ULTRAFAST INTERFACIAL ELECTRON TRAPPING AND RECOMBINATION IN PHOTOEXCITED COLLOIDAL CADMIUM SULFIDE

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Abstract – We measured, using femtosecond pump-probe experiment, the time evolution of transient absorption in aqueous CdS colloids. The signal rises within the time resolution ($\sim$ 0.5 ps) of the experiment and decays with two exponential time constants, 4.8 ps and 132 ps. The ultrafast rise of the transient absorption is considered to be for shallowly trapped conduction band electrons after photoexcitation. The amplitude ratio of the two decaying components varies with the pump intensity and the decay times increase in the presence of hole scavengers. Even though a biexponential function fits the decay well, we object that two independent first order processes (geminate and nongeminate recombinations) are responsible for the decay. A function with an integrated rate equation for second order nongeminate recombination plus a long background fits the decay well. The long background is considered to be for deeply trapped charges at the CdS particle.

INTRODUCTION

Electrons and holes generated by photoexcitation of wideband-gap semiconductors undergo electrochemical reactions to produce (or decompose) organic (or inorganic) materials.[1,2] Electron transfer at the semiconductor-liquid interface may be a key process in the photocatalysis. For better photocatalytic efficiency, nanometer size semiconductors have been tested[1-5] expecting following advantages; first, because of larger band-gap than their bulk counterparts, they can be used as photocatalysts in more electrochemical reactions and can store larger chemical energy; second, because of larger surface area per volume than their bulk counterparts, higher efficiency of charge transfer at the interface is possible; third, they can be synthesized easily on the laboratory bench. Disadvantages may be inhomogeneity and impurity in the synthesized materials but they can be improved. Most serious problem would be a large number of defect sites which are inevitable due to lack of crystallinity on the surface. Photogenerated electrons and holes are easily trapped at the defect sites, thus decreasing photocatalytic efficiency. In this case, the surface needs to be treated with suitable metals or ions that intercept the charges before trapping.

Nanometer size CdS colloid, along with TiO_2, is probably the most studied semiconductor, especially on the purpose of understanding photoinduced interfacial charge transfer process. It has been synthesized in narrow size distribution using numerous methods.[6-11] Its uv-visible spectral properties[12-15] have been well characterized. Time-resolved photoemission,[6,16] resonance Raman,[9] and transient absorption[17] experiments have been carried out. Recent ultrafast transient absorption studies[11,18-20] in aqueous solution suggest ultrafast charge trapping after the photoexcitation, on the ground that transient absorption ranging from 400 nm to 800 nm is observed within some subpicoseconds after the photoexcitation. Then, the transient absorption signal decays rapidly in picosecond time scale, to whose behavior Zhang *et al.*[11] have assigned geminate and nongeminate recombination between trapped electrons and holes. However, as explained later in this paper, such assignment needs further justification. In this work, we reanalyze the time evolution of the transient absorption signal that was obtained in femtosecond pump-probe experiment and discuss the identity and the fate of the transient.

MATERIALS AND METHODS

The most common method of preparing aqueous CdS colloid would be passing a quantitative amount of H_2S gas into an aqueous solution of ionic cadmium compound.[6-9] However, we used an alternative method to avoid complexities in the preparation apparatus; CdS colloids can be slowly grown from reactants $CdCl_2$ and Na_2S in the presence of an inhibitor.[10,11] 50 ml solution of 7.5 mM CdS and 50 ml solution of 11 mM $Na_2S \cdot 9(H_2O)$ are each allowed to drop very slowly from separate burets into a reaction vessel that contains 50 ml solution of 12 mM sodium mercaptoacetate as the inhibitor. Well-dispersed aqueous CdS colloids can be prepared, especially when the reaction vessel is agitated inside an ultrasonicator. pH of the prepared solution is measured to be 9.3.

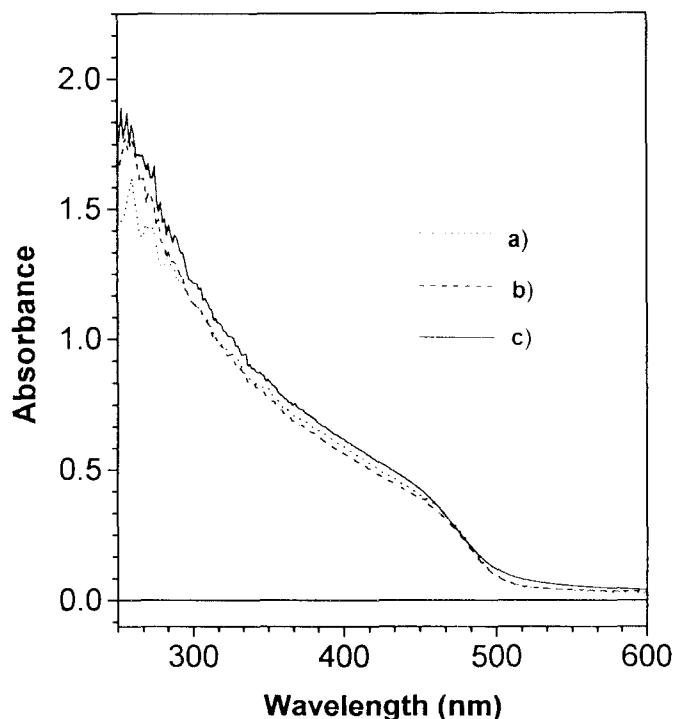* To whom correspondence should be addressed.

Figure 1. UV- visible absorption spectra of aqueous CdS colloids; (a) 2 hours after preparation (b) 1 week after preparation (c) 1 month after preparation

Figure 2. Amplified Ti:Sapphire laser system and pump-probe transient absorption setup

Figure 1 shows uv-visible spectra of the aqueous CdS colloid that were kept under dark for 2 hours, 1 week, and 1 month after the preparation. It shows the prepared solution is stable for several months; however, the pump-probe experimental data of this work were obtained for the samples that were less than 20 hours old. In taking the spectra of Fig. 1, the original CdS solution was diluted by 5 times to use 1 cm cuvette cell instead of 2 mm cell in the femtosecond pump-probe experiment. This dilution process results in the drop of pH by 0.7 but since the band-gap is independent of pH the shape of uv-visible spectra does not change. In the spectra one can identify the band-gap at approximately 500 nm and exciton band at 450 nm. Comparing the band-gap with those published,[11] we estimate the diameter of CdS colloids to be 30-40 Å .

The femtosecond pump-probe experiment of this work used the setup of Korea Research Institute of Standard and Science and is depicted in Fig. 2. About 350 μJ, 300 fs pulses of 800 nm wavelength were generated at the repetition rate of 1 kHz from the laser system that consists of a Ti:Sapphire oscillator (Spectra Physics, Tsunami), a Ti:Sapphire regen-erative amplifier (Quantronix, 4810), and a pulse stretcher and compressor (Quantronix, 4820). After splitted by a 50/50 beam splitter, half the splitted pulse passed through a variable delay line controlled by a stepper motor and was focused onto a 5 mm thick β-barium borate crystal for frequency doubling. About 15 μJ frequency doubled (400 nm) pulse was then generated and used as the pump for the photoexcitation of CdS; it was focused by a 30 cm focal length lens onto a 2 mm flowing sample cell, through which the CdS colloid solution was circulated. The other half of the splitted pulse was
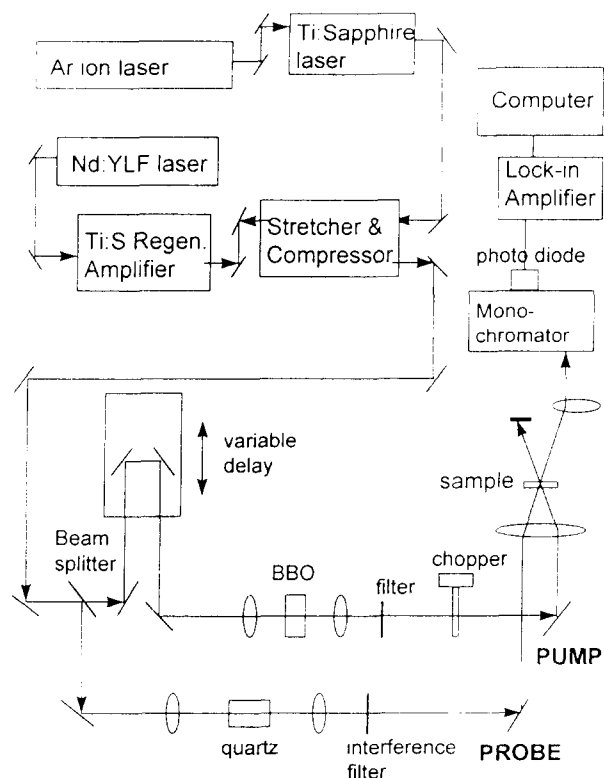
focused by 15 cm focal length lens onto a quartz to generate white light continuum Then, a pulse of probe wavelength (640 nm) was selected by a 10 nm band-width interference filter and was focused by a 25 cm focal length lens onto the sample cell. The transmitted probe pulse after transient absorption created by the pump pulse passed a monochromator followed by photodiode detection and lock-in-amplifier average with 40 Hz chopping frequency.

RESULTS

Figure 3 shows the time evolution of transient absorption of aqueous CdS colloids. Figure 3(a) and 3(b) were obtained by scanning the delay between the pump (400 nm) and the probe (640 nm) with 2 ps time step and 0.2 ps time step, respectively, and repeating the scan 10 times. Overall, each data point in Fig. 3(a) corresponds to average of 75,000 pump-probe cycle. The signal rises with 0.5 ps, which is the time resolution of the setup and decays nonexponentially. The shape of the signal decay in Fig. 3 suggests that either a sum of independent first order kinetics or a second order kinetics occurs after the photoexcitation. For the better understanding, we have conducted a rough test with pump intensity variation and found that the signal intensity at 1 ps time delay is almost proportional to the pump intensity while the signal intensity after 50 ps time delay has a small (~ 0.5)
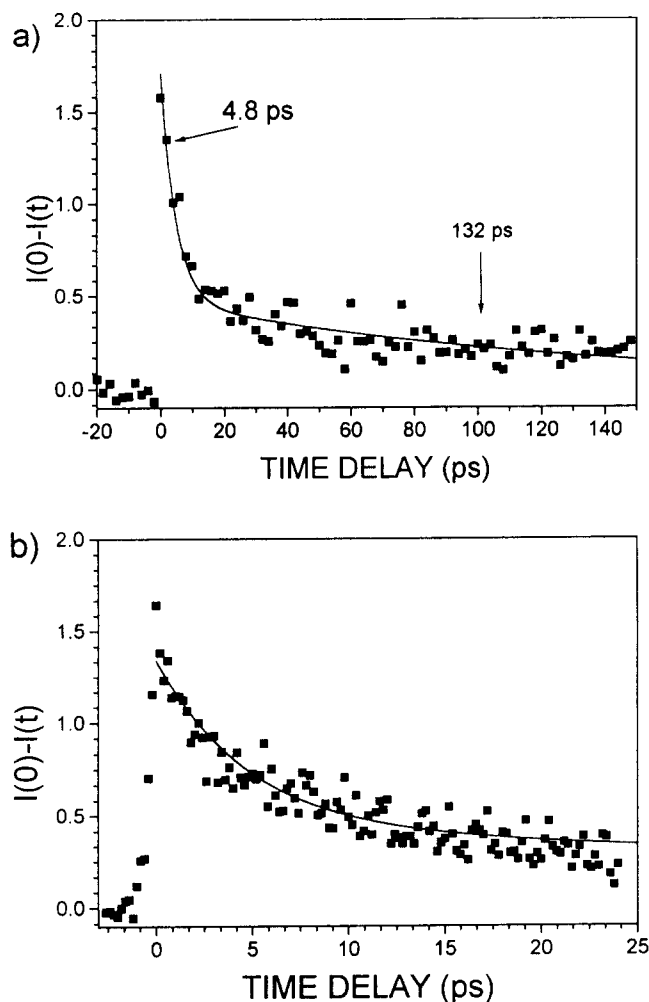
a)

b)

Figure 3. Time evolution of transient absorption of aqueous CdS colloids; (a) step size = 2 ps, the solid curve fit function represents $I_0 - I(t) = 1.24\{\exp(-t/4.8ps) + 0.38\exp(-t/132ps)\}$; (b) step size = 0.2 ps, the solid curve fit function represents $I_0 - I(t) = 0.91\{\exp(-t/4.8ps) + 0.38\exp(-t/132ps)\}$

fractional dependence on the pump intensity. It suggests that two (or more) independent processes are responsible for the shape of the signal. Therefore, we first fit the decay data with a biexponential function and show the result in the solid curves in Fig. 3. The fitted decay constants are 4.8 ps and 132 ps and the amplitude ratio of the two decaying components is approximately 1 to 0.4.

DISCUSSION

We consider three possible transient states that are responsible for the observed transient absorption; the first would be the conduction band electron inside CdS particle, the second would be the conduction band electron trapped at the surface defect sites of CdS particle, and the third would be the electron that is ejected into and solvated by water. If the conduction band electron

inside CdS particle induced the transient absorption, the decay would have been independent of solvent. However, we note that both decay times become shorter if pH of the solution is lowered; Zhang et al.[11] reported the two decay time constants are 2 ps and 50 ps, respectively when pH of the solution is 8.0 instead of our value of pH 9.3. In addition, as stated later, the decay times become longer when hole scavenging ions are added. Thus, we eliminate the possibility of conduction band electron inside the CdS particle for the ultrafast transient absorption.

Next, we consider the other two possibilities for the ultrafast absorption: the hydrated electron and the trapped electron. The conduction band electron can be ejected into solvent by the Auger-like multiphoton process, as suggested by Kaschke et al.[18] According to a simulation,[21] the ejected electron is solvated by water molecules in less than 50 fs. This mechanism is consistent with ultrafast risetime (< 500 fs) of the transient absorption but can not explain decay times in the picosecond regime. The solvated electron is unlikely the major transient in our time regime. Therefore, the most probable transient would be the trapped electron at the semiconductor-water interface. Wave function of the photoexcited conduction band electron extends to the surface; the trapping at the surface can be made instantaneously. Or it can be made by diffusion. Zhang et al.[11] estimated the diffusional trapping time to be 3 fs for 30 Å. Such ultrafast trapping time makes it difficult for the Auger-like multiphoton ejection process to take place. Therefore, we suggest that the instantaneous rise is due to ultrafast trapping of photoexcited electrons and the decay is due to a recombination of the trapped electrons with holes.

pH dependence of the decay times could be due to changes in electromotive potential by 0.059 V per one pH unit or can be due to changes of hole scavenging OH$^-$ concentration. Zhang et al.[11] showed and we also confirmed that additions of hole scavenging NaI at constant pH's (8.0 in Zhang et al.'s and 9.3 in ours) result in longer decay times. Increased hole scavenger concentration at the interface will reduce the recombination rate. Thus, pH dependency in decay times is more likely due to changes in hole scavenging OH$^-$ concentration.

Figure 3 is obtained with the pump energy of about 15 μJ. The amplitude of the faster decaying component is almost proportional to the pump energy but that of slower component has a fractional (~ 0.5) dependence on the pump energy. Similar behavior was observed in 2 ps and 50 ps components in Zhang et al.'s experiments[11] for CdS colloids and in 1-2 ps and 30 ps components in Ernsting et al.'s transient bleaching experiments[22] for ZnCdS. Because of this pump energy dependency, Zhang et al.[11] suggested that the faster decay is due to nongeminate recombination process and the slower decay is due to the geminate recombination.

At this point, we raise the question whether the biexponential function that was used to fit the decay in
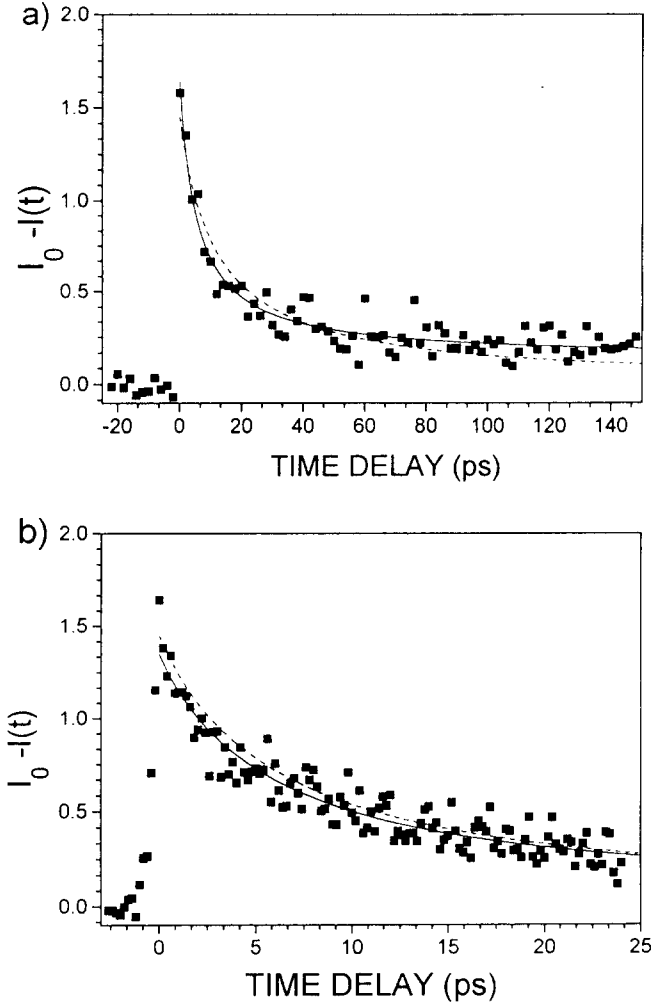
Figure 4. Time evolution of transient absorption of aqueous CdS colloids; (a) step size = 2 ps, the solid line fit function represents $I_0 - I(t) = 1.51/(1 + 0.175t) + 0.134$, the dotted curve represents $I_0 - I(t) = 1.45/(1 + 0.085t)$; (b) step size = 0.2 ps, the solid curve fit function represents $I_0 - I(t) = 1.34/(1 + 0.175t) + 0.106$, the dotted curve represents $I_0 - I(t) = 1.45/(1 + 0.176t)$

Fig. 3 is adequate for the geminate and nongeminate recombination process. Gemination recombination is induced from electron-hole pairs that are tied together like exciton and should follow a first order kinetics, but nongeminate recombination should follow second order kinetics as in Eq. (1)

$$\frac{dN_c}{dt} = -k_2 N_c N_h \tag{1}$$

where k_2 is the second order nongeminate recombination rate constant and N_c, N_h are number densities of trapped conduction band electrons and valence band holes, respectively. It is reasonable to assume that $N_c = N_h$ and then the solution of Eq. (1) is

$$N_c = \frac{N_c^0}{1 + N_c^0 k_2 t} \tag{2}$$

where N_c^0 is the number density of initially trapped electrons. The dotted curves in Fig. 4 represent the best fits of the decay to Eq. (2). The best fits in Fig. 4(a) and Fig. 4(b) give a big difference in $k_2 N_c$; $8.5 \times 10^{10} s^{-1}$ in (a) and $1.8 \times 10^{11} s^{-1}$ in (b). Overall, the function of Eq. (2) does not show the necessary curvature to fit the data in the entire time range.

In the mechanism where the trapped electron undergoes geminate recombination in competition with nongeminate recombination, the rate equation can be written

$$\frac{dN_c}{dt} = -k_1 N_c - k_2 N_c^2 \tag{3}$$

where k_1 is the first order geminate recombination rate constant. The solution of differential Eq. (3) is

$$N_c = \frac{k_1 N_c^0 \exp(-k_1 t)}{k_2 N_c^0 \{1 - \exp(k_1 t)\} + k_1} \tag{4}$$

Fitting the data with Eq. (4) gives the result as good as that fitted with eq. (2). Fitting parameters are $k_2 N_c^0 = 8.47 \times 10^{10} s^{-1}$ and $k_1 = 2.47 \times 10^7 s^{-1}$. In other words, the contribution of the first order geminate recombination process is negligible.

One may suppose that the absorption coefficient of the trapped electron undergoing geminate recombination is different from that undergoing nongeminate recombination since the former can be tied up with a hole. In this case, the following trial function may be tested.

$$N_c = (1 - R)N_c^0 \exp(-k_1 t) + R \frac{N_c^0}{1 + N_c^0 k_2 t} \tag{5}$$

where R is the ratio of absorption coefficients at 640 nm of trapped electrons undergoing the geminate and the nongeminate recombinations. Eq. (5) fits the data in excellence. However, this is because one more fit parameter is used. The fit parameters are $k_2 N_c^0 = 1.75 \times 10^{11} s^{-1}$ and $k_1 = 3.4 \times 10^{-11} s^{-1}$. In other words, the first term in Eq. (5) contributes only as a background. Therefore, the following equation is most adequate.

$$N_c = \frac{N_c^0}{1 + N_c^0 k_2 t} + B \tag{6}$$

where B is a background.

The fit with Eq. (6) is indicated in the solid curves in Fig. 4 and gives $k_2 N_e^0 = 1.75 \times 10^{11} s^{-1}$. The ratio N_e^0/B is about 12.

Then, what is the meaning of the background B? Long lived transient state is often observed in aqueous semiconductor colloids.[23] In ns and longer time regimes, the hydrated electron can be thought of the long lived transient. However, the hydrate electron, if formed ultrafast, needs the Auger-like ejection process by multiphoton, but the pump energy dependence of signal does not support it. It is more likely the hydrated electron is formed from relaxed states of electron at later stage. On the contrary, deeply trapped electrons (or holes) can be formed within our laser pulse duration and may live over many hundred picoseconds, thus contributing as the background transient. Thus, we suggest two states of trapped charge at the interface for the observed time behavior of the transient absorption: the shallowly trapped electron and the deeply trapped electron (or hole). Both the states are formed within the time duration of our laser pulse. The shallowly trapped state is initially formed with 12 times more concentration than the deeply trapped ones when our pump energy is 15 μJ. It undergoes nongeminate recombination with hole and dispappears mostly within 10 ps. Therefore, the relative contribution of it to the transient absorption is smaller as longer and weaker excitation pulses are used. The deeply trapped charge does not undergo the recombination immediately and lives for many hundred picoseconds. As the excitation pulse is weaker and longer, its relative contribution increases.

The two different trapped states are also suggested by Hässelbarth et al. with time-resolved fluorescence quenching experiment.[16] Following their suggestion one shallowly trapped state is the precursor of the other deeply trapped state. However, this is another story since the lifetimes of the two trapped states in their work are in the nanosecond regime. The deeply trapped state that we assigned is created independently after the photoexcitation and can be a precursor of further deeply trapped states found in photoemission and transient absorption experiments in longer time regimes.

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