Communication

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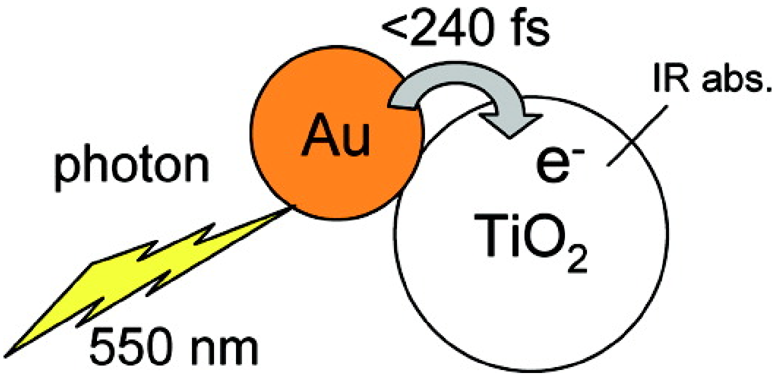

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Ultrafast Plasmon-Induced Electron Transfer from Gold Nanodots into TiO_2 Nanoparticles

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Spherical gold nanoparticles (called gold nanodots) are attracting much interest since they are chemically stable and optically sensitive, showing unique size and shape-dependent optical properties.[1,2] The gold nanodots have a plasmon absorption band at around 550 nm, which shifts when the particle size or environmental dielectric property changes. In this way, detection of the plasmon resonance wavelength can be used to sense the dielectric constant of the adjacent local volume.[3−5] Furthermore, strong electric fields near the nanodots can enhance Raman scattering, fluorescence, and nonlinear response of adsorbed molecules, leading to application in single molecule detection[6] and a new type of laser.[7]

In accord with the strong interactions between the environment and oscillating electrons in the gold nanoparticle, recently it was evidenced that electron transfer from gold nanodots into a TiO_2 semiconductor nanocrystalline electrode occurs because the system exhibited photocurrent under excitation of the plasmon band.[8−11] Note that the reverse electron transfer from TiO_2 to gold is already known to occur under UV illumination of TiO_2.[12]

Since the plasmon band is due to a collective motion of conductive electrons induced by the electric field of incident light, the photon energy is shared by numerous electrons and individual electrons are not expected to have sufficient energy to get over a ~1.0 eV Schottky barrier at the interface between gold and TiO_2.[13] To obtain direct evidence of electron transfer from gold nanodots to TiO_2 and, furthermore, to evaluate the rate and yield of the reaction, femtosecond transient absorption spectroscopy was used. Since electrons injected in the TiO_2 conduction band are known to show strong intraband absorption in the IR region,[14] femtosecond IR probing was used to directly observe any injected electrons from the plasmon band of the gold nanodots that were attached to TiO_2 nanoparticles (Figure 1).

To make TiO_2 films with gold nanodots (Au/TiO_2), a colloidal solution of gold nanodots with an average diameter of 10 nm (Sumitomo Osaka Cement) was mixed with TiO_2 powder (Degussa P25) with ~20 nm mean particle diameter (~10 wt %). The resulting slurry was put on a glass plate and heated at 500 °C to decompose any organic molecules between gold and TiO_2. Complete decomposition was proved from no vibrational band signals observed by IR absorption. In the film, the number of gold nanodots was much fewer than that of TiO_2 particles. Optical density spectra of Au/TiO_2 and the original gold solution showed plasmon peaks at ~550 and 515 nm, respectively (Figure 2). The Au/TiO_2 optical spectrum includes a strong scattering effect due to the TiO_2 film. For comparison of the electron transfer yield, a dye-sensitized TiO_2 film using a ruthenium complex dye (*cis*-bis(4,4′-dicarboxy-2,2′-bipyridine)dithiocyanato ruthenium(II), generally referred to as N3) was prepared ($N3/TiO_2$) by immersing a bare TiO_2 (P25) film in the dye solution. This system is known to give a very efficient charge separation yield of nearly 100%.[15] In addition, by using ZrO_2 nanoparticles instead of TiO_2, another comparison sample (Au/ZrO_2) was made and the optical density spectrum is also shown in Figure 2. Since the conduction band edge of ZrO_2 is located 0.9 V above that of TiO_2,[15] no electron transfer from gold nanodots to ZrO_2 is expected and the sample can be used as a reference to monitor the response of excited gold nanodots. The surface plasmon band at 550 nm was excited by ~150 fs laser pulses, and transient absorption at 3500 nm was recorded. An IR band-pass filter was placed before the probe light detector (Hamamatsu, P3257-10) to efficiently remove IR emission from the excited gold nanodots. The samples measured were sufficiently stable during experiments. Details of our femtosecond transient absorption spectrometer have been described previously.[16] The measurements were performed in air at room temperature (22 °C).

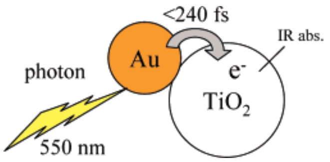

Figure 1. Schematic diagram of a gold nanodot attaching on a TiO_2 nanoparticle, also indicating the revealed electron injection process.

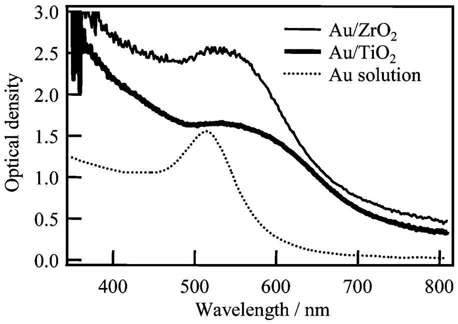

Figure 2. Optical density of the gold nanodots on ZrO_2 and TiO_2 nanocrystalline film (thin and thick solid lines, respectively) and in solution (dotted line).

As shown in Figure 3, for Au/TiO_2, a prompt transient absorption rise was clearly observed and the absorption decayed slowly with time. Since Au/ZrO_2 did not show any transient absorption under identical experimental conditions, excited gold nanodots were confirmed to produce no transient absorption at the probe wavelength of 3500 nm. Hence, the observed transient absorption for Au/TiO_2 can be assigned to electrons injected in TiO_2 as expected. The absorption rise was within 240 fs (the time resolution of the apparatus, given by reference to the charge carrier absorption rise for a silicon plate), and no subsequent rise was observed (Figure 3), indicating that electron injection was complete within 240 fs. It is known that, after photoexcitation of gold nanoparticles, the electrons with a non-Fermi distribution relax through electron−electron (<100 fs), electron−phonon (1−10 ps), and phonon−phonon (~100 ps) interactions;[1,2] therefore, the electron injection

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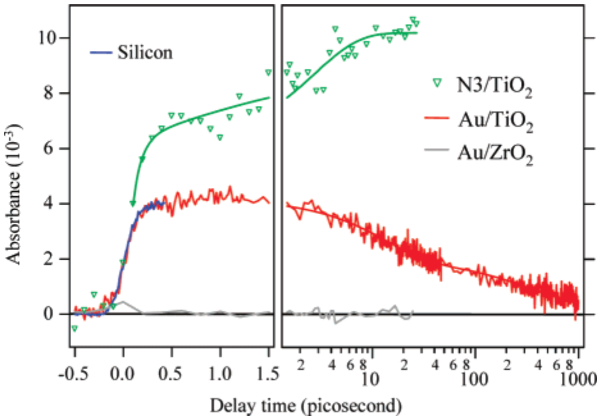

Figure 3. Transient absorption kinetics at 3500 nm of nanocrystalline films (green: N3/TiO$_2$, red: Au/TiO$_2$, gray: Au/ZrO$_2$). The blue line shows the response of the apparatus, obtained using a silicon plate.

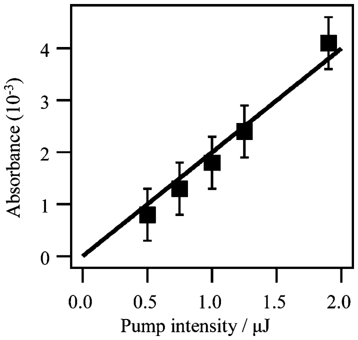

Figure 4. Transient absorption intensity just after the excitation plotted against excitation laser intensity.

process was found to occur before or during thermalization due to the electron−electron scattering.

The electron injection yield was evaluated to be about 40% by comparison with N3/TiO$_2$ (Figure 3), which is already well understood to give ∼100% injection efficiency following a biphasic reaction path; the first path within 100 fs followed by another on a tens of picoseconds time scale.[14] Note that, at 550 nm pump wavelength, both Au/TiO$_2$ and N3/TiO$_2$ had an optical density larger than 1, indicating that most incident photons were absorbed by the samples and the transient absorption intensity ratio directly corresponds to the ratio of the electron injection yields.

The amplitudes of the transient absorption signals for Au/TiO$_2$ were measured as a function of the excitation light intensity (Figure 4), showing a linear relationship. This result suggests that the obtained electron injection yield under intense femtosecond laser excitation is the same as that under weak light excitation such as conventional lamps and sunlight. The number of absorbed photons per gold nanodot was estimated to be a few thousands at the experimental condition of 2 μJ pump intensity.

Up to 1 ns, the injected electrons were observed to decay through back electron transfer to gold nanodots (Figure 3). The nonexponential kinetics will be due to diffusion of many electrons within TiO$_2$ particles. Further experiments are underway investigating particle size dependence and excitation power dependence, and these results will be published elsewhere.

It should be noted that the yield of electron transfer measured just after excitation is similar to that reported by a steady state photocurrent experiment using a solar cell configuration;[10] therefore, the decay observed up to 1 ns may be sensitive to sample preparation methods and possibly be suppressed by the presence of electrolyte.

The detailed mechanism on the efficient electron injection upon plasmon band excitation is not clear at the present. The plasmon band overlaps with an interband transition in gold, where electrons in the filled d-band are excited to electronic states above the Fermi level in the sp conduction band. Electrons oscillating collectively may lead to interband excitation, giving enough energy to electrons moving to the interface to overcome the Schottky barrier, since the ballistic mean free path of electrons in gold is 20−150 nm at energies ∼1 eV above the Fermi level.[13]

To check if such interband excitation assists electron transfer upon plasmon excitation or not, we are planning to measure excitation wavelength dependence on the electron transfer yield as well as to examine other systems such as gold nanorods on TiO$_2$, which have a plasmon band in the near IR region without overlapping with the interband transition. Also, using silver nanodots instead of gold nanodots would be effective to avoid the overlap problem with interband transitions.

TiO$_2$ is known as a good electron-accepting metal oxide through many transient absorption experiments comparing with other dye-sensitized semiconductors, such as ZnO, SnO$_2$, and In$_2$O$_3$.[17,18] The excellent electron-accepting property or the very fast electron injection can be understood from the high density of states in the conduction band of TiO$_2$. The electron transfer yield may be affected for different semiconductors. These systematic experiments will be necessary for understanding the mechanism of plasmon-induced electron transfer.

In conclusion, by using femtosecond transient absorption spectroscopy with an IR probe, we could directly observe plasmon-induced electron transfer from 10 nm gold nanodots to TiO$_2$ nanoparticles. The reaction time was within 240 fs, and the yield was about 40%. Since gold nanodots have an extremely high absorption coefficient compared with usual dye molecules, they may be utilized as a good electron source in nanodevices if back electron transfer can be suppressed efficiently.

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