Nanoparticle Assemblies

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Charge Transfer between Metal Nanoparticles Interconnected with a Functionalized Molecule Probed by Surface-Enhanced Raman Spectroscopy**

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The assembly of nanosized metal particles with functionalized molecules is a rapidly emerging field of great fundamental and practical interest because of the prospective applications in nanoelectronic devices.[1] The charge transfer (CT) properties of individual particles are dependent on the particle size and the distance between the particles. Importantly, the activation energy for electron transfer between the particles can be varied by the structure of the interconnecting molecule. In particular, tunneling CT may occur for particles covalently linked with π-conjugated molecules.[2] Recent progress in surface-enhanced Raman spectroscopy (SERS) has made single-molecule detection possible, which is of considerable interest to the communities concerned with nanomaterials, analytical chemistry, and single-molecule spectroscopy. An enhancement factor of approximately 10^{11} has been estimated at the junctions between the closely spaced nanoparticles, as a result of the electromagnetic (EM) enhancement mechanism.[3] The CT mechanism has also been suggested to play an important role in single-molecule SERS.[4] Herein, we investigate the Raman scattering of molecules in the assembled structures of metal nanoparticles.

The present study is of interest from two points of view. First, by using layer-by-layer (LBL) self-assembly, a molec-

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ular-scale gap can be spontaneously formed between the metal nanoparticles through interconnecting functionalized 4-aminothiophenol (PATP) molecules, which is a typical "push–pull"-type molecule with the electron-donating and electron-accepting groups connected by a conjugated π system. Second, SERS measurements were performed with near-IR excitation (1064 nm), which is far away from the surface plasmon resonance of the metal nanoparticles. This strategy may distinctly demonstrate the CT behavior of metal contacts, which play a significant role in metal–molecule–metal nanosystems.

The LBL assembly of the metal nanoparticles is illustrated in Figure 1 A. The protonated pyridine groups of polyvinylpyridine (PVP) derivatized on a glass slide provided the active sites for the adsorption of negatively charged gold

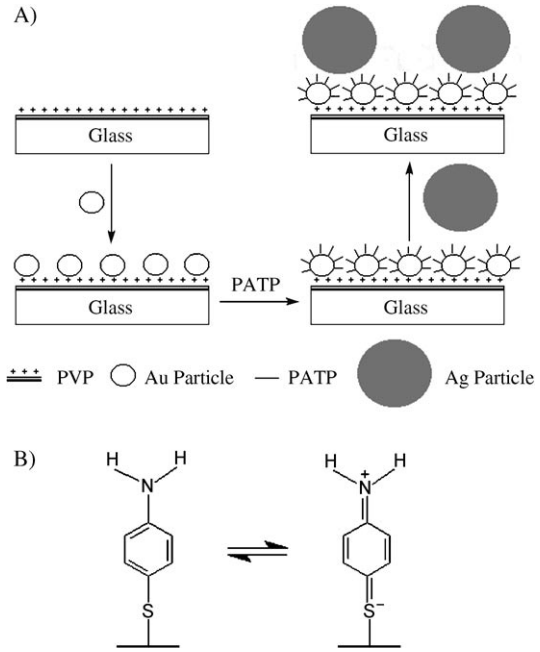

Figure 1. Illustration of A) the assembly of gold and silver nanoparticles and B) the resonance structures of the adsorbed PATP molecule.

nanoparticles. A layer of gold nanoparticles ($\approx$30 nm in diameter) was assembled on the surface by electrostatic interaction. PATP molecules were then adsorbed on the surface of the assembled gold nanoparticles through the formation of Au–S bonds. Similar to *p*-nitroaniline,[5] the PATP molecule possesses two resonance structures: the benzenoid and quinonoid forms (Figure 1 B). In the quinonoid form, it can further interact electrostatically or covalently with silver nanoparticles. As a result, a layer of silver nanoparticles ($\approx$100 nm in diameter) can be assembled on top of the gold nanoparticle layer.

Scanning electron microscopy (SEM) images of the surface morphologies of the single and double assemblies of the metal nanoparticles are shown in Figure 2. As can be seen, the gold nanoparticles were uniformly assembled into a submonolayer structure on the PVP-derivatized glass surface. Most of the particles existed separately as a result of the

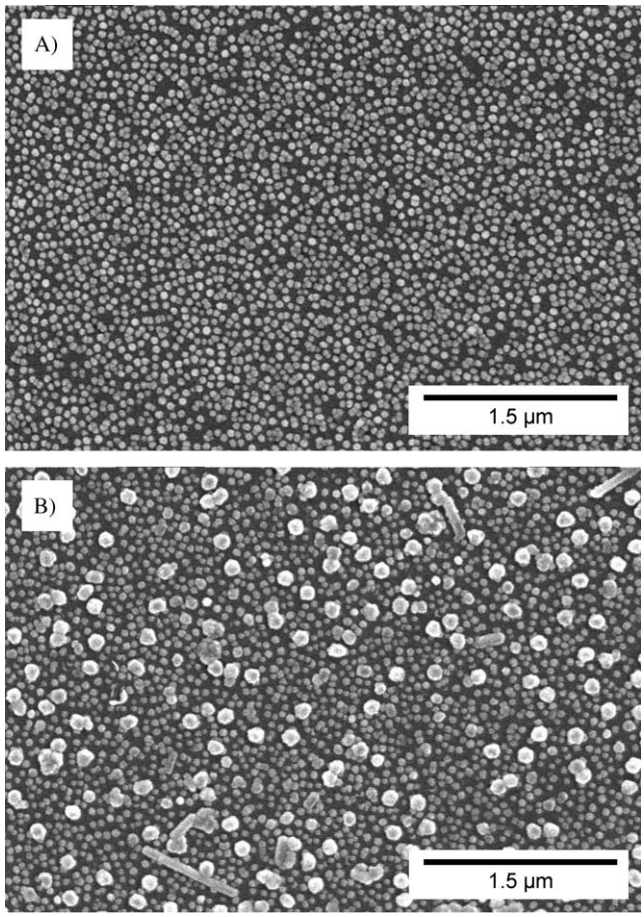

Figure 2. SEM images of A) gold nanoparticle and B) gold/PATP/silver assemblies.

electrostatic repulsion because of their negative charge. No apparent change in the assembled structure of the nanoparticles was observed after the adsorption of PATP, which indicates that the PATP molecules adsorbed on the surface of the individual gold nanoparticles did not disturb the distribution of the particles on the slide surface. The second layer of metal nanoparticles is distinguishable after the assembly of the silver nanoparticles (Figure 2 B). A single silver nanoparticle may be attached to several underlying gold nanoparticles because of the difference in the particle size.

As a result of the dipole–dipole EM interaction between the particles,[6] the surface plasmon resonance (SPR) of the gold nanoparticles shifted from 527 nm for the particles in the colloid (Figure 3, curve a) to 531 nm for the particles immobilized on the surface of the PVP-derivatized glass slide (Figure 3, curve b). The adsorption of the PATP molecules on the gold nanoparticles caused negligible spectral change. Further assembly of a layer of silver nanoparticles resulted in the appearance of the SPR band of the silver nanoparticles at 432 nm, along with the SPR band of the gold nanoparticles (Figure 3, curve c). However, a shift of the SPR of the gold nanoparticles to 528 nm was observed. This shift could result from either EM interaction of the metal particles in different layers, or CT through the linked PATP molecules, as demonstrated by SERS.

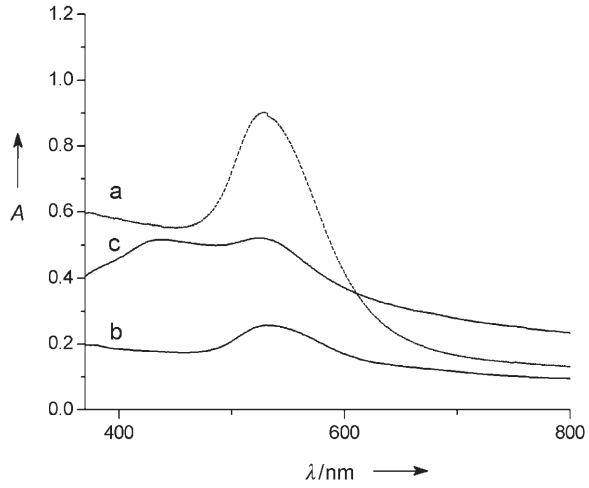

Figure 3. Extinction spectra of a) a gold colloid, b) the gold nanoparticle assembly, and c) the gold/PATP/silver assembly.

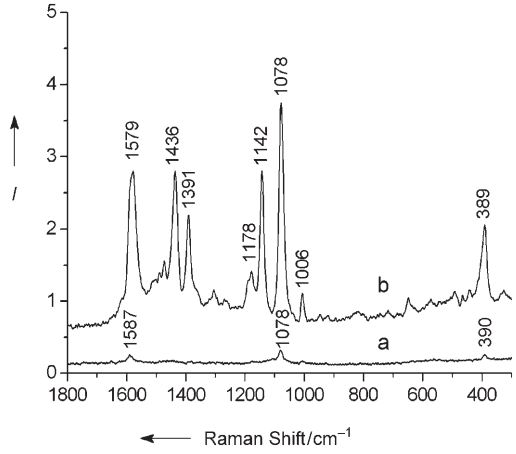

Figure 4. Surface-enhanced Raman spectra of PATP molecules a) adsorbed on the assembled gold nanoparticles and b) interconnected in the gold/PATP/silver assembly.

In most of the SERS studies, the difficulty in experimentally gaining deep insight into the enhancement associated with the CT mechanism is that the chemical enhancement is normally inextricably linked with the EM enhancement. For example, in a recent SERS study of the assembly of silver nanoparticles interconnected with symmetric 1,4-benzenedithiol molecules, Moskovits and Jeong[7] demonstrated a large SERS enhancement of the interconnecting molecules as a result of the strong local EM field produced in the interstitial regions between the neighboring nanoparticles. However, the contribution from the CT mechanism was not described in their study. It is probable that the EM mechanism, which is strongly related to the SPR of the metal particles in the visible spectral region, is the main factor responsible for the overall SERS enhancement under their experimental conditions (with excitation at 514 nm). In the present study, we measured the surface-enhanced Raman spectra with excitation at 1064 nm, which is far away from the SPR bands of the nanoparticles in the assemblies. Therefore, the Raman spectral features obtained under our experimental conditions may be largely associated with the CT effect.

The surface-enhanced Raman spectra of the PATP molecules adsorbed on the gold nanoparticle assembly and cross-linked in the layers of the gold and silver nanoparticles are shown in Figure 4. The PATP molecules on the gold nanoparticles exhibited three major bands at 1587, 1078, and 390 cm^{-1} (Figure 4, curve a), which are the a_1 modes of the PATP molecule.[8] Interestingly, the assembly of the layer of silver nanoparticles caused a large increase in the intensity of the spectrum (Figure 4, curve b). In particular, in addition to the bands observed in curve a of Figure 4, additional bands appeared at 1142, 1391, 1436, and 1579 cm^{-1}. These new bands were assigned to the nontotally symmetric b_2 vibrational modes of the PATP molecule.[8] The selective enhancement of the b_2 modes (Figure 4, curve b) cannot be explained by the EM mechanism.

According to the surface-selection role of the EM model, the SERS enhancement order for the vibrational modes of molecules with C_{2v} symmetry should be $b_1 = b_2 > a_2$ for molecules with a standing-up orientation, and $a_2 = b_1 > b_2$ for molecules with a lying-down orientation, respectively. In Figure 4, curve b, only the b_2 modes among the three vibrational modes are enhanced. The possibility of a difference between bonding geometries in the assembly structures is also excluded, because no noticeable difference in the frequencies of the a_1 modes was observed in the two spectra. Therefore, we consider that the b_2 modes are enhanced by the CT mechanism through the Herzberg–Teller contribution.[9] That is, the enhancement of the b_2 modes of PATP is associated with CT between the metal nanoparticles and the adsorbed molecules, and is dependent on the degree of matching between the energy level of the adsorbed molecules and the metal nanoparticles, and the extent of the CT. On the other hand, curve a in Figure 4 indicates that there is no clear enhancement of the b_2 modes on the assembled gold nanoparticles alone. Our previous study also indicated that only slight enhancement of the b_2 modes of the PATP molecules can be obtained on assembled silver nanoparticles under 1064-nm excitation conditions.[10] In other words, the individual nanoparticles of the two metals cannot provide such a large enhancement of the b_2 modes as that observed in curve b of Figure 4; such a large enhancement should be related to the particular assembly structure of the gold and silver nanoparticles.

The assembly of the nanoparticles through the PATP molecules (Figure 1 A) generated an exactly asymmetric metal–molecule–metal nanosystem. Accordingly, the CT model of the "donor–bridge–acceptor" system may be applicable to the present nanosystem.[2] In this case, dynamic CT between the particles could occur through coupling with the vibrations of the bridging molecules, as the energy levels of the metal nanoparticles match the HOMO and LUMO energy levels of the molecules under excitation by light. The selective enhancement of the b_2 modes of the PATP molecules may be indicative of such a CT process. The work function of silver ($\approx$4.3 eV) is lower than that of gold ($\approx$5.0 eV),[11] and therefore we consider that the overall CT could be from silver to gold by tunneling through the interconnecting PATP molecules.

Furthermore, the quinonoid form of the adsorbed PATP may play a very important role in the CT process in this system, because the CT direction is parallel to the dipolar direction of the PATP molecule, which may be favorable to the overall CT process between the metal nanoparticles. To verify this point, the nanoparticles were assembled inversely, with the silver nanoparticles as the first layer and the gold nanoparticles as the second. The surface-enhanced Raman spectrum of the PATP molecules adsorbed on the silver nanoparticle assembly (Figure 5, curve a) is comparable to that reported previously.[10] Importantly, the assembly of the gold nanoparticles on the silver nanoparticle layer did not result in an enhancement of the b_2 modes of the interconnecting PATP molecules (Figure 5, curve b), because the possible

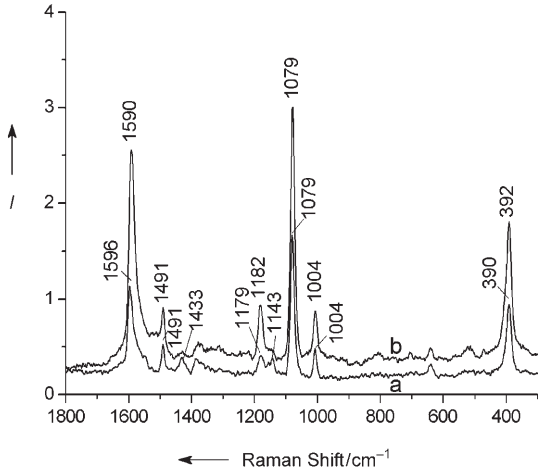

Figure 5. Surface-enhanced Raman spectra of PATP molecules a) adsorbed on the assembled silver nanoparticles and b) interconnected in the silver/PATP/gold assembly.

CT from silver to gold is opposite to the dipolar direction of the PATP molecule. The enhancement of the a_1 modes at 1590, 1079, and 392 cm^{-1} in curve b of Figure 5 could be related to the enhancement of the EM field between the metal particles. Notably, the EM mechanism, as demonstrated by Moskovits and Jeong,[7] should also contribute to the overall SERS enhancement in the present study, as a result of the broad SPR of the assembled metal nanoparticles. Further theoretical analysis is necessary for a better understanding of the CT mechanism in this particular system.

In summary, a metal–molecule–metal nanosystem has been fabricated by the self-assembly of gold and silver nanoparticles interconnected with PATP molecules. The b_2 vibrational mode in the surface-enhanced Raman spectrum of the interconnecting PATP molecules, which is characteristic of CT between the metal nanoparticles and PATP molecules, is likely greatly enhanced by CT from the silver to gold nanoparticles by tunneling through the PATP molecules. The CT process is dependent on the dipolar direction of the PATP molecules. Together with the SPR data for the metal nanoparticle assemblies, the greatly enhanced SERS signal of the interconnecting PATP molecules may demonstrate the importance of the contribution of the CT mechanism in single-molecule SERS.

Experimental Section

Gold and silver colloids were prepared according to literature protocols.[12] The metal nanoparticles were assembled on glass slides according to the following procedure. The surface of the glass was derivatized by immersing the slides in a solution of PVP (5 wt%) in ethanol. After washing with ethanol and water, the slides were immersed in a colloidal solution of silver or gold nanoparticles for 6 h. The slides covered with a surface layer of metal nanoparticles were then immersed in a solution of PATP in ethanol (1 mM) for 3 h. After adsorption of the PATP molecules, the slides were transferred into a colloidal solution of gold or silver nanoparticles to allow the assembly of the second layer of metal nanoparticles.

The extinction spectra were measured on a Shimadzu UV-3150 spectrometer. The surface morphologies of the samples were measured on a Hitachi 7350G scanning electron microscope. The surface-enhanced Raman spectra were measured on a Nicolet 960 FT-Raman spectrometer equipped with a liquid-nitrogen-cooled Ge detector and a Nd:VO_4 laser (1064 nm) as excitation source. The laser power used was about 300 mW at the samples. The spectral resolution was 4 cm^{-1} at the excitation wavelength.

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