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Photodriven Charge Separation Dynamics in CdSe/ZnS Core/Shell Quantum Dot/Cobaloxime Hybrid for Efficient Hydrogen Production

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Supporting Information

ABSTRACT: Photodriven charge-transfer dynamics and catalytic properties have been investigated for a hybrid system containing CdSe/ZnS core/shell quantum dots (QDs) and surface-bound molecular cobaloxime catalysts. The electron transfer from light-excited QDs to cobaloxime, revealed by optical transient absorption spectroscopy, takes place with an average time constant of 105 ps, followed a much slower charge recombination process with a time constant of ≫3 ns. More interestingly, we also observed photocatalytic hydrogen generation by this QD/cobaloxime hybrid system, with >10 000 turnovers of H_2 per QD in 10 h, using triethanolamine as a sacrificial electron donor. These results suggest that QD/cobaloxime hybrids succeed in coupling single-photon events with multielectron redox catalytic reactions, and such systems could have potential applications in long-lived artificial photosynthetic devices for fuel generation from sunlight.

Direct sunlight-to-fuel conversion offers one of the best solutions for meeting long-term global energy demands. Inspired by natural photosynthesis, current solar fuel research involves developing systems to capture and convert solar energy and store it in the form of chemical bonds in small, energy-dense molecules, such as hydrogen.[1−3] A technologically significant solar driven H_2 production system requires not only efficient and long-lasting functional sites for light-harvesting, charge transport, and redox reactions but also minimal reliance on sacrificial donors and acceptors. Inspired by natural photosynthesis, a number of synthetic systems designed toward such an ideal model use single chromophores for both light-harvesting and electron-transfer (ET) functions, but most of these systems suffer from inefficient coupling of single-photon/electron events with multielectron redox reactions necessary for fuel generation (i.e., hydrogen from water and hydrocarbons from CO_2).[4] Therefore, new systems for solar fuel generation must be able to accumulate and transfer *multiple* electrons and/or holes to catalytic sites. Quantum dots (QDs) have high extinction coefficients across a broad spectral range in the solar spectrum, and hence QDs can simultaneously absorb multiple photons, or continuously absorb multiple photons even after electrons or holes are accumulated, and can link catalysts directly onto the surface via appropriate functional groups.[5−7] These characteristics make QDs superb candidates to fulfill multiple functionalities required in solar fuel generation as photosensitizers, electron/hole accumulation sites, and electron donors when they are properly coupled to efficient catalysts for H_2 generation. For these reasons, there is significant interest in developing new light-driven systems using QDs as light-harvesting materials for H_2 generation. To date there have been only a handful of published studies employing QDs in H_2 production systems,[8−12] and the fundamental charge-transfer dynamics as well as the detailed reaction pathways in these systems remain unclear. Here we report photoinduced ET dynamics and light-driven H_2 production activities of a new hybrid photocatalytic system containing CdSe/ZnS core/shell QDs functionalized with a molecular cobaloxime catalyst.

The core/shell CdSe/ZnS QDs were used as photosensitizers, which are preferable for photocatalysis applications over the more common CdSe QDs because the ZnS shell dramatically enhanced photostability[13] and fluorescence quantum yields[14,15] of the QDs compared to those without the shell. The molecular cobaloxime catalyst was chosen since they are among the best transition metal complexes known for H_2 production, tolerant to oxygen,[16] readily synthesized,[17,18] and composed of earth-abundant elements. In this study, we have anchored the cobaloxime catalyst molecules to the surface of CdSe/ZnS QD via a phosphonate linkage[19] (Figure 1a inset). Details of synthesis and QD/cobaloxime functionalization are described in the Supporting Information (SI). Two-electron reduction of the starting cobaloxime (Co^{III}) is necessary to initiate the catalytic cycle for H_2 generation.[20]

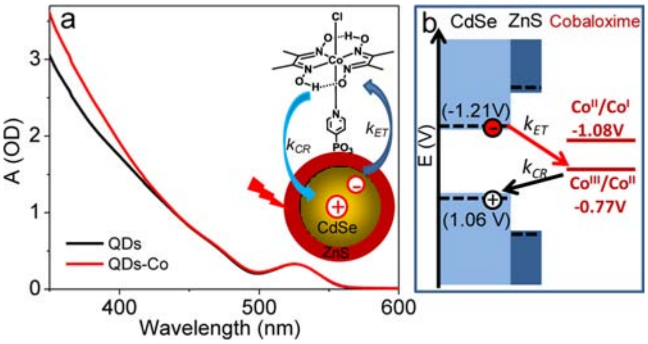

Figure 1. (a) UV−vis absorption spectra of CdSe/ZnS core/shell QDs with (red) and without cobaloxime (black). The inset depicts an idealized photoinduced charge separation process from CdSe/ZnS core/shell QDs to cobaloxime catalyst. (b) Energetic diagram of CdSe/ZnS core/shell QDs and cobaloxime hybrid.

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The estimated reduction and oxidation potentials of the QDs in the 1S exciton state are −1.21 and 1.06 V (vs SCE), respectively,[21−23] and the reduction potentials of the functionalized cobaloxime in this study are approximately −0.77 V vs SCE for $Co^{III} \rightarrow Co^{II}$, and −1.08 V vs SCE for $Co^{II} \rightarrow Co^{I}$.[18] These values give an estimated Gibbs free energy change $\Delta G°$ for the first and second step ET from the excited QDs to cobaloxime to be −0.44 eV and −0.13 eV, respectively, which makes the multistep photoinduced ET thermodynamically possible for H_2 generation in this catalyst system.

The UV/vis spectra of CdSe/ZnS core/shell QDs in toluene with and without cobaloxime (Co^{III}) (Figure 1a) show the first exciton (1S) peak of the QDs only solution at 525 nm (black). While the same exciton band is essentially unchanged in the QDs/cobaloxime hybrid solution (red), an additional absorption feature below 400 nm appears due to the cobaloxime absorption. Because cobaloxime (Co^{III}) is insoluble in toluene, the additional absorbance below 400 nm is due to the cobaloxime adsorbed directly onto the QDs. From the measured absorbance and the approximate extinction coefficients of cobaloxime and QDs,[24] we estimated a maximum average surface coverage of 66 cobaloxime on each QD (Figure S5).

The dynamics of the excited QDs and the ET to surface bound cobaloxime catalysts are characterized by transient absorption (TA) spectra under the excitation of 415-nm light. The TA spectra of CdSe/ZnS core/shell QDs (Figure 2a) show bleaches of the 1S (525 nm) and 1P (475 nm) exciton transitions at different delay times as well as a red-shifted absorption feature at early delay times due to the carrier-induced Stark effect.[25,26] The 1S exciton bleach recovers only by <30% within 3 ns, suggesting that most excited QDs have one exciton[27,28] with a long lifetime (≫3 ns). In contrast, the TA spectra of CdSe/ZnS/cobaloxime (Co^{III}) hybrid show nearly 95% of the bleach recovery within the delay time of 3 ns (Figure 2b). Because of the Pauli exclusion principle, the filling of the additional electrons to the 1S level in the conduction band leads to the bleach of the 1S exciton band.[25,29] Therefore, the faster recovery of the 1S exciton bleach in the QDs/cobaloxime hybrid system suggests a fast 1S electron depopulation dynamics. Although the TA spectra of the hybrid system within 10 ps delay times are characteristic of the exciton band bleach, a distinct absorption feature in the 440−450 nm region appears after 100 ps delay time (Figure 2b inset), which resembles the absorption feature of the reduced cobaloxime (Co^{II}).[18] Moreover, the TA spectra of the hybrid system show clear redshifts in the bleach band peak with increasing delay. This spectral feature is similar to those observed in the other QD-acceptor complexes in the presence of charge separated state and can be attributed to the Stark effect induced exciton band shift,[30−33] further supporting the formation of $QD^{+}-Co^{II}$ charge-separated state. These spectral features all indicate that at least the first step of reduction from Co^{III} to Co^{II} has been successfully phototriggered via ET from QD to cobaloxime catalyst.

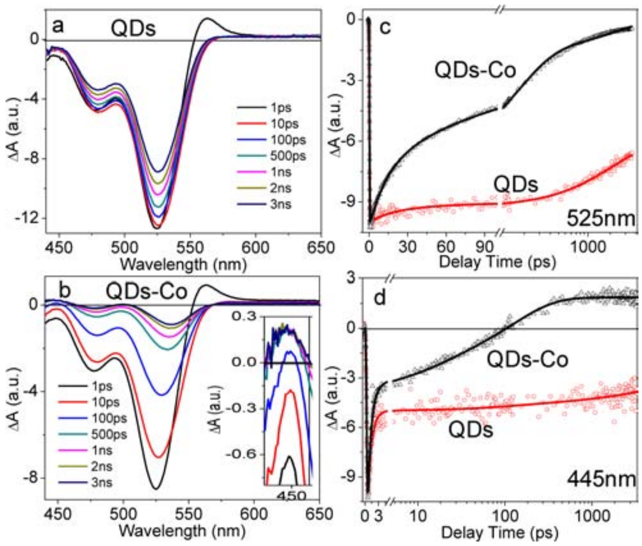

Figure 2. Femtosecond transient absorption spectra of (a) CdSe/ZnS core/shell QDs and (b) CdSe/ZnS core/shell QDs/cobaloxime hybrid in toluene at indicated delay times after 415 nm excitation. The inset shows the expanded view of the same TA spectra of QDs/cobaloxime in 430−460 nm region. (c) Comparison of the femtosecond TA kinetics of QDs excited state at 525 nm in free QDs (red open circle) and QDs/cobaloxime hybrid (black open triangle). (d) Comparison of the femtosecond TA kinetics at 445 nm in free QDs (red open circle) and QDs/cobaloxime hybrid (black open triangle).

Further evidence of the ET process from QDs to cobaloxime can be seen by comparing TA kinetic traces of QDs at 525 and 445 nm without and with surface bound cobaloxime molecules. The exciton bleach recovery kinetics (Figure 2c) of the QDs/cobaloxime hybrid (black triangle) at 525 nm show much faster recovery than that the QDs alone (red circle), suggesting an accelerated exciton dissociation kinetics. The TA signals at 445 nm in QDs/cobaloxime hybrid have contributions from both the exciton bleach of QDs and the absorption of cobaloxime (Co^{II}) reduced from the starting material which are clearly seen in Figure 2d as positive signals after 100 ps delay (black triangle). Based on our analysis, the TA kinetics at 445 nm are the superposition of the exciton bleach recovery of QDs during the first 100 ps and the rise of cobaloxime (Co^{II}) absorption thereafter. To quantify the ET rate, we fit the kinetics shown in Figure 2c according to eq 1,where $[QD^*](t)$ represents the

$$[\mathrm{QD}^*](t) = [\mathrm{QD}^*](0) \sum_{j} B_j \sum_{i} A_i \, \mathrm{e}^{-(k_{0j}+k_{i\mathrm{ET}})t} \tag{1}$$

concentration of excited QDs at time t, A_i and $k_{i\mathrm{ET}}$ are the ith amplitude and rate constant of ET process from QDs to cobaloxime, and B_j and k_{0j} are the jth amplitude and rate constant of intrinsic decay process in QDs without cobaloxime and have been predetermined by fitting the kinetics at 525 nm for the QDs sample without cobaloxime. Fitting the TA kinetics at 525 nm for the QDs/cobaloxime hybrid by eq 1, we obtained the amplitude-weighted ET time constant τ_a = 105 ps. The fitting parameters are listed in Table 1. Meanwhile, the kinetics of reduced cobaloxime (Co^{II}) at 445 nm in QDs/cobaloxime hybrid shows negligible recovery on the <3 ns scale, indicating a long-lived charge-separated state (≫3 ns). The fast charge separation rate coupled with slow recombination rate suggests potential utility of CdSe/ZnS core/shell QDs/cobaloxime hybrids in artificial photosynthetic devices. Ideally, one should also capture the dynamics of the second step ET process from the excited QDs to the already reduced cobaloxime (Co^{II}) to form Co^{I} species from which the catalytic H_2 generation takes place. However, the TA signal of Co^{I} species is too weak to be

Table 1. Fitting Parameters for Exciton Bleach Recovery Kinetics of CdSe/ZnS Core/Shell QDs with and without Cobaloxime

sample	k_{01}^{-1} (ps) (B_1, %)	k_{02}^{-1} (ns) (B_2, %)	$k_{1\mathrm{ET}}^{-1}$ (ps) (A_1,%)	$k_{2\mathrm{ET}}^{-1}$ (ps) (A_2,%)	τ_a (ps)
QDs	65 (10)	$\gg$3 (90)			
QD-Co			9 (27)	140 (73)	105

[a] A_i, $k_{i\mathrm{ET}}$, B_j, and k_{0j} (i,j = 1,2) are fitting parameters for eq 1. τ_a is the amplitude-weighted average lifetime.

used. Nevertheless, the hydrogen generation described below has proven multiple ET processes in the hybrid system.

With this promising display of photoinduced charge separation in the QD/cobaloxime hybrid, we proceeded to carry out photochemical hydrogen evolution experiments. Illumination of a toluene solution of the QD/cobaloxime hybrids with continuous and broadband visible light ($\lambda > 400$ nm) in the presence of triethylamine hydrochloride and triethanolamine (used as proton source and sacrificial donor, respectively; see SI for details) produced a significant quantity of H_2 gas. Control experiments that omitted either CdSe/ZnS core/shell QDs or cobaloxime catalyst yielded no appreciable amount of H_2, indicating that both components were essential for photodriven H_2 production. Figure 3 shows the H_2 production as a function of illumination time where an 2-h induction period was observed, which is consistent with previous reports and attributed to the multiple equilibriums for the conversion of Co^{III} to Co^{II} followed by a secondary ET from Co^{II} to Co^{I} for the proton reduction.[18] After a 10-h period of illumination, >10 000 turnovers of H_2 per QD were obtained, demonstrating the applicability of this hybrid system for solar-to-fuels conversion.

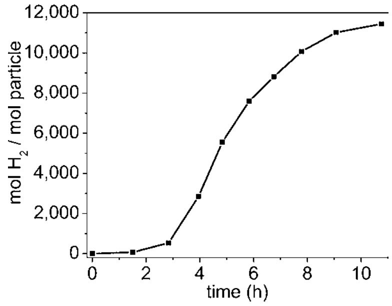

Figure 3. Time profile of H_2 production following illumination of CdSe/ZnS core/shell QDs/cobaloxime hybrids in toluene.

In order to investigate the reason(s) for the cease of H_2 generation after the 10-h illumination, we carefully replaced toluene by methanol in the reaction solution after photocatalysis to remove QDs in the solution. The resulting methanol solution after removing the QD precipitates shows very different absorption spectrum from that of the starting cobaloxime (Figure S2), suggesting the degradation of the catalyst during photocatalysis. Meanwhile, the morphology of the hybrid in solution was also investigated by TEM with EDS analysis before and after the photocatalysis (Figure S3), which revealed that no Co nanoparticles were formed during photocatalysis.[34] A blue-shift of the first exciton peak of QDs accompanied by a reduced intensity in higher energy exciton transition bands was observed in the UV/vis spectrum of the hybrid solution after photocatalysis (Figure S4), suggesting a decrease of the average QD size during photocatalysis due to photocorrosion of the QDs as reported previously.[35,36]

In summary, we have prepared a new photocatalyst system for H_2 generation by linking a known hydrogen generation catalyst, cobaloxime, to light-harvesting/electron-donating CdSe/ZnS core/shell quantum dots. The results of photoinduced electron transfer dynamics in this QDs/cobaloxime system reveal the QD exciton dissociation due to the ET to the cobaloxime catalysts with an average time constant of 105 ps, which is much faster than that for the charge recombination, resulting in long-lived catalytically active sites. Consequently, this hybrid system is capable of catalyzing H_2 generation photochemically in the presence of a proton source and a sacrificial electron donor. We therefore confirmed that (1) multiple photodriven redox equivalents have been successfully accumulated in the QDs, and (2) the accumulated redox equivalents have been successfully harvested by cobaloxime catalyst in the hybrid system through ET from excited CdSe/ZnS core/shell QDs to the surface-bound catalyst, reducing the Co^{III} ground state to Co^{II} and Co^{I} species and leading to hydrogen production. Undoubtedly, the ability of the QDs to store and donate *multiple* electrons to the adsorbed cobaloxime catalysts plays a key role in the H_2 photocatalytic efficiency. Future studies are aimed at examining core/shell QDs/catalyst hybrids that are active for H_2 photocatalysis in neutral water, fixing new QDs/catalyst hybrids to electrodes to remove the need for sacrificial donors, and characterizing structural dynamics of the catalyst during the H_2 generation with X-ray transient absorption spectroscopy.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Sample preparation, experimental setup, and data analysis procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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