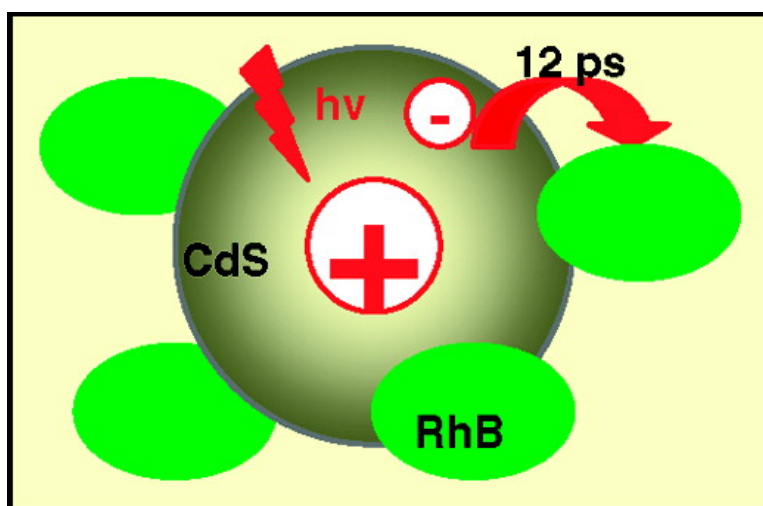## Communication

Ultrafast Charge Separation at CdS Quantum Dot/Rhodamine B Molecule Interface

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Ultrafast Charge Separation at CdS Quantum Dot/Rhodamine B Molecule Interface

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Multiple exciton generation,[1,2] a process by which an absorbed photon generates multiple excitons (electron−hole pairs), was reported recently in a series of semiconductor quantum dots (QDs).[3,4] This process allows for over 100% quantum efficiency in generating electron−hole pairs, providing a potential way for dramatically improving the solar-to-electric power conversion efficiency in QD-based solar cells.[5] The next major technical advance that enables the realization of this potential is the separation of the electron−hole pairs before the exciton−exciton annihilation processes, which occurs on the 10s−100s picosecond (ps) time scale for many QDs.[6] Previous studies have reported that excitons in QDs could dissociate by either electron or hole transfer, although the factors that control the dissociation pathways and rates remain not well understood.[7] In this Communication, we demonstrate ultrafast dissociation of excitons in CdS QDs via electron transfer (ET) to adsorbed rhodamine B (RhB) molecules on the 10 ps time scale. Furthermore, we show that the charge separation rate can be controlled by the number of adsorbates attached on the nanoparticle. The rapid and controllable charge separation in this model QD−adsorbate complex provides a potential approach for separating multiple excitons generated by the MEG process.

The CdS−RhB complex was chosen for this study because of its well-separated spectral signatures and appropriate redox potentials. As shown in the inset of Figure 1a, RhB (with reduction and oxidation potentials of −0.8 V and +1.2 V (vs SCE), respectively[8]) can act as both electron and hole acceptors. Its strong and distinct absorption bands in ground, excited, reduced, and oxidized states allow for an unambiguous probe of the exciton dissociation pathways.[8] Treating the QD as a spherical well with infinite potential barrier, the energy of the lowest exciton state (E_{CdS*}), a bound pair of 1S electron in the conduction band (CB) and 1S hole in the valence band (VB), is given by[9]

$$E_{CdS*}[1s_e, 1s_h] = E_g + \frac{\hbar^2 \pi^2}{2R^2}\left[\frac{1}{m_e^*} + \frac{1}{m_h^*}\right] - \frac{1.8e^2}{4\pi\epsilon_0\epsilon R} \quad (1)$$

where E_g is the bulk bang gap, R is the radius of the QD, and m_e^* and m_h^* are the effective masses of electrons and holes. The second and third terms are the confinement energy of the 1S electron and 1S hole, respectively, and fourth term results from electron−hole coulomb attraction. Adopting $m_e^* = 0.2m_0$ (m_0 is the free electron rest mass), $m_h^* = 0.8m_0$, $\epsilon = 5.4$, $E_g = 2.42$ V,[20] a CdS QD with the first exciton peak at 386 nm has an estimated radius of 1.45 nm. Following the model of Brus,[9] we estimated an excited-state oxidation potential (CdS*[1s$_e$,1s$_h$] → e + CdS$^+$[1s$_h$]) of −1.27 V(SCE) and reduction potential (CdS*[1s$_e$,1s$_h$] → h + CdS$^-$[1s$_e$]) of +1.61 V(SCE), shifted from the corresponding bulk CB (−0.7 V SCE) and VB (+1.72 V vs SCE) flat band potentials.[10]

CdS QDs were synthesized by established literature procedure.[11] Figure 1a shows the absorption spectrum of these QDs in heptane.
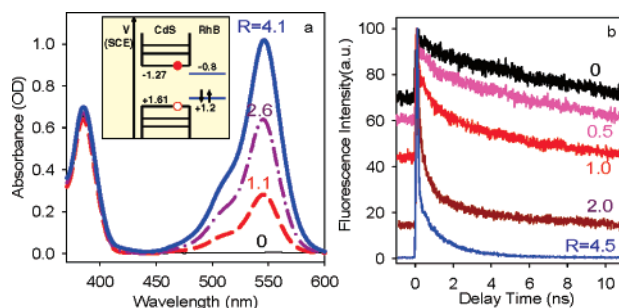

Figure 1. (a) UV−vis absorption spectra of CdS QDs and QD-Dye assemblies of indicated dye/QD ratios (*R*). The inset shows the redox potentials of RhB and CdS QDs. (b) Fluorescence decay for CdS−RhB nanoassembly in heptane with indicated RhB/QD ratios. The samples were excited at 400 nm, and their emissions in the 415−450 nm region were measured by time-correlated single photon counting.

QD-dye assemblies with different concentration ratios were prepared by adding different amounts of dye to the QD solution followed by sonication and filtration to remove undissolved dyes. Since RhB is not soluble in heptane, all dissolved dyes are believed to be bound with CdS QDs. This was confirmed by the observation of ca. 8 ns RhB fluorescence anisotropy decay in the RhB/CdS/heptane sample (see figure S1), which is much slower than that of free RhB in ethanol (0.2 ns).[12] The spectra of the CdS−RhB complex can be well reproduced by the sum of the spectra of CdS (<400 nm) and RhB (>450). The average number of the adsorbed RhB per QD particle was calculated on the basis of the measured absorbance and known extinction coefficients of RhB (ϵ_{543} nm = 106 000 M^{-1} cm^{-1})[13] and CdS (ϵ_{386} nm = 280 000 M^{-1} cm^{-1}).[14]

Because RhB molecules have negligible absorption at 400 nm, illumination of the CdS QD−RhB complex at this wavelength selectively excites the QDs, generating 1S$_{3/2}$(h)−1S(e) excitons.[6] The interaction of adsorbed RhB with CdS QDs can be monitored by their effect on exciton lifetime, which was measured by time-correlated single photon counting of the QD emission between 415 and 450 nm. As shown in Figure 1b, at low RhB ratio, the exciton is long-lived, similar to that of CdS in heptane (~42 ns). The exciton lifetime decreases as the number of adsorbed RhB molecules increases, suggesting the quenching of excitons in CdS by the RhB molecules.

There are three possible pathways for the quenching of QD excitons by the adsorbate: (1) ET from QD CB to the unoccupied molecular orbitals of RhB, producing a reduced RhB (RhB$^-$) and a hole in the QD; (2) hole transfer from VB of QD to the occupied molecular orbital of RhB (or ET from RhB to VB of QD), producing an oxidized RhB (RhB$^+$) and an electron in the QD CB; and (3) energy transfer from QD to RhB, producing an excited RhB (RhB*) and QD in its ground state. All three quenching pathways reduce the lifetime of excitons and cannot be differentiated by the fluorescence measurement alone. However, these processes produce
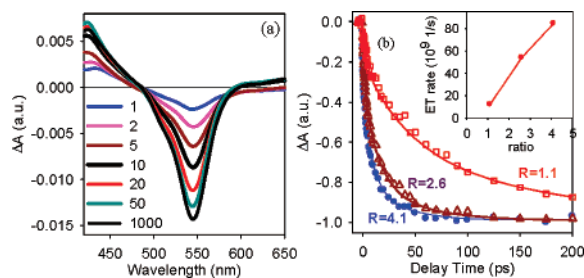
Figure 2. (a) Transient absorption spectra of RhB−CdS nanoassembly (ratio of RhB/CdS = 2.6) recorded at indicated delay times (in units of picoseconds) following 400 nm excitation. (b) Transient bleach formation (at 545 nm) kinetics of CdS−RhB assembly with indicated dye/QD ratio. Solid lines are fits to biexponential rise function (see table S1). The signal size has been normalized for better comparison. The inset shows the charge separation rate as a function of the dye/QD ratios.

different transient products (i.e., reduced, oxidized, and excited RhB, respectively) that have distinct transient visible absorption bands.[8]

The transient absorption spectra of sample with dye/QD ratio (R) of 2.6 recorded at delay times up to 1 ns after 400 nm excitation are shown in Figure 2a. The spectra at all delay times consist of two features, the ground-state bleach of RhB at 545 nm and an absorption band peaked at ∼425 nm, which are separated by a clear isosbestic point at 482 nm. In addition, as shown in Supporting Information Figure S2, the kinetics of these features (probed at 435 and 545 nm, respectively) show identical rates, indicating the conversion of ground-state RhB molecules to the new absorbing species at ∼425 nm as a result of QD excitation. The spectra of the bleach agree well with the UV−visible spectra of the RhB adsorbed on CdS. The lack of RhB stimulated emission (∼600 nm) and excited-state absorption (∼450 nm[8]) indicates the absence of excited RhB molecules, which excludes the possibility of both energy transfer from CdS to RhB or direct excitation of RhB by the pump pulse at 400 nm. The pathway of hole transfer from QD VB to RhB can also be ruled out because its product, oxidized RhB (absorption peak at 500 nm[8]), was not observed in the transient spectra. The absorption band at ∼425 nm can be assigned to that of one-electron reduced RhB, whose absorption band was reported at ∼420 nm.[8] These results suggest that excitons in CdS QDs dissociate by ET from CdS CB to the unoccupied orbitals of RhB, forming a reduced RhB:

$$\text{CdS*}(1S_e, 1S_h) + \text{RhB} \xrightarrow{k_S} \text{CdS}^+(1S_h) + \text{RhB}^- \quad (2)$$

Two other samples with a RhB/CdS ratio of 1.1 and 4.1 were also studied under the same condition. The transient spectra of these samples, shown in Figure S3 and S4, are similar to the sample with ratio of 2.6 (Figure 2a). They consist of an absorption band centered at ∼425 nm, a bleach of RhB ground-state absorption centered at 545 nm, and an isosbestic point at 482 nm, suggesting that QD excitons in these samples also dissociate by ET from CdS CB to RhB. The rate of the charge separation process, k_s, can be measured by monitoring the growth of the ground-state bleach. Shown in Figure 2b is a comparison of the kinetics monitored at the center of the ground-state bleach in these samples, showing that the charge separation rate increases with the number of adsorbed RhB molecules per QD, consistent with the fluorescence quenching measurement shown in Figure 1b.

The kinetics in Figure 2b can be well fit by a tri-exponential rise function. The parameters for these fits are shown in Table S1, from which the amplitude-weighted average time constants were

calculated. The average charge separation times are 90, 19, and 12 ps for samples with RhB/CdS ratios of 1.1, 2.6 and 4.1, respectively. The average charge separation rate increases with the number of adsorbates per QD, as shown in the inset of Figure 2b. In all cases, the lifetime of the charge separated state [CdS($1s_h$) + RhB$^-$] is much longer than 1 ns, as indicated by the lack of bleach recovery on this time scale.

Transient absorption spectra of RhB on a larger size CdS (first exciton peak at 446 nm, estimated radius of 1.95 nm, shown in Figure S5) measured under similar conditions show much smaller bleach of RhB ground state, suggesting much slower ET to RhB than the smaller CdS QDs (radius of 1.45 nm). The observed faster ET from the smaller CdS can be attributed to the quantum confinement effect, which increases the energy of its 1s electrons and the ET driving force. The latter is estimated to be −0.5 V for the smaller QDs, significantly higher than that of −0.1 V for the larger QDs.[9] It is interesting to note the lack of hole transfer on the <1 ns time scale in these samples, despite sufficient driving force (ca. −0.4 V) for this process.

In conclusion, we have shown that in the CdS QD (386 nm)-RhB complex, excitons in QDs dissociate by electron transfer to RhB molecules. The electron-transfer rate increases with the number of adsorbed RhB molecules on the QD. The transfer time is about 12 ps in QDs with an average of 4.1 adsorbed RhB molecules. This time is similar to and shorter than the lifetime of multiexcitons observed in some quantum dots,[6] suggesting the possibility of separating multiple excitons before the exciton−exciton annihilation process.

Supporting Information Available: Experimental methods and fluorescence anisotropy, transient spectra and kinetics of RhB/CdS. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0773406