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Modulation of Electron Injection in CdSe−TiO$_2$ System through Medium Alkalinity

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Photosensitization of TiO$_2$ nanostructures with semiconducting quantum dots is useful in the development of all inorganic type solar cells.[1,2] Previous studies have shown that the charge injection from excited CdSe nanocrystals into TiO$_2$ can be tuned by controlling the CdSe particle size.[3] Decreasing the particle diameter increases the driving force for the charge injection as the energy difference between the two conduction bands increases. For example, decreasing the particle diameter of CdSe from 7.5 to 2.8 nm resulted in a 3 orders of magnitude increase in the charge injection rate.

An alternate way to modulate the energy difference between CdSe and TiO$_2$ conduction bands is to tune the band edge of TiO$_2$. Since it is difficult to obtain quantized TiO$_2$ particles with varying size (particle diameter less than 1 nm), one needs to seek alternate means to tune the conduction band edge of TiO$_2$.[4,5] It has been established earlier that the pH-induced protonation of surface groups is useful to shift the band edges of TiO$_2$ (a Nernstian shift of 59 mV/pH unit).[6,7] The band edges shift to more negative (vs. NHE) potentials with increasing pH. Prior study on a dye sensitized TiO$_2$ surface has shown that the oxidation potential of the dye itself changes with pH upon complexation with the surface; therefore it does not induce a major energy difference between the band edge of TiO$_2$ and the excited state oxidation potential of the dye.[8] In this regard, CdSe passivated with hydrophobic functional groups such as trioctyl phosphine oxide (TOPO) is useful as it renders the semiconductor surface insensitive to pH. Thus, any change in the solution pH only affects the energetic band position of TiO$_2$. We have now capitalized on this ability to tune the band edge of TiO$_2$ and established the importance of energy gap on the charge injection process between excited CdSe and TiO$_2$. Here, we discuss modulation of the emission response of the CdSe−TiO$_2$ system in the pH range 5−12.

Nanostructured TiO$_2$ and SiO$_2$ films were prepared on fluorine-doped tin oxide (FTO) glass slides using respective colloidal nanoparticle suspensions. TOPO-capped CdSe quantum dots (3.5 nm in diameter) in toluene were prepared using a previously reported procedure.[9] See Supporting Information (SI) for more details on the deposition of CdSe nanoparticles on TiO$_2$ and SiO$_2$ films. Fluorescence spectra were recorded using a 1 cm quartz cuvette that has provision to flow water of desired pH. All measurements were done by placing the films at 45° angle between the excitation source and the detector.

Figure 1A shows the emission spectra of 3.5 nm CdSe nanocrystals deposited on TiO$_2$ films that are in contact with solutions of three different pH values. While the TOPO-capped CdSe deposited on SiO$_2$ substrate show little or no dependence (see Figure S2 in SI), we observe an increase in CdSe emission on TiO$_2$ substrate as we increase the pH. As shown earlier, SiO$_2$ is an inert substrate and does not directly influence the radiative recombination process in CdSe.[10] On the other hand, the TiO$_2$ substrate participates in a charge transfer interaction with excited CdSe. The fact that we observe an increased emission with increasing medium pH only in the case of TiO$_2$ indicates that this effect is likely to arise from the altered rates of charge transfer. Interestingly, this change in the emission response is reversible if we allow enough time to equilibrate with the solution of different pH. Figure 1B shows the emission response monitored at 560 nm of CdSe−TiO$_2$ film during the flow of solution of varying pH through the cell. The prompt response of the CdSe emission to the pH of the medium as well as its reversibility opens up the possibility of using CdSe−TiO$_2$ systems for sensing medium pH. Unlike previous work, the present work does not employ dye or Förster resonance energy transfer (FRET mechanism) for sensing of pH.[11]

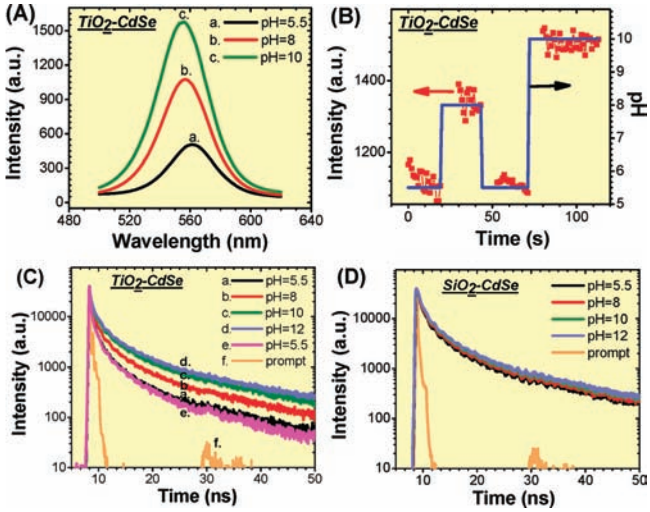

Figure 1. (A) Emission spectra and (B) emission response of CdSe on TiO$_2$ film at three different pH values. Distilled water was flowed through the cell before changing pH. (C and D) Emission lifetime response of CdSe on TiO$_2$ and SiO$_2$ films at varying pH.

We further probed the influence of pH on the charge injection process by monitoring the emission decay of CdSe−TiO$_2$ and CdSe−SiO$_2$ films submerged in an aqueous solution of known pH (Figure 1C and D). The emission of CdSe−TiO$_2$ film exhibits slower decay with increasing pH and, thus, confirms a longer radiative lifetime in alkaline pH. The emission decay exhibited a relatively smaller variance in the same pH range for CdSe−SiO$_2$ films. We also further confirmed the reproducibility of the emission decay response to pH by comparing the emission−time profile at pH 5.5 before and after exposure to a solution of pH 12 (traces a and e in Figure 1C, respectively). Trace e was recorded after washing the TiO$_2$ films with a copious amount of distilled water. The similarity of the emission decay lifetimes further confirms the reproducibility of the pH effect on the radiative recombination of CdSe deposited on TiO$_2$ film.

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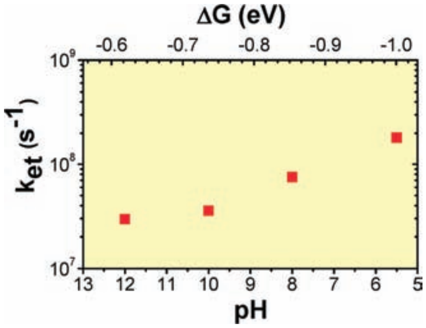

Figure 2. Dependence of electron injection rate constant, k_{et}, on the pH for a TiO_2−CdSe film (see SI for analysis).

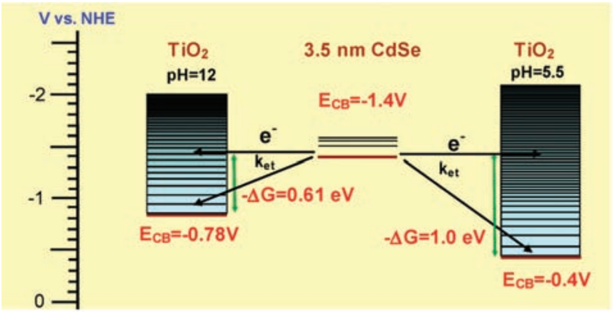

Figure 3. Scheme illustrating the electron injection processes from CdSe band edge to TiO_2 nanoparticle conduction band at two different pH conditions.

The emission decay was analyzed by a three exponential fit. The kinetic parameters are summarized in the Supporting Information (Table S1). The average lifetime of CdSe−TiO_2 film increased nearly 2-fold (from 3.17 to 6.20 ns) as we increased the pH from 5.5 to 12. Under similar experimental conditions, CdSe quantum dots attached to SiO_2 exhibit little variation in the average emission lifetime (6.84−7.58 ns). The change in average lifetime agrees with the trend observed with the emission yield (Figure 1A). On SiO_2 substrate, the CdSe quantum dots are nonresponsive to pH since radiative charge recombination is the only dominant process. However, on the TiO_2 semiconductor surface the electron transfer to TiO_2 competes with charge recombination and its dependence on pH causes the emission to vary.

As shown earlier,[10] we can use the average lifetime of the CdSe emission on SiO_2 and TiO_2 substrates to obtain an apparent electron transfer rate constant (k_{et}). The k_{et} values determined at different pH values are plotted in Figure 2. See Table S2 in the SI for details. A nearly 5-fold increase in the apparent electron transfer rate constant is seen upon decreasing the pH from 12 to 5.5.

Figure 3 shows the energy levels of CdSe and TiO_2 at two different pH values. The value of the conduction band edge of TiO_2 at pH 12 and 5.5 is assumed to be −0.78 and −0.4 V vs NHE, respectively.[7] For 3.5 nm diameter CdSe colloids, the conduction band is assumed to be −1.4 versus NHE.[12] The band energies of TOPO-capped CdSe dots are independent of pH while the conduction band of TiO_2 shifts to more negative potentials with increasing pH. As a result of this altered energetics of the CdSe−TiO_2 system, we anticipate a decreased band energy difference to retard the rate of electron transfer from CdSe to TiO_2. For pH 5.5 and 12 this energy difference ($-\Delta G$) decreases from ~1.0 to ~0.61 eV and a drop in the rate constant of 2×10^8 s^{-1} to 3×10^7 s^{-1} occurs respectively. The increased rate constants with decreasing pH further supports our earlier argument[3] that the energy difference between the conduction bands of CdSe and TiO_2 is important to attain an efficient charge injection process, and hence higher photoconversion efficiency. The modulation of the energy difference between conduction bands of CdSe and TiO_2 was achieved through size quantization.[3] In the present study we varied the energy difference by varying the band energy of TiO_2 by means of medium pH while maintaining the same size of quantum dot.

According to Marcus theory,[13−15] for a nonadiabatic reaction in the activation limit, the rate of electron transfer depends on the electronic coupling between the donor and acceptor states, the density of states (DOS) per unit volume, and the driving force, which is the Gibbs free energy difference ($-\Delta G$) between the two states. Hence, as the driving force increases, the rate of charge transfer also increases until it reaches a maximum when the driving force is equal to the reorganizational energy. Because of the quasi continuum of states in the TiO_2 conduction band, the total electron transfer rate depends on the sum of all possible electronic transitions. Lian and co-workers have calculated the DOS dependent k_{et} for Re-bipyridyl complexed to TiO_2 and shown that electron transfer rate modulation per unit pH is greatest near the band edge and becomes nearly invariant for $\Delta G > 1$ eV.[16] Our experimental data are consistent with their observation. At lower pH, the greater availability of DOS is likely to make the electron transfer more efficient. Preliminary measurements on CdSe−TiO_2 films at different pH values using femtosecond transient absorption spectroscopy show a trend similar to that for the emission decay results (see Figure S6). Efforts are currently underway to probe these processes at different excitation wavelengths and elucidate the role of DOS in the charge injection process.

The ability to promote the charge injection from excited CdSe into TiO_2 has important implications in the design of quantum dot sensitized solar cells. The results presented here demonstrate the modulation of the charge injection process by means of solution pH. The reversible emission response of the CdSe−TiO_2 system to solution pH is also of interest in monitoring solution alkalinity.

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Supporting Information Available: Experimental details, emission spectra of CdSe on silica, and emission lifetime analysis are presented. This material is available free of charge via the Internet at http://pubs.acs.org.

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