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Efficient Hot Electron Transfer by Plasmon Induced Interfacial Charge Transfer Transition

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Surface plasmon resonance in metal nanostructures has been widely used to enhance the efficiency of semiconductors and/or molecular chromophore based solar energy conversion devices by increasing the absorption or energy transfer rate through the enhanced local field strength. In more recent years, it has been shown that excitation of plasmons in metal nanostructures can lead to the injection of hot electrons into semiconductors and enhanced photochemistry. This novel mechanism suggests that plasmonic nanostructures can potentially function as a new class of widely tunable and robust light harvesting materials for solar energy conversion. However, plasmon-induced hot electron injections from metal to semiconductor or molecules are still inefficient because of the competing ultrafast hot electron relaxation processes within the metallic domain. In this paper we discuss a recent study on the plasmon-exciton interaction mechanisms in colloidal quantum-confined semiconductor-gold nanorod heterostructures. In CdSe NRs with Au tips, the distinct plasmon band of the Au nanoparticles was completely damped due to strong interaction with the CdSe domain. Using transient absorption spectroscopy, we show that optical excitation of plasmons in the Au tip leads to efficient hot electron injection into the semiconductor nanorod. In the presence of sacrificial electron donors, this plasmon induced hot electron transfer process can be utilized to drive photoreduction reactions under continuous illumination. We propose that the strong metal/semiconductor coupling in CdSe/Au heterostructures leads to a new pathway for this surprising efficient hot electron transfer. In this plasmon induced interfacial charge transfer transition (PICTT) the a plasmon decay by direct excitation of an electron from the metal to semiconductor, bypassing the competition with hot electron transfer in metal. Ongoing studies are examining the generality of this mechanism and exploring possible approaches for improving its efficiency through controlling the size and shape of the plasmonic and excitonic domains.