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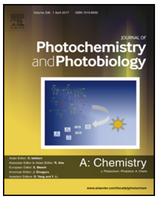

Charge transfer dynamics between MPA capped CdTe quantum dots and methyl viologen

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ABSTRACT

The understanding of charge carrier dynamics in hybrid materials based on colloidal semiconductor nanocrystals (or quantum dots) and organic moieties is fundamental for the design of efficient photonic and photovoltaic devices. In the present work, we investigate the interactions occurring between CdTe quantum dots, capped with a strong capping agent such as 3-mercaptopropionic acid, and a well known electron acceptor such as methylviologen molecule. The nature of the interactions and of exciton dynamics is investigated by stationary and time-resolved spectroscopies. Luminescence data recorded in presence of increasing methylviologen concentrations, indicate that the organic molecule is able to statically interact with the surface sites of CdTe quantum dots; a biphasic interaction behavior is evidenced by determining the apparent association constants. These latter are obtained through the analysis of luminescence data, and values in the range 10^3–10^4 are determined.

The nature of the interactions is characterized by nanosecond and femtosecond transient absorption spectroscopies, to clarify the dynamics and the conditions able to foster charge mobility. Nanosecond flash photolysis measurements, carried out upon quantum dots excitation, shows the absorption of methylviologen radical cation specie at 605 nm, suggesting the occurrence of electron transfer from CdTe nanocrystals to the organic acceptor; the relatively long decay time of the transient signal ($10.3\ \mu s$) indicates that back electron transfer processes are negligible. Ultrafast transient absorption measurements confirm the occurrence of an ultrafast electron transfer process; spectral and kinetic analysis of the transient data show that methylviologen radical cation is formed almost instantaneously on the ps-time scale but mainly when the samples are pumped in the energy continuum at 400 nm. This finding suggests that electron mobility from the nanocrystals to the organic units is achieved mainly when the excitonic states possess an excess of energy. The comparison of the kinetic behaviour of the signals at increasing methylviologen concentrations indicates that the electron transfer process competes with the radiative exciton recombination. In addition, the kinetic data suggests that surface trapping and Auger recombination processes might slow down the charge mobility.

1. Introduction

The unique tunable optical properties of colloidal semiconductor nanocrystals (or quantum dots, QDs) belonging to the II–VI groups have attracted much research and industrial attentions [1].

It is well established that upon light absorption QDs generate exciton species, which can act as charge carriers. Exciton dynamics and mobility strongly depend on the structure of the nanocrystals and on the nature of the ligands adsorbed on the nanocrystal surface [2–4]. The possibility to tune the dynamic processes of the

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excitonic state (and the efficiency of the deactivation pathways) through organic ligands can broaden the industrial opportunities of the QDs for the development of more efficient photovoltaic devices [5–8] and the design of photocatalytic platforms [9–12].

Several works report that surface defects impact the carrier dynamics [10,13–16]; in particular midgap defect states, associated with the uncapped surface atoms, have been recently identified as carrier traps [14].

The role of ligand molecules to drive the dynamics of the excitonic state has not been clearly defined, since in many cases the ligand molecules used during the synthesis affect the lattice properties of the colloids as well as the nanocrystal growth process. Ligand exchange experiments indicate that the electronic properties of the ligand molecules affect the dynamics and the deactivation path of the exciton state in colloidal QDs. In many cases, hole transfer processes from QDs to organic ligands have been observed [17–20]. Many reports support the occurrence of electron transfer processes from QDs to organic capping agents. Monitoring exciton dynamics by ultrafast transient absorption, Tseng et al. suggested that multistep electron transfer interactions initiated by a hole transfer process occur from CdS nanorods to a Ru− mononuclear complex [21]. More recently, Chen et al. presented experimental evidences for electron transfer from CdSe QDs to 4,4′-Bipyridine assisted by an interfacial proton transfer [22]. In agreement with the electron shuttling process across the interface of CdSe nanoparticles observed for the first time by El-Sayed et al. [23], Cui et al. observed for CdTe nanocrystals with pyromellitimide units on the surface, that the organic unit shuttles the electron from the conduction band (CB) to the valence band (VB), thus enhancing the recombination [24].

In this context, the study of charge carrier dynamics in functionalized QDs appears interesting for the exploitation of QDs-hybrids properties in real devices.

In this work we focused our attention on the study of the dynamics of charge carriers when capped CdTe-QDs interact with organic electron acceptor molecules adsorbed on their surface.

The relaxation dynamics of the excitonic states that occurs in capped CdTe-QDs system were widely described in previous works [25,26]. The results indicate that charge carriers decay in a quite short time scale (tens of ps) through either Auger recombination or trapping by surface defects thus reducing the charge mobility efficiency. When CdTe-QDs are capped by ligands able to passivate more efficiently their surface, as observed for 3-mercaptopropionic acid (MPA), a lengthening of the excitonic states' decay times is observed [25].

These findings lead to the question whether MPA-capped CdTe-QDs are able to transfer charge carriers toward organic units on their surface.

Recently, Jhonsi et al. [15] reported that CdTe-QDs luminescence is less efficiently quenched by methylviologen when MPA is used as capping agent compare to other ligands.

Thus, it appears interesting to investigate the ultrafast dynamics of CdTe nanocrystals capped with 3-mercaptopropionic acid (MPA) in the presence of methylviologen (MV^{2+}), which is a well known electron acceptor molecule [19,27–30].

In the present work, luminescence quenching experiments and transient absorption measurements, in the femtosecond to nanosecond temporal interval, are reported. Our work extend in a lower quencher concentration regime the study reported in Ref. [15]. In addition, a complete description of the overall interaction mechanism is obtained. In particular, the use of ultrafast transient absorption spectroscopy (TAS) gives us valuable pieces of information concerning the dynamics of charge carriers when the surface of the nanocrystals is progressively modified by MV^{2+}.

2. Experimental section

2.1. Materials

$Cd(NO_3)_2 \cdot 4H_2O$, 3-mercaptopropionic acid (MPA), $NaBH_4$, methyl viologen dichloride are purchased from Sigma-Aldrich. MilliQ water is freshly prepared in our laboratory.

2.2. Synthesis

MPA-capped CdTe-QDs are synthesized following literature procedures, with minor modifications [31,32]. Briefly, the solutions of the reactants are freshly prepared as follows: 0.2 mmol of $Cd(NO_3)_2 \cdot 4H_2O$ and 0.4 mmol of MPA are added to 40 ml of milliQ water under vigorous magnetic stirring. After complete dissolution of the two reagents, 1 M NaOH is added drop-wise until obtaining a pH of 12; the solution of Te^{2-} precursor is prepared adding 0.4 mmol of tellurium powder and 1 mmol of $NaBH_4$ in 10 ml of milliQ water; the reduction is carried out at 80 °C under a nitrogen atmosphere.

The two stock solutions of the precursors are then mixed with a Cd/Te molar ratio of 1:1 in order to obtain the nanocrystals. The nucleation and the growth stage of the reaction is carried out at 100 °C in an inert atmosphere. The progress of the reaction is spectrophotometrically checked and the samples analysed for particle dimensions.

2.3. Photophysical characterization

UV-VIS absorption spectra are recorded with a Perkin-Elmer Lambda 800 spectrophotometer on air-equilibrated solutions. Photoluminescence spectra, corrected for the instrumental response, are measured with a Fluorolog (Spex F112AI) spectrofluorometer. Time Correlated Single Photon Counting (TCSPC) measurements are performed to characterize the radiative electron-hole recombination. The luminescence decay (mean deviation of three independent experiments, ca. 5%) is measured by TCSPC method using an Edinburgh Instrument 199S setup. A 460-nm nanoLED with a 1.3 ns pulse duration is used as excitation source and the signal is acquired by a Hamamatsu R7400U-03 detector.

The nanosecond to microsecond transient behaviour is investigated by using a flash photolysis setup previously described [33,34] and based on an Nd:YAG Continuum laser (Surelite II, third harmonics, $\lambda^{exc} = 355$ nm, pulse width ca. 7 ns and energy ca. 1 mJ pulse). The transient spectra are obtained by monitoring the optical density changes every 5–10 nm over the 300–800 nm range and averaging at least 10 decays at each wavelength. The kinetic analysis of the signals at selected wavelengths allows the transient decay time to be determined. The experimental errors on the transient decay time values are estimated to be about 10%. All the measurements are performed in air-equilibrated samples.

The apparatus used for TAS measurements has been described in detail in previous works [35,36] and only a brief description of the system is given here. The fs-laser oscillator is a Ti:sapphire laser (Spectra Physics Tsunami). The short (≤70 fs) pulses are stretched and amplified at 1 kHz repetition rate by a regenerative amplifier (BMI Alpha 1000). After compression a total average power of 500 mW and a pulse duration of 100 fs are obtained. The repetition rate of the output beam is reduced to 100 Hz by a mechanical chopper. UV–vis pump pulses are produced by Second Harmonic Generation (SHG) and by mixing the output of an optical parametric generator and amplifier (OPG-OPA) based on a BBO crystal (TOPAS by Light Conversion, Vilnius, Lithuania) [37,38]. The sample was excited by pumping at 400 and 520 nm with an excitation energy of 150 nJ in both cases and the same focus