

Photoinduced Charge Transfer between CdSe Nanocrystal Quantum Dots and Ru–Polypyridine Complexes

Milan Sykora,^{*,†} Melissa A. Petruska,[†] James Alstrum-Acevedo,[‡] Ilya Bezel,[†] Thomas J. Meyer,[‡] and Victor I. Klimov^{*,†}

Chemistry Division, Los Alamos National Laboratory, MS J567, Los Alamos, New Mexico 87545, and Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514

Received March 9, 2006; E-mail: sykoram@lanl.gov; klimov@lanl.gov

Ru–polypyridine complexes have been studied extensively with one point of interest being their possible inclusion in solar energy conversion schemes either as light sensitizers or as molecular catalysts. Utilization of Ru complexes in practical technologies requires that they are incorporated in or immobilized on surfaces of matrices or supports. For example, sensitization of high surface area nanocrystalline titanium dioxide (TiO₂) with Ru–polypyridine complexes has led to the development of a new class of photovoltaic cells.¹ Recently, Meyer and co-workers have shown that the oxidizing equivalents stored in a sensitizer following electron injection into TiO₂ can be used to activate a catalyst and ultimately drive oxidation of organic substrates.² In the photocatalytic assembly, a Ru catalyst was activated by a Ru-based sensitizer and TiO₂ semiconductor functioned as an electron transfer medium.

In this communication, we demonstrate a new approach to sensitization of Ru complexes by using semiconductor nanocrystal quantum dots (NQDs). NQDs of semiconductor materials with band gaps <2.5 eV (e.g., CdSe and CdTe) are well suited for applications as solar-light sensitizers. They have broad, size-controlled absorption spectra, large extinction coefficients, and their electronic structure can be size-tuned to optimize the driving force for charge transfer (CT) processes in coupled NQD/catalyst assemblies. Additionally, NQDs can respond to absorption of a single photon by generating up to seven excitons.³ If generated charges can be extracted rapidly, such large yields of charge carriers can be very useful in photocatalysis, especially for driving multielectron/multiproton chemical reactions.

Here we report studies of photoinduced CT between CdSe NQDs and a series of Ru–polypyridine complexes (Scheme 1) in solution. The Ru complexes and NQDs were prepared by established literature procedures.^{4,5} The mean NQD radius and the NQD size dispersion were 2.3 nm and ~5%, respectively, as calculated from absorption spectra.⁶ The room temperature photoluminescence (PL) quantum efficiency of the NQDs was ~5%. NQD/complex mixtures were prepared by mixing stock solutions of the NQDs and the complexes in benzonitrile. Control solutions were prepared by appropriate dilution of stock solutions.

Figure 1 shows emission spectra of the mixture of the CdSe NQD with complex **3** at various times following the mixing of stock solutions. Emission features due to NQDs and complex **3** are observed as distinct maxima at 614 and 673 nm, respectively. Both features decrease in intensity with time upon mixing.

The emission from the NQDs is completely quenched within hours following the mixing with less time required for higher complex/NQD ratios. At low concentrations of the NQDs and complexes used in this study, the quenching is likely not collisional in nature. Rather, it is attributed to gradual adsorption of the complexes onto the NQD surface. This is consistent with the observed increase in quenching over time. As shown in the inset

Scheme 1^a

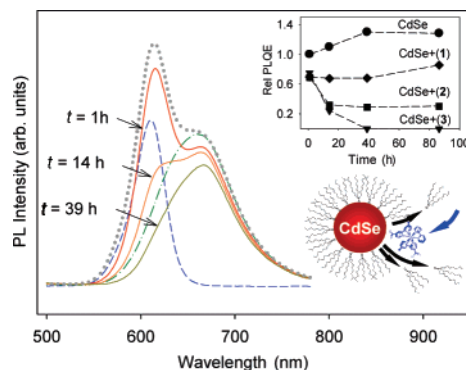
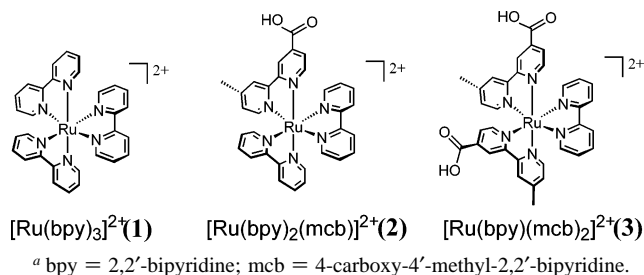


Figure 1. Room temperature, steady-state PL spectra of CdSe NQDs with [Ru(bpy)(mcb)₂]²⁺ (**3**) in benzonitrile (excitation at 400 nm). The concentrations of NQDs and metal complexes are $\sim 5 \times 10^{-7}$ and $\sim 5 \times 10^{-5}$ M, respectively.⁷ The solid lines are the spectra of the NQD/**3** mixture at different times after mixing. The dashed line shows the emission spectrum of CdSe NQDs, and the dash–dotted line the spectrum of **3**. The dotted line is a numerical sum of the two latter spectra. The inset shows the CdSe NQD relative PL quantum efficiency changes following mixing of NQDs with the complexes.

of Figure 1, the efficiency of NQD PL quenching in studied NQD/complex mixtures increases in the order **1**, **2**, **3**. On the basis of the previous observation that carboxylate-containing ligands can anchor to the surface of the CdSe NQDs,⁸ this trend most likely reflects an increased affinity of complexes **2** and **3** to the NQD surface due to their ability to attach via the carboxylate functionalities (as shown schematically in Figure 1). Further studies are required to confirm this means of surface attachment.

One possible mechanism for NQD emission quenching is distorted surface passivation. However, the fact that emission intensities of both the NQDs and complexes are affected simultaneously (Figure 1) suggests that quenching is caused by electronic interactions that occur upon attachment. We can exclude energy transfer as a possible mechanism for NQD PL quenching because of a very small spectral overlap between the absorption spectrum of the complexes and the NQD emission spectrum (Figure 2a). This conclusion is also consistent with the fact that quenching of the NQD emission is not accompanied by a complementary growth of the complex PL intensity. Instead, the PL intensity is reduced for

[†] Los Alamos National Laboratory.

[‡] University of North Carolina.

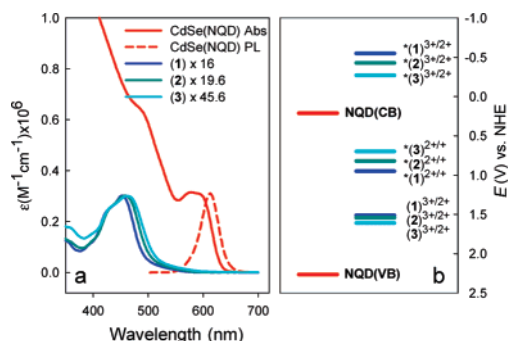


Figure 2. (a) Optical absorption spectra of NQDs and metal complexes 1, 2, and 3 (solid lines) and the PL spectrum of the NQDs (dashed line). (b) The relative positions of conduction and valence band edges in NQDs⁹ and reduction potentials of metal complexes as measured in acetonitrile at room temperature. The star indicates the excited-state reduction potentials estimated using ground-state potentials and the E_{em}^{0-0} values determined by the PL spectral fitting procedure described in ref 10.

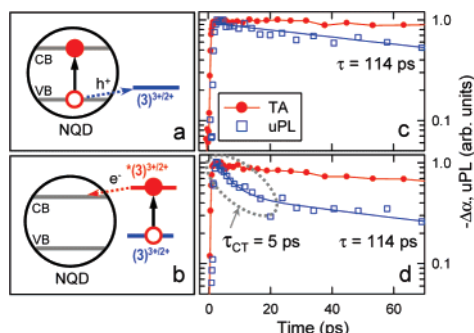


Figure 3. Left: Two possible CT processes leading to NQD quenching (see text). Right: A comparison of the TA (solid circles) and uPL (open squares) dynamics measured for the CdSe NQDs (a) and the NQD/3 mixture (b) at room temperature, 80 h after mixing ($\Delta\alpha$ is the pump-induced absorption change). The concentrations of NQDs and metal complexes are as in Figure 1. The TA and PL signals were collected at 600 and 615 nm, respectively. The excitation wavelength was 400 nm, the pulse width was 100–200 fs, and the pump per-pulse fluence was $25 \mu\text{J cm}^{-2}$.

both the NQDs and the complexes (Figure 1). The latter observation is consistent with CT between the complexes and the NQDs.

There are a number of CT processes that are thermodynamically favorable based on the NQD valence and conduction band energies and the reduction potentials of the complexes (Figure 2b). However, if processes requiring simultaneous excitation of NQDs and the adsorbed complex are excluded (they are not likely at low excitation intensities used in the PL quenching studies), only two possible processes remain that are shown schematically in Figure 3 (panels a and b). In case “a”, a hole is transferred from the NQD to the complex following NQD photoexcitation, implying that the NQD serves as both a sensitizer and a hole donor. In case “b”, the electron is injected into the conduction band of the NQD following photoexcitation of the complex, and hence, the NQD acts as an electron acceptor but not as a sensitizer. While utilizing different photoexcitation pathways, these two processes produce the same final state in which the hole resides on the complex and the electron resides on the NQD. This state is nonemissive because it is comprised of the nonemissive Ru(III) form of the complex and a charged NQD, which is “dark” because of high-efficiency nonradiative Auger recombination.⁶

To determine the exact role of the NQDs in the CT process (i.e., to distinguish between processes shown in panels a and b of Figure 3), we performed ultrafast studies of charge carrier dynamics using femtosecond transient absorption (TA) and time-resolved PL up-conversion (uPL) experiments. In CdSe NQDs, the dynamics of pump-induced absorption changes recorded at the position of the lowest energy, 1S transition using the TA experiment provide

information about the depopulation rate of the electron 1S state.¹¹ On the other hand, the PL intensity is determined by the product of electron and hole population numbers. Consequently, PL relaxation is dominated by hole dynamics if they are significantly faster than electron dynamics.¹² The latter is the case in the NQD/complex mixtures (see below).

Figure 3 displays TA and uPL time transients (collected at 600 and 615 nm, respectively) for the NQD solution (c) and the NQD/3 mixture (d). In the case of the NQD-only solution, uPL relaxation is slightly faster than TA relaxation, suggesting more efficient surface trapping of holes compared to electrons.¹¹ While electron dynamics remain almost unchanged in the mixture, the hole dynamics develop a short-lived, 5 ps component (derived from the uPL trace), indicating fast depopulation of NQD hole states. This process is consistent with the CT mechanism shown in Figure 3a, indicating that in the NQD–complex assemblies studied here the NQDs serve as sensitizers of complexes.¹³

In conclusion, we have shown that mixing of NQDs and Ru–polypyridine complexes results in formation of electronically coupled assemblies. Photoexcitation of these assemblies leads to oxidation of the adsorbed complex via efficient hole transfer from the NQD. To our knowledge, this is the first demonstration of a semiconductor/Ru complex system in which the semiconductor, rather than the complex, functions as a light sensitizer. The CT occurs on ultrafast time scales, and for the systems studied here, it is characterized by a 5 ps time constant. This constant is shorter than the characteristic Auger recombination times in NQDs, suggesting that the NQD/Ru complex assemblies can be utilized for extraction of multiple redox equivalents produced in the NQD via the carrier multiplication process.

Acknowledgment. This work was supported by the Office of Basic Energy Sciences, U.S. Department of Energy, and Los Alamos LDRD funds. We thank Dr. M. Achermann for helpful discussions.

Supporting Information Available: Supporting discussion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- O'Regan, B.; Gratzel, M. *Nature* **1991**, *353*, 737–740.
- (a) Treadway, J. A.; Moss, J. A.; Meyer, T. J. *Inorg. Chem.* **1999**, *38*, 4386–4387. (b) Gallagher, L. A.; Serron, S. A.; Wen, X. G.; Hornstein, B. J.; Dattelbaum, D. M.; Schoonover, J. R.; Meyer, T. J. *Inorg. Chem.* **2005**, *44*, 2089–2097.
- (a) Schaller, R. D.; Klimov, V. I. *Phys. Rev. Lett.* **2004**, *92*, 186601–1–186601–4. (b) Schaller, R. D.; Sykora, N.; Pietryga, J. M.; Klimov, V. I. *Nano Lett.* **2006**, *6*, 424–429.
- Peek, B. M.; Ross, G. T.; Edwards, S. W.; Meyer, G. J.; Meyer, T. J.; Erickson, B. W. *Int. J. Pep. Protein Res.* **1991**, *38*, 114–123.
- Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706–8715.
- Klimov, V. I. *J. Phys. Chem. B* **2000**, *104*, 6112–6123.
- The concentration of NQDs was determined using the calculated extinction coefficient $\epsilon_{NQD} = 1.04 \times 10^6 \text{ M}^{-1} \text{ cm}^{-1}$ at 400 nm. The concentrations of Ru complexes were calculated using experimentally measured extinction coefficients (shown in Figure 2a).
- Petruska, M. A.; Bartko, A. P.; Klimov, V. I. *J. Am. Chem. Soc.* **2004**, *126*, 714–715.
- The energy of the conduction band edge (electron affinity) in NQDs is estimated as $E_{CB}(NQD) = E_{CB}(\text{bulk}) + \Delta E_{conf}(m_h + m_e)^{-1}$, where $\Delta E_{conf} = E_{1s}(NQD) - E_g(\text{bulk})$ is the total confinement energy and m_h and m_e are the hole and electron effective masses, respectively. We used $E_{CB}(\text{bulk}) = 4.95 \text{ eV}$ (vs vac) and $E_g(\text{bulk}) = 1.74 \text{ eV}$.
- Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722–3734.
- Klimov, V. I.; Schwartz, C. J.; McBranch, D. W.; Leatherdale, C.; Bawendi, M. *Phys. Rev. B* **1999**, *60*, 13740–13749.
- Klimov, V. I. In *Semiconductor and Metal Nanocrystals. Synthesis and Electronic and Optical Properties*; Klimov, V. I., Ed.; Marcel Dekker: New York, 2004; pp 159–214.
- Photoinduced hole transfer from CdSe NQD to a surface-adsorbed acceptor has been observed previously. See for example: (a) Sharma, S. N.; Pillai, Z.; Kamat, P. V. *J. Phys. Chem. B* **2003**, *107*, 10088–10093. (b) Burda, C.; Link, S.; Mohamed, M.; El-Sayed, M. J. *J. Phys. Chem. B* **2001**, *105*, 2286–2292.

JA061556A