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Research paper

Electron transfer dynamics and yield from gold nanoparticle to different semiconductors induced by plasmon band excitation

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ABSTRACT

Photoinduced electron transfer from gold nanoparticles (NPs) to semiconductor under plasmon excitation is an important phenomenon in photocatalysis and solar cell applications. Femtosecond plasmon-induced electron transfer from gold NPs to the conduction band of different semiconductor like TiO₂, SnO₂, and ZnO was monitored at 3440 nm upon optical excitation of the surface plasmon band of gold NPs. It was found that electron injection was completed within 240 fs and the electron injection yield reached 10–30% under 570 nm excitation. It means TiO₂ is not the only proper semiconductor as electron acceptors in such gold/semiconductor nanoparticle systems.

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1. Introduction

Surface plasmon resonance (SPR) has been widely studied in the surface science field since R. H. Ritchie had done the initiating work in 1957 [1]. SPR is a wave of collective motion of numerous conductive electrons induced by the electric field of incident light, which are sensitive to the condition of circumstance such as the shape and size of the metal and the surrounding refractive index [2,3]. The resonant interaction between the surface charge oscillation and the electromagnetic field of the light gives rise to enhancement of fluorescence, Raman scattering light, second-harmonic light from absorbed molecules. The plasmon features of the gold nanoparticle have many applications such as photocatalysis and solar cell devices [4–6] due to the stability of gold nanoparticles and charge transfer between gold nanoparticles and contacting semiconductors.

It is already well-known that the dynamics of photoexcited gold nanoparticles give three representative time constants, which are respectively assigned to relaxation of electrons with a non-Fermi distribution to the Fermi electron distribution through electron–electron scattering (<100 fs), cooling of hot electron through electron–phonon scattering (1–10 ps), and heat dissipation from the gold nanoparticles to the environment through phonon–phonon scattering (~100 ps) [7–10]. Considering these dynamics, only

electrons with high energy before deactivating through electron–electron scattering (less than 100 fs) seem to have a chance of electron transfer going across the surface of gold nanoparticle. Efficient electron transfer, however, may occur in such a short time if electronic coupling with the electron acceptor is large enough.

Contact between gold and semiconductor can form a metal–semiconductor Schottky junction [11,12], which possibly blocks the charge separation because electrons are difficult to go across the interface. The interaction between gold and semiconductor can be influenced by the plasmon-induced strong electronic field upon photo-excitation. More than a decade ago, Y. Tian and T. Tatsuma proposed the mechanism that the charge separation was accomplished by electron transfer from the photo-excited gold particles to TiO₂ [13]. In our previous study using femtosecond spectroscopy, electron injection from the 10 nm gold nanoparticle to TiO₂ nanoparticle (P25) had been directly observed [14]. We have proved plasmon excitation induced free electron transfer occurred in gold/TiO₂ systems by using femtosecond IR probe transient spectroscopy. We found electron injection process was completed within 50 fs and the yield was about 40%. But the electron injection mechanisms are still not fully clear. TiO₂ usually works as a very excellent electron acceptor because TiO₂ has a larger density of states in the conduction band due to the d-orbital nature, differing from the other typical metal oxides such as ZnO and SnO₂, whose conduction band basically is composed of the s or sp orbitals of metal atoms. To clarify the electron injection mechanism, three types of different semiconductors (TiO₂, SnO₂, and ZnO) are used as electron acceptor, respectively.

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Here we report that plasmon-induced electron transfer dynamics in gold nanoparticle loaded with different semiconductor systems of TiO₂, SnO₂, and ZnO. Transient absorption kinetics up to 1 ns in the IR range were measured by exciting plasmon band of gold nanoparticles located at 570 nm. Electron injection yields for different gold/semiconductor systems were also studied. The transient absorption kinetics probed at 3440 nm reflected that the free electrons are injected into the conduction band of these semiconductors, clearly indicating that TiO₂ is not the only suitable semiconductor in such metal–semiconductor systems showing light-energy conversion.

2. Experimental section

2.1. Sample preparation

Bare TiO₂ (99.8%TiO₂, anatase, Aladdin, China) and SnO₂ (Alfa-Aesar, China) NP films with the average diameter of 10 nm were prepared by respectively mixing the powders with two droplets Triton and a certain amount of acetylacetone using the doctor blade method. ZnO (99.9% ZnO, Cw-nano, Shanghai) NP film with the average diameter of 30 nm was produced by electric deposition method. All samples were made by heating at 450 °C for 1 h. Au-modified procedure was done after heating, and the above heated samples were put into a beaker in 100 mL 0.001 M HAuCl₄ and 1 mL CH₃OH, then irradiated with a UV lamp for 30 min. Dye-sensitized TiO₂, SnO₂ and ZnO films using an efficient sensitizer Ru-complex dye (N719) were prepared as the reference samples with 100% electron injection efficiency to the semiconductor NP, by immersing a bare TiO₂, SnO₂ or ZnO film in a N719 dye solution for 12 h. The molecular structure of N719 dye is shown in Fig. 1.

2.2. Femtosecond transient absorption spectrometer

Transient absorption kinetics were measured by the femtosecond VIS-pump/IR-probe transient absorption spectrometer based on an amplified Ti: sapphire laser system (1 kHz repetition frequency, 800 nm center wavelength, 150 fs pulse width) combined with two optical parametric amplifiers. The pump beam radius on the film surface was about 0.36 mm. The details of our spectrometer had been described previously [15,16]. The gold/semiconductor NP and N719/semiconductor NP films were placed in air and stable enough during the transient absorption measurements. The samples were mechanically scanned to avoid the degradation of N719 dye and gold nanoparticle due to pump light irradiation during the experiments. All the transient absorption measurements were performed at 295 K.

2.3. Steady state spectrometer

The prepared samples scatters visible light strongly. A spectrophotometer (Shimadzu, MPC-3100) equipped with an integrat-

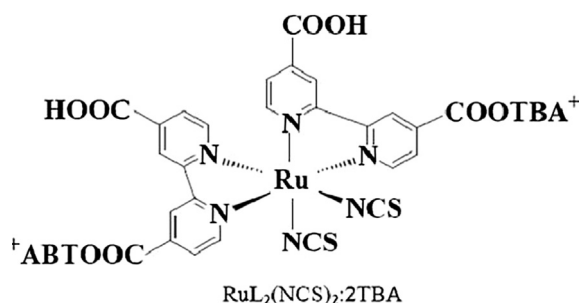


Fig. 1. The molecular structure of N719 dye.

ing sphere was used to accurately obtain the absorption fraction for each sample. Details of the procedure are described as below. An incident light with intensity I_0 enters the integrated sphere through the entrance window. First the samples were placed before the sphere to measure the transmission fraction (F_T) for each gold/semiconductor and N719/semiconductor sample. F_T can be obtained from the ratio of transmitted light I_T to the incident light I_0 (Eq. (1)). Then the sample was placed behind the sphere to obtain the reflection fraction (F_R) for each gold/semiconductor and N719/semiconductor sample. F_R can be obtained from the ratio of reflected light I_R to the incident light I_0 (Eq. (2)). So the absorption fraction F_A can be calculated from F_T and F_R (Eq. (3)) because the total of F_A , F_T and F_R is 100%.

$$F_T = I_T/I_0 \quad (1)$$

$$F_R = I_R/I_0 \quad (2)$$

$$F_A = 1 - (F_R + F_T) = 1 - I_T/I_0 - I_R/I_0 \quad (3)$$

3. Results and discussion

3.1. Optical characterization

Fig. 2(a,b,c) show each F_A as a function of wavelength for the TiO₂, Au/TiO₂, N719/TiO₂, SnO₂, Au/SnO₂, N719/SnO₂, ZnO, Au/ZnO, and N719/ZnO systems. For Au/TiO₂ system, the absorption band at 550 nm originating from the plasmon band of gold nanoparticles were observed. The F_A value was close to 0.8 due to strong absorption of gold nanoparticles. For Au/SnO₂ system, the F_A value was close to 0.4 due to weaker absorption of gold nanoparticles at 550 nm. For Au/ZnO system, the F_A value was close to 0.35 due to weaker absorption of gold nanoparticles at 515 nm. For N719/TiO₂ and N719/SnO₂ systems, the F_A values for the absorption band peak at around 530 nm were also close to 0.6–0.8. For N719/ZnO system, the F_A values for the absorption band peak at around 515 nm were close to 0.4. The plasmon band peak of different semiconductor loaded with gold nanoparticle is slightly different each other due to the particle size effect of gold, different refractive index and reflection characteristics of semiconductors. It is known that large refractive index and large Au diameter make red-shift to the peak wavelength. The band peak of bare TiO₂, SnO₂, ZnO absorption give the value at around 380 nm, 369 nm, 360 nm. We chose 570 nm light as a pump pulse to excite the plasmon band of gold nanoparticle.

3.2. Electron injection in different semiconductor systems

Transient absorption signals of Au/TiO₂, N719/TiO₂, bare TiO₂, Au/SnO₂, N719/SnO₂, bare SnO₂ and Au/ZnO, N719/ZnO, bare ZnO systems observed at 3440 nm upon excitation at 570 nm were shown in Fig. 3(a,b,c). All amplitudes had been corrected by the absorption fraction at pump light wavelength of 570 nm. At this probe wavelength, absorption due to free electrons injected from gold nanoparticle into the conduction band of TiO₂, SnO₂ or ZnO can be monitored. Bare TiO₂, SnO₂ or ZnO show no transient absorption signals due to no absorption at 570 nm (Fig. 2), the excitation intensity at the sample point is 1mw. For Au/semiconductor systems, we found the electron injection process was completed within less than 240 fs (the time resolution of our apparatus) [14] and following was the decay process. From the data, there may be a small rising component after response rise. This might be relaxation of injected electrons as we discussed in our previous work [16,17]. The following decay was assigned to the back electron transfer from the semiconductor to gold nanoparticle. The

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