Nanoparticle Metal–Semiconductor Charge Transfer in ZnO/PATP/Ag Assemblies by Surface-Enhanced Raman Spectroscopy

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The ZnO/PATP/Ag sandwich structure and its reverse Ag/PATP/ZnO were fabricated using ZnO nanorods and silver nanoparticles with functional molecules 4-aminothiophenol (PATP) through layer-by-layer self-assembly techniques. Under near-IR excitation (1064 nm, far from the surface plasmon resonance of the Ag nanoparticles in the assemblies), the enhancement of surface-enhanced Raman spectra (SERS) from the charge-transfer mechanism can be readily observed only in the former structure. The considerably larger enhancement of the b2 modes, relative to those of the a1 modes, is ascribed to the charge transfer between the silver nanoparticles and ZnO tunneling through the interconnecting PATP molecules. This is not observed in the second structure. The result demonstrates for the first time that directional charge transfer between nanoscale metal and semiconductor tunneling through the interconnecting molecules may be examined by SERS.

I. Introduction

Surface-enhanced Raman spectroscopy (SERS) has become a widely used tool for the investigation of properties of various nanoscale structures. The high sensitivity and resolution of the technique make it ideal for extracting detailed information as to the nature of molecular interactions with both metal and semiconductor nanoparticles.1−6 SERS is characterized by both surface plasmon resonance as well as charge-transfer effects.7−14 The surface plasmon resonance comes about due to the interaction of the exciting laser frequency with the metal conduction band electrons, and at certain particle sizes very large electric fields are produced at the nanoparticle surface. When these fields interact with an adsorbed molecule, enormous enhancements are observed in the molecular Raman signal. Additional contributions to the observed enhancements have been attributed to charge-transfer transitions induced by the molecule−metal interaction.11 At certain excitation wavelengths, electrons can be transferred between the molecule either to or from the metal conduction band, adding additional intensity to the enhanced Raman signal. However, the charge-transfer mechanism has a strong effect on the observed Raman spectrum. Although the vibrational frequencies of the molecule are not strongly affected by SERS, their relative intensities are. As a result charge transfer is often accompanied by drastic changes in the observed SERS spectrum.

SERS has also recently been observed in semiconductor nanoparticles.15−19 Since these particles often have plasmon resonances far from the excitation wavelengths used, it is widely assumed that the charge-transfer mechanism dominates these spectra. This line of research holds great promise in that it is increasingly possible to produce samples of well-controlled nanoparticle sizes and shapes.

It is also possible to combine both metals and semiconductors into composite systems, with interesting properties. The interface between metals and semiconductors is often called a “Schottky barrier”, and these have been widely investigated in bulk systems.20,21 An important feature of such systems is the appearance of a dipolar layer at the junction, which mediates the energies of the interconnecting systems. More recently a ZnO core−Ag shell quantum dot system was studied by Shan et al.22 They used SERS to observe enhancements in the LO phonon modes of the ZnO core, observing up to five overtones. They attributed the observations to charge transfer from the silver conduction band into the ZnO core, red-shifting the plasmon resonance and greatly enhancing the (normally weak) phonon spectrum.

In another study, Zhou et al.23 investigated charge transfer between adjacent Ag nanoparticles mediated by a connecting molecule p-aminothiophenol (PATP). The thiol (−SH) end of the molecule forms a strong bond to the first silver nanoparticle, and a subsequent addition of additional Ag nanoparticles can then bind to the remaining amino group, forming a sandwich-like structure connecting two Ag particles. The resultant SERS spectrum showed very strong enhancement of the nontotally symmetric b2 vibrational modes relative to the a1 modes. This has been shown to be characteristic of charge transfer in a metal−PATP system24 by a density functional theory (DFT) calculation with PATP on Au nanoparticles. In a further study25,26 in which PATP was sandwiched between Au and Ag nanoparticles (Au/PATP/Au; taking advantage of the differential adsorption of the thiol and amino ends of the molecule), the authors were able to effect charge transfer between two different types of particles (i.e., Ag → Au) with different work functions (4.3 eV for Ag and 5.0 eV for Au). The mechanism was attributed to tunneling through the intermediate PATP molecule. Once again the enhancement of the b2 modes of the PATP was considered important in the conversion. The charge transfer was aided by the quinoid dipolar resonance structure forming a net positive charge on the −NH2 and negative charge on the −SH...
ends of the molecule. When the sandwich was reversed (i.e., Ag/PATP/Au) no enhancement of the b2 modes was observed.

In this work we explore the results of fabrication of a sandwich structure between a metal (Ag) and a semiconductor (ZnO) mediated by PATP. The band gap of ZnO is rather large (3.35 eV) so that net charge transfer can only be achieved from the metal to the semiconductor. We consider two systems: the first involves depositing a layer of PATP on a ZnO film and then adding Ag nanoparticles. This system (ZnO/PATP/Ag) has the thiol attached to the ZnO and the amino group attached to the Ag nanoparticle. In the second system the order is reversed (Ag/PATP/ZnO), and the thiol is attached to the Ag, with the amino end attached to the ZnO. In the former assembly we find that the b2 modes of PATP are strongly enhanced in the SERS spectrum, whereas in the latter, they are not. The appearance of nontotally symmetric (b2) modes is diagnostic of a charge-transfer process. This indicates that charge is transferred in the ZnO/PATP/Ag system but not in the reverse system. We examine the likely mechanism of charge transfer in this system.

II. Experimental Procedures

Chemicals. All the reagents were used as received without further purification. Silver nitrate was obtained from Aldrich. 4-Aminothiophenol (PATP) was obtained from Acros Organics Chemical Co. Poly(diallyldimethylammonium chloride) (PDDA) with medium molecular weight (200 000–350 000) was obtained from Sigma Chemical Company. Zinc nitrate was obtained from the Beijing Chem. Co. (China). Ethanol was purchased from Beijing Chem. Co. (China).

Apparatus and Methods. Synthesis of Silver Colloid. Silver colloid was prepared according to the literature protocols. The particular description is as follows: AgNO3, (36 mg) was dissolved in 200 mL of H2O and brought to a boil. A solution of 1% sodium citrate (4 mL) was added. The solution was kept boiling for about 1 h. The Ag colloid was greenish yellow and displayed an absorption maximum at 410 nm.

Preparation of ZnO Nanorod Films. ZnO nanorod films were prepared according to literature protocols. Glass slides were suspended in an aqueous solution of zinc nitrate hydrate, Zn(NO3)2·H2O, (0.025 M) and methenamine (0.025 M) at 90 °C for 3 h. ZnO nanorods were grown directly on the glass substrates, and they were removed from the solution, rinsed with deionized water, dried, and stored in the dark under clean air.

Preparation of ZnO/ATP/Ag Sandwich Structure (Figure 1a). Self-assembled monolayers were deposited by immersing freshly prepared ZnO nanorod film substrates into 0.1 mM PATP solution in ethanol at room temperature for 24 h. After deposition, the sample was taken out from the reactor and rinsed three times with ethanol and deionized water, respectively. Then the prepared ZnO/PATP film was immersed in silver colloid for 30 min, the sample was taken out from the reactor, rinsed three times with deionized water, and dried under N2 stream.

Preparation of Ag/ATP/ZnO Sandwich Structure (Figure 1b). The glass slides were cleaned by immersion in a boiling solution prepared by mixing 30% H2O2 and concentrated H2SO4 with a volume ratio of 3:7. After cooling, the substrates were rinsed repeatedly with deionized water. The slides were then immersed in a 0.5% PDDA solution for about 40 min and finally rinsed with triply deionized water. The slides were immersed into the silver colloid for about 3 h. The slides were then rinsed with deionized water and immersed in 0.1 mM PATP solution for 30 min and rinsed with ethanol and deionized water, respectively. Finally, a film of ZnO nanorods was deposited on the prepared Ag/ATP substrate through the method mentioned above.

The extinction spectra were measured on a Shimadzu UV-3600 spectrometer. The surface morphologies of the samples were measured on a JEOL JSM-6700F field emission scanning electron microscope (FE-SEM) operating at 3.0 keV. Surface-enhanced Raman spectra were measured on a Nicolet 960 FT-Raman spectrometer equipped with a liquid-nitrogen-cooled Ge detector and a Nd:VO4 laser (1064 nm) as excitation source (the laser power used was about 250 mW at the samples) and a Renishaw Raman system model 1000 spectrometer with the 514.5 nm argon ion laser exciting source (the laser power at the sample position was typically 400 μW with an average spot size of 1 μm in diameter). The spectral resolution was 4 cm⁻¹ at the excitation wavelength.

III. Results

In Figure 2 we show the SEM images of (Figure 2a) ZnO crystal film and (Figure 2b) ZnO/PATP/Ag assemblies. The ZnO film is seen to be composed of a collection of hexagonal nanorods approximately 0.5–2 μm in diameter. They are little changed by absorption of PATP, whereas the Ag colloid particles can clearly be seen in the image Figure 2b.

In Figure 3 we present the extinction spectra of (Figure 3a) the ZnO film, (Figure 3b) the ZnO/PATP assembly, (Figure 3c) the ZnO/PATP/Ag assembly, (Figure 3d) a Ag colloid, and

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**Figure 1.** Schematic illustration of the structure of ZnO/PATP/Ag (a) and Ag/PATP/ZnO (b) molecular junctions on glass substrates.
Figure 3. Extinction spectra of (a) ZnO film, (b) the ZnO/PATP assembly, (c) the ZnO/PATP/Ag assembly, (d) a Ag colloid, and (e) PATP molecules in ethanol solutions.

Figure 2. SEM images of (a) ZnO crystal film and (b) ZnO/PATP/Ag assemblies.

(Figure 3e) PATP molecules in ethanol solutions. The ZnO film shows a broad band below 400 nm, while addition of the PATP introduces a UV peak near 290 nm (similar to a broadened solution spectrum of PATP shown in Figure 3e). Addition of the Ag nanoparticles causes the two PATP bands to shift to around 300 nm. For comparison, we show the Ag colloid spectrum, in which a characteristic single broad band centered at around 400 nm is seen. There is little hint of this band in the ZnO/PATP/Ag assembly spectrum, probably due to the relatively low concentration of Ag particles in the assembly, as shown in Figure 2.

In Figure 4, we show the Raman spectra excited at 1064 nm of the PATP molecules (Figure 4a) adsorbed on the silver nanoparticle monolayer, (b) in the Ag/PATP ZnO assembly, and (c) the ZnO/PATP/Ag assembly.

In Figure 5, we show the results of Raman spectra excited at 514.5 nm of the PATP molecules (Figure 5a) adsorbed on the surface of a ZnO nanoparticle, (b) adsorbed on the silver surface, and (c) the ZnO/PATP/Ag assembly.
disubstituted benzenes are given by notations of the correspond-
that the lines at 1144, 1306, 1390, and 1437 cm
modes.

The assignments were taken from ref 25 and confirmed with
and assignments of the modes observed in the various spectra.

In Table 1 we present a summary of the observed wavenumbers
the ZnO/PATP/Ag assembly and the Ag/PATP/ZnO assembly.

is a sharp difference in the observed Raman spectrum between
attached to a SERS-active Ag colloid. In the latter case the
ZnO substrate alone but does appear when the molecule is

In Figure 6, we illustrate the fact that for the ZnO/PATP/Ag
assembly there is a strong propensity for the dipolar quinoid-
like resonance structure NH2+=ϕ=S− to be an important contributor to the stability of the assembly. The electronegative
=− atom is attached to a Zn2+ site on the semiconductor,
whereas the =NH2+ end of the molecule is attached to the Ag
nanoparticle. With charge transfer from the conduction band
of the Ag nanoparticle to the π* level (LUMO) of the molecule,
the added electron weakens the resonance structure, lowering
the bond order, resulting in downshifts in the vibrations sensitive
to this resonance structure. These are, namely, the 1595 and
1089 cm−1 lines, which shift to 1576 and 1074 cm−1,
respectively. The 1595 cm−1 line is the C=− stretch, and the 1089 cm−1 line is the C=S stretch. The frequency shifts are
due to the strong interaction between adsorbate and substrate.
The difference of substrate also caused little difference in the
Raman shift.

In Figure 7, we illustrate the difference between the two
assemblies. Note that for the ZnO/PATP/Ag assembly the Ag
nanoparticles can readily donate electrons to the relatively
electropositive NH2+ site on the semiconductor, while the =S− end
can readily donate an electron to the ZnO. Thus, the direction
of charge transfer, from Ag to ZnO, is facile. However, in the
Ag/PATP/ZnO structure, the relatively negative =S− resists
electron transfer from the Ag nanoparticles, and the same is
true for the =NH2+/ZnO interface.

These ideas are made more concrete by the energy level
diagram in Figure 8. The Fermi level for Ag is 4.3 eV below
the vacuum level, while the ionization potential of PATP is 7.16
eV.31 This is the location of the lowest filled orbital (HOMO).
The lowest unfilled orbital (LUMO) should correspond to the
300 nm transition, putting it at 3.03 eV. The valence band
of ZnO is at 7.7 eV below the vacuum level, and the band gap is
3.35 eV, locating the bottom of the conduction band at 4.3 eV.
The Fermi level of ZnO is just slightly below this. It can readily
be seen from this diagram, that the introduction of a photon at

| TABLE 1: Raman Frequencies and Assignments of 4-Aminothiophenol (PATP) in the 800−1800 cm−1 Regiona |
|---|---|---|---|---|---|
| solid 1064 nm | 1064 nm | 514.5 nm | 1064 nm | 514.5 nm | assignment | mode/sym. |
| 1595s | 1591s | 1578m | 1576m | 1577m | C=C str | 8a1 |
| 1572v | 1491w | 1474w | 1475w | 1473w | C=C str + CH ip bend | 19a1 |
| 1490w | 1442w | 1432s | 1437s | 1433s | C=− str + CH ip bend | 19b2 |
| 1403v | 1392w | 1389s | 1390m | 1390s | CH ip bend + C=C str | 3b2 |
| 1310w | 1182w | 1191w | 1190m | 1190w | CH ip bend | 9a1 |
| 1173m | 1144wv | 1141s | 1144s | 1044s | CH ip bend | 9b |
| 1089s | 1078s | 1077m | 1074s | 1075m | C str | 7a1 |
| 1011w | 1005w | 1005w | 1005w | 1005w | CC ring def | 18a |

a Intensities: s = strong, m = medium, w = weak. b Frequencies (in cm−1) followed by relative intensities (s, strong; m, medium; w, weak, vw, very weak). c Bands observed only in the UVRR spectrum at 309.1 nm excitation (ref 30).
514.5 nm (2.40 eV) will be sufficient to easily transfer an electron to an excited unfilled level of PATP, which can then easily transfer it to the conduction band of ZnO. As the ZnO conduction band is filled, the ZnO Fermi level rises, while the Ag Fermi level falls. Equilibrium is reached when both Fermi levels (or chemical potentials) are the same. At this point the Ag Fermi level falls. Equilibrium is reached when both Fermi levels are measured from the vacuum. The highest filled electron level in ZnO is 7.7 eV below the vacuum, and there is not enough energy in the incoming photon to initiate a charge-transfer process in this direction.

The system examined here can be regarded as part of a class of assemblies, which behave as molecular rectifiers. In a recent electrochemical study of nonequilibrium electronic charge transport in 4,4′-bipyridine sandwiched between two Au(111) surfaces, Wu et al. showed that when the Fermi level of the metal lies close to an unoccupied π* molecular orbital energy, electronic charge transfer is facilitated. Kim and Yoon examined PATP sandwiched between Ag or Au nanoparticles and a smooth Au surface. Using SERS they examined the relative contribution of plasmonic coupling and charge transfer to the Raman signal. A more complete discussion of molecular rectifiers is provided in a review by Metzger, concentrating on single-molecule effects.

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References and Notes

(2) Nie, S. M.; Emory, S. R. Science 1997, 275, 1102–1106.