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Ultrafast Charge Separation in Multiexcited CdSe Quantum Dots Mediated by Adsorbed Electron Acceptors

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A lot of recent efforts aim to establish colloidal quantum dots (QDs) instead of organic molecules as light-emitters in electroluminescent devices,[1−3] lasing materials,[4,5] or light-absorbers[6,7] in photovoltaics. A unique potential advantage of QDs over organic dyes in QD-sensitized solar cell is the production of multiexcitons by charge carrier multiplication (CM)[8] that is not possible in organic molecules.[9] Efficient generation of multiexcitons by one absorbed photon in QDs could improve performance of QD-sensitized cells beyond the efficiencies achievable with dye-sensitized solar cells.[10−12] However, the successful application of CM in QD-based cells requires ultrafast charge separation in order to minimize the losses due to Auger recombination.[12] Although the charge transfer between semiconductor QDs and the molecular electron or hole acceptors adsorbed on the surface has been previously observed on a subpicosecond and picosecond time scale,[13−17] the possibility of charge extraction from QDs which contain multiexcitons has not been demonstrated yet. Recently, the energy transfer in QD conjugated with phthalocyanines was studied upon one- and two-photon excitation.[18] The authors show that the energy transfer occurs mainly from the lowest one-exciton state and only to a minor extent from the multiexcited states.

In this Communication we report on the study of ultrafast electron transfer (ET) between multiexcited CdSe QDs and the molecular electron acceptor methylviologen (MV^{2+}) adsorbed on the surface of the nanoparticles. An ET with a characteristic time constant of ∼70 fs from the conduction band of the QDs to MV^{2+} upon excitation of the transition involving the lowest electron state (1S) in CdSe is observed. Our studies show that 4 or even more electron−hole (e−h) pairs created upon excitation at 387 nm can be separated in the QD/MV^{2+} coupled system.

The CdSe QDs with mean radii of 1.4 nm were synthesized following a published procedure.[19] The absorption and fluorescence spectra of QDs in chloroform are shown in Supporting Information, Figure S1. The preparation of the QD/MV^{2+} coupled systems was carried out by adding an excess amount of MV^{2+} dissolved in methanol to the QDs solution in chloroform at a molar ratio of 7:1; here efficient adsorption of MV^{2+} molecules on the surface of QDs can be expected.[20] Finally, the QD/MV^{2+} couple in a chloroform-methanol mixture (33:1, v/v) was used in the experiments.

The photoluminescence of CdSe samples was completely quenched upon mixing with MV^{2+}. This effect in the QD/MV^{2+} system is explained by ET from the conduction band of CdSe to MV^{2+}. The addition of MV^{2+} to the CdSe solution also leads to drastic changes in the transient absorbance (TA) spectra. First, the presence of the MV^{2+} leads to an ultrafast recovery of the 1S absorption band (in the following the transition $1S(e)-1S_{3/2}(h)$ will be denoted as 1S) of the CdSe samples probed at 539 nm (Figure 1b). Second, a new positive absorbance change instead of a negative signal at 411 nm is observed (Figure 1a). The TA signal at 411 nm observed for the QD/MV^{2+} couple is caused by the absorption band of the $MV^{\bullet+}$ radical with its maximum at 400 nm.[21] Since the formation of $MV^{\bullet+}$ radicals upon direct photoexcitation of MV^{2+} can be excluded,[20] appearance of the radical in the sub-100 fs time scale also supports ultrafast ET from photoexcited QDs to MV^{2+}.

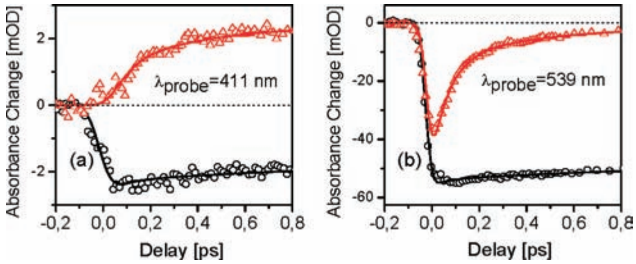

Figure 1. Comparison of the transient absorbance kinetics probed at (a) 411 nm (i.e., in the absorption band of the $MV^{\bullet+}$ radical) and (b) 539 nm (the bleach of the lowest 1S optical transition in QDs) for CdSe with (red triangles) and without (black circles) adsorbed MV^{2+} after excitation at 539 nm. Symbols are experimental data points; the solid lines are the result of a multiexponential fit. The fast component of the fit yields an ET time of 70 fs.

A global fit analysis of the complete set of the time-resolved data for the QDs/MV^{2+} coupled system (Figure S3b) results in an ET time of 70 fs after excitation at 539 nm with a pulse energy equivalent to the average number of absorbed photons per QD $\langle N_0 \rangle = 0.5$. To the best of our knowledge this is the fastest ET that has been directly measured between a photoexcited QD and a molecular electron acceptor. The ultrafast ET reaction suggests the possibility of efficient separation of the multiple e−h pairs in the CdSe QD/MV^{2+} system.

The average number of photons absorbed per QD can be calculated using the expression:[22,23]

$$\langle N_0 \rangle = J(0)\frac{1-\exp(-\mathrm{OD}\ln 10)}{cL} \qquad (1)$$

Here $J(0)$ is the photon flux at the cuvette's entrance, OD is the optical density at the excitation wavelength, c is the concentration of the QDs and L is the optical path length within the cuvette.

If the pump photon energy is much higher than the band gap of the QD sample, the probability for a QD to absorb N photons is independent of the number of e−h pairs already created in the particle and can be described by the Poisson distribution:[12,22]

$$P_{\langle N_0 \rangle}(N) = \langle N_0 \rangle^N \exp(-\langle N_0 \rangle)/N! \qquad (2)$$

Here $P_{\langle N_0 \rangle}(N)$ is the probability of QD to have N e−h pairs if the average number of photons absorbed per particle is $\langle N_0 \rangle$.

The recombination of multiple excitons in QDs occurs as a sequence of quantized steps from the N to N-1, N-2,..., to 1 e−h pair state due to Auger processes.[4] Taking the sequential recombination of excitons and the Poisson distribution $P_{\langle N_0 \rangle}(N)$ (eq 2) into account and assuming

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that only Auger and ET processes play the main role in the relaxation of multiple excitons, the average number of reduced electron acceptor molecules per nanoparticle $N^{MV\bullet+}$ can be calculated as a function of n_{max} and $\langle N_0 \rangle$:

$$N^{MV\bullet+}(\langle N_0 \rangle, n_{max}) = \sum_{i=1}^{n_{max}} (i-1)P_{\langle N_0 \rangle}(i-1) + n_{max}\left(1 - \sum_{i=1}^{n_{max}} P_{\langle N_0 \rangle}(i-1)\right) \quad (3)$$

Here we assume that ET can occur from the states which contain not more than n_{max} e−h pairs. Figure 2a shows the dependence of the relative TA signal for the $MV^{\bullet+}$ radical (color curves), calculated on the basis of eq 3, from the number of photons absorbed per particle $\langle N_0 \rangle$. Here n_{max} = 1, 2,..., 6 was assumed. To compare with the experimental results all calculated curves were normalized to 1 at $\langle N_0 \rangle = 0.5$.

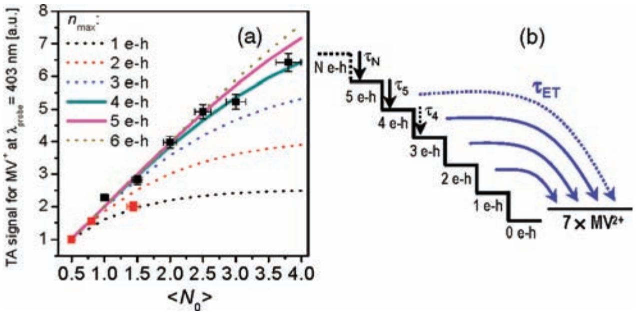

Figure 2. (a) Comparison of the predicted dependence (lines) of the TA signal for the $MV^{\bullet+}$ radical in the case of ET from multiple-pair states with the data obtained from the experiments after excitation at 387 nm (black squares) and at 539 nm (red squares). The experiments with λ_{exc} = 387 nm show that at least 4 e−h pairs can be separated by ET to the electron acceptor MV^{2+}. For the comparison with the experimental results all calculated curves were normalized to 1 at $\langle N_0 \rangle = 0.5$. (b) Schematic representation of the ET from CdSe to MV^{2+} upon multiple excitation of QDs.

The TA spectra for the CdSe QDs with the adsorbed electron acceptor MV^{2+} were measured in the visible spectral region at various excitation intensities corresponding to an initial carrier density $\langle N_0 \rangle$ from 0.5 to 3.8 e−h pairs per dot on average. To ensure the Poisson distribution of the probability for a QD to absorb N photons (eq 2), a pump photon (387 nm), which has an energy much greater than the band gap of the CdSe QD sample was used. The TA traces at λ_{probe} = 403 nm (the absorption band of the $MV^{\bullet+}$ radical[21]) for the QD/MV^{2+} coupled system measured at different $\langle N_0 \rangle$ are shown in Figure S4. The $MV^{\bullet+}$ radicals are considered as main contributors to the TA signal at 403 nm and τ_{delay} between 1.8 and 4 ps, because QDs exhibit a negligibly small TA signal at this wavelength and delay time (see Figure S5). Therefore the amplitudes of the TA traces (1.8 ps $< \tau_{delay} <$ 4 ps, Figure S4) were related to the concentration of the reduced acceptor.

The relative amplitudes of the TA traces[20,24] probed at 403 nm for the QD/MV^{2+} couple are included in Figure 2a as a function of $\langle N_0 \rangle$. The experimental points are in agreement with the theoretical curve calculated for n_{max} = 4. Taking into account the uncertainties of the experimental data we can conclude, that the ET can occur from multiple excited states with N = 4 or even 5. In other words, at least 4 e−h pairs can be separated in the QD/MV^{2+} coupled system.

Based on the previous discussion, the ET between photoexcited CdSe QDs and the molecular acceptor MV^{2+} adsorbed on the surface can be represented as shown in Figure 2b. Upon high pump power excitation, N e−h pairs can be formed. Because Auger-type relaxation dominates over the ET at higher multiexcited states, QDs relax through the Auger processes (shown by the black arrows in Figure 2b) to the excited states with N = 4 or 5 e−h pairs. At these states the ET to MV^{2+} becomes the main relaxation path for multiexcitons in CdSe QDs with adsorbed electron acceptor.

Interestingly, upon photoexcitation of the lowest 1S transition in CdSe QDs at 539 nm the dependence of the $MV^{\bullet+}$ concentration from $\langle N_0 \rangle$ indicates that the ET mainly occurs from the state with 1 e−h pair (Figure 2a, red squares). The optical transition, which determines the position of the band-edge 1S absorption peak in CdSe QDs, is 2-fold spin degenerate.[12] Therefore, the probability of generation of e−h pairs is strongly dependent on the number of already existing pairs due to carrier induced saturation of absorption at the pump wavelength. Consequently, the data for the QDs/MV^{2+} coupled system excited in the lowest 1S transition of CdSe QDs cannot be interpreted in the same way as the data for λ_{exc} = 387 nm.

In summary, the ultrafast ET (∼70 fs) between photoexcited CdSe QDs (1.4 nm radius) and the molecular electron acceptor MV^{2+} adsorbed on their surface was observed upon photoexcitation of the 1S transition in CdSe QDs at 539 nm. Our studies for the coupled system as a function of excitation intensity at λ_{exc} = 387 nm show that the ET processes compete efficiently with exciton−exciton annihilation in CdSe QDs and at least 4 e−h pairs can be separated by ET to the electron acceptor MV^{2+}.

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Supporting Information Available: Experimental methods and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) Here exponential decrease of the photon flux in an optically dense sample was taken into account.
(24) The ratio $A_{403nm}(\langle N_0 \rangle)/A_{403nm}(0.5)$ was defined as the relative amplitudes of the TA traces measured for initial carrier density $\langle N_0 \rangle$ and used in Figure 2a (black squares). Here $A_{403nm}(\langle N_0 \rangle)$ is the mean amplitude of the TA traces probed at λ_{probe}= 403 nm and τ_{delay} between 1.8 and 4.0 ps.

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