was dried under vacuum at room temperature for 4 h and then subjected to SERS measurement. If the Ag NPs were not fully covered with carbon shells, 4-MBA must have been chemisorbed onto the Ag NPs surfaces, due to its strong adsorbability for Ag and small molecular structure. Thus, 4-MBA cannot be washed out by sonication and solvent washes. On the contrary, if the carbon shells were free of pin-holes, any 4-MBA that might be physisorbed on the carbon shells should be washed out by sonication and solvent washes. No SERS peak was observed using 632.8 nm laser light as the excitation source (Fig. 3B), indicating the pin-hole of the carbon shells smaller than 4-MBA. This is important for the SHINERS technique, because a shell without any defect prevents direct contact of the detected molecules with the Ag core. For some molecules, a photochemical reaction could be stimulated owing to direct contact of the molecules with the Ag NPs, resulting in new products.[15] Thus, we have demonstrated that an ultrathin carbon shell without any defects can be readily synthesized by using the alternate adsorption and carbonization method. To the best of our knowledge, this is the first synthesis of ultrathin carbon shell coated Ag NPs. In comparison to silica or alumina shells, two features become apparent: (1) Since carbon is far more stable than silica or alumina with respect to resistance to acids, bases, and solvents, the carbon shell should have clear advantages over silica or alumina shells in environmental and biological detection fields based on SHINERS. (2) Our approach is easier to control than that needed for silica. During the fabrication, the thickness of the carbon layer could be controlled very easily, so that the carbon layer covered the entire Ag NPs uniformly. Also, our approach does not need special equipment in comparison with that needed for alumina shells.

The SERS activity of the carbon-coated Ag NPs was evaluated using 4-MBA as the probing adsorbate with excitation at 632.8 nm. The strong Raman signals at $\sim$1584 and 1072 cm^{-1} arose from ν_{8a} and ν_{12} aromatic ring vibrations, respectively, when 4-MBA was physisorbed onto the carbon-coated Ag NPs, and no characteristic peak for 4-MBA was observed when it was physisorbed onto a borosilicate cover glass. The results indicate that the carbon-coated Ag can induce a significant enhancement of the Raman signal. The enhancement factor was estimated to be $\sim$1 $\times$ 10^4 (see ESI†), suggesting that the carbon-coated Ag can be applied in SHINERS.

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