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SERS of Semiconducting Nanoparticles (TiO_2 Hybrid Composites)

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Renewed interest in surface-enhanced Raman scattering (SERS) spectroscopy has been stimulated by the possibility of single molecule detection sensitivity.[1] This presents new approaches for studying the biophysical and biomedical properties of complex biologically relevant systems *in situ* deep inside the tissues.[2] For this purpose abundant, nontoxic, and biologically compatible materials must be used as SERS active supports.

So far, SERS experiments have been dependent on the use of metals, in particular Ag and Au nanocrystalline aggregates or roughened substrates. The primary mechanism for SERS from metal nanoparticles (NPs) is a combination of an electromagnetic and a chemical effect. The former is due to resonant excitation of surface plasmons in NPs, and the latter is related to the formation of charge transfer (CT) states between the adsorbed molecule and the NPs.[3]

Herein, we report strong enhancement of selected Raman-active modes of biologically active enediol molecules adsorbed on the surface of TiO_2 NPs (Figure 1). We found that a CT complex is necessary for the enhancement. CT complexes of molecules with TiO_2 NPs that previously demonstrated having tunable optical properties throughout the visible spectrum[6] were selected for our study. We found that all investigated CT systems show enhanced Raman intensities and that the enhancement is correlated to a shift in absorption. Only a few studies have reported Raman spectra of molecules adsorbed on TiO_2.[4,5] Previous studies have involved dye-sensitized NPs[4] making the interpretation of the possible enhancement mechanisms ambiguous as it can be attributed to either CT or resonance enhanced Raman (RERS). Recently, SERS attributed to *TiO_2-to-molecule* CT was published.[5] In contrast, we present evidence of a different electronic mechanism involving *molecule-to-TiO_2* CT, which results in significantly larger enhancement factors.

The hybrid CT−NP complexes exhibited wavelength-dependent Raman signal intensities, with the enhancement of selected vibrations and the appearance of new bands. This indicates that distinct binding and orientation of the adsorbed molecules on the TiO_2 surface contributes to the molecular specificity of the SERS. We observed an enhancement up to ~10^3 in NP solutions (Figure 1). Although the enhancement factor is similar to that predicted for RERS, the fact that the excitation wavelengths used in our experiments do not have enough energy to excite molecular electronic transitions as would be the case for dye-sensitized NPs[4] and that there is a substantial dependence of the Raman signal on the size and shape of the NPs rules out RERS as the predominant mechanism for the observed enhancement. As a comparison, we investigated surface modification of TiO_2 NPs with sodium benzoate where there is chemical binding but no formation of the CT complex. A weak 3-fold enhancement in the Raman signal was observed, having the same peak position and relative intensities as observed for free molecules in solution.

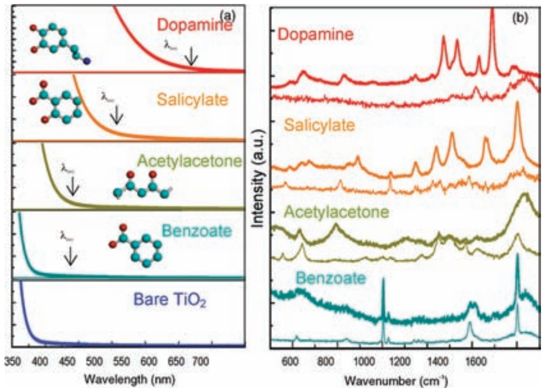

Figure 1. Absorption (a) and SERS (b) spectra of 5 nm TiO_2 NPs (1×10^{-4} M NP solution) modified with different ligands (4×10^{-2} M). Laser excitation (λ_{exc}) is indicated on the figure. The spectra of free molecules (0.1 M) are shown below each curve for the different ligands.

The CT mechanism for SERS requires a specific interaction between the adsorbed molecules and the NP surface that, in some cases, leads to the formation of a CT complex. The complex absorbs light at the excitation frequency, producing resonant Raman scattering that appears as SERS.[7,8] The observed optical properties of examined molecules adsorbed on TiO_2 NPs support the existence of a CT complex. The emergence of SERS in this system is not expected because the existing theoretical models require a metallic NP for the chemical mechanism of enhancement to operate. However, we observe SERS for dopamine (DA) on TiO_2 NPs. New band positions and different relative intensities are detected with energies similar to those observed in SERS on Ag NPs.[9] The strongest band in the spectra is a phenolic mode appearing at 1489 cm^{-1} on TiO_2 and 1479 cm^{-1} on Ag colloids. All enhanced vibrations are found to be associated with nontotally symmetric ring vibrations of DA molecules[9] indicating that chemical attachment to the NPs leads to selective enhancement of nontotally symmetric vibrations. DA molecules bind bidentately to surface Ti atoms and lie perpendicular to the NP surface, preserving their symmetry upon binding. Nontotally symmetric vibrations lead to deviations in the symmetry of DA and are necessary for the CT transitions and consequently to the surface enhancment.[10]

The intensity of the spectra for DA adsorbed on 5 nm TiO_2 spherical NPs does not show a linear dependency with concentration of adsorbed DA but rather an asymptotic behavior until the concentration reaches a maximum at 130 DA per particle (~$^1/_3$ coverage,[6] Figure 2). The intensity decays at higher surface coverages probably due to an interaction between closely packed DA molecules. Note low concentrations of adsorbed DA show the

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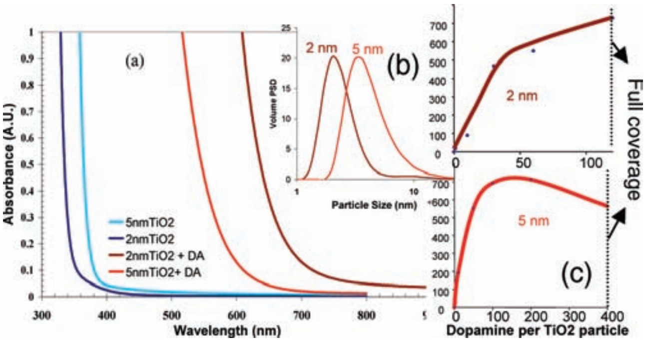

Figure 2. Absorption spectra of bare and dopamine modified 0.04 M spherical 2 and 5 nm TiO_2 NPs (a) in conjunction particle size measurements obtained with dynamic light scattering of the two solutions (b) and the dependence of the intensity of the strongest Raman vibration band at 1480 cm^{-1} on the DA surface coverage for 2 and 5 nm modified TiO_2 NPs (1×10^{-4} M NP) (c).

greatest enhancement, indicating that, regardless of the specific mechanism of enhancement, it is observable at low densities of transferred electrons to the conduction band of TiO_2 upon light excitation. This is one of the most striking experimental results as it seems to indicate a saturation effect of SERS. The dependence of the SERS intensity on DA concentration adsorbed on 2 nm NPs that have a much larger surface curvature shows only asymptotic behavior reaching a maximum at full coverage of the Ti surface sites. Note the intensity of the signal for the same amount of DA−surface Ti complex (10 DA per particle, 1×10^{-4} M of particles) is 1.6 times smaller in 2 nm particles compared to 5 nm NPs.

Figure 2 shows the absorption spectra of bare TiO_2 and TiO_2−DA conjugates in which all surface atoms are bound to DA molecules.[5] As the size of TiO_2 NPs becomes smaller than 3 nm, electrons and holes become confined within the boundaries imposed by the interface resulting in the appearance of quantization effects. These effects are responsible for the hypsochromic shift seen in the absorption spectrum of bare 2 nm NPs compared to the spectrum of 5 nm NPs.[11] The apparent bathochromic shift of the absorption spectra of surface modified 2 nm NPs compared to 5 nm NPs is a consequence of the increase of the absorbance as the number of surface atoms increases.

There are two opposite contributions to the observed SERS that can occur in the semiconductor NPs. First, as the particle size decreases the amount of exposed surface atoms and subsequent adsorbed molecules increases, an effect that should increase the SERS signal. Second, the CT mechanism of enhancement on a metallic surface is based on borrowing intensity from the allowed transitions within continuum states through Herzberg−Teller vibronic coupling.[12] Similarly, the CT transition in molecules that are strongly coupled to metal oxide NPs can also borrow intensity from the continuum states within the conduction band, giving rise to Raman transitions of adsorbed molecules. However, in small TiO_2 NPs (Bohr radius 1.5 nm) where quantization effects occur, the electron and hole wave functions experience boundary conditions that select discrete allowed levels from the conduction and valence band continuum. This lowers the vibronic coupling between allowed transition states and reduces the enhancement of Raman transitions. The net result is that the enhancement due to the CT mechanism will increase with decreasing particle size until the size quantization regime is reached at which point SERS enhancement is expected to diminish due to the decrease in the vibronic coupling between allowed discrete states.

The SERS signal intensity follows the extinction coefficient of the CT complex, increasing beyond the absorption threshold, reaching the strongest signal using 442 nm excitation. However, under 325 nm irradiation when the TiO_2 NPs are excited instead of the CT complex, a sharp decrease in intensity was observed. Also, when the excitation energy was smaller than the energy of the CT complex no enhancement was observed. These results suggest that the CT transition is also in resonance with the laser implying that in CT nanocrystallites we are observing surface enhanced resonance Raman (SERRS). Both SERS and SERRS are usually described as the coincidence of electromagnetic and chemical effects that cooperatively contribute to the overall enhancement.[10] In TiO_2, the electromagnetic component is only contained within the light excitation and the whole enhancement is a result of a CT complex. While SERS on metallic supports is initiated by the excitation of a solid matrix (plasmon resonance) that is transferred to adsorbed molecules, CT induced SERRS is initiated by interfacial electron transfer from the adsorbed molecule to the solid support resulting in the formation of an electron gas that can transfer the excitation back to the adsorbed molecules. However, not all nanostructures that form a CT complex with DA show the same enhanced signal. Raman spectra of a DA−nanotube complex show different band positions and relative intensities and weak SERS enhancement (~10-fold), compared to spherical NP solutions or their films.

In conclusion, we report the measurement of SERS in a hybrid system consisting of a semiconducting NP and a CT molecular moiety. The existence of the phenomenon is unambiguous as the experiments show dependence on both the NP surface features and the frequency of excitation. Future work will address the detailed nature of the enhancement mechanism, the specific mechanism of the saturation effect observed on the number of electrons injected in the conduction band, and interpretation of the mode selectivity for Raman enhancement and their consequences on selection rules for efficient charge separation.

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Supporting Information Available: Detailed SERS spectra, position of SERS peaks and EPR characterization. This material is available free of charge via the Internet http://pubs.acs.org.

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