Ultrafast Electron Dynamics of Plasmonic Nanoparticles under Modal Strong Coupling Conditions

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In our previous study, we have developed an efficient photoelectrochemical energy conversion system based on an Au nanoparticle (Au-NP)/TiO_2 thin-film/Au-film photoelectrode, which exhibits modal strong coupling between the localized surface plasmon resonance (LSPR) and the cavity resonance. [1,2] Employing this unique photoelectrode under strong coupling conditions, the quantum efficiency of water oxidation is enhanced as compared to the general photoelectrode without strong coupling. The dynamics of hot electrons, such as the electron-electron scattering, electron-phonon scattering, under the photon excitation, and the interfacial charge transfer at Au-NPs/TiO_2 interface should be essential factors for the efficient energy conversion in this strong coupling system. In this study, we explored the dynamics of hot electron in Au NP and the charge transfer at the interface of Au-NPs/TiO_2 under strong coupling conditions using femtosecond transient reflection spectroscopy. Substrates consist of TiO_2 thin film (~ 170 nm) on Au film and a Au-NPs layer that inlaid inside the TiO_2 thin film. The inlaid position of the Au-NPs was controlled to tune the strong coupling conditions between the LSPR and the cavity resonance. Generally, besides the resonant frequencies overlap between the LSPR and the cavity resonance, the local electric field intensity also determines the strong coupling strength. Because the electric field distribution in the cavity varies as a function of its location, the strong coupling between LSPR and cavity resonance could be controlled by varying the position of Au-NPs layers inside the TiO_2 thin film. Femtosecond transient reflection measurements were performed to study the dynamics of the electron transfer from Au-NPs to the conduction band of TiO_2 using a visible pump and IR probe at 2000 nm. The pump fluence was set at a range of 2-4 mJ/cm^2; the probe fluence was set at a range of several μJ/cm^2. Based on this measurement, we observed the electron transfer efficiency as a function of the strong coupling conditions. Besides, transient measurements using a visible pump and white light probe were carried out to study the dynamics of the decay of excited electron in the Au-NPs. Combining these two transient measurements, we will discuss the electron dynamics of Au-NPs under the strong coupling conditions.

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