Blocking Plasmon-Molecule Charge Transfer Using Surface Ligands

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Abstract

Hot electron transfer to unoccupied molecular orbital is the most popularized mechanism for plasmon enhanced photocatalytic reactions, while a few reactions have been attributed to near-field enhanced intramolecular adsorbate electronic photoexcitation. In this presentation, we will present experimental data that show distinct outcomes of electron transfer and energy transfer depending on the adsorption condition of the analyte molecule (methylene blue, MB). In the presence of cetyl trimethyl ammonium bromide (CTAB) surface ligand on gold nanoparticles, MB is selectively transformed to thionine at 633 nm excitation wavelength that overlaps with the electronic transition of the adsorbate. This mechanism involves near-field enhanced intramolecular electronic excitation of the MB adsorbate, and the process is favored by the presence of CTAB that appears to increase the rate of adsorbate excitation by orienting the molecular dipole along the driving surface field and to prolong the lifetime of the excited state by slowing down adsorbate-to-metal energy transfer. On the other hand, when MB is directly adsorbed on the nanoparticles, the mechanism involves electron transfer that appears to lead to formation of anionic complex. In situ surface enhanced Raman scattering spectra suggest that the complex remains stable at long excitation wavelengths (808 and 785 nm), while at shorter wavelengths (671, 633 and 561 nm), it undergoes non-selective N-demethylation, yielding partially N-demethylated derivatives in addition to thionine. These experimental observations underscore the importance of adsorption condition in determining the mechanism of plasmon enhanced photocatalytic reactions.

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