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From Hot Carrier Cooling to Auger Recombination of Negative Trions

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Photoexcitation Dynamics in Electrochemically Charged CdSe Quantum Dots: From Hot Carrier Cooling to Auger Recombination of Negative Trions

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ABSTRACT: Fulfilling the potential of colloidal semiconductor quantum dots (QDs) in electrically driven applications remains a challenge largely since operation of such devices involves charged QDs with drastically different photophysical properties compared to their well-studied neutral counterparts. In this work, the full picture of excited state dynamics in charged CdSe QDs at various time scales has been revealed via transient absorption spectroscopy combined with electrochemistry as a direct manipulation tool to control the negative charging of CdSe QDs. In trions, excited states of single charged QDs, the additional electron in the conduction band speeds up the hot electron cooling by enhanced electron–electron scattering followed by charge redistribution and polaron formation in a picosecond time scale. The trions are finally decayed by the Auger process in a 500 ps time scale. Double charging in QDs, on the other hand, decelerates the polaron formation process while accelerates the following Auger decay. Our work demonstrates the potential of photoelectrochemistry as a platform for ultrafast spectroscopy of charged species and paves the way for further studies to develop comprehensive knowledge of the photophysical processes in charged QDs more than the well-known Auger decay, facilitating their use in future optoelectronic applications.

KEYWORDS: single charged, double charged, semiconductor nanocrystals, spectroelectrochemistry, transient absorption spectroscopy, polaron, tetron, Auger decay, solar cells, optoelectronics

1. INTRODUCTION

Quantum dots (QDs), as semiconductor nanocrystals with a size smaller than Bohr’s radius, have been widely investigated both as model systems for fundamental research and for numerous applications. The applications typically rely on separation and extraction of photogenerated electron–hole pairs for the efficient conversion of photons to free charge carriers. This can be achieved through transfer of photogenerated charges to electron (hole) acceptors, which highly depends on the relative position of the band edges. Charge dynamics in such systems have been extensively investigated by time-resolved spectroscopies. Most of these studies are implemented on half-cell systems (i.e., only photoanodes or photocathodes) or under open-circuit conditions where electron/hole extraction through external circuits does not occur. In full functioning devices, extraction of charges to/from the electrodes is essential for device operation, which means that under working conditions, the photoactive layer can accumulate charges due to defects or Schottky barrier formation at the interfaces. Charge accumulation at the interfaces and also in the QDs considerably influences the device performance and optoelectronic behavior. Therefore, understanding of the effect of an external bias and the presence of extra charges in the QD-acceptor system is of great importance for the development of high-performance QD devices.

By absorption of light in a semiconductor, an electron–hole pair, exciton, is created. Two excitons in a QD interact and form a biexciton, which rapidly decays through the Auger process leaving behind a single exciton. The Auger recombination in QDs is efficient and drastically influences the performance of the corresponding devices at high excitation intensities. Photoexcitation of a charged QD leads to the so-called trion, which is a three-body state of an electron–hole pair and an additional charge. Depending on the charge, a trion can be either positive or negative. Analogously to the biexciton, the trion also can decay through Auger recombination. The depopulation of trions through the Auger process competes with the extraction of charges and consequently undermines the charge separation efficiency in the devices. Most of the existing studies on trion dynamics utilized time-resolved
phosphoroluminescence spectroscopy to measure radiative trion decay in core/shell heterojunction structures where the shell structure has a direct effect on the trion recombination. Such a core–shell structure isolates the QD core from surface defects, and at the same time, the shell also slows down or even prevents charge carrier transport to and from the core, making integrated optoelectronics based on QDs difficult.

In this work, we combine electrochemistry with ultrafast transient absorption spectroscopy (TA) to monitor changes in the excited state dynamics of the QD under controlled charging. By observing the changes in the steady state absorption during spectroelectrochemistry measurement, we have identified distinct potentials that correspond to the injection of one and two electrons to the QDs. The presence of these negative charges leads to negative trions and tetrions upon excitation by laser light in the TA measurement. We observed a series of changes in the relaxation processes due to the extra electrons including nonradiative Auger recombination in a 500 ps time scale. We anticipate that our findings will pave the way to comprehensive knowledge and better understanding of the photophysical processes in charged QDs, leading to their efficient use in future nanotechnology applications.

2. ELECTROCHEMISTRY

In electrochemistry, the applied potential induces electron exchange between working electrodes and the sample under study. By changing the potential of the working electrode linearly with time (vs a reference electrode) from one set initial potential to another preset chosen potential and then reversing the scan linearly back to the initial potential while measuring the current that passes to the counter electrode, a cyclic voltammogram (CV) is obtained showing distinct bands at the potentials where charge carriers can enter the electronic states of the system. Monodispersed CdSe QDs with a diameter of ~3 nm were used for sensitization of TiO2-coated flouroine-doped tin oxide (FTO) (Supporting Information). Such a TiO2-FTO system is analogous to the photoanode architecture of QD-sensitized solar cells. CVs of CdSe QDs were measured in a conventional three-electrode electrochemical cell configuration, where the QD-TiO2-FTO assembly serves as the working electrode, a plasless pseudo-AgAgCl electrode is used as reference, and a platinum wire acts as a counter electrode. The detailed description is given in the Supporting Information. All of the potentials in this work are reported vs the AgAgCl pseudo-reference. In equilibrium, the Fermi levels of the semiconductors that are in contact with each other are considered to be equal, which will equilibrate the charges through QD-TiO2-FTO layers. In that respect, the TiO2-FTO layer can be considered to be as one system with a common Fermi level, while CdSe QDs are separate semiconductors attached to the TiO2-FTO layer by a linker molecule. The reference electrode is considered to have a fixed potential, and thus applying a negative bias corresponds to an increase in the TiO2-FTO Fermi level. At sufficiently high negative potentials, electrons in the conduction band (CB) of the TiO2-FTO layer can reach energies equal to or higher than those of the CdSe CB; hence, electrons can be injected into the QDs. When electrons are exchanged between QDs and TiO2-FTO, a current change can be detected in the CV, which is represented in Figure 1a. For a better understanding of the electrochemical measurements and changes in the current, it is essential to define the relation between energy levels of the QDs and the applied potentials. By identifying the electrochemical potential for the CB minimum (first excited state) of the QDs $U_{1S_e}$ (in V), the electrochemical potential for the valence band energy levels $U_h$ can be expressed as

$$U_h = U_{1S_e} + \Delta E_{opt}/\epsilon + 1.86/(4\pi \epsilon_0^2 \epsilon r)$$

where $\Delta E_{opt}$ is the energy of the optical transition from the corresponding energy level in the valence band to $1S_e$, $\epsilon$ is the elementary charge, $\epsilon_0^2$ is the medium’s relative permittivity at high frequencies, $\epsilon_r$ is the vacuum permittivity, and $r$ is the radius of the QDs. The approximate electrochemical potentials for the energy levels obtained from the CV and the discrete energy levels of 3 nm CdSe QDs with their corresponding optical transitions are depicted in Figure 1b,c.

In CV, Figure 1a, with the increasing negative bias, we see a steady raise of the current due to faradic processes. At ~1.5 V, a clear peak emerges since the Fermi level reaches the conduction band of TiO2 and, consequently, additional electrons can be injected into the CB of TiO2. At ~1.75 V, another peak indicates the electrochemical potential where electrons can be transferred from TiO2 to the 1S_e level in the QDs. The next peak at ~1.9 V is at too low a potential to correspond to the next energy level, 1P_e, as illustrated in Figure 1b,c. Accordingly, we interpret the peak as further charging of the QDs since the 1S_e level can simultaneously accommodate two electrons. Due to the Coulomb repulsion, it is expected that addition of the second electron requires more energy, which corresponds to a higher negative potential in electrochemistry. Since the features between ~1.5 and ~1.75 V are a combination of those of the QDs and TiO2-FTO, exact description of them solely based on the CV.
measurement is not straightforward. In addition, as one can see from the CV measurement in Figure 1a and as reported previously in the literature, the electrochemical measurements on QDs have an irreversible character.\textsuperscript{14,30,31} This indicates that the charges injected into the QDs do not fully return on the time scale of the electrochemical cycle when the potential is reversed.\textsuperscript{30} Previous studies have shown that charging can induce surface modifications, which lead to the formation of traps in QDs without inducing significant changes in absorption and photoluminescence.\textsuperscript{12,29} It has also been shown that it is possible to charge QDs without reducing the surface using a passivating ligand or by building core–shell structures to eliminate such surface species.\textsuperscript{12,21,31} For precise scrutiny of the effect of external bias on the QD assembly, as the main goal of this study, a combination of electrochemistry with spectroscopy\textsuperscript{13} is used. Changes of the absorption spectra due to the state filling can further identify the energy levels that are involved in charging.\textsuperscript{13,34}

3. SPECTROELECTROCHEMISTRY

The spectroelectrochemistry\textsuperscript{15} measurements were carried out by following the absorption spectra at different negative potentials during the CV scan. The initial spectrum was taken at the open-circuit potential (OCP) corresponding to $-0.25$ V vs Ag/AgCl, and the potential-dependent spectral changes were obtained by subtracting this initial spectrum from the measured absorption spectra at each potential as represented in Figure 2.

The absorption spectra show two clear bands at around 550 nm for $1S_{3/2} - 1S_e$ and $2S_{3/2} - 1S_e$ transitions and at 450 nm for the $1S_{1/2} - 1S_e$ transition. At all negative potentials, an increasing featureless background from 600 to 1000 nm (Figure S5) is due to absorption of the charges in TiO$_2$.\textsuperscript{36} Until the potential reaches $-1.5$ V, the Fermi level in the TiO$_2$–FTO layer is lower than the QD conduction band; hence, the induced absorption changes at 535 and 565 nm are due to the Stark shift.\textsuperscript{37} At $-1.6$ V and a higher negative bias, a strong bleach of the transitions at 550 and 450 nm shows that the electrons fill the QD $1S_e$ state, and consequently, the absorption of all transitions to this level becomes partially bleached. At $-1.8$ V, the bleach amplitude becomes 2 times larger. These observations provide strong evidence that at $-1.6$ V the QDs are charged by one and at $-1.8$ V by two electrons, which fill the doubly degenerate $1S_e$ state. These results demonstrate that spectroelectrochemistry provides a convenient direct manipulation tool for a controlled charge injection to the QDs. In the following, we will use this method to prepare negatively charged QDs for the transient absorption measurements. We also point out that we are well aware of the limitations of the effective mass theory description and in reality the colloidal QDs have much more energy levels shown by atomistic calculations.\textsuperscript{38} Such a quasi-continuum view is important for understanding the excited electron relaxations in QDs, as discussed in the next section. However, the main spectral features of these two approaches are in good agreement, justifying our interpretation of electrochemistry in terms of $k\cdot p$ effective mass theory and state filling. It is worth mentioning that even at $-1.8$ V the band edge transition is not fully bleached. This may be due to a subset of QDs with incomplete charging. This may also be the result of the size distribution of the QDs as the smaller dots are less likely to become fully charged. This means that in reality at $-1.8$ V there is a mixture of states, which is making precise distinction of the processes in the following analyses complicated and thus the proposed models need to be considered as simplification of the full complexity of the real situation.

4. TRANSIENT ABSORPTION SPECTROSCOPY

Combination of spectroelectrochemistry with time-resolved femtosecond TA spectroscopy allows in situ probing of the excited state dynamics in well-controlled charged QDs. A detailed description of the TA measurements is given in the Supporting Information. Excitation at 400 nm was used to populate higher-energy levels ($2P_{3/2} - 1P_e$ transition) so that the absorption changes under different electrochemical potentials do not affect the excitation conditions. The initial hot electron relaxation provides valuable information about the details of the carrier cooling process. Decay-associated spectra (DAS) were obtained from global fitting of the TA data and used for mapping of the population and depopulation pathways of the excited states. The DAS spectra without normalization are presented in the Supporting Information.

The TA measurements at OCP ($-0.25$ V vs Ag/AgCl) are taken as reference. In the following, the TA features are discussed in a consecutive order.

4.1. OCP and Negative Bias

Relaxation of the initially excited hot electrons and holes occurs in a sub-ps time scale.\textsuperscript{39} All DAS components of TA consist of a negative peak at 550 nm corresponding to a decay of the bleach signal related to the almost instantaneous state filling of $1S_{1/2} - 1S_e$ and $2S_{3/2} - 1S_e$ transitions. Since at OCP, after the laser excitation, only one electron and hole are present in QDs, electron–electron scattering cannot take place; hence, the relaxation is induced only by electron–phonon scattering. Since the phonon frequencies are significantly smaller than the level spacing in
the effective mass description, the hot carrier cooling corresponds to relaxation through a quasi-continuum of the energy levels.  

The small positive band at 600 nm in the 500 fs DAS is the excitation-induced spectral shift and also reflects the hot carrier arrival to the band edge. It is followed by two slower processes corresponding to the initial electron injection (9 ps) to a charge transfer state where the electron still interacts with the hole and the full charge separation via electron diffusion to the bulk of TiO$_2$ (95 ps). The broad positive signal at longer wavelengths is attributed to the excited state absorption (ESA) of free electrons in the CB of TiO$_2$. 

Eventually, the photogenerated charges are recovered within a time scale that is longer than our experimental limit noted as $>10$ ns in all cartoon illustrations of the decay processes in Figure 3.

Figure 3. (A–C) Summary of TA measurements and their corresponding fitted exponents with normalized decay-associated spectra (DAS) of the 3 nm CdSe QD assembly on TiO$_2$ at OCP, $-1$, and $-1.5$ V applied bias vs Ag/AgCl, respectively. The corresponding unnormalized DAS component is shown in the Supporting Information. (D–F) Cartoon depiction of electron transitions at the given potentials. Black arrows indicate laser excitation connecting corresponding energy levels for photogenerated charges, and blue down arrows are used to show electron decaying pathways and recombination mechanisms.

4.2. Single and Double Charged QDs. When an external voltage is applied to the photoanode, at potentials up to $-1.5$ V, no electrons are electrochemically injected into the QDs, but the excess electrons in TiO$_2$:FTO do affect the excited state dynamics in the QDs as well as charge transfer to TiO$_2$ due to long-range Coulomb interactions in QDs. At $-1.0$ V, the Fermi level is still below the CB of TiO$_2$ and the electrons can only enter the TiO$_2$ shallow traps. The time scale of the hot electron relaxation is not influenced by this, while the photoexcited electron injection from the QDs to TiO$_2$ and the following diffusion of the injected electron away from the QD vicinity into the bulk of TiO$_2$ are both significantly slowed down from 9 to 80 ps and from 95 to 900 ps, respectively. At $-1.5$ V, when electrons fill the lowest levels of the TiO$_2$ conduction band, the charge separation process is further slowed down up to ns. The fast component that was earlier related to the hot carrier cooling has also become significantly slower, representing a combination of the cooling and some other slower process.

When the applied negative bias reaches $-1.75$ V, the Fermi level of the TiO$_2$:FTO layer is shifted higher than the QD 1$S_0$ level, which becomes populated by one electron. Excitation of such charged QDs creates trions. The hot electron relaxation in the trion is shortened to 370 fs due to the electron–electron scattering, which is now possible because of the extra electron. Since at $-1.75$ V, the electron density in the CB of the TiO$_2$ is high, the electron injection from QDs to TiO$_2$ is very unlikely to occur. The 5.8 ps component is interpreted as a combined effect of Coulombic repulsion between the electrons and polaron formation. The repulsion is likely to push the extra electron to the surface of the QDs. Such a new charge distribution is followed by nuclear rearrangement, forming a polaron and thereby stabilizing the charge distribution. Observation of a strong Stokes shift of the fluorescence in electrochemically single and double charged CdSe QDs gives strong evidence for polaron formation and for the related nuclear rearrangement. The following 510 ps component is assigned to negative trion Auger recombination (see Figure 4A,C), which is in good agreement with the previous reports.

After the Auger recombination, the QDs return back to the initial unexcited charged state, but the DAS analysis still shows a 12 ns component (10% of the TA signal, Table S2) with a clear ground state bleach at the main absorption band. This minor long component corresponds to the QDs that have remained uncharged.

At $-2$ V, since QDs become double charged, the corresponding excited states are called tetrions, with three electrons and a hole. The hot electron relaxation (380 fs) has about the same time scale as in the case of the negative trions. The relaxation due to polaron formation becomes longer since stronger electrostatic repulsion can lead to larger charge redistribution and the corresponding rearrangement of the QDs’ lattice needs more time to reach the new minimum-energy level. As expected, the Auger process in the tetrion is slightly shorter (415 ps) than in the trion.

5. CONCLUSIONS

In conclusion, spectroelectrochemistry is used to directly manipulate and monitor charging of the QD photoanode assembly in a well-controlled manner. Combination of spectroelectrochemistry with in situ TA provided a convenient tool for the study of the excited state dynamics of the QDs under different potentials mimicking realistic working conditions in an optoelectronic device. At low potentials, the electrons cannot reach the CB of the TiO$_2$ but populate the shallow traps, which appear as a constant featureless background over the whole visible spectral range. Next, the electrons start filling the CB of TiO$_2$ without entering the QDs and the photoinduced electron transfer from the QDs to TiO$_2$ is significantly slowed down. At even higher negative
potentials, −1.75 and −2.0 V, spectroelectrochemistry confirmed that the QDs are charged by one and two electrons, respectively. Now the hot electron cooling process becomes faster due to the electron–electron scattering. In the charged QDs, a process in the picosecond time scale occurs, which is attributed to polaron formation. In addition, Auger relaxation with a 500 ps time constant is observed in our TA measurements. The Auger process becomes faster in the case of double charging, in tetrons. Thereby, we provide a thorough in situ spectroscopic investigation of QDs at operational conditions of devices, which depend on charge separation or electrocharging of the particles.

The work can lead to a novel photophysical view on the design of QDs in optoelectronic devices. Our exploration of the effect of slight variation of charging that causes diminution of charge extraction provides understanding of the photophysical ground for efficiency limits of the QD devices.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.0c02478.

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**Author Contributions**

A.H. and H.M. contributed equally. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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**ABBREVIATIONS**

QD, quantum dot  
CB, conduction band  
CV, cyclic voltamogram  
FTO, fluorine-doped tin oxide  
OCP, open-circuit potential  
TA, transient absorption spectroscopy  
DAS, decay-associated spectra  
ESA, excited state absorption

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