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Surface-Enhanced Raman Scattering inside Metal Nanoshells

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Surface-enhanced Raman scattering (SERS) has been known and investigated for over 30 years.[1,2] While the mechanisms of SERS had been well studied before the 1990s,[3] reports of giant SERS enhancement had reignited tremendous interest.[4,5] Various types of metal substrates have been shown to give rise to SERS.[6,7] The consensus view on the SERS mechanisms is that the enhancement comes from two components: an electromagnetic (EM) enhancement as the major contribution and a chemical enhancement as the minor contribution.[8] It has long been understood that the Raman signals can be significantly enhanced when two or more metal nanoparticles (NPs) are brought together closely.[9,10] Recent theoretical interrogations have shown that the electromagnetic field strength in the interstice between two NPs can be significantly increased when the two are placed close together (i.e., <1 nm), leading to SERS enhancements of up to $\sim 10^{11}$ for molecules locating at that spot.[11,12] Based on this, one might expect similarly significant SERS enhancements exist for molecules if they are surrounded by more than two metal NPs in close distances, such as, a metal nanoshell.

Metal nanoshells, especially those with SiO_2-cores, have been extensively studied as SERS substrates in the past decade.[13,14] Yet all the experimental SERS studies related to nanoshells consider the SERS effect in the proximal distance outside the nanoshells. There has been limited theoretical investigation on SERS inside a nanoshell, which suggested that a large field enhancement was to be expected for a large volume of the spherical cavity inside the nanoshell.[15] Still, there has not been any experimental attempt reported to investigate such a large enhancement inside a nanoshell and exploit its potential applications. Here we report the design and development of a type of nanostructure that demonstrates, experimentally for the first time, the giant SERS enhancement inside the metal nanoshell.

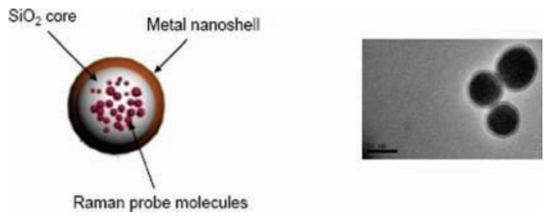

Figure 1. (Left) Schematic of the design of the probe-embedded dielectric-core metal-nanoshell structure. (Right) TEM image of RuBPy-embedded SiO_2-core Au-shell NPs.

The schematic of the design of the probe-embedded dielectric core/metal shell nanostructure is illustrated in Figure 1. A Raman-active probe molecule is embedded into a dielectric NP, such as a SiO_2 NP. This probe-embedded SiO_2 NP is subsequently coated with a thin layer of either a Au or Ag metal. As an example, we use tris(2,2′-bipyridyl)ruthenium(II) chloride (RuBPy) as the probe molecule and Au as the coating metal. Other probe molecules and metal coating are also used as discussed later.

The synthesis of the probe-embedded dielectric core/metal shell nanostructures is achieved through reduction of $AuCl_4^-$ ions by citrate solution, using the probe-embedded SiO_2 NPs as the template for growth. It starts with the synthesis of RuBPy-embedded SiO_2 NPs in reverse microemulsion (Supporting Information, SI).[16] The surface of these NPs is then coated with amine (NH_2-) groups by reacting with a small amount of 3-aminopropyltriethoxysilane (APTS). The resulting NPs disperse thoroughly in water under sonication into yellow solution, an indication that RuBPy molecules are entrapped inside the SiO_2 matrix. The formation of metal nanoshells is carried out using the RuBPy-embedded NH_2-functionalized SiO_2 NPs as templates. By adjusting the ratio of the SiO_2 NPs and $AuCl_4^-$ while maintaining citrate in excess, different thicknesses of the Au shell could be achieved. A TEM image of typical RuBPy-embedded SiO_2-core Au-shell NPs is shown in Figure 1.

Figure 2 shows a series of SERS spectra of RuBPy-embedded SiO_2-core Au-shell NPs under different excitations. Estimation of SERS enhancement factors can be carried out by comparing the SERS signals of such NPs with the fluorescence signals of RuBPy-embedded SiO_2-core NPs without the Au-shell, both excited by the 532 nm laser (SI). The SERS enhancement factors for our RuBPy-embedded SiO_2-core Au-shell NPs are estimated to be on the order of 10^{11} to 10^{14}. This is in line with previous reports in the single molecule SERS studies, where single molecules displaying giant SERS enhancement were believed to reside in the so-called "hot spots".[4,5] The actual locations of those "hot spots", which were few and far between within the metal colloidal substrates, were difficult to be predicted, if possible at all. In contrast, the interior of our SiO_2-core Au-shell NPs is a "hot zone" that can be constructed and prepared easily and reproducibly.

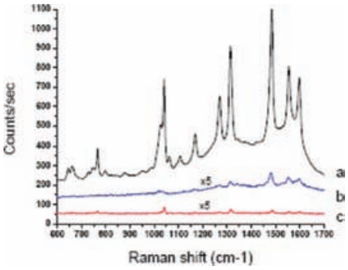

Figure 2. SERS spectra of RuBPy-embedded SiO_2-core Au-shell NPs under three laser excitations: (a) 632.8, (b) 532, (c) 785 nm.

We note that the SERS enhancement observed in these NPs are probably solely due to EM enhancement, as there is no direct contact between the entrapped RuBPy and the Au shell. Furthermore, all enhancements are attributed to the near-field effect, considering that all probe molecules are within the near field of the metal shell because of the size of the NPs (<100 nm). This is further confirmed by comparing the SERS spectra we obtain with those in a recent study on the near-field SERS of RuBPy absorbed on Ag NPs, where Raman peaks between the two bands of 1318 and 1486 cm^{-1} only appeared in the near-field SERS spectra and not in the far-field SERS spectra.[17]

The fact that the probe molecules are embedded inside the SiO_2 matrix allows one to measure the EM enhancement completely

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separated from the chemical enhancement. By embedding different probe molecules inside the SiO_2 core, one can investigate the EM enhancement for different probe molecules under similar conditions. SERS spectra of SiO_2-core Au-shell NPs doped with different probe molecules (RuBPy, dichloro tris(1,10-phenanthroline) ruthenium (RuPhen) and dichloro tris(1,10-phenanthroline) copper (CuPhen)) are shown in Figure 3. Notice that, not surprisingly, the SERS spectra of RuPhen and CuPhen are very similar, indicating that only the chelating ligand plays a significant role in the SERS spectra.

Among the probe molecules tested, RuBPy appears to give the most intense SERS signals under similar conditions. Nevertheless, the results in Figure 3 show that, although there is some difference in SERS enhancement from one probe molecule to another, all SERS enhancements are within 1 order of magnitude. This is consistent with the notion that the EM enhancement should be independent to the type of the probe molecules. Furthermore, it is direct experimental evidence to support that notion.

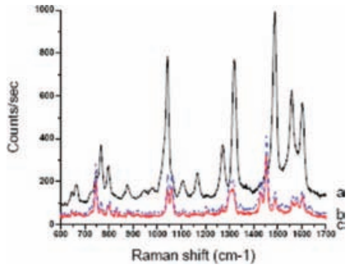

Figure 3. SERS spectra of SiO_2-core Au-shell NPs with different probe molecules embedded: (a) RuBPy, (b) RuPhen, (c) CuPhen. Excited at 632.8 nm.

The SERS enhancement of the probe molecules inside the nanoshells is dependent on the shell thickness. When the RuBPy-embedded SiO_2-core NPs are coated with a small amount of gold, resulting in incomplete or very thin Au shells, the SERS signal of RuBPy is moderate. When the amount of the coated Au increases, the SERS signal of RuBPy first increases then decreases as the Au shells become thicker. As shown in the SI, there appears to be an optimal shell thickness for SERS signals. This may be understood from two aspects. On the one hand, SERS becomes stronger when the metal shell becomes complete, as compared with incomplete coverage. On the other hand, as the thickness of the metal shell increases, the dielectric property of the RuBPy-embedded SiO_2-core Au-shell NPs would approach that of pure Au NPs. This would lead to (a) the change of conditions for EM enhancement and the decrease of such enhancement and/or (b) the decrease in Raman emission of RuBPy as it needs to penetrate the thick metal shells to be detected.

Note that both Au and Ag nanoshells work similarly in generating SERS inside the metal nanoshells (Figure 4). Interestingly, for the RuBPy-embedded SiO_2-core Au-shell NPs, SERS enhancement is the strongest for the 632.8 nm excitation, less stronger for the 532 nm excitation and least for the 785 nm excitation, while, for the Ag-shell counterparts, SERS enhancement is stronger for 532 nm excitation than for 632.8 nm excitation. Considering the surface plasmon band for the RuBPy-embedded SiO_2-core Au-shell NPs (Supporting Information), our observations are in line with the notion that the excitation of maximum SERS enhancement does not necessarily coincide with the peak of the plasmon resonance.[18]

We further coat the RuBPy-embedded SiO_2-core Au-shell NPs with another thin layer of SiO_2 and observe that SERS signals of RuBPy inside the metal nanoshells remain after the coating (SI). With this SiO_2 coating, the NPs can be easily decorated with recognition elements to target specific objects of interest. The results pave the way for a new design of NPs to be used as SERS-tags for Raman-based assays and imaging with the following features: (1) strong SERS signals due to the high enhancement; (2) versatility, so the type of probe molecules embedded inside the nanoshell can be readily changed and the size and type of the dielectric core can also be changed; (3) reasonably reproducible and uniform SERS signals; (4) easy to synthesize; (5) very stable with a long shelf life. Further research will realize the full potential of such SERS-tags in Raman detection and imaging applications.

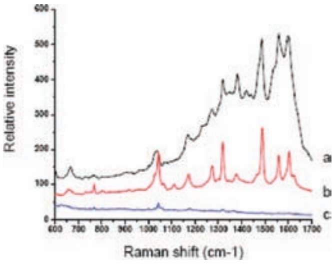

Figure 4. SERS spectra of RuBPy-embedded SiO_2-core Ag-shell NPs under three laser excitations: (a) 532, (b) 632.8, (c) 785 nm.

Lastly, the observation of a giant enhancement of SERS indicates that the inside of metal nanoshells may behave as a cavity to concentrate EM radiation within.[19] The ease of changing the type and size of the dielectric core and the type and thickness of the nanoshell allows one to readily tune the parameters of the cavity. NPs of such structures will have a profound implication in the future design of plasmonic devices.

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Supporting Information Available: Full experimental details, additional TEM images, UV−vis absorption spectrum, and Raman spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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