J|A|C|S
ARTICLES

Published on Web 03/10/2010

Multiple Exciton Dissociation in CdSe Quantum Dots by Ultrafast Electron Transfer to Adsorbed Methylene Blue

Jier Huang, Zhuangqun Huang, Ye Yang, Haiming Zhu, and Tianquan Lian*

Department of Chemistry, Emory University, Atlanta, Georgia 30322

Received January 6, 2010; E-mail: tlian@emory.edu

Abstract: Multiexciton generation in quantum dots (QDs) may provide a new approach for improving the solar-to-electric power conversion efficiency in QD-based solar cells. However, it remains unclear how to extract these excitons before the ultrafast exciton−exciton annihilation process. In this study we investigate multiexciton dissociation dynamics in CdSe QDs adsorbed with methylene blue (MB^+) molecules by transient absorption spectroscopy. We show that excitons in QDs dissociate by ultrafast electron transfer to MB^+ with an average time constant of ~2 ps. The charge separated state is long-lived (>1 ns), and the charge recombination rate increases with the number of dissociated excitons. Up to three MB^+ molecules per QD can be reduced by exciton dissociation. Our result demonstrates that ultrafast interfacial charge separation can effectively compete with exciton−exciton annihilation, providing a viable approach for utilizing short-lived multiple excitons in QDs.

Introduction

Multiexciton generation (MEG) is a process by which an absorbed photon generates multiple excitons. MEG in bulk semiconductors is typically inefficient and occurs at a high threshold photon energy.[1,2] Much more efficient MEG processes with lower threshold photon energies were reported recently in PbX (X = S, Se, Te),[3−8] Si,[9,10] CdSe[11,12] and InAs[13,14] quantum dots (QDs) and in carbon nanotubes.[15] Generation of as many as seven excitons per photon was reported in PbSe QDs at an excitation photon energy of 7.8 E_g (band gap energy, defined as 1S exciton energy in QDs).[6] If these findings are proven to be true, efficient MEG in QDs may be a transformative discovery, as it provides new approaches for improving the solar-to-electric power conversion efficiency in QD-based solar cells[16,17] and for designing novel QD-based multielectron or hole photocatalysts.[18] However, there are two main challenges regarding the generation and application of MEG in QDs. First, the mechanism, efficiency, and generality of this process are subjects of intense ongoing debates.[7,19−27] Some recent studies refute the claims of efficient MEG in CdSe[19] and InAs[20] and report similar MEG efficiencies in PbS bulk semiconductor and quantum dots.[28] These reports suggest the need to further improve MEG efficiencies in QDs for practical applications. Second, it remains unclear how to extract multiple excitons in

---

(1) Wolf, M.; Brendel, R.; Werner, J. H.; Queisser, H. J. *J. Appl. Phys.* **1998**, *83*, 4213.
(2) Kolodinski, S.; Werner, J. H.; Wittchen, T.; Queissera, H. J. *Appl. Phys. Lett.* **1993**, *63*, 2405.
(3) Schaller, R. D.; Klimov, V. I. *Phys. Rev. Lett.* **2004**, *92*, 186601–186604.
(4) Ellingson, R. J.; Beard, M. C.; Johnson, J. C.; Yu, P.; Micic, O. I.; Nozik, A. J.; Shabaev, A.; Efros, A. L. *Nano Lett.* **2005**, *5* (5), 865–871.
(5) Luther, J. M.; Beard, M. C.; Song, Q.; Law, M.; Ellingson, R. J.; Nozik, A. J. *Nano Lett.* **2007**, *7* (6), 1779–1784.
(6) Schaller, R. D.; Sykora, M.; Pietryga, J. M.; Klimov, V. I. *Nano Lett.* **2006**, *6* (3), 424–429.
(7) Trinh, M. T.; Houtepen, A. J.; Schins, J. M.; Hanrath, T.; Piris, J.; Knulst, W.; Goossens, A. P. L. M.; Siebbeles, L. D. A. *Nano Lett.* **2008**, *8* (6), 1713–1718.
(8) Murphy, J. E.; Beard, M. C.; Norman, A. G.; Ahrenkiel, S. P.; Johnson, J. C.; Yu, P.; Micic, O. I.; Ellingson, R. J.; Nozik, A. J. *J. Am. Chem. Soc.* **2006**, *128* (10), 3241–3247.
(9) Beard, M. C.; Knutsen, K. P.; Yu, P.; Luther, J. M.; Song, Q.; Metzger, W. K.; Ellingson, R. J.; Nozik, A. J. *Nano Lett.* **2007**, *7* (8), 2506–2512.
(10) Sykora, M.; Mangolini, L.; Schaller, R. D.; Kortshagen, U.; Jurbergs, D.; Klimov, V. I. *Phys. Rev. Lett.* **2008**, *100* (6), 067401/1−067401/4.
(11) Schaller, R. D.; Sykora, M.; Jeong, S.; Klimov, V. I. *J. Phys. Chem. B* **2006**, *110* (50), 25332–25338.
(12) Schaller, R. D.; Petruska, M. A.; Klimov, V. I. *Appl. Phys. Lett.* **2005**, *87* (25), 253102/1–253102/3.
(13) Schaller, R. D.; Pietryga, J. M.; Klimov, V. I. *Nano Lett.* **2007**, *7* (11), 3469–3476.
(14) Pijpers, J. J. H.; Hendry, E.; Milder, M. T. W.; Fanciulli, R.; Savolainen, J.; Herek, J. L.; Vanmaekelbergh, D.; Ruhman, S.; Mocatta, D.; Oron, D.; Aharoni, A.; Banin, U.; Bonn, M. *J. Phys. Chem. C* **2007**, *111*, 4146–4152.
(15) Gabor, N. M.; Zhong, Z.; Bosnick, K.; Park, J.; McEuen, P. L. *Science* **2009**, *325* (5946), 1367–1371.
(16) Nozik, A. J. *Phys. E* **2002**, *14* (1−2), 115–120.
(17) Klimov, V. I. *Appl. Phys. Lett.* **2006**, *89* (12), 123118/1–123118/3.
(18) Klimov, V. I. *Annu. Rev. Phys. Chem.* **2007**, *58*, 635–673.
(19) Nair, G.; Bawendi, M. G. *Phys. Rev. Lett.* **2007**, *76*, 081304.
(20) Ben-Lulu, M.; Mocatta, D.; Bonn, M.; Banin, U.; Ruhman, S. *Nano Lett.* **2008**, *8* (4), 1207–1211.
(21) Shabaev, A.; Efros, A. L.; Nozik, A. J. *Nano Lett.* **2006**, *6* (12), 2856–2863.
(22) Rupasov, V. I.; Klimov, V. I. *Phys. Rev. B: Condens. Matter* **2007**, *76* (12), 125321/1–125321/6.
(23) Schaller, R. D.; Agranovich, V. M.; Klimov, V. I. *Nat. Phys.* **2005**, *1* (3), 189–194.
(24) Prezhdo, O. V. *Chem. Phys. Lett.* **2008**, *460*, 1.
(25) Franceschetti, A.; An, J. M.; Zunger, A. *Nano Lett* **2006**, *6*, 2191.
(26) Allan, G.; Delerue, C. *Phys. Rev. B: Condens. Matter* **2008**, *77*, 125340.
(27) McGuire, J. A.; Joo, J.; Pietryga, J. M.; Schaller, R. D.; Klimov, V. I. *Acc. Chem. Res.* **2008**, *41*, 1810.
(28) Pijpers, J. J. H.; Ulbricht, R.; Tielrooij, K. J.; Osherov, A.; Golan, Y.; Delerue, C.; Allan, G.; Monn, M. *Nat. Phys.* **2009**, *5*, 811–814.

10.1021/ja100106z

QDs before the ultrafast (10s to 100s ps) exciton−exciton annihilation process.[29,30]

One potential approach for extracting multiple excitons in QDs is through ultrafast interfacial electron transfer (ET). In the presence of electron acceptors or donors, the excitons in QDs can dissociate by transferring the electrons to the acceptors or holes to the donors. Such charge transfer processes have been observed in bulk semiconductors[31,32] and QDs.[33−37] Various molecular acceptors and donors have been used to prepare p and n type QDs[38,39] and to selectively trap electrons or holes to facilitate the study of carrier relaxation dynamics in QDs.[40−44] There have been studies of ET and hole transfer dynamics from various QDs to molecular acceptors[45−58] and nanoporous oxides.[59−65] Some of these studies reported ET times on the 10s of picoseconds and faster time scale,[45−50,56,57] suggesting the possibility of separating multiple excitons by ultrafast ET to adsorbates before the exciton−exciton annihilation process.

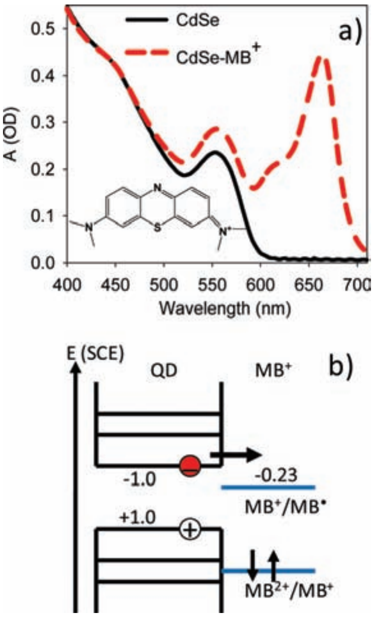

Figure 1. (a) UV−visible absorption spectra of CdSe (solid black line) and CdSe−MB$^+$ complex (dashed red line), and (b) potential of 1S electron and hole in CdSe QDs and the reduction potential of MB$^+$ molecule.

In a recent report, Matylitsky and co-workers showed that, in CdSe QDs adsorbed with methylviologen (MV^{2+}), up to four excitons can be dissociated by ultrafast electron transfer from QD to MV^{2+}.[66] The number of excitons dissociated was determined by the absorption of MV$^{+•}$ at ~400 nm which overlapped with the much stronger absorption of QDs in this region. In an effort to determine whether multiple exciton dissociation can be achieved with other molecular acceptors as well as to overcome the spectral overlap problems mentioned above, we have investigated the dynamics of dissociating multiple excitons in CdSe adsorbed with methylene blue (MB$^+$). MB$^+$ (molecular structure shown in Figure 1a) has been shown to be an efficient acceptor for conduction band electrons from semiconductor colloidal particles because of its low reduction potential (−0.231 V vs SCE).[51] Its ground state absorption band, at ~660 nm, is well separated from the QD absorption, allowing unambiguous determination of the exciton dissociation rate and yield. In this work, as well as in the previous study,[66] multiple excitons are generated by absorbing multiple photons with an energy below the MEG threshold. Although simultaneous absorption of multiple photons by one QD has negligible probability under solar flux, it can be readily accomplished with femtosecond laser excitation and has been used as a convenient approach to generate and study multiple exciton states.[18,30,68−70] Once generated and after initial relaxation, these multiple-exciton states should have the same annihilation and dissociation dynamics regardless of their generation process (either by one

---

(29) Nozik, A. J. *Annu. Rev. Phys. Chem.* **2001**, *52*, 193–231.
(30) Klimov, V. I.; Mikhailovsky, A. A.; McBranch, D. W.; Leatherdale, C. A.; Bawendi, M. G. *Science* **2000**, *287* (5455), 1011–1013.
(31) Seker, F.; Meeker, K.; Kuech, T. F.; Ellis, A. B. *Chem. Rev.* **2000**, *100*, 2505–2536.
(32) Finklea, H. O. *Semiconductor Electrodes*; Elsevier: New York, 1988; Vol. 55.
(33) Henglein, A. *Chem. Rev.* **1989**, *89*, 1861–1873.
(34) Kamat, P. V. *Chem. Rev.* **1993**, *93*, 267–300.
(35) Kamat, P. V. *Prog. React. Kinet.* **1994**, *19* (3), 277–316.
(36) El-Sayed, M. A. *Acc. Chem. Res.* **2004**, *37* (5), 326–333.
(37) Kamat, P. *J. Phys. Chem. C* **2008**, *112*, 18737–18753.
(38) Yu, D.; Wang, C.; Guyot-Sionnest, P. *Science* **2003**, *300* (5623), 1277–1280.
(39) Wehrenberg, B. L.; Guyot-Sionnest, P. *J. Am. Chem. Soc.* **2003**, *125* (26), 7806–7807.
(40) Guyot-Sionnest, P. In *Semiconductor Nanocrystals and Silicate Nanoparticles*; Peng, X., Mingos, D. M. P.; Structure and Bonding; Springer: Berlin, Germany, 2005; Vol. 118, pp 59−77.
(41) Klimov, V. I. *J. Phys. Chem. B* **2000**, *104*, 6112.
(42) Klimov, V. I.; Mikhailovsky, A. A.; McBranch, D. W.; Leatherdale, C. A.; Bawendi, M. G. *Phys. Rev. B: Condens. Matter* **2000**, *61* (20), R13349–R13352.
(43) Burda, C.; Link, S.; Mohamed, M.; El-Sayed, M. *J. Phys. Chem. B* **2001**, *105* (49), 12286–12292.
(44) Burda, C.; Link, S.; Mohamed, M. B.; El-Sayed, M. *J. Chem. Phys.* **2002**, *116* (9), 3828–3833.
(45) Rossetti, R.; Beck, S. M.; Brus, L. E. *J. Am. Chem. Soc.* **1984**, *106*, 980–984.
(46) Rossetti, R.; Brus, L. E. *J. Phys. Chem.* **1986**, *90*, 558.
(47) Ramsden, J. J.; Gratzel, M. *Chem. Phys. Lett.* **1986**, *132*, 269.
(48) Henglein, A. *Pure Appl. Chem.* **1984**, *56*, 1215–1224.
(49) Logunov, S.; Green, T.; Marguet, S.; El-Sayed, M. A. *J. Phys. Chem. A* **1998**, *102*, 5652–5658.
(50) Burda, C.; Green, T. C.; Link, S.; El-Sayed, M. A. *J. Phys. Chem. B* **1999**, *103*, 1783–1788.
(51) Kamat, P. V.; Dimitrijevic, N. M.; Fessenden, R. W. *J. Phys. Chem.* **1987**, *91*, 396.
(52) Sharma, S. N.; Pillai, Z. S.; Kamat, P. V. *J. Phys. Chem. B* **2003**, *107* (37), 10088–10093.
(53) Landes, C. F.; Burda, C.; Braun, M.; El-Sayed, M. A. *J. Phys. Chem. B* **2001**, *105*, 2981.
(54) Landes, C. F.; Braun, M.; El-Sayed, M. A. *J. Phys. Chem. B* **2001**, *105* (43), 10554–10558.
(55) Sykora, M.; Petruska, M. A.; Alstrum-Acevedo, J.; Bezel, I.; Meyer, T. J.; Klimov, V. I. *J. Am. Chem. Soc.* **2006**, *128* (31), 9984–9985.
(56) Boulesbaa, A.; Issac, A.; Stockwell, D.; Huang, Z.; Huang, J.; Guo, J.; Lian, T. *J. Am. Chem, Soc.* **2007**, *129* (49), 15132–15133.
(57) Huang, J.; Stockwell, D.; Huang, Z.; Mohler, D. L.; Lian, T. *J. Am. Chem. Soc.* **2008**, *130*, 5632–5633.
(58) Huang, J.; Huang, Z.; Jin, S.; Lian, T. *J. Phys. Chem. C* **2008**, *112*, 19734–19738.
(59) Plass, R.; Pelet, S.; Krueger, J.; Gratzel, M.; Bach, U. *J. Phys. Chem. B* **2002**, *106*, 7578.
(60) Vogel, R.; Hoyer, P.; Weller, H. *J. Phys. Chem.* **1994**, *98* (12), 3183–3188.
(61) Blackburn, J. L.; Selmarten, D. C.; Nozik, A. J. *J. Phys. Chem. B* **2003**, *107* (51), 14154–14157.
(62) Robel, I.; Kuno, M.; Kamat, P. V. *J. Am. Chem. Soc.* **2007**, *129* (14), 4136–4137.
(63) Robel, I.; Subramanian, V.; Kuno, M.; Kamat, P. V. *J. Am. Chem. Soc.* **2006**, *128*, 2385–2393.
(64) Spanhel, l.; Weller, H.; Henglein, A. *J. Am. Chem. Soc.* **1987**, *109*, 6632.
(65) Blackburn, J. L.; Selmarten, D. C.; Ellingson, R. J.; Jones, M.; Micic, O.; Nozik, A. J. *J. Phys. Chem. B* **2005**, *109* (7), 2625–2631.
(66) Matylitsky, V. V.; Dworak, L.; Breus, V. V.; Basche, T.; Wachtveitl, J. *J. Am. Chem. Soc.* **2009**, *131*, 2424.
(67) Quitevis, E. L.; Martorell, J.; Chang, Y.; Scott, T. W. *Chem. Phys. Lett.* **2000**, *319* (1,2), 138–144.

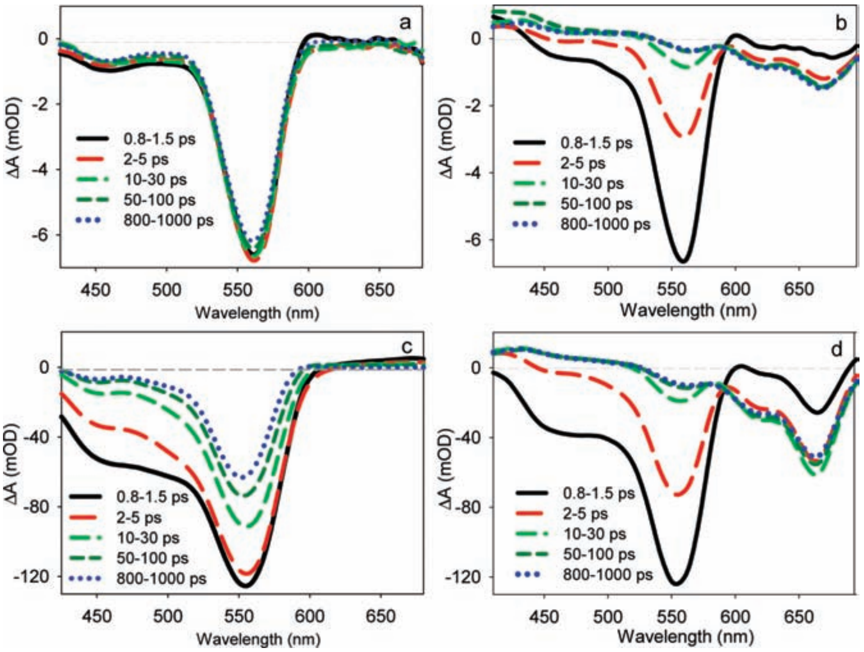

Figure 2. Transient visible absorption spectra of CdSe (a, c) and CdSe−MB$^+$ complexes (b, d) at indicated delay times after 400 nm excitation. Spectra (a, b) and (c, d) were measured with excitation pulse energy of 11 and 847 nJ, respectively.

high energy photon or by multiple low energy photons). Furthermore, the number of excitons in QDs, generated by the absorption of multiple photons, can be quantified and controlled by excitation power, facilitating the study of multiexciton dissociation dynamics.[18,30] We show that excitons in CdSe dissociate by electron transfer to adsorbed MB$^+$ with an average time constant of 2 ps and as many as three MB$^+$ molecules per QD can be reduced at high excitation power.

Experimental Section

Oleic acid (OA)-capped CdSe QDs were synthesized according to an established literature procedure.[71] The fluorescence quantum yield for the CdSe QDs used for this study was determined to be ∼6% (Supporting Information). Methylene Blue Chloride (MB$^+$Cl$^-$) was purchased from Aldrich and was used without further purification. The CdSe−MB$^+$ complex was prepared by adding MB$^+$ to CdSe QD solution in heptane followed by sonication and filtration to remove undissolved MB$^+$. Since MB$^+$ is not soluble in heptane, all dissolved dyes are believed to be bound with QDs. For all spectroscopic measurements, the obtained CdSe−MB$^+$ samples were sealed in Harrick IR cells with a 400-μm-thick spacer sandwiched between two sapphire windows. The UV−vis absorption spectra were recorded using a Cary 50 Bio UV−visible spectrophotometer. The pump−probe transient absorption setup used for this study was based on a regeneratively amplified femtosecond Ti:sapphire laser system (1 kHz repetition rate at 800 nm, 150 fs, 2.5 mJ/pulse). Pump pulses at 400 nm were generated by frequency doubling of ∼100 μJ of the fundamental in a BBO crystal. The pump beam at the sample had a diameter of 300 μm. The energy of the 400 nm pulse used for the measurement was controlled by a variable neutral-density filter wheel. The visible probe was generated by attenuating and focusing ∼10 μJ of the 800 nm pulse into a 2 mm thick sapphire window to produce a white light continuum from 410 to 750 nm. The probe was focused on the sample using protected Al parabolic reflectors to a spot size of 150 μm at 400 nm. After the sample, the probe was focused into a fiber-coupled spectrometer (Ocean Optics HR4000Plus, 2048 pixel CCD, ∼0.25 nm/pixel readout) and detected at a frequency of 10 Hz. The pump pulses were chopped by a synchronized chopper to the same frequency. During the data collection, samples were constantly translated at a speed of 2 mm/min to avoid photodegradation.

The absorption spectra of free CdSe, CdSe−MB$^+$ complex in heptane are shown in Figure 1a. The $1S_{3/2}(h)-1S_{1/2}(e)$ (or 1S) and $1P_{3/2}(h)-1P(e)$ (or 1P) exciton absorption bands of these QDs are at 553 and 460 nm, respectively.[72] The peak due to the $2S_{3/2}(h)-1S_{1/2}(e)$ exciton, expected at 525 nm,[72] is not clearly observed, which is likely caused by poor size distribution and partial overlap with the 1S exciton peak. Compared to the spectrum of free QDs, CdSe−MB$^+$ complexes exhibit an additional absorption band at 664 nm which has been attributed to the ground state absorption of the MB$^+$ molecule. The average number of adsorbed MB$^+$ per QD is estimated to be ∼3 based on the measured absorbance and known extinction coefficients of MB$^+$ (7.4×10^4 M^{-1} cm^{-1})[73] and CdSe (1.17×10^5 M^{-1}cm^{-1}).[74]

Results and Discussion

Single Exciton Dissociation. The transient visible spectra of CdSe and the CdSe−MB$^+$ complex after 400 nm excitation are shown in Figure 2a and b, respectively. These spectra were taken under the same conditions with low excitation energy (11 nJ) to ensure negligible populations in multiple exciton states. For QDs only, the transient spectrum show bleaches of 1S (553 nm) and 1P (460 nm) exciton transitions at all delay times. The 1S exciton bleach decays by ∼10% within 1 ns, suggesting a ≫1 ns decay time. In contrast, as shown in Figure 2b, in the

---

(68) Kaschke, M.; Ernsting, N. P.; Mueller, U.; Weller, H. *Chem. Phys. Lett.* **1990**, *168* (6), 543–50.

(69) Ernsting, N. P.; Kaschke, M.; Weller, H.; Katsikas, L. *J. Opt. Soc. Am. B* **1990**, *7* (8), 1630–7.

(70) Zhang, J. Z. *Acc. Chem. Res.* **1997**, *30* (10), 423–429.

(71) Yu, W. W.; Wang, Y. A.; Peng, X. *Chem. Mater.* **2003**, *15* (22), 4300–4308.

(72) Norris, D. J.; Bawendi, M. G. *Phys. Rev. B: Condens. Matter* **1996**, *53* (24), 16338–16346.

(73) Narband, N.; Uppal, M.; Dunnill, C. W.; Hyett, G.; Wilson, M.; Parkin, I. P. *Phys. Chem. Chem. Phys.* **2009**, *11*, 10513–10518.

(74) Yu, W. W.; Qu, L.; Guo, W.; Peng, X. *Chem. Mater.* **2003**, *15* (14), 2854–2860.

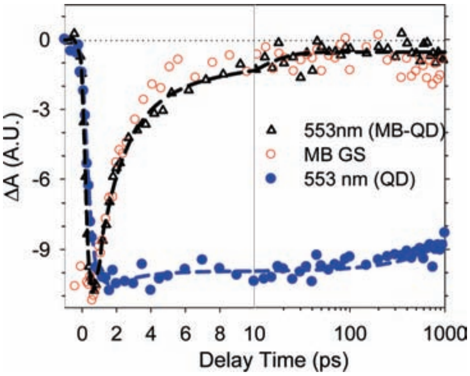

Figure 3. Comparison of the recovery kinetics of QD 1S exciton bleach (black open triangles) and the formation kinetics of MB^+ ground state bleach (red open circles) in CdSe−MB^+ complexes. Also shown is the exciton bleach recovery kinetics of QD only (blue filled circles). The MB^+ ground state bleach signal has been normalized and inverted for better comparison.

QD−MB^+ complex, the bleach of 1S exciton bands nearly fully recovers by 100 ps. It has been shown that 1S exciton bleach is caused by the filling of the 1S electron level in the conduction band.[18] The long-lived exciton bleach in QD (without MB^+) indicates long-lived electrons in the 1S level and negligible multiple excitons under this low excitation energy. Therefore, the accelerated recovery of exciton bleach kinetics for CdSe−MB^+ suggests short-lived 1S electrons in CdSe QDs in the presence of adsorbed MB^+. We have previously shown in related systems that CdSe QD 1S exciton bleach recovers when excitons dissociate by ET to the adsorbate, while it remains constant when the holes are transferred.[57,58] Furthermore, as shown in Figure 2b, the spectra of the CdSe−MB^+ complex exhibit two additional features, a broad bleaching band in the 610−680 nm region and an apparent absorption band at ∼430 nm. The former agrees well with the UV−visible spectra of MB^+ and can be attributed to the depletion of MB^+ molecules in the ground state. The absorption band at 430 nm can be assigned to the absorption of $MB^\bullet$ semiquinone,[51] which was observed in previous studies of ET in the CdS−MB^+ complexes.[51,67] These spectral signatures suggest that, in CdSe−MB^+, single exciton states decay by ET to adsorbed MB^+.

The kinetics of QD exciton bleach recovery and MB^+ ground state depletion for CdSe−MB^+ complexes are compared in Figure 3. The exciton bleach kinetics trace was obtained by averaging the data from 545 to 560 nm. The depletion kinetics of MB^+ ground state was monitored at ∼664 nm. The MB^+ bleach has been normalized and inverted for a better comparison of its growth with the recovery of QD exciton bleach. These kinetics traces agree well with each other within 1 ns, supporting the assignment that excitons in CdSe QDs dissociate by transferring electrons to MB^+. The best fit to the exciton bleach recovery kinetics for the CdSe−MB^+ sample is shown in Figure 3, from which we obtain an amplitude-weighted average ET time of ∼2.3 ps.

Comparison of static emissions of CdSe and CdSe−MB^+ shows that >99% of QD emission is quenched in the presence of MB^+ (Figure S1 in Supporting Information). Thus, the remaining bleach signal at 553 nm at 100 ps−1 ns in the transient spectra (Figure 2b) can be attributed to that of MB^+ ground state bleach. In addition to electron transfer, QD excitons can also be quenched by energy transfer to MB^+. Direct measurement of static emission of MB^+ molecules indicates an ∼6% energy transfer efficiency from excited CdSe to MB^+. A detailed analysis can be found in the Supporting Information (Figure S1). Despite good overlap of the QD emission and MB^+ absorption spectra, energy transfer is inefficient in this system because of the presence of a much faster electron transfer channel. These results suggest that, in CdSe−MB^+, single exciton states in QDs dissociate by ET to the adsorbed MB^+ with a rate constant of $(2.3\ \text{ps})^{-1}$ and near unity quantum efficiency. The efficient exciton dissociation is consistent with the observed ET time which is much faster than the intrinsic single exciton lifetime in QDs.

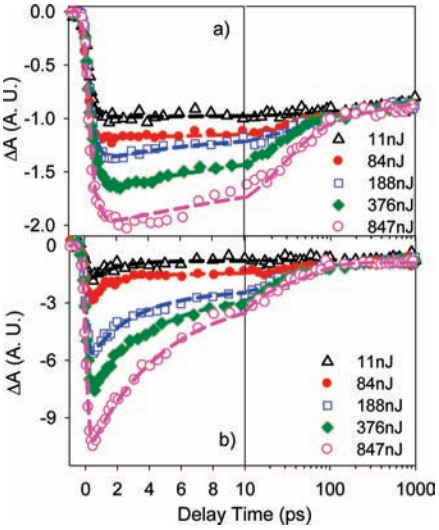

Figure 4. Comparison of (a) 1S and (b) 1P exciton bleach recovery kinetics of CdSe at indicated excitation energy. Kinetic traces have been normalized to the same value at 1 ns. The left panel shows the data up to 10 ps in linear scale, and the right panel displays the data from 10 ps to 1 ns in logarithmic scale.

Exciton−Exciton Annihilation. The exciton−exciton annihilation in CdSe and exciton dissociation dynamics in CdSe−MB^+ complexes were studied as a function of excitation energy from 11 to 1187 nJ/pulse. Shown in Figure 2c and d are the transient absorption spectra recorded at the excitation power of 847 nJ. Similar spectra for selected intermediate pump powers are shown in Figure S2 in the Supporting Information. As shown in Figure 2c, at high excitation power, the 1S exciton bleach in CdSe recovers by ∼50% within 1 ns, in contrast to long-lived exciton bleach under low excitation energy (Figure 2a). The fast exciton bleach recovery in CdSe (in the absence of MB^+) indicates the fast exciton−exciton annihilation process under these conditions. Furthermore, there is an increase in the 1P exciton bleach amplitude, indicating the presence of 1P electrons. Figure 4a shows the normalized exciton bleach kinetic traces for CdSe measured under different excitation intensities. These kinetic traces have been normalized to unity at 1 ns. They show a larger fast recovery component at higher pump power, indicating an increasing percentage of QDs with multiple excitons.

The number of excitons per QD generated by the excitation pulse is assumed to obey a Poisson distribution:[18,30]

$$P_n(w) = \sum_n \frac{w^n}{n!} e^{-w} \qquad (1)$$

where $P_n(w)$ is the probability of having QDs with n excitons and w is the average number of excitons per QD. With a 2-fold spin degeneracy in the 1S electron level, in QDs with one

Table 1. Exciton Lifetime (CdSe and CdSe−MB$^+$) and MB$^+$ Bleach Formation Time (CdSe−MB$^+$)[a]

	CdSe			CdSe−MB$^+$		
Power	τ_{1X}/ps	τ_{2X}/ps	τ_{3+X}/ps	τ_{1S}/ps	τ_{1P}/ps	τ_{MB}/ps
11 nJ	≫1000	50.6	1.5	2.5	1.4	2.3
84 nJ		52.2	1.2	3.2	1.2	2.5
188 nJ		44.2	2.6	4.7	1.3	2.1
376 nJ		44.6	3.5	4.1	1.1	2.0
847 nJ		50.7	4.5	4.7	1.2	2.0
τ_{ave}		49 ± 4			1.2 ± 0.2	2.2 ± 0.2

[a] τ_{1X}, τ_{2X} and τ_{3+X} are single-, bi-, and n(>2)-exciton lifetimes calculated from multiple exponential fits to the exciton bleach recovery kinetics of CdSe; τ_{1S} and τ_{1P} are exciton dissociation times for 1S and 1P excitons, respectively, calculated from multiple exponential fits to the exciton bleach recovery kinetics of CdSe−MB$^+$; τ_{MB} is the MB$^+$ ground state bleach formation time calculated from multiple exponential fits to MB$^+$ ground state bleach kinetics of CdSe−MB$^+$; τ_{ave} is the averaged time constants. These fitting parameters are listed in Tables SI−III in the Supporting Information.

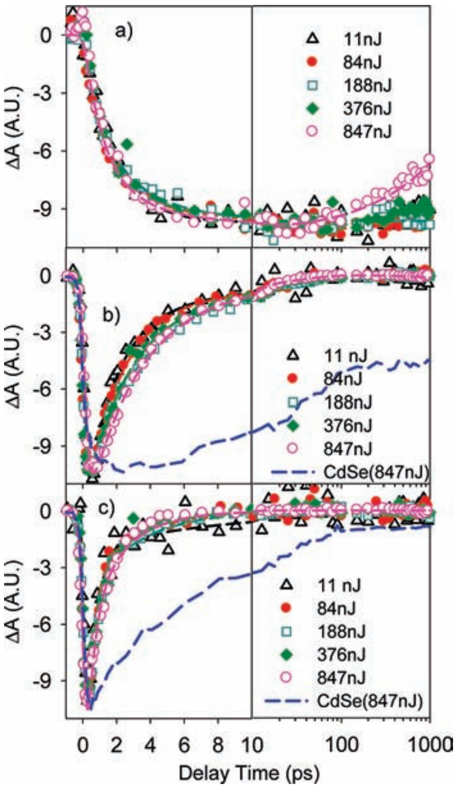

Figure 5. Comparison of the kinetics of (a) MB$^+$ bleach formation, (b) 1S exciton bleach recovery, and (c) 1P exciton bleach recovery in CdSe−MB$^+$ at indicated excitation energy. Also shown in (b) and (c) are the 1S and 1P exciton bleach recovery in CdSe only at the highest excitation energy (blue dashed line). All kinetic traces have been normalized to the same maximum amplitude. The left panel shows the data up to 10 ps in linear scale, and the right panel displays the data from 10 ps to 1 ns in logarithmic scale.

exciton the 1S exciton absorption is reduced by half and in QDs with two or more excitons the 1S exciton absorption is completely bleached. For this reason, the 1S bleach signal is assumed to be unaffected by decay between n (>2) to $n - 1$ exciton states. It depends only on the decay of biexciton (with lifetime of τ_{2X}) and single exciton (with lifetime of τ_{1X}) states. The normalized absorbance change in the 1S exciton peak at delay time t is

$$\Delta S_{1S}(t) = -\frac{\Delta A_{1S}(t)}{0.5A_{1S}(L_e/L)} = (1 - P_0 - P_1)e^{-t/\tau_{2X}} + (1 - P_0)e^{-t/\tau_{1X}} \quad (2)$$

where L_e is the effective length of the sample probed in the transient absorption measurement, L is the sample path length, and $\Delta A_{1S}(t)$ and A_{1S} are the transient absorbance change and static absorbance of the 1S exciton band, respectively. The first term in eq 2 is the contribution of the short-lived biexciton state, and its amplitude is given by the probability of finding QDs with two or more excitons. The second term reflects the decay of long-lived single exciton states, and its amplitude is given by the probability of finding excited QDs (with one or more excitons). The transient kinetics of the 1S exciton bleach are fitted according to this equation, from which we obtain an average biexciton decay time of 49 (±4) ps and single exciton decay time of ≫1 ns. The fitting parameters are listed in Table S1 (Supporting Information), and the average decay times are shown in Table 1. The best fit also reveals a rise time of ∼350 fs for the 1S exciton bleach, which is attributed to the relaxation of electrons from the initially excited 1P level to the 1S level. This relaxation rate is similar to those reported for other QDs and is believed to occur via an Auger process.[42,75]

The kinetics of 1P exciton bleach is shown in Figure 4b. Even at the lowest excitation energy (11 nJ), when the average number of excitons per QD is smaller than 1, there is a long-lived 1P exciton bleach. This is attributed to the effect of the long-lived 1S exciton on the 1P exciton absorption. In addition, there is also a fast recovery component. The origin of this decay component is not clear. With increasing excitation power, the amplitude of 1P exciton bleach increases, and the percentage of fast recovery components increases. The 1P exciton bleach recovery can be fitted by a three-exponential recovery. The fitting parameters are listed in Table SI (Supporting Information) and summarized in Table 1. The time constants of the long-lived and intermediate components are fixed at >1 ns and 48.5 ps to account for the effect of single and biexciton states on the 1P bleach. The short-lived component (τ_{3+X}) has a time constant of 2.6−4.5 ps for an excitation energy of 188−847 nJ and is attributed to the decay of n(>2)-exciton states. The decay rate of multiple exciton states should increase with the number of excitons because of the increase in Auger relaxation channels.[30] Here, the decay time is used to qualitatively describe the average lifetime of n(>2)-exciton states and to compare with the electron transfer time. The best fit of these data shows an instantaneous rise time of 1P exciton bleach, consistent with the initial excitation of electrons to near the 1P level.

Multiexciton Dissociation Dynamics. In the presence of MB$^+$, the exciton bleach of QDs shows a much faster decay, and there is a corresponding growth of the bleach of MB$^+$ ground state absorption and MB• anion absorption. Whereas the amplitude of the MB$^+$ bleach increases with excitation power, its growth kinetics appears to be unaffected, as shown in Figure 5a. The growth kinetics can be fit by a biexponential function. The fitting parameters are listed in Table SI. The amplitude weighted average rise times at varying excitation power are listed in Table 1, resulting in an average rise time of the MB$^+$ bleach of 2.2 (±0.2) ps. At low excitation power, the MB$^+$ bleach shows negligible recovery on the <1 ns time scale. With increasing

---

(75) Cooney, R. R.; Sewall, S. L.; Dias, E. A.; Sagar, D. M.; Anderson, K. E. H.; Kambhampati, P. *Phys. Rev. B: Condens. Matter* **2007**, *75* (24), 245311/1–245311/14.

excitation power, the recovery of MB^+ bleach become faster, suggesting an increased recombination rate of the MB• with the holes in QD to reform the ground state of MB^+. As a bimolecular process, the recombination rate should increase with the concentration of MB• and holes in the QD. The pump-power dependent recombination rates suggest the dissociation of multiple excitons under high excitation power.

The 1S exciton bleach recovery kinetics at varying excitation power are compared in Figure 5b. Because of the overlap of the 1S exciton with MB^+ ground state absorption, we have subtracted out the MB^+ contribution to the bleach. The latter is obtained by scaling the MB^+ bleach signal at 664 nm such that the subtracted exciton bleach amplitude is zero at 1 ns. These kinetics traces were fitted by multiexponential decay functions. The fitting parameters are listed in Table SII (Supporting Information), and average recovery times are shown in Table 1. The 1S exciton bleach recovery time at 11 nJ is the same as that for the MB^+ bleach formation, indicating that single exciton states in QDs decay by electron transfer to MB^+. At higher excitation power, the exciton bleach recovery becomes slower than the MB^+ bleach formation. It indicates that, in the multiexciton states, not all excitons are dissociated by electron transfer to the adsorbates and some of the excitons decay by Auger recombination with a time constant that is slower than the ET time.

The 1P bleach recovery kinetics traces for CdSe$-$$MB^+$ at different pump energies are compared in Figure 5c. The recovery kinetics are similar and have an average recovery time of ~1.2 ps. These recovery times are faster than those of 1S exciton bleach and the MB^+ bleach formation, indicating that the exciton dissociation rate in the n(>2)-exciton states is faster than those in the bi- and single-exciton states. Furthermore, in the QD with n(>2) excitons, the first ET event generates a reduced adsorbate and an additional hole in the QD. Because both the electron energy and wave function depend on the number of electrons and holes in the QD, as well as surface charges,[76] the rates of the subsequent ET processes are likely different. Because of these differences, it is puzzling that the MB^+ bleach formation does not show any noticeable dependence on excitation power. The reasons for this puzzling observation and the dependence of ET rate on the number of electrons and holes in QDs are being investigated in ongoing studies.

A comparison of the 1S exciton bleach in CdSe$-$$MB^+$ and CdSe, shown in Figure 5b, suggests that exciton decay in CdSe$-$$MB^+$ is much faster than the biexciton lifetime of QDs. Similarly, a comparison of the 1P exciton bleach in CdSe$-$$MB^+$ and CdSe, shown in Figure 5c, also indicates that the 1P exciton recovery in CdSe$-$$MB^+$ is much faster than that in CdSe. These comparisons suggest that interfacial ET is a competitive pathway for the dissociation of bi- and multi- (>2) exciton states.

Quantifying the Number of Excitons and Reduced MB^+. The number of excitons in QDs can be quantified by examining the exciton bleach amplitude as a function of excitation power. According to eqs 1 and 2, in a QD sample with an average of w excitons per QD, the amplitudes of normalized exciton bleach signals are given by

$$\Delta S_{1s}(0) = 2 - (2 + w)e^{-w} \qquad (3)$$

$$\Delta S_{1s}(T) = 1 - e^{-w}$$

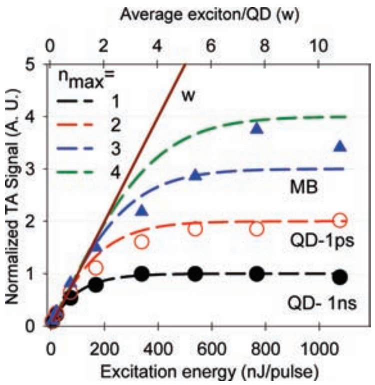

Figure 6. Excitation power dependence of the amplitudes of normalized exciton bleach at $t = 1$ ps (red open circles) and $t = 1$ ns (black solid circles) in QDs and normalized MB^+ bleach in QD-MB^+. Normalized QD bleach signals are calculated from the transient bleach amplitudes at 1 ps and 1 ns (data shown in Figures 2 and S2) according to eq 2. The MB^+ bleach signal is normalized such that it equals the normalized QD 1S exciton bleach signal at the lowest excitation energy. The solid line is the average number of excitons per QD, and dashed lines are fits according to eq 4. The curves for $n_{max} = 1$ and 2 (eq 4) are the same as those for $\Delta S_{1S}(T)$ and $\Delta S_{1S}(0)$ (eq 3), respectively.

In eq 3 $\Delta S_{1S}(0)$ is the normalized bleach signal at $t = 0$, when no exciton decay has occurred, and $\Delta S_{1S}(T)$ is the normalized exciton bleach signal at T ($\tau_{2X} \ll T \ll \tau_{1X}$), when the biexciton states have decayed to single exciton states and there is negligible decay of single exciton states. Because $\tau_{1X} \gg 1$ ns and $\tau_{2X} \gg 1$ ps, it was assumed that $\Delta S_{1S}(0) = \Delta S_{1S}(1\text{ ps})$ and $\Delta S_{1S}(T) = \Delta S_{1S}(1\text{ ns})$.

The values of $\Delta S_{1S}(1\text{ ps})$ and $\Delta S_{1S}(1\text{ ns})$ are obtained by scaling the QD 1S exciton transient bleach signal $\Delta A_{1S}(1\text{ ps})$ and $\Delta A_{1S}(1\text{ ns})$ by $-0.5A_{1s}(L_e/L)$ according to eq 2. The transient spectra of CdSe at various excitation pulse energies are shown in Figures 2 and S2. These normalized bleach signals as a function of pump energy are shown in Figure 6. According to eq 3, the $\Delta S_{1S}(1\text{ ns})$ value saturates at 1 at high excitation power. This is observed in our data when the value of L_e/L is set to 0.58. This ratio is less than 1 because of the noncollinear pump/probe geometry in the transient absorption measurement, in which optimal overlap of the pump and probe beams was achieved for only part of the sample volume. The pump power dependent normalized bleach amplitudes can be fitted according to eq 3. Because w is linearly proportional to the pump power, the proportionality constant is the only fitting parameter. From these fits, the average number of excitons at each excitation energy is obtained and has been plotted as the top horizontal axis in Figure 6. Equation 3 predicts that, at $w \ll 1$, both $\Delta S_{1S}(0)$ and $\Delta S_{1S}(T)$ are equal to w and, at $w \gg 1$, the ratio of $\Delta S_{1S}(0)/\Delta S_{1S}(T)$ saturates at 2, all of which are consistent with the data shown in Figure 6.

To determine how ET competes with exciton$-$exciton annihilation, we analyze the amplitude of MB^+ bleach as a function of pump power. As shown in Figure 3, at low excitation energy (11 nJ), there is negligible population of multiexcitons in QDs and the single excitons dissociate by ET to MB^+ with near unity efficiency. Under these conditions, the ratio of reduced MB^+ to excitons per QD is 1:1. We have normalized the maximum MB^+ bleach amplitude (at ~10 ps) in QD$-$$MB^+$ to the normalized 1S exciton bleach at 1 ns in QDs. Because the latter is the average number of excitons per QD, w (eq 3, at $w \ll 1$), the normalized MB^+ bleach amplitude represents the average number of reduced MB^+ per QD (N_{A-}). The same normalization factor is applied to the MB^+ bleach signals at higher

---

(76) Wang, L.-W. *J. Phys. Chem. B* **2001**, *105*, 2360.

excitation powers. The normalized MB^+ bleach signal (N_{A-}) as a function of excitation power is also shown in Figure 6. If all excitons are dissociated by ET, the normalized MB^+ bleach signal should be given by w. This is observed at w (<2). At $w > 2$, the normalized MB^+ bleach signal becomes smaller than w, indicating that not all excitons are dissociated. At $w > 5$, we observe approximately three reduced adsorbates per QD.

To model the excitation power dependence of the average number of reduced MB^+, it is assumed that there is a maximum number of reduced adsorbates per QD, n_{max}.[66] In QDs with exciton number $n < n_{max}$, all excitons are dissociated and each contributes to one reduced adsorbate. In QDs with $n > n_{max}$, the maximum number of reduced adsorbate is n_{max}. The average number of reduced MB^+ per QD, N_{A-}, is given by

$$N_{A^-} = \sum_{n=0}^{n_{max}-1} P_n(w) \times n + \sum_{n=n_{max}}^{\infty} P_n(w) \times n_{max} \qquad (4)$$

It can be shown that, for $n_{max} = 1$ and 2, N_{A-} is given by $\Delta S_{1S}(T)$ and $\Delta S_{1S}(0)$ (eq 3), respectively, and for $n_{max} \gg n$, $N_{A-} = w$. Figure 6 shows the predicted N_{A-} values as a function of the excitation energy for $n_{max} = 1-4$. The curve for $n_{max} = 3$ is in good agreement with the experimental data. It is interesting to note that this n_{max} value appears to be similar to the average number of adsorbates per QD in this sample. It may suggest that, in the current system, all adsorbates can be reduced by electron transfer from QDs under high excitation power. However, the current model has not taken into account the distribution of the number of adsorbates per QD, which should give rise to distribution of n_{max} values. Furthermore, the accuracy of the extinction coefficient for QDs is unclear, which leads to an uncertainty of the estimated adsorbate/QD ratio. It should also be noted that the maximum number of dissociated excitons is the same as the n_{max} value if each adsorbate can only undergo one electron reduction. However, MB^+ can be a two-electron acceptor.[77] In that case, the maximum number of dissociated excitons is $2n_{max}$. Although the second reduction process does not lead to a change of MB^+ bleach amplitude, it should affect the amplitude of MB• radical absorption at ~430 nm. Unfortunately, because of its overlap with the much stronger exciton bleach signal at that region, a quantitative analysis of the extent of two-electron transfer in this system is difficult.

In summary, exciton quenching dynamics in the CdSe QD−MB^+ complex has been investigated by transient visible absorption spectroscopy. We show that excitons in QDs dissociate by ET to MB^+ with an average time constant of ~2 ps with negligible dependence on the excitation energy. The separated charges are long-lived (>1 ns), and the charge recombination rate increases with the number of dissociated excitons. The recovery of 1P exciton bleach is faster than that of 1S exciton bleach, indicating a faster rate of exciton dissociation in the n(>2)-exciton states than those in single or biexciton states. Comparison of ET time in QD−MB^+ complexes with the exciton decay dynamics in QDs shows that the ultrafast ET process competes effectively with exciton−exciton annihilation. We show that up to three MB^+ molecules per QD can be reduced by ultrafast ET from the QD. This study demonstrates that ultrafast interfacial charge separation can be a viable approach for extracting multiple excitons before their annihilation.

Acknowledgment. The work was supported by the National Science Foundation (CHE-0848556) and Petroleum Research Fund (PRF#49286-ND6).

Supporting Information Available: Fluorescence and transient absorption spectra. This information is available free of charge via the Internet at http://pubs.acs.org.

JA100106Z

---

[77] Wopschall, R. H.; Shain, I. *Anal. Chem.* **1967**, *39*, 1527.