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Impact of capping agent on the electron transfer dynamics of CdTe QDs with methyl viologen

Mariadoss Asha Jhonsi ^{a,*}, Sekar Thulasi ^a, Arunkumar Kathiravan ^{b,*}^a Department of Chemistry, B.S. Abdur Rahman University, Chennai 600048, Tamil Nadu, India^b National Centre for Ultrafast Processes, University of Madras, Taramani Campus, Chennai 600113, Tamil Nadu, India

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ABSTRACT

The primary process in quantum dot solar cells is electron transfer between excited state QDs and semiconductor. There are several key factors controlling this electron transfer process including capping agents. Therefore fundamental understanding of capping agent dependent electron transfer dynamics is much needed. Here, we have employed two capping agents namely thioglycolic acid (TGA) and mercapto propionic acid (MPA) in which the later has one additional methylene group in its structure which plays a significant role on electron transfer process. Hence, we have studied the electron transfer dynamics of TGA and MPA capped CdTe QDs with methyl viologen (MV) in aqueous medium by using steady state and time resolved absorption and fluorescence techniques. The results show that MV quenches the fluorescence of CdTe QDs which is capping agent dependent. The obtained quenching rate constant for TGA and MPA capped CdTe QDs are $8.04 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $1.66 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ respectively. From the quenching rate constant values, it is clear that there is a significant role of capping agent on electron transfer process. This is due to MPA passivate the surface of QDs more than TGA, which slow down the electron transfer process from QDs to MV. Moreover, the observed radical cation ($\text{MV}^{\bullet+}$) from transient absorption measurements confirms that the fluorescence quenching of CdTe QDs by MV is attributed to electron transfer. These experimental results will help to understanding the behavior of QDs with various acceptors towards the applications of quantum dot solar cells.

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1. Introduction

Quantum dots (QDs) are defined as a class of quasi-zero-dimensional nanoparticles in which carrier motion is restricted in all three spatial dimensions [1]. Semiconductor QDs have been widely explored in fundamental research due to their optical properties, such as narrow and tunable emission spectra, high quantum yields, and photochemical stabilities [2,3]. Particularly, cadmium based QDs such as CdS, CdSe and CdTe were used in many applications, such as in light emitting devices, photovoltaic cells, photonics, transistors and biological labeling [4–8]. In particular, exploiting QDs as solar harvesters constitutes a promising approach toward low-cost third-generation solar cells owing to their band gap tunability, high absorption coefficient, solution processability, and multiple exciton generation possibilities [7–12]. Among them, Cadmium telluride (CdTe) QDs are the subject of intense studies due to they absorb throughout the visible and

near-infrared region, and display narrow and widely tunable photoluminescence together with a high stability against photobleaching when compared with other QDs and traditional organic dyes [7–9]. Moreover, CdTe is one of the leading thin film materials for photovoltaic (PV) applications. The advantage of using CdTe in thin-film solar cells lies on the fact that it is a direct band gap material with high absorption compared to silicon and the ease of device processing and high stability [10].

Generally, bare QDs are not stable in water or organic solvents and thus need surface capping reagents to help them stabilize. However, surface reagents such as organic molecules with long alkyl chains, polymers, or inorganic shells decelerate the rate of electron transfer (ET) between the excited QDs and electron acceptors because of the increased distance from the QD core to the adsorbates [13,14]. There are reports available for the effect of capping agent and size of QDs on the excited state electron transfer studies [15–17] which clearly indicates that the properties of molecular linkers can significantly influence the deactivation pathways of QDs and the efficiency of interfacial electron-transfer reactions between QDs and other molecules. For instance, Weiss reported the photoinduced electron transfer (PET) rate for a Cds QDs-Viologen complex. They demonstrate the use of transient

* Corresponding authors.

E-mail addresses: asha@bsauniv.ac.in (M.A. Jhonsi), akathir23@gmail.com (A. Kathiravan).

absorption to simultaneously investigate the PET process of a single QD–ligand couple and quantify the affinity of the ligand for the QD surface under the conditions of the PET experiment [18]. Later, they describe a study of the rates of photoinduced electron transfer (PET) from CdSe.

QDs to poly(viologen) within thin films, as a function of the length of the ligands passivating the QDs. They have shown, for the first time, a dramatic decrease of the PET rate upon increasing the length of the ligands on the QDs [19]. In 2013, the same author reported the evidence for a through-space pathway for electron transfer from QDs to carboxylate-functionalized viologens [20]. The rate constant for PET from colloidal CdS QDs to alkylcarboxylate-functionalized viologens is independent of the number of methylene groups in the alkyl chain (n). The insensitivity of the electron transfer rate constant to the length of the functional groups on the viologen suggests that a “through-space” pathway.

Kamat et al. reported that the electron transfer between methyl viologen radicals and graphene oxide [21]. The methyl viologen radicals are capable of transferring electrons to graphene oxide and partially restore the sp^2 network. Lian et al. reported the interfacial charge separation and recombination in Core/Shell QDs-molecular acceptor [22]. They concluded that, III–V and II–VI semiconductors provides a promising approach for optimizing their light harvesting and charge separation for solar energy conversion applications. Yang et al. reported the supramolecular self-assembly and photophysical properties of pillar [5] arene-stabilized CdTe QDs mediated by viologens [23]. CP[5]As could efficiently trap bridged bis(MV) inside the cavities through host-guest binding interactions, and thus efficiently prevent the electron transfer from CdTe QDs to bridged bis(MV). Based on the context, we would like to investigate the effect of thiol capping agents on CdTe QDs surface and their excited state properties. For electron transfer studies, we have chosen a well known electron acceptor namely methyl viologen (MV), since it has similar reduction potential compared with TiO_2 conduction band. In addition, steady state and time resolved techniques are used to probe the role of capping agent on the electron transfer between CdTe QDs and MV.

2. Experimental

2.1. Materials and methods

Thioglycolic acid (TGA, 98%), Mercapto propionic acid (MPA, 98%), $CdCl_2 \cdot 2.5H_2O$ (99.99%), tellurium powder (99.997%), sodium borohydride (95%) and Methyl viologen dichloride hydrate (98%) were purchased from Sigma–Aldrich and used as such without further purification. Other chemicals and solvents were of analytical grade and purchased from LOBA Chemicals (India). Milli-Q water was used to prepare the samples for spectral measurements. The synthesis of thiol-capped colloidal CdTe QDs was performed by using $CdCl_2$ and $NaHTe$ as precursors followed by the previously reported methods with some modifications [24–26]. The optimized reaction condition, characterization (XRD and TEM) and Tauc plot for the prepared QDs were given in the supporting information (Figs. S1, S2 and S3). The particle size of the prepared QDs is provided in Table 1.

X-ray powder diffraction patterns were recorded on a Rigaku MiniFlexII-C system using $CuK\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) radiation and a graphite monochromator in the diffracted beam. TGA and MPA capped CdTe QDs samples were recorded in the form of powder. A scan rate of 1° min^{-1} was applied to record a pattern in the $2\theta = 25^\circ$ in the range of $2\theta = 20^\circ$ – 80° . Morphology of the synthesized TGA and MPA-capped CdTe QDs were investigated by high resolution transmission electron microscopy (HRTEM, JEOL

Table 1

Absorption (λ_{max}), emission (λ_{emi}) wavelength, particle size from powder XRD, TEM, absorption measurements and band gap energy (E_g) of prepared TGA and MPA capped QDs.

Parameters	TGA–CdTe	MPA–CdTe
λ_{max} (nm)	522	536
λ_{emi} (nm)	576	583
^a Band gap (eV)	2.15	2.12
^b Particle size	2.7	2.9
^c Particle size	3.1	3.3
^d Particle size	2.84	3.07
^e Radii	1.90	1.98

^a From Tauc relation.

^b From Scherer equation.

^c From TEM measurement.

^d From absorption measurement.

^e From Brus equation.

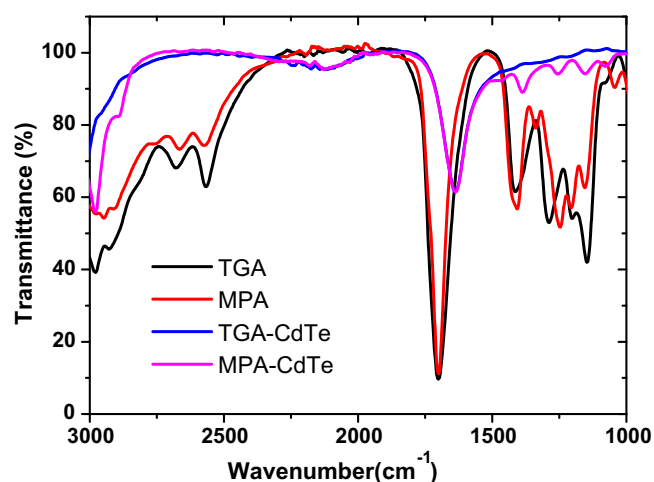


Fig. 1. FT-IR spectra of TGA, MPA and capped CdTe QDs.

JEM-1230 with accelerating voltage of 120 kV). FT-IR spectra were obtained by using JASCO FT-IR ATR 6300 spectrometer at room temperature in the range of 4000 – 400 cm^{-1} . The samples were placed in a liquid cell between two windows (CaF_2). Mirror velocity is 0.3 cm s^{-1} and numbers of co-added scans are 4 then total collection times is less than 2 min. Absorption spectra were recorded using Perkin-Elmer Lambda 25 UV–visible spectrophotometer. The fluorescence quenching measurements were carried out with Perkin-Elmer LS 45 spectrofluorometer. The excitation and emission slit width (each 5 nm) and scan rate (200 nm min^{-1}) were maintained constant for all the measurements. For fluorescence studies, more diluted solutions were used to avoid spectral distortions due to the inner-filter effect and emission reabsorption. Transient absorption experiments were carried out using nanosecond laser flash photolysis (Applied Photophysics, UK). The third harmonic (355 nm) of a Q-switched Nd:YAG laser (Quanta-Ray, LAB 150, Spectra Physics, USA) with 8 ns pulse width and 150 mJ pulse energy was used to excite the samples. The transients were probed using a 150 W pulsed xenon lamp, a Czerny–Turner monochromator, and Hamamatsu R-928 photomultiplier tube as detector. The transient signals were captured with an Agilent infinity digital storage oscilloscope, and the data were transferred to the computer for further analysis. For laser flash photolysis studies, samples were purged with argon gas for about 45 min prior to the laser irradiation. Time-resolved fluorescence decays were obtained by the time correlated single-photon counting (TCSPC) technique exciting the sample at 400 nm. Data analysis was carried out by the software provided by IBH

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