Femtosecond studies of interparticle electron transfer in a coupled CdS–TiO$_2$ colloidal system

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We report the direct femtosecond measurements of the electron transfer process from CdS to TiO$_2$ particles in a coupled colloidal system. The electrons initially created in the conduction band and quickly trapped at the liquid–solid interface in aqueous CdS colloids are found to be transferred to the colloidal TiO$_2$ particles with a time constant of 2 ps, resulting in significantly slower electron–hole recombination. These coupled semiconductor colloids provide a potentially useful system for achieving efficient charge separation, which is important for many chemical reactions involving heterogeneous electron transfer.

I. INTRODUCTION

Coupled semiconductor colloidal systems have recently received a great deal of attention in research.[1–10] There are at least two important reasons. First, coupled colloids with different energy levels provide the intriguing possibility of using small bandgap semiconductors to photosensitize large bandgap semiconductors that have no visible absorption. This is significant for many photoelectrochemical reactions involving large bandgap semiconductors as photocatalysts. Second, charge injection from one colloidal semiconductor into another can lead to efficient and longer charge separation by minimizing the unwanted electron–hole recombination pathway.[1,2] Therefore, coupled semiconductors are potentially useful in improving the photocatalytic efficiency in photoelectrochemical systems, including solar energy conversion through hydrogen generation. Enhanced yields of hydrogen generation from the reduction of H$_2$S has been observed in the CdS particulate system upon the addition of TiO$_2$ powders.[4] A tenfold enhancement in the efficiency of methylviologen reduction has also been found upon increasing the colloidal TiO$_2$ content in a CdS–TiO$_2$ system.[5] Also, the charge transfer processes in several coupled semiconductor colloids, including CdS–TiO$_2$, CdS–ZnO, PbS–TiO$_2$, AgI–Ag$_2$S, and Cd$_3$P$_2$–ZnO, have been reported.[1–10]

To understand the mechanism of charge transfer in coupled colloidal semiconductors, it is essential to study the primary dynamical events involved in the charge injection process. One of the prototypical systems used to study charge transfer dynamics in coupled semiconductor colloids is CdS–TiO$_2$.[1–5] In this system, CdS has a bandgap (2.5 eV for bulk) smaller than that of TiO$_2$ (3.2 eV), while the bottom of the conduction band for TiO$_2$ is lower than that of CdS by about 0.5 eV.[11] This makes it possible to use CdS as a photosensitizer for TiO$_2$ by injecting the conduction band electron from CdS to TiO$_2$ following photoexcitation of CdS. Kamat and co-workers have found that the fluorescence of CdS is quenched significantly when coupled to TiO$_2$ and the quenching is attributed to electron injection from CdS and TiO$_2$.[2] An injection time constant of <20 ps was indicated from their study. A direct probe of the charge injection process is yet to be carried out and such a probe should help to better understand the interparticle charge transfer mechanism.

In this paper, we report a direct femtosecond measurement of the electron transfer dynamics in a coupled aqueous CdS–TiO$_2$ colloidal system. We found that electrons initially trapped at the CdS particle surface are injected into TiO$_2$ with a time constant of 2 ps following photoexcitation of CdS at 390 nm. We also found that the electron transfer affects mainly the early time dynamics, <10 ps. Implications of this study in the potential development of a coupled nanoelectrode for photoelectrochemical reactions are discussed.

II. EXPERIMENT

The CdS colloids used in the experiment were prepared by first lowering the pH of 100 ml of 3.2 mM sodium mercaptoacetate (inhibitor) with 4 ml of 60 mM HCl.[12] Then, with constant stirring, 200 ml of 2 mM CdCl$_2$ and 30 ml of 20 mM Na$_2$S were both added dropwise from two separate burets.[13] The final pH of the colloidal solution is between 8–10. Particles with a 40 Å diameter were obtained, as confirmed by the electronic spectrum and transmission electron microscopy (TEM).

The preparation of the TiO$_2$ colloids was adapted from the following procedures detailed by Gratzel *et al.*[14] and Henglein *et al.*[15] TiO$_2$ was prepared by first adding 0.50 g of titanium tetraisopropoxide (Alpha) to 20 ml of spectral grade 2-propanol (Aldrich), avoiding moisture. Then 2 ml of this titanium solution was added slowly at a constant rate via a 0.7 mm diameter needle to 20 ml HCl-acidified water (pH 1.5) under nitrogen gas with constant stirring. The TiO$_2$ colloidal solution was clear with a silver sheen upon completion. The final pH of the colloidal solution is between 2–3. The particles obtained had a 120 Å diameter, as determined by TEM. Both CdS and TiO$_2$ colloids were typically stable for months. The coupled aqueous CdS–TiO$_2$ colloids were prepared by combining with stirring two parts aqueous CdS colloid to one part aqueous TiO$_2$ colloid, and the solution was basified to pH=8–10 with 0.1 M NaOH. The final solution is stable and has no precipitation.

The experiments were performed using a pump–probe scheme with a regeneratively amplified, mode-locked femto-

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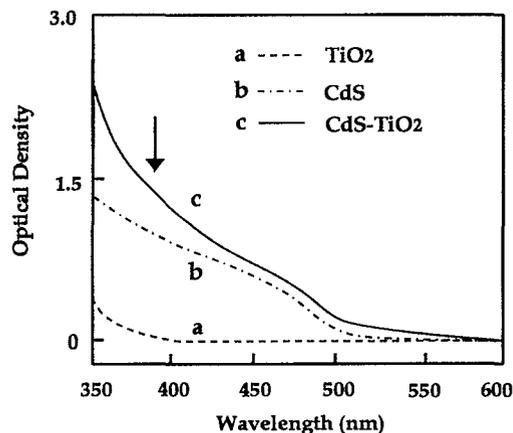
FIG. 1. Electronic absorption spectra of different colloids (a) aqueous TiO_2 (2.0 mM); (b) aqueous CdS (0.06 mM); and (c) CdS (0.06 mM)–TiO_2 (2.0 mM) colloids. The arrow in the figure indicates the excitation wavelength (390 nm) used in the transient absorption experiment.
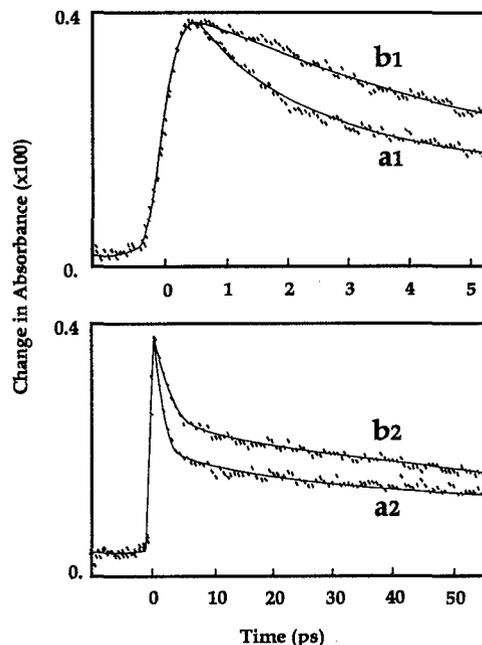

FIG. 2. The time evolution of the photoinduced electrons probed at 780 nm following excitation at 390 nm on two different time scales. The dotted lines are the experimental data. The solid lines (a) are fits using a function including a 100 fs exponential rise and a fast 2.5 ps exponential decay, followed by a slower 50 ps exponential decay plus an offset of 20% of the maximum absorbance change. The solid lines (b) are fits using the same function with a 100 fs rise and a fast 4.0 ps decay, followed by a slower 50 ps decay plus an offset of 30% of the maximum absorbance change. (a) For CdS alone, $c = 0.06$ mM; (b) for CdS–TiO_2 with 0.06 mM CdS and 2.0 mM TiO_2.

second Ti–sapphire laser. The laser system and the experimental setup have been described before.[13] Briefly, pulses of 40 fs duration with 5 nJ/pulse energy at a repetition rate of 100 MHz were generated and amplified in a Ti–sapphire regenerative amplifier using chirped-pulse amplification. The final output pulses obtained were typically 150 fs with a pulse energy of 350 μJ, centered at 780 nm at 1 kHz. The amplified output was doubled in a 1 mm KDP crystal to generate 30 μJ/pulse of 390 nm light, which was used as a pump source to excite the colloids contained in a quartz cell of a 1 cm optical path length. The remaining fundamental was focused into quartz to generate a white light continuum and the desired probe wavelength was selected by using an interference bandpass filter. The probe beam was split into a signal and a reference, which were detected by two photodiodes and processed by a computer-controlled, gated integrator in conjunction with an analog-to-digital converter (ADC). Pulse-to-pulse fluctuation (about 3%–5%) of the laser beam was eliminated by dividing the signal by the reference for each laser shot. The delay between the pump pulse and probe pulse was controlled by an optical delay line based on a translation stage. The pump and probe beams were focused with a 10 cm focal length lens and cross overlapped over a spot size of 0.5 mm in the sample slightly before the focal point. The pump power was attenuated to about 5 μJ/pulse so that there was no signal from the pure solvent, i.e., water. No signal was observed from TiO_2 colloids alone.

III. RESULTS AND DISCUSSION

The electronic absorption spectra for CdS, TiO_2, and CdS–TiO_2 are shown in Fig. 1. For TiO_2 alone, there is very little absorption at 390, while there is strong absorption at 390 nm for CdS alone. For the coupled colloids CdS–TiO_2 the spectrum shifts slightly to the red compared to that of CdS alone, indicating some interaction between CdS and TiO_2 particles. Even though several coupled colloidal systems have been studied before, including CdS–TiO_2 in organic solvents such as acetonitrile[2] and in aqueous solution[5]

using picosecond and nanosecond fluorescence techniques, to our knowledge, the present report is the first femtosecond study on coupled CdS–TiO_2 in aqueous solution. In our previous study on aqueous CdS colloids, we found that the electron trapping and electron–hole recombination dynamics were insensitive to the size of CdS particles between 20–40 Å, despite the strong size dependence of the static electronic absorption spectrum.[16–20] Thus, only one size (40 Å) of particles for CdS is reported here for the dynamical measurements. The strong correlation between the position of the excitonic peak or the onset of the static absorption and the size of the particles is usually used to infer the particle size of the CdS colloids.

TEM measurements established that the CdS and TiO_2 particles are attached, similar to that observed before by Kamat *et al.* in a different solvent (acetonitrile).[2] We have also found that the TiO_2 particles are larger in diameter (120 Å) than the CdS particles (40 Å) and that there are, on average, either one or two CdS particles attached to one TiO_2 particle.

The time evolutions of the photoinduced electrons probed at 780 nm for both CdS alone and CdS–TiO_2 coupled colloids are shown in Fig. 2 for two different time scales. There was no signal for TiO_2 alone since there is no absorption at the pump wavelength of 390 nm. For CdS colloids alone [Fig. 2(a)], the transient spectra feature a very fast rise followed by a fast and a slow decay; it then levels off up to 1 ns, as confirmed by a separate long time scan. The data are fit to a single exponential rise and a *double exponential de-*

cay plus an offset, convoluted with a 200 fs Gaussian representing the laser pulse. The results fit well to a 100 fs exponential rise and a fast 2.5 ps exponential decay followed by a slower 50 ps exponential decay, plus an offset of 20% of the maximum absorbance change. The transient absorption has been assigned to trapped electrons at the liquid–solid interface of the CdS colloids and the double exponential decay has been attributed to geminate and nongeminate electron–hole recombination.[13,21] The initial fast rise indicates that the trapped electrons are formed with a time constant of <100 fs. The population reaches a maximum in 500 fs and then starts to decay. More than 50% of the initially generated population decays in less than 10 ps. This exceedingly fast electron–hole recombination suggests the need to develop techniques to lengthen the lifetime of the electron, so that it will proceed to participate in photoreactions rather than recombine with the hole. A detailed analysis of the data for CdS colloids alone has been reported previously.[13,21]

For the coupled colloids CdS–TiO$_2$ [Fig. 2(b)], the decay dynamics are significantly different from that of CdS alone. The experiments were repeated several times to ensure that the data were reproducible. The rise time for the CdS–TiO$_2$ colloids is about the same as in CdS alone, but the decay is much slower on the short time scale of <10 ps. The fast decay component is slowed down to about 4.0 ps. We attribute this slower decay to less efficient electron–hole recombination in CdS as a result of electron transfer from CdS to TiO$_2$, since once the electron is injected into TiO$_2$, the probability for recombination with the hole in CdS is much lower.[2] This argument is based on the assumption that the electron in the conduction band or trapped at the surface of TiO$_2$ has a similar absorption at 780 nm as that in CdS. This assumption is supported by the known similar red-infrared absorption of the electron in both CdS and TiO$_2$ colloids.[1,22–25] Since there has been no data available on the absolute cross sections of the trapped electrons in CdS or TiO$_2$ on the ultrafast time scales, the validity of this assumption remains to be verified. This interpretation is qualitatively consistent with the shorter fluorescence decay lifetime observed in CdS–TiO$_2$ in acetonitrile than that in CdS alone.[2] The fact that the early time dynamics are affected more than the longer time dynamics also suggests that the electron transfer must be very fast, most likely in less than 10 ps. The rate, not the amplitude, of the slower 50 ps exponential decay, attributed to geminate electron–hole recombination,[13] was almost unchanged in the coupled colloids compared to CdS alone (Fig. 2). The rapid nature of the electron transfer process also indicates that the transfer occurs between CdS and TiO$_2$ particles that are in close proximity or attached and that the transfer is not diffusion controlled.

In order to obtain an estimate of the rate constant of electron transfer from CdS to TiO$_2$ in this coupled colloidal system, we use a simple kinetic model to extract the time constant from the fast decay component. The fast decay, which has been attributed to nongeminate electron–hole recombination in CdS,[13] has a time constant of about 2.5 ps for CdS alone [Fig. 2(a)]. This decay is slowed down to about 4 ps in the coupled CdS–TiO$_2$ system (assuming a single exponential). As mentioned above, we attribute the slowdown

of this decay to electron transfer from CdS to TiO$_2$. If the decays due to electron–hole recombination and electron transfer are both assumed to be first order and if the absorptions of the electron at the 780 nm probe wavelength are assumed to be the same in CdS and TiO$_2$, we can derive a simple equation for the total population of the electrons (N_e) in CdS and in TiO$_2$ as follows:

$$N_e = N_e^0 \{ k_2/(k_1+k_2) + [k_1/(k_1+k_2)]$$
$$\times \exp[-(k_1+k_2)t] + c \}, \qquad (1)$$

where N_e^0 is the initial population of the electrons produced by photoexcitation of CdS at 390 nm, c is an offset used to account for the longer time decays (50 ps plus offset), and k_1 and k_2 are the rate constants corresponding to electron–hole recombination and electron transfer from CdS to TiO$_2$, respectively, and are related to the corresponding decay time constants τ_1 (electron–hole recombination) and τ_2 (electron transfer) through $k_1 = 1/\tau_1$ and $k_2 = 1/\tau_2$.

This simple model gives a reasonable fit of the decay profile for CdS alone with a time constant of $\tau_1 = 2.5$ ps for electron–hole recombination when there is no electron transfer to TiO$_2$, i.e., the rate constant $k_2 = 1/\tau_2 = 0$. For the coupled system, while keeping the time constant for electron–hole recombination as 2.5 ps, we found that a time constant of 2 ps for electron transfer provides a good fit to the major features of the decay profile. Even though this calculation is very rough, especially considering that the first order assumption about the electron–hole recombination may not be valid, it does provide an estimate of the time scale for electron transfer from CdS to TiO$_2$. This conclusion is consistent with the earlier suggestion of a transfer rate of <20 ps based on the picosecond fluorescence study by Kamat et al.[2] An attempt to fit the data using a second order process for the electron–hole recombination did not produce an analytical solution for the population of the electrons, making it difficult to obtain a simple physical understanding of the problem. More sophisticated computer simulations may help to gain further insight into this issue.

The concentration ratio between CdS and TiO$_2$ in the above experiment is about 0.06–2.0 mM (1 to 33). For a fixed concentration of 0.06 mM for CdS, the observed fast decay becomes slower as the TiO$_2$ concentration increases from 1.0 to 2.0 mM. At a TiO$_2$ concentration of 1.0 mM or less, no significant change in the dynamics was observed. The reason for this is not quite clear, however, it is consistent with the observation in the nanosecond fluorescence quenching experiment that "strong effects were observed when the concentration of TiO$_2$ particles substantially exceeded that of the CdS particles."[5] One possible explanation is that the particle size of TiO$_2$ (120 Å) is much larger than that of CdS (40 Å), a higher TiO$_2$ concentration is needed in order to have a similar number of particles for each colloid. Assuming similar crystal structure for CdS and TiO$_2$, a simple argument based on volume would suggest that the TiO$_2$ concentration needs to be 27 times that of CdS in order to have a particle ratio of 1:1. This is actually close to the concentration ratio of 33 to 1 for TiO$_2$ to CdS used in the current experiment. Attempts to use an even higher concentration of TiO$_2$(>2

mM) produced an unstable coupled colloidal system due to the instability of TiO_2 at high concentration at the $pH=8-10$ used.

This study strongly indicates that more efficient charge separation can be achieved in a coupled $CdS-TiO_2$ system, as suggested before.[2] Since CdS has reasonably strong absorption in the visible region and TiO_2 is a readily available material, there is a great potential for building a photoelectrochemical system based on this coupled colloidal semiconductor system, which is essentially a nanoelectrode. The separation of the electrons and holes into two different colloidal particles enhances the opportunity for carrying out efficient reduction and oxidation reaction separately. The recent development in dye photosensitization of TiO_2 in Gratzel's group presents another interesting approach for manipulating the charge transfer mechanism of photocatalytic systems.[26–28] However, the coupled semiconductor system is more attractive since there are indications that the charges injected into TiO_2 from CdS live longer than that originating from dye molecules[2] and that sensitization using quantum colloidal particles such as CdS has less photodegradation.[3] Another attractive feature with sensitization using quantum colloidal semiconductors such as CdS is that the absorption range is adjustable with the particle size due to the quantum size confinement effect.[3,16–20] A direct probe of the charge injection process of dye sensitization will help to better evaluate the advantages and disadvantages of these two different approaches and the study of dye sensitization is currently in progress.

IV. CONCLUSION

In summary, we have performed direct femtosecond measurements of the electron transfer process from CdS to TiO_2 particles in a coupled colloidal system. The electrons initially created in the conduction band and trapped at the liquid–solid interface of aqueous CdS colloids are found to be transferred to the colloidal TiO_2 particles with a time constant of about 2 ps. This results in significantly slower electron–hole recombination due to better separation of the charge carriers into two different colloidal particles. These coupled semiconductor colloids are potentially useful in developing efficient photoelectrochemical systems for solar energy conversion as well as for other heterogeneous photoreactions.

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