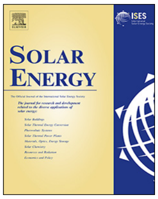
Solar Energy 169 (2018) 75–83

Contents lists available at ScienceDirect

Solar Energy

journal homepage: www.elsevier.com/locate/solener



# Photovoltaic-targeted photoluminescence lifetime engineering in bright type-II alloy quantum dots

Qinghua Li[a,*], Xiao Jin[a], Yin Yang[b], Zihan Chen[c], Degui Kong[d], Chao Nie[b], Haiyang Li[b], Yinglin Song[e,*]

[a] School of Physics Science and Technology, Lingnan Normal University, Zhanjiang 524048, PR China
[b] Jiangxi Engineering Laboratory for Optoelectronics Testing Technology, Nanchang Hangkong University, Nanchang 330063, PR China
[c] School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, Sydney, NSW 2052, Australia
[d] College of Electronic Engineering, Heilongjiang University, Harbin 150080, PR China
[e] Department of Physics, Harbin Institute of Technology, Harbin 150001, PR China

ARTICLE INFO

*Keywords:*
Type-II quantum dots
Charge transport
Quantum dot solar cells
Excited state lifetime

ABSTRACT

A crucial issue faced by quantum dot solar cells (QDSC) is how to achieve a quantum dot material with high photoluminescence (PL) quantum yield and long excited state lifetime at the same time to maximize charge carrier collection efficiency. Here, we present a new type of $Zn_{0.9}Cd_{0.1}S/ZnSe$ hetero-nanocrystals that have a staggered band alignment, i.e., a type-II structure by which the wave function overlap between electrons and holes is reduced, thereby leading to a significant enhancement in the PL lifetime. The resultant QD also exhibits a QY up to 75.4%, which is, to the best of our knowledge, the highest one for a type-II QD to date. In particular, we explore the underlying relationship between the broad tunability and energy level alignment of these hetero-nanocrystals, and we highlight the properties that have delivered QDSCs and light-emitting diodes.

## 1. Introduction

Colloidal quantum dots (CQDs) have many advantages including low cost fabrication through solution process and tunable band gaps that can cover the whole solar spectrum. Therefore they are promising materials for photovoltaic devices (Polman et al., 2016). The development of quantum dot solar cells (QDSCs) was impressively fast during the past several years, whereas this type of solar cells is still in its infancy as their power conversion efficiencies (PCEs) are still far below commercialization (Kovalenko, 2015; Kramer and Sargent, 2014; Rath et al., 2012; Yuan et al., 2016). Many efforts have been made aiming to harvest more photons through controlling the QD's morphologies (Choi et al., 2015; Tang and Sargent, 2011), introducing intermediate layer (Santra and Kamat, 2013), improving conductivity by ligand exchange (Zhitomirsky et al., 2014), reducing the mid gap states via surface passivation (Cao et al., 2016; Carey et al., 2015; Chuang et al., 2015) and others (Aqoma et al., 2015; Kim et al., 2015; Stavrinadis et al., 2013). Apart from these strategies, an ideal QD PV absorber also needs long lifetime for the high lying excited state, which enables the photoexcited excitons to have enough time to be extracted prior to carrier recombinations (Stranks et al., 2013). Unfortunately, this important prerequisite is rarely considered in designing QDSCs.

Previously, many attempts have been devoted to explore QDs with high photoluminescence (PL) quantum yield (QY), and now in some QD systems the QYs are approaching unity (Huang et al., 2015; Lim et al., 2015), even in plain core nanocrystals (Gao and Peng, 2015). It is believed that the high QY implies the QD either has a small number of defects or short radiative recombination lifetime, and therefore the photoexcited carriers are less likely to undergo non-radiative recombinations. As a result, QDs with high QY offer opportunities to achieve high PCE devices if charged carriers can be effectively extracted to external circuits. Nevertheless, the significance of pursuing QDs with extraordinary QY is somewhat overestimated, especially in PV applications. For instance, the widely used lead sulfide (PbS) QDs can have considerable QYs (above 60%) together with a narrow bandgap (Greben et al., 2015), which should guarantee a reasonably good utilization of the solar spectrum (Zhao et al., 2010). However, the current highest PCE of PbS QDSCs is still far behind their theoretical limit, and one of the contributing factors is the short carrier lifetimes (Carey et al., 2015). Theoretical calculations reveal that the PbS QD active layer should be at least 1 μm in thichness in order to absorb 90% of the solar energy (Tang and Sargent, 2011), while the photoexcited carriers cannot diffuse for such a long distance to the electron/hole transport layers before they undergo non-radiative recombinations (Zhitomirsky

---

* Corresponding authors.
*E-mail addresses:* qhli@hqu.edu.cn (Q. Li), ylsong@hit.edu.cn (Y. Song).

https://doi.org/10.1016/j.solener.2018.04.034
Received 11 December 2017; Received in revised form 12 April 2018; Accepted 16 April 2018

et al., 2013). As a result, only the carriers which reside near the donor/acceptor interfaces can be effectively extracted. Therefore, the charged carrier lifetime is also a critical criterion in designing robust QDs for PVs.

Strategies to extend the carrier lifetime and suppress the non-radiative recombinations typically include controlling the QD stoichiometry (Weidman et al., 2014), proper selection of surface organic ligands (Carey et al., 2015) and passivating the surface (Jeong et al., 2012). However, these solutions, on one hand, may create inter-dot transport obstacles which can deteriorate the mobility of the carriers. On the other hand, the charge carrier lifetime adjustability still remains limited through these methods. Thanks to the versatile type-II QDs, which enables a more effectively way to tune electronic and optical properties of the QDs (Cirloganu et al., 2014; Granados Del Aguila et al., 2016; Jiao et al., 2015; Smith et al., 2009). Type-II QD is a core-shell hetero-nanocrystal that combines two semiconductor materials with staggered band alignment between the core and the shell (Kim et al., 2003). Unlike the type-I QD whose electrons and holes are both confined at the core, in type-II QD, only holes (electrons) are localized in the core while electrons (holes) can be delocalized into the shell. In other words, electrons and holes are separated spatially and behave more individually. Herein, the overlap of the wave functions between electrons and holes are greatly suppressed, along with the decrease of the corresponding oscillator strength of non-radiative recombination, hence the carrier lifetimes are lengthened (Granados Del Aguila et al., 2016). As reported by Smith and co-workers, CdTe/ZnSe type-II QDs where elastic core/shell are employed, are capable of bearing a large stress rather than forming defect trap states, which ensures a continuous increase in the exciton radiative lifetimes instead of self-quenching from undesired trap states (Smith et al., 2009). Besides, QD with type-II structure is promising in light harvesting applications, owing to their ability of modulating the absorption and emission spectra across a broad range that otherwise cannot be achieved with the single core or shell constituent. Moreover, the intrinsic separation of electrons and holes in type-II QD favors the initial charged carrier separation in the absorber and thus provides an increase in photocurrent in the corresponding solar cells (Jiao et al., 2015), owing to the less tightly bonded excitons (Kim et al., 2003).

Despite recent development in Cd(Zn)-chalcogenide based binary type-II systems (Cirloganu et al., 2014; Granados Del Aguila et al., 2016; Jiao et al., 2015; Tyrakowski et al., 2015), it remains a challenging task to simultaneously achieve high quality QDs with good QYs and long excited state lifetimes. Current type-II QDs suffer from the lattice mismatch of the core-shell materials, which potentially tends to form surface defects that provides extremely fast non-radiative channels for photogenerated excitons, therefore quenching the PL and reducing the excited state lifetimes. To illustrate, Kim et al. described a type-II ZnSe(5.668 Å)/CdS(4.136 Å, 6.714 Å) QD with QY of 20% and PL lifetime ranging from 9.6 ns to 57 ns (Kim et al., 2003). Later, a CdTe (6.482 Å)/ZnSe(5.668 Å) system demonstrated a longer PL lifetime (115 ns), whereas its quantum yield was below 40% (Smith et al., 2009). Recently, a ZnS passivating shell was employed to modify the ZnSe(5.668 Å)/CdS(4.136 Å, 6.714 Å) type-II QD, where the non-radiative processes were greatly suppressed and the corresponding QY was enhanced up to 61%. However, the PL lifetimes of these QDs were still within tens of nanosecond (Tyrakowski et al., 2015).We believe that the intrinsic core-shell component especially the lattice match is also of great importance as the preparation procedures in designing proficient type-II structures. Besides, the excited state lifetimes rely more on the material system, because they are determined by the extent of the wave function overlap. Therefore, it is meaningful to utilize new QDs to construct robust type-II architectures beyond above mentioned binary systems.

Here, we present a new type of $Zn_{0.9}Cd_{0.1}S$/ZnSe alloy type-II QDs that are proficient in pursuing high PL QYs and long excited state lifetimes. We demonstrate a gentle ZnSe shell with less compressive strain on a $Zn_{0.9}Cd_{0.1}S$ core also capable of tuning the absorption and emission wavelengths which are difficult to attain by the single component, changing the conduction energy band, and modulating the excited state lifetimes by simply altering the initial adding amounts of Se precursor. The optimized QDs-$TiO_2$ planar heterojunction exhibits efficient charge transfer and a PCE of 5.8%, owing to the intrinsic electron-hole separation behavior in type-II structures which offers facile channels for the initial charge dissociation.

## 2. Experimental section

### 2.1. Materials

CdO (99.999%), Zn acetate (98%), 1-octadecene (1-ODE, 90%), oleic acid (OA, 90%), 1,2-ethanedithiol (EDT, 98%), tributylphosphine (TBP, 90%), sulfur (S, 99.998%, powder), selenium (Se, 99.9%) and $MoO_3$ (99.97%), reagent grade hexane methanol, ethanol and acetonitrile were purchased from Sigma-Aldrich. All the chemicals were used as received.

### 2.2. Synthesis of $Zn_{0.9}Cd_{0.1}S$/ZnSe quantum dots

$Zn_{0.9}Cd_{0.1}S$ seeds were synthesized following a procedure adapted from Lee et al. (2013). In a typical procedure, 10 mmol Zn acetate and 1 mmol CdO were dissolved in 7 mL OA in a 3-neck reactor and heated at 150 °C with Ar purging. After that, 15 mL 1-ODE was added into the mixture and the reactants were further heated to a specific temperature (270–310 °C). A S precursor was prepared by dissolving 2.0 mmol sulfur in 2.0 mL 1-ODE at 100 °C and was quickly injected into the above mentioned mixture. The temperature was kept for 10 min for the growth of $Zn_{0.9}Cd_{0.1}S$ core. And then a second Se precursor was prepared by dissolving 0.5 mmol Se in 3 mL TBP at room temperature. In order to form a ZnSe shell, an appropriate and varied amount Se precursor was dropwisely added into the reactor to overcoat the obtained $Zn_{0.9}Cd_{0.1}S$ seeds without any purification steps and the reaction was maintained for 20 min. The resultant $Zn_{0.9}Cd_{0.1}S$ and $Zn_{0.9}Cd_{0.1}S$/ZnSe QDs were purified by adding ethanol to precipitate followed by centrifugation and dispersion into hexane. After three times precipitation and dispersion the purified QDs were dried under nitrogen flow and stored in solid form in a nitrogen filled glove box.

### 2.3. Device fabrication

The ITO substrates were ultrasonically cleaned with acetone and isopropanol and were treated under ultraviolet-ozone for 20 min. A layer 50 nm thick $TiO_2$ film was prepared by spin coating the $TiO_2$ colloid on ITO glass, followed by sintering in air at 200 °C for 30 min in air, which is in a similar way in our previous studies. The $Zn_{0.9}Cd_{0.1}S$/ZnSe QDs layer was fabricated by layer-by-layer spin coating methods. First, the QD solution was dropped to cover the substrate, followed by spinning at 2500 r.p.m. for 20 s. Then EDT acetonitrile solution ($2 \times 10^{-3}$ M) was spin-coated on the $Zn_{0.9}Cd_{0.1}S$/ZnSe layer. In order to remove the excess ligand, the substrate was washed by 10 drops of acetonitrile solution and spun for 30 s to dry the film. The spinning and EDT treating process were until the QD layers with desired thickness were achieved. Finally, a 50 nm thick $MoO_3$ layer and a 250 nm thick Al electrode were in sequence thermally deposited onto the top of QD layer in a high vacuum ($< 10^{-6}$ Torr).

### 2.4. Characterization

Absorption and steady-state PL spectra were measured by a Varian Cary 300 spectrophotometer. Absolute quantum yields of the QDs were tested by an absolute QY test system (Quantaurus-QY C11347-11, Hamamatsu Photonics Co., Ltd.). The surface electron concentrations and the charge carrier diffusion constants were determined with a Hall-