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Ultrafast dynamics in QD based photoelectrochemical cells

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ABSTRACT

We have prepared electrodes for photo-electro-chemical cells which have enabled to pre-charge colloidal quantum dots in well-controlled fashion. Femtosecond transient absorption measurements were carried out revealing clear speed-up of the photo-induced charge carrier dynamics, particularly the recombination. Such studies allow to understand the behavior of light harvesting materials in operational conditions of optoelectronic devices giving new recipes for improvements.

Keywords: Femtosecond spectro-electrochemistry, quantum dots, CdSe, trion, exciton

1. INTRODUCTION

Colloidal semiconductor nanocrystals, so called quantum dots (QDs) and their assemblies have been extensively studied for light harvesting and photo-catalytic applications due to their high absorption coefficient, size-tunable optical band gap and possible multiple exciton generation.¹⁻³ Recent years have shown the potential of QDs from the new perovskite solar energy material for optoelectronics applications.⁴⁻⁸ Such applications rely on separation of photo-generated electron-hole pairs for efficient photon to electron conversion, which is typically carried out through charge transfer from the QDs to electronically coupled electron (or hole) acceptors. Charge transfer in QD-acceptor systems have been extensively investigated by time-resolved spectroscopies.⁹⁻¹³ However, most of the earlier studies have been implemented in half-cell systems (i.e. only photoanodes or photocathodes) in open-circuit condition. Under such circumstances, the initial conditions of the measured QDs is zero charge despite of the photoinduced charge separation at the QD/acceptor interface during the measurements. In full devices, however, injection or extraction of charges by an external electric field to/from the electrodes is essential for device operation. Consequently, the QD-acceptor system is usually charged during the functioning of the device. Previous studies by optical spectroscopy,¹⁴ electrochemistry¹⁵⁻¹⁸ and combination of both¹⁸⁻²¹ show that the presence of extra charges does influence the electronic structure of the QDs. For instance, one electron injection into the conduction band (CB) of the nanoparticles provides a chemical reduction significantly affecting the steady state absorption at the excitonic band²² and the addition of two electrons to the CB simultaneously by using electrochemistry makes the absorption of the excitonic band completely bleached. In semiconductors the change of optical properties due to the Fermi level shift toward the carrier bands by using high doping concentrations is explained as the Burstein-Moss effect, which recently has been used for evaluation of the absolute position of band edges of semiconductor nanoparticles.²³ However, recent studies by time resolved spectroscopy revealed very unconventional excited state photophysics of charged QDs.²⁴ It was explained via so called trions, which induce fast non radiative recombination of the charged exciton, electron-hole pair together with an additional electron or hole, similar to the Auger process. By considering these effects, one can expect very different charge transfer dynamics in QD-acceptor systems when QDs are pre-charged due to an external applied electric field compared with open-circuit conditions. Previously it was reported that, filling trap states by controlled the potential in a QDs assembly results in enhanced charge transfer between nanoparticles.²⁵ In this work we will investigate how the charge transfer dynamics in the QD-acceptors system is influenced in case the nanoparticles are fully charged by application of an external bias. We will probe the dynamics by using femtosecond electrochemical time resolved transient absorption spectroscopy (FECTA). We demonstrated clear changes in ultrafast exciton dynamics in QDs attached to TiO₂ under the applied potential. The findings give new hints for rational design of QD-based optoelectronic devices.

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2. MATERIALS AND METHODS

Octadecene (ODE), Cadmium oxide (CdO), Selenium powder (Se), Oleic acid (OLEA), Trioctylphosphine (TOP), Dichloromethane (DCM), Methanol (MEOH), Acetone, 3-mercaptopropionic acid (3-MPA), Fluorine doped tin oxide on glass (FTO), tetrabutylammonium hexafluorophosphate (TBAPF6) were purchased from Sigma-Aldrich and were used as received without any purification or distillation. 3 Å molecular sieves powder were activated by heating and vacuum then used for drying and storage of solvents if needed.

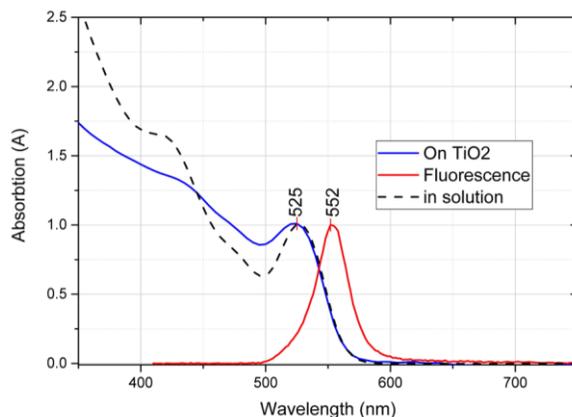


Figure 1. Absorption and photoexcited luminescence spectra of the CdSe QDs used in this study. Also the absorption spectrum of the QD-TiO₂ film is shown.

Conventional hot injection method was used for QD synthesis. 1500 mgr of CdO was dissolved in 7 ml of OLEA and 50 ml of ODE at 270°C in a three-neck flask. Selenium precursor was prepared by sonication of Se powder in 10 ml of ODE for 10 min in an Ar purged flask then by adding 0.5 mL of trioctylphosphine and then stirred until it became a transparent solution. When the Cd precursor solution became clearly transparent the temperature was lowered to 240°C, then the Se solution was quickly injected at 240°C and stirred for 2 min. Then the flask was removed from the heater and the hot solution was quickly poured into a metallic bucket, which was placed in a cold bath filled with dry ice. This immediate cooling proved to be very efficient to keep the size distribution of the nanoparticles very narrow. The synthesized CdSe QDs were characterized to ensure the quality, size distribution and shape of the nanoparticles. The absorption spectrum shows a very distinctive excitonic peak around 545 nm, see Figure 1. From the excitonic peak, we evaluated the size of the QDs to be 3.5 nm. Photoluminescence of the QDs excited at 400 nm, shows a narrow emission band at 550 nm with FWHM 29 nm. The capping ligand was changed to 3-MPA. The FTO slides were coated with TiO₂ paste, sintered at 480°C and cooled overnight. Films, see Figure 2, were prepared by soaking TiO₂ coated FTO slides in a MPA capped QDs solution at basic pH for more than 24 h, then washed with distilled water and heated to 150°C. Films were stored in a vacuum desiccator over drying agents. Films were kept in dark, since photo-degradation could be observed for samples under illumination due to charge transfer.²⁶

3 electrode system was used for electrochemistry. TiO₂ coated FTO glass was used as working electrode, Pt wire as counter electrode and leak-less Ag/AgCl as reference electrode. The electrochemical cell was made from glass with a 3 mm spacer, see Figure 2. For electrolyte solution 0.1M tetrabutylammonium hexafluorophosphate in DCM was used. Electrolyte selection is a critical decision, because adsorption and intercalation of electrolyte molecules into the nanoparticles shows significant effects on the electrochemistry.²⁷

Output of amplified laser system provided 796 nm, 6mJ, 100fs pulses which used to generate both pump and probe light. Second harmonic of the fundamental laser was used as the pump pulses with central wavelength 400 nm. White light generated in CaF₂ crystal was used as probe (350 nm to 1200 nm). The collected data is a 2D map consisting of the

evolution of the absorption difference in time after excitation by pump pulse. In our measurement the negative signal corresponds to the ground state bleach.

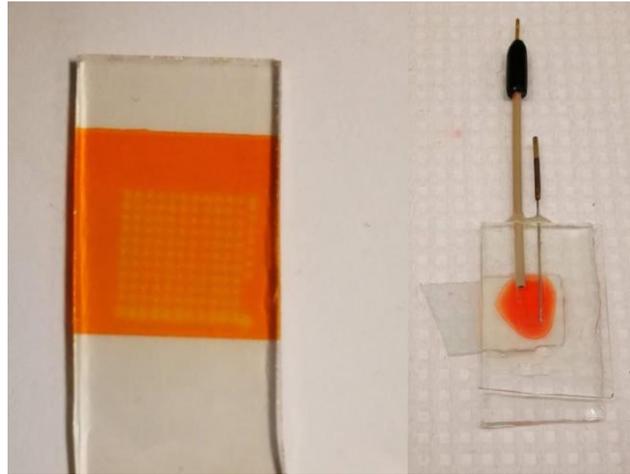


Figure 2. Left: film of CdSe QDs on TiO₂ coated FTO. The dotted matrix in the film represents the photodegradation of QDs due to charge transfer during TA measurements. Right: homemade electrochemical cell consisting of TiO₂ coated FTO as working electrode, leak-less Ag/AgCl reference electrode and a Pt wire as counter electrode.

3. RESULTS AND DISCUSSION

The CdSe QDs films on TiO₂, can be considered as two semiconductors, which are attached by 3MPA as linker. In equilibrium the Fermi levels of the semiconductors that are in contact with each other, will be equal through the junction. In that respect we can consider the FTO-TiO₂ layer all together to be as one system with a common Fermi level. If a bias voltage is applied, it causes a shift in the electrodes' Fermi level relative to each other, which causes band bending at the junction of two semiconductors and consequently forces charges to move through the junction to reach a new equilibrium, which can be measured as an electrical current. Since in electrochemistry the potential is measured versus a reference electrode, which has a fixed potential over a wide range, negative potentials can be considered as an increase in the TiO₂-FTO Fermi level, such that electrons in TiO₂-FTO can reach energy levels equal or higher than those of CdSe CB. So, if the negative potential is high enough, electrons can leave FTO-TiO₂ and enter the CdSe QDs. At positive potentials by lowering the Fermi level until carriers in FTO-TiO₂ have lower energy than their counterparts in the CdSe valence band (VB), electrons can leave CdSe VB and migrate into TiO₂-FTO. When the Fermi level is moved so high (down) that it merges with the conduction (valence) band then the semiconductor can act like a N type (P type) semiconductor with very high doping.

Femtosecond transient absorption spectroscopy (TA) was used to probe the excited state dynamics of the QDs under the applied potentials. Global analysis and Single Value Decomposition (SVD) fitting of the TA data were used to quantify the population and depopulation pathways of the excited states.

As a reference, first the transient absorption measurements of the CdSe QDs in solution and on TiO₂ film were carried out, see Figure 3. The TA spectra consist of a negative bleach band with a maximum at 550 nm corresponding to the state filling of band edge after excitation and thermalization of the charges. There also exists a weak broad positive signal from 650 nm to 1100 nm attributed to the excited state absorption (ESA). From the spectrograms it is already clear that the bleach signal of the QDs attached to the TiO₂ acceptor is decaying significantly faster. This behavior is expected owing to the charge carrier injection from the QD donor to the acceptor. The global analyses of the decay provide 5 components. The shortest subpicosecond component is clearly the hot carrier relaxation. The two picosecond components of low amplitude most likely correspond to a minor proportion of QDs with traps while the ns components correspond to the lifetime of the excited state. After attachment of the QDs the hot carrier relaxation remains unchanged while the ps components' amplitude is significantly increased. The three components of about 2, 50 and 600 ps have rather similar spectrum and amplitude. The two longer ones we assign to the electron injection while the 2 ps component

can be either injection or partially due to the surface defects generated by the attachments of the QDs. The ns component can be the minor proportion of unattached QDs or reflects the back electron transfer to the QDs.

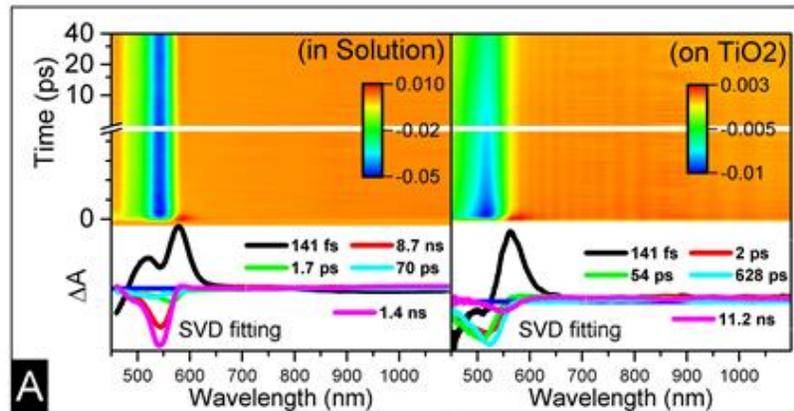


Figure 3. Transient absorption spectrograms of the CdSe QDs in solution and attached to TiO₂ mesoporous film. The amplitude spectra of the kinetic components obtained by global analyses using singular value decomposition are also provided.

By application of negative potentials, when the voltage is lower than the band edge potential of the QDs no significant changes were observable. This means that no significant charging of the QDs due to the electron transfer from TiO₂ occurs since the electrochemical driving force is insufficient to overcome the potential barrier. When the negative voltage reaches -1.5 V and higher, however, we observe significant increase of the band edge ground state bleach amplitude at 500 nm, see Figure 4.

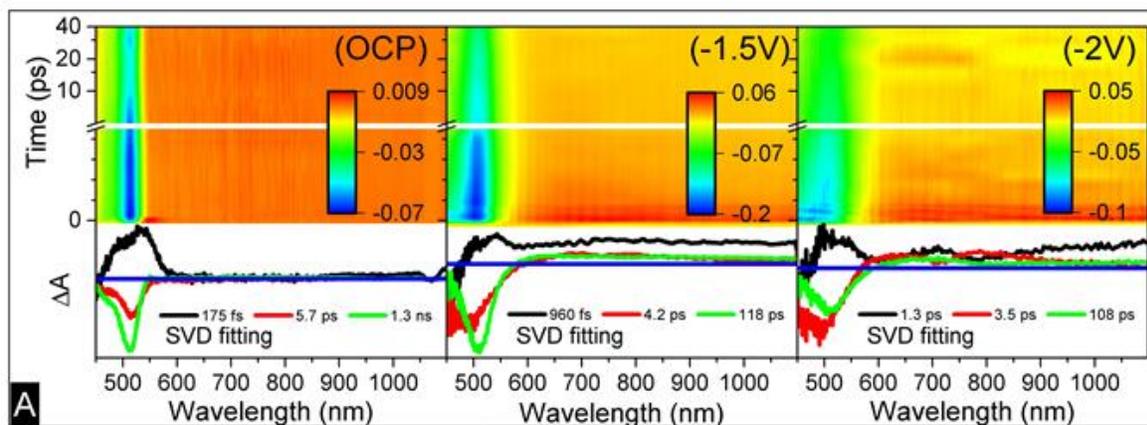


Figure 4. Transient absorption spectrograms of the CdSe QDs attached to TiO₂ mesoporous film at different applied electrochemical potential. The amplitude spectra of the kinetic components obtained by global analyses using singular value decomposition are also provided.

We interpret the spectral feature of the QD-TiO₂ at high negative applied voltages by the following model. If the applied negative potential is so high that the Fermi level in the CB of TiO₂ is higher than the CB edge in CdSe QDs, electrons will move into the QDs. The charges will first fill the doubly degenerate band edge states. If now the pump pulse generates an electron-hole pair, the band-edge transition would be saturated. The corresponding bleach effect would be stronger. We can also see that the bleach decay dynamics becomes significantly faster which we explain by the decay of negative trion. Based on the negative trion mechanism we propose that due to the electrochemical band filling in CB of the QDs, while photogenerated electrons are decaying, some electrons gain enough energy to jump to higher excited states of the QDs, which gives broadband featureless absorption in the IR region. Such positive absorption is so broad that it cannot be attributed to the Stark shift from the excitation of the QDs. In addition, such a featureless broad positive ESA is very similar to the state filling of free charges in the CB of perovskite QDs but with much lower exciton binding

energy.²⁸ Since TiO₂ has more density of states these electrons in the higher excited states of the QDs have a higher probability of being trapped in the excited states of TiO₂ and follow their relaxation in TiO₂, which leads to separation of charges. We point out that the holes cannot transport through the TiO₂ barrier at these conditions.

In case of positive bias (data not shown) the behavior is different. We first observed that the ground state bleach is significantly diminished with positive applied voltage. Such suppression on the band edge bleach can be attributed to an ESA signal under the bleach band which suppresses the signal amplitude. The signal corresponds to the transition from the deeper VB levels to the band edge holes. The decay of the bleach band becomes slower with positive voltages, which is due to the evacuated trap states at the QDs interface. The longer wavelength ESA becomes negligible at positive voltage. Unfortunately, the hole dynamics are not clearly visible in the TA measurement and TiO₂ is also considered to be mainly a hole blocking layer, which makes it difficult to conclude the exact hole dynamics from these measurements. The holes in VB have a small energy level splitting and much larger density of states in comparison with the electrons in CB and the hole transfer is not energetically favorable.

4. CONCLUSIONS

We have demonstrated clear electrochemical charging of colloidal QDs and related trion effects in photoinduced dynamics. Such trions would negatively influence most of the optoelectronic devices. In order to avoid them, proper trion neutralization strategies need to be implemented in real life applications of QDs.

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