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7.1. Summary

The present thesis aims at two aspects of semiconducting NCs or QDs. Part of the thesis deals with the fundamental understanding of charge carrier dynamics in heterostructured and Cu-doped NCs which has been investigated through femtosecond TA spectroscopy. The other part of the thesis focused on the improvement of photo-voltaic performance of QD sensitized solar cells. The first chapter describes some of the fundamental aspects of QDs including a brief overview of their electronic structure focusing on the prototype CdSe QDs, the wide variety of NCs that can be synthesized today and their potential applications detailing QDSSCs. The second chapter deals with the synthesis methodologies and device fabrication protocols used in this thesis along with experimental techniques utilized to characterize the NCs as well as the devices.

The third chapter focuses on the detailed analysis on charge separation energetics and dynamics for CdTe/ZnS NCs have been carried out with varying shell thickness to elucidate quasi type-II behavior in a standard type-I system. Separation of charge arises as the lattice strain at the core/shell interface alters the CB energy levels for both core and the shell in an opposite way extending the electronic wave-function towards the shell. To find out the energetics of the charge separation the steady state spectra were analyzed in the realm of Marcus theory to reveal charge separation occurring in the inverted region with \(-\Delta G_{\text{ET}}^\circ > \lambda\). Slow electron cooling as observed from ultrafast TA measurements with increasing shell thickness also confirms electron being decoupled from the hole as the electronic wave-function spreads out to the shell. For CdTe/ZnSe spherical core/shell NCs the optical spectra and charge carrier dynamics can be tuned depending on the synthetic conditions employed. When ZnSe is coated on top of CdTe core at nominal (~220°C) reaction temperature the effect of interfacial alloying is less pronounced. Interestingly, as the reaction temperature is sequentially changed between 220-280°C during core/shell synthesis a blue-shifted short lived (~10 ns) emission appears accompanied with the normal long lived (~36 ns) core/shell emission. This blue shifted emission has its origin in the interfacial alloyed layer which forms due to ionic diffusion. At elevated temperature (~280°C) this blue emission diminishes with increase in overall QY for the core/shell emission around 700 nm. Ultrafast TA spectroscopy reveals the
interplay of carrier population dynamics in first and higher excitonic states which are subsequently affected by interfacial alloying.

The fourth chapter discusses about the one pot synthesis and the underlying reaction mechanism of CdSe/PbSe Janus HNCs along with the epitaxy at the hexagonal CdSe-cubic PbSe hetero-junction. During the initial stages of reaction, unusually large CdSe NCs were formed due to rapid growth in presence of Pb-olate which cation exchanged asymmetrically to form the Janus structures. Distinct PbSe and CdSe domains were visualized after sufficient growth as seen from the HRTEM images with an unique rock salt PbSe and wurtzite CdSe interface. The core Pb-Se bonds were differentiated from interfacial Pb-Se bonds through the XPS measurements. TA spectroscopy of the Janus NCs revealed intriguing spectroscopic signatures both in the spectral and time domain as manifested by the early population of higher excitonic states upon pulsed laser excitation along with broad TA spectra rich in higher excitonic states due to the intricate hybridization between the electronic states of two disparate materials. The TA measurements were well correlated with the formation of the Janus structure as new states emerged at the longer wavelength side in the TA spectra due to PbSe accompanied with a slow ~5 ps additional electron cooling component arising due to hole localization in the PbSe domain. The charge separation was further aided upon deposition of Au NPs in CdSe/PbSe HNCs forming a tri-phasic structures.

Cyclic voltammetric and TA measurements on Cu$^+$ doped CdSe NCs were utilized to reveal the energetics of the electroactive Cu$^+$ dopant with respect to the band energies of CdSe NC host and the influence of Cu in tuning the carrier dynamics, respectively which is the focus of chapter five. Oxidation-reduction peaks due to an electroactive dopant within CdSe NC host have been traced to determine its energy level which was correlated to the dopant emission energy and Stokes shift. The low doping density of Cu does not significantly alter the band structure of CdSe as the shape of the TA spectra remains similar before and after doping. However, Cu$^+$ acts as a hole localizing center decoupling the electronic wave function from the hole leading to slower Auger assisted electron cooling in doped NCs. As hole localization to Cu$^+$ is the primary step for dopant emission, in presence of hole quenchers (aminophenols) the dopant emission gets
drastically quenched. Interestingly, once hole is captured by Cu due to strong affinity for electron, external quenchers (nitrophenols) are unable to capture the electron as confirmed from steady state and time resolved measurements establishing the role of Cu as an internal sensitizer for the charge carriers.

The last and sixth chapter deals the application of QDs for sensitized solar cells. The CdZnS and CdZnSe alloy NCs were synthesized and the photo-voltaic performance was compared with their binary counterpart. The alloy NCs were found to be superior sensitizer than pure NCs because of less defect states that acts as charge trapping centers with PCE of 3.11% (compared to 1.32% for pure CdS) and 3.78% (compared to 3.21% for pure CdSe). This was also corroborated through ultrafast TA measurements which demonstrated slower recombination in alloy NCs essential for carrier extraction. To further enhance the PCE of QDSSCs we have designed a method by introducing a hole transporting layer (HTL) of p-type CuS through cation exchange process in post synthetic ligand assisted assembly of NCs. High quality CdSe and CdSSe gradient alloy NCs were synthesized through colloidal method and the charge carrier dynamics was monitored through ultrafast TA measurements. Notable increase in the short circuit current concomitant with the increase in open circuit voltage and fill factor lead to 45% increment in PCE for CdSe based solar cell upon formation of the CuS HTL. EIS measurements further revealed that the CuS layer formation increases recombination resistance at the TiO\textsubscript{2}/NC/electrolyte interface implying interfacial recombination gets drastically reduced due to smooth hole transfer to the redox electrolytes. Utilizing the same approach for CdSSe alloy NCs highest 4.03% PCE was obtained upon CuS layer formation compared to 3.26% PCE for the untreated one and 3.61% PCE with the conventional ZnS coating. Therefore, such strategies will help to cross the kinetic barriers for hole transfer to electrolyte which is major obstacle in the high performance device. Moreover, to overcome the severe electron recombination due to slow charge transport, cold argon plasma treatment was performed on TiO\textsubscript{2} nanoparticulate photoanodes under ambient conditions, resulting tremendous ~65% increase in the PCE to 6.26% utilizing CdSe\textsubscript{0.4}S\textsubscript{0.6} alloy NCs as sensitizers. This remarkable performance was attributed to the increased surface conductivity of TiO\textsubscript{2} due to improvement in inter-particle connectivity.
and formation of Ti$^{3+}$ electron donor states along with increase in surface hydrophilicity due to enhanced roughness factor upon plasma etching. The fast charge transport through TiO$_2$ results almost 3.5 times reduction of recombination rate at the TiO$_2$/NC/electrolyte interface significantly increasing the short circuit current. The PCE was further enhanced to 7.41% with the aid of a hole transporting CuS layer facilitating hole transfer from the NCs to the electrolyte. Thus, our investigation opens up a promising direction in the advancement of QDSSCs attracting further research to optimize the device fabrication viable for highly efficient devices.

7.2. Future Scope

Investigation of the basic photo-physics of QDs will help to understand the optical and material properties in detail. For core/shell NCs the interfacial strain and alloying plays an important role in exciton dynamics which was investigated for CdTe/ZnS and CdTe/ZnSe NCs. Recent literature has suggested the importance of alloying and strain. The alloyed interface can improve PL QY, and slow down the Auger recombination rates.$^{1,2}$ On the other hand, in CdSe/PbSe Janus NCs both electron and hole are easily accessible compared to core/shell structures. The slow electron cooling found in Janus NCs will be beneficial for carrier extraction. With Janus structures fabrication of solar cells is expected in future having possibility of MEG and better carrier extraction. The tri-phasic Au-CdSe/PbSe NCs represents an interesting system both in terms of synthesis and applications. The synthesis can be optimized to have better quality NCs with less defects and selective deposition of Au in one region. With optimum charge separation this kind of material will be useful for photo-voltaic and photo-catalytic applications.

Luminescent Cu-doped NCs have potential application as potential light emitters and as luminescent solar concentrators. Our work reveals the role of Cu$^+$ in controlling the exciton dynamics of CdSe NC host. Electrochemical measurements in form of cyclic voltammetry were used to trace the signatures of Cu-dopant within the CdSe NC host. Our findings will help to understand the exciton-dopant coupling in a more elaborate way, which might be helpful for future developments of Cu-doped NCs in photo-voltaics and sensor applications.
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The PCE of quantum dot based solar cells is still low for practical applications. Therefore, the research is continuing to improve each and every component of the solar cell device. One of the limiting factors in the QDSSC device architecture is the slow hole transport to the electrolyte. To alienate this problem we investigated the role of CuS as a hole transporting material coated on the NC sensitizers. This method apart from being efficient is simple and inexpensive. The other factor that restricts the PCE is slow charge transport through mesoporous TiO2 NPs. To increase the conductivity of the TiO2 layer cold argon plasma treatment was performed on TiO2 nanoparticulate photo anodes under ambient conditions, resulting 65% increase in the PCE for QDSSCs.

The PCE is still limited in our work due to several reasons such as unavailability of state of the art device fabrication protocols restricting the Jsc and FF (~40%), use of polysulfide electrolyte having high redox potential and Cu2Se/FTO CE limiting the Voc <0.7 V.3,4 Still we have achieved Jsc ~21mA/cm2 using CdSe0.4S0.6 NC sensitizer having absorption onset ~600 nm, which is comparable to best efficiencies reported so far for QDSSCs.5 In this regard enormous scope is present to further optimize the PCE through exclusion of human errors during device fabrication improving Jsc and FF, using near-IR NCs as sensitizers for better light harvesting and improving the electrolyte/CE material enhancing the Voc. In fact, with the use of graphene hydrogel-CuS composite, mesoporous carbon, nitrogen doped mesoporous carbon CE or tetraethyl orthosilicate added polysulfide electrolyte Voc close to 0.8V can be achieved with FF nearing 70% and PCE exceeding 10%.6,8 Therefore, we truly believe the novel plasma treatment approach for surface engineered TiO2 photoanodes if combined with a better sensitizer and CE-electrolyte combination can lead to highly efficient QDSSC devices.

7.3. References


List of Thesis Publications


Chapter 7

8. Sourav Maiti, Jayanta Dana and Hirendra N. Ghosh*. "Exciton-Plasmon Coupling in Tri-phase Au/CdSe/PbSe Hetero-nanocrystals." (Manuscript under preparation)

List of Other Publications During Thesis


6. Tushar Debnath, Deepa Sebastian, Sourav Maiti, and Hirendra N. Ghosh*. “Tuning Hole and Electron Transfer from Photoexcited CdSe Quantum Dots to
Phenol Derivatives: Effect of Electron-Donating and -Withdrawing Moieties.”


Conference Attended

(1) Sourav Maiti; Tushar Debnath; Partha Maity; Hirendra N. Ghosh*. “Effect of Interfacial Alloying and Lattice Strain on Exciton Dynamics of CdTe/ZnSe Core/Shell Nanocrystals.” *Frontiers in Advanced Materials (FAM-2015)*, IISC Bangalore, Bangalore, India.


(3) Sourav Maiti; Jayanta Dana; Tushar Debnath; Ghosh, H. N. Effect of Molecular Interaction on Cu-doped CdSe Nanocrystals. *The International Conference on Nanoscience and Technology 2016 (ICONSAT-2016)*, IISER Pune, Pune, India.


(5) Sourav Maiti; Yogesh Jadhav; Jayanta Dana; Santosh K. Haram; Hirendra N. Ghosh*. “Exciton dynamics and cyclic voltammetric studies with Cu-CdSe NCs.” *DAE-BRNS Theme Meeting on Ultrafast Science-2016 (UFS-2016)*, BARC, Mumbai, India.

(6) Sourav Maiti; Farazuddin Azlan; Pranav Anand; Jayanta Dana; Hirendra N. Ghosh*. Improvement of Efficiency after Cation Exchange with Cu$^{2+}$ in Quantum Dot solar Cells. *Nanolndia 2017*, IIT Delhi, Delhi, India.

Oral Presentation

Lattice-Strain-Induced Slow Electron Cooling Due to Quasi-Type-II Behavior in Type-I CdTe/ZnS Nanocrystals

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ABSTRACT: Detailed analysis on charge separation energetics and dynamics for CdTe/ZnS nanocrystals have been carried out with varying shell thickness to elucidate quasi-type-II behavior in a standard type-I system. Redshift in the absorption–photoluminescence spectra and increase of the excited state lifetime in the core/shell nanocrystals with a thick ZnS shell (2 and 4 ML of ZnS) indicate quasi-type-II behavior caused by charge separation. Separation of charge arises as the lattice strain at the core/shell interface alters the conduction band energy levels for both the core and the shell in an opposite way, extending the electronic wave function toward the shell. To find out the energetics of the charge separation, the steady-state spectra were analyzed in the realm of Marcus theory to reveal charge separation occurring in the inverted region with \(-\Delta G_{et} > 0\). Slow electron cooling as observed from ultrafast transient absorption measurements with increasing shell thickness also confirms electron being decoupled from the hole as the electronic wave function spreads out to the shell. Consistent with the Marcus theory analysis, the separation of charge is clearly exhibited in the nanocrystal with the highest ZnS shell thickness because the excitonic bleach shows a slower electron cooling rate and increased amplitude of a slow recovery component in the red region of transient absorption spectrum.

1. INTRODUCTION

Semiconductor nanocrystals have emerged as a versatile material for solar energy conversion, light-emitting devices, and bioimaging because of their shape, size, and surface dependent optoelectronic properties originating from quantum confinement. This charge-carrier confinement can be tuned by suitable surface-bound surfactants and impurity doping as well as by introducing a shell material either in a type-I structure where both the electrons and holes are confined only in the core or through a type-II structure where one of the charge carriers leaks to the shell, leading to charge separation. The charge-separated state in type-II nanostructures has been a subject of intense investigation because of its long-lived nature. Schmickler et al. have analyzed the steady state absorption and emission spectra to demonstrate the energetics of charge-transfer state in CdSe/CdTe type-II nanorods with the help of Marcus theory, concluding that charge separation occurs in the Marcus inverted region. The dynamics of the charge-transfer state has also been analyzed in detail for different type-II nanocrystals utilizing femtosecond transient absorption spectroscopy. Burda et al. have studied both energetics and dynamics of charge transfer in CdTe/CdSe core/shell spherical nanocrystals demonstrating charge separation in the inverted region with \(-\Delta G_{et} > 0\) build-up time for the CT state. Furthermore, Zanck et al. have inferred the dynamics of charge-transfer state in ZnSe/CdS/ZnSe nanobars along with the Marcus inverted behavior of charge transfer from ZnSe to CdS.

Although formation of type-I or type-II nanocrystals depends entirely on the band alignment of the core and shell materials, Nie et al. have shown type-I to type-II conversion is feasible utilizing lattice strain at the core/shell interface when a compressive shell is put over soft CdTe core. The lattice strain at the core/shell interface tends to alter the conduction band alignment of both the core and the shell material, leading to charge carrier leaking. However, the energetics and dynamics of this strain-induced charge separation is still obscure. To shed light on what was unexplained, we have provided an in-depth analysis of strain-induced charge separation energetics and dynamics in type-I CdTe/ZnS nanocrystals, employing both steady-state and time-resolved measurements.

To demonstrate quasi-type-II behavior through strain-induced charge carrier leaking we have synthesized two different CdTe/ZnS nanocrystals with varying shell thickness from CdTe core through a successive ionic layer adsorption and reaction (SILAR) method using literature reports with some modifications. The CdTe core is termed (a) and core/shell nanocrystals are termed as (b) and (c) for 2-monolayer (ML) and 4-ML of ZnS thickness respectively, with 1 ML \(\approx 0.32\) nm.
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Lattice-Strain-Induced Slow Electron Cooling Due to Quasi-Type-II Behavior in Type-I CdTe/ZnS Nanocrystals

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Tuning the Charge Carrier Dynamics via Interfacial Alloying in Core/Shell CdTe/ZnSe NCs

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Supporting Information

ABSTRACT: For core/shell semiconducting nanocrystals, the interfacial alloy has an important role governing the charge carrier dynamics. This work focuses on CdTe/ZnSe spherical core/shell NCs where the optical spectra and charge carrier dynamics can be tuned depending on the synthetic conditions employed. When ZnSe is coated on top of CdTe core at a nominal (~220 °C) reaction temperature, the effect of interfacial alloying is less pronounced. Interestingly, as the reaction temperature is sequentially changed between 220 and 280 °C during core/shell synthesis a blue-shifted short-lived (~10 ns) emission appears accompanied by the normal long-lived (~60 ns) core/shell emission. This blue-shifted emission has its origin in the interfacial alloyed layer which forms due to ionic diffusion. At elevated temperature (~280 °C) this blue emission diminishes with an increase in the overall QY for the core/shell emission around 700 nm. Ultraviolet transient absorption spectroscopy reveals the interplay of carrier population dynamics in first and higher excitonic states which are subsequently affected by interfacial alloying.

1. INTRODUCTION

Copious synthetic strategies developed during the past two decades have made size, shape, and composition control of semiconducting nanocrystals (NCs) readily attainable.1–4 Because of this synthetic flexibility and tunable optoelectronic properties these NCs have become lucrative candidates for solar energy harvesting, photocatalysis, bioimaging, light-emitting devices, and electronics. The optical properties can be further improved or even altered when two or more semiconducting materials are put together forming a heterostructure either in an alloyed material without any interface or in a core/shell structure with a well-defined interface (or interfaces).5–8 This heterojunction can be very sharp where the carrier confinement potential varies steeply from core to shell or can be an alloyed interface with a swift change of confinement potential. Thus, tailoring the structure of this heterojunction provides a unique way to control the carrier confinement which in turn affects the overall NC properties. Two vital factors controlling the nature of the interface are interfacial strain and alloying. The interfacial strain arises due to lattice mismatch between core and shell materials as the core and shell have different lattice parameters. If the strain is high enough the band alignment of the core and shell can be modulated so that the electronic wave function leads to the shell, converting a type-I structure to a type-II one. Recent literature has documented the effect of lattice strain on the optical properties of core/shell NCs along with the energetics and dynamics of strain-induced charge separation.9–12 However, the strain tends to create interfacial defects, which is detrimental for high photoluminescence (PL) quantum yield (QY). Having an alloyed interface between the core and the shell releases the strain making a smooth interface, thereby decreasing the defects. For cadmium and zinc chalcogenide-based quantum dots this interfacial alloying process has been extensively studied.2,3,9–12 The interionic diffusion between core and shell materials becomes fast enough at temperatures higher than 270 °C, which promotes significant alloying at the core/shell interface.13 The alloyed interface is capable of reducing the interfacial defects, resulting in highly luminescent NCs.9–12 Also, smoothing of the confinement potential in the alloyed layer results in slow Auger recombination rate for CdSe/CdS NCs.13–15 Zamkov et al. reported the blue-shifted emission in CdTe/ZnSe tetrapod NCs, which was attributed to alloy formation at the core/shell interface.16 Thus, both interfacial alloying and lattice strain at the interface are the two dominating factors that control the charge carrier confinement and exciton dynamics.

Here, we report a case of CdTe/ZnSe NCs where both the blue-shifted interfacial alloyed emission and the strain-induced red-shifted core/shell emission were found compared to the CdTe core. The core/shell NCs were synthesized using a spherical CdTe core onto which a thin layer of ZnSe shell (~1–1.5 ML) was introduced through successive ionic layer
Elucidating the Electronic Cross-Talk Dynamics across the Heterointerface of Janus CdSe/PbSe Nanocrystals

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ABSTRACT: CdSe/PbSe Janus heteronanocrystals (HNCs) were synthesized in one pot, and the underlying reaction mechanism along with the epitaxy at the heteroepitaxial CdSe—CdSe PbSe heterointerface were investigated. During the initial stages of reaction, unusually large CdSe nanocrystals were formed due to rapid growth in the presence of Pb oleate which cation exchanged anisotropically to form the Janus structures. Distinct PbSe and CdSe domains were visualized after sufficient growth as seen from the high-resolution transmission electron microscopy images with a unique rock salt PbSe and wurtzite CdSe interface. The core Pb—Se bonds were differentiated from interfacial Pb—Se bonds through the X-ray photoelectron spectroscopy measurements. Transient absorption spectroscopy of the Janus NCs revealed intriguing spectroscopic signatures in both the spectral and time domains as manifested by the early population of higher excitonic states upon pulsed laser excitation along with broad TA spectra rich in higher excitonic states due to the intrinsic hybridization between the electronic states of two disparate materials. The TA measurements were well correlated with the formation of the Janus structure as new states emerged at the longer wavelength side in the TA spectra due to PbSe accompanied by a slow ~5 ps additional electron cooling component arising due to hole localization in the PbSe domain.

1. INTRODUCTION

The desire to architect heteronanocrystals (HNCs) comprising two or more semiconducting materials having different physiochemical properties emerges due to the outstanding optoelectronic properties they possess important for both technological applications and fundamental research. The optoelectronics of these HNCs often surpass their individual components providing a unique way to control and/or create new properties. Recent progress in synthetic methodologies has provided several types of HNCs forming either symmetric core/shell or anisotropic structures. All these HNCs rely upon the tunability of the charge carrier confinement, either confining them in a type-I structure to recombine with high photoluminescence quantum yield or separating them in a type-II structure to get extracted for catalysis or harnessing solar energy. The intermixing of electronic states between the constituting components in these HNCs often leads to unique charge carrier dynamics very different from the excitonic properties of the individual components.

In this regard, Cd and Pb chalcogen especially CdSe and PbSe based HNCs score considerable attention representing a unique system where two structurally immiscible materials with very less crystal mismatch, extremely different charge carrier effective masses, and different band alignments coexist forming a sharp heterointerface. Both the symmetric and asymmetric structures are possible depending on the reaction conditions employed providing fundamental information about the reaction mechanisms and tunable properties. Anisotropic structures are derived either from restructuring the core/shell NCs or direct Pb (Cd) to Cd (Pb) cation exchange with judicious change in the reaction conditions. Partial cation exchange on presynthesized CdSe NCs often leads to anisotropic Janus HNCs where one part is composed of CdSe and the other is PbSe. For Janus HNCs both CdSe and PbSe are surface exposed in contrast to the core/shell NCs where the shell creates a barrier for charge transfer interactions. In CdSe/PbSe HNCs due to quasi type-II band alignment the hole localizes in the PbSe region while the electron is spread throughout the NC. Thus, Janus HNCs are advantageous as both electron and hole are specially decoupled and accessible to the surface beneficial for photocatalytic reactions and photovoltaics. However, the behavior of the photoexcited charge carriers which is the key to optimize the excitonic properties is rather obscure in these Janus structures.

In this work, we have synthesized CdSe/PbSe Janus NCs to investigate the heterogeneous exciton dynamics across the interface. Moreover, in contrast to the present literature we have synthesized the Janus HNCs in one pot and shed light on the mechanistic aspects of partial cation exchange. The modulation of charge carrier dynamics with the mechanism through which the Janus structure forms has also been elaborated in this study. The Janus NCs were synthesized by injecting Se-trioctylphosphine at ~250 °C in a mixture of Cd and Pb-oleate and growing the NCs at 270 °C. In the presence...
Electrochemical Evaluation of Dopant Energetics and the Modulation of Ultrafast Carrier Dynamics in Cu-Doped CdSe Nanocrystals

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Supporting Information

ABSTRACT: Cyclic voltammetric and femtosecond transient absorption (TA) measurements on Cu-doped CdSe nanocrystals (NCs) were utilized to reveal the energetics of the electroactive Cu' dopant with respect to the band energies of CdSe NC host and the influence of Cu in tuning the carrier dynamics, respectively. Oxidation-reduction peaks due to an electroactive dopant within CdSe NC host have been traced to determine its energy level which was correlated to the dopant emission energy and Stokes shift. The low doping density of Cu does not significantly alter the band structure of CdSe as the shape of the TA spectra remains similar before and after doping. However, Cu acts as a hole localizing center decoupling the electronic wave function from the hole leading to slower Auger-assisted electron cooling in doped NCs. As hole localisation to Cu' is the primary step for dopant emission, in the presence of hole quenchers (aminophenols) the dopant emission gets drastically quenched. Interestingly, once hole is captured by Cu' due to strong affinity for electron, external quenchers (nitrophenols) are unable to capture the electron as confirmed from steady state and time-resolved measurements establishing the role of Cu as an internal sensitizer for the charge carriers.

1. INTRODUCTION

Doping transition metal ions in a semiconducting nanocrystalline host efficiently introduces new optoelectronic properties resulting from dopant–exciton interaction. In this regard, Cu-doped semiconducting NCs are promising candidates for light emitting devices and display technologies due to tunability of emission, long radiative lifetimes with high quantum yields, and large Stokes shift. In Cu-doped NCs, a broad tunable dopant photoluminescence (PL) arises from the recombination of delocalized conduction band (CB) electron with the Cu-localized hole. The photophysical properties of Cu-doped NCs have been extensively studied including tunability of the dopant emission, single particle spectroscopy, electronic structure of doped NCs revealed through density functional theory (DFT) calculations, and use of Cu dopant as nanosensor to monitor the optoelectronic properties of NC host. However, electrochemical measurement on doped NCs where the signal due to an electroactive dopant is traced to determine the energetics of the dopant relative to the NC host is rare. Electrochemical measurements based on cyclic voltammetry (CV) are one of the simplest ways to determine the band-edge parameters and trap along with midgap state energetics of NCs. Considering this, the present study presents cyclic voltammetric measurements on Cu-doped CdSe NCs explicitly determining the dopant energy level and thus correlating the large Stokes shift and dopant emission energy with band-edge energies of CdSe NC host. Previously, few attempts were made for bulk materials in the case of bulk ZnSe, CdSe, CdS, and CdTe crystals and in CdSe NCs through sophisticated ultraviolet photoelectron spectroscopy (UPS); however, determination of energy levels for the Cu dopant in the NC host through electrochemical technique still remains elusive.

Recently Fuhr et al. have determined the Cu-related defect state energy in CIS NCs through electrochemistry correlated with the photoluminescence Stokes shift. Moreover, the role of Cu dopant in affecting the exciton dynamics in ultrastark time scale for Cu-doped II–VI NCs has not been elucidated in detail so far. Earlier Gal et al. have reported charge carrier dynamics in nanosecond time scale for Cu-doped II–VI NCs through measuring the effect of Cu doping in the luminescence decay of the band-edge emission. However, to fully explore the optoelectronic properties, the exciton dynamics needs to be investigated in picosecond to femtosecond time scale. The influence of Cu on the exciton

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Boosting the Efficiency of Quantum Dot-Sensitized Solar Cells through Formation of the Cation-Exchanged Hole Transporting Layer

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ABSTRACT: In search of a viable way to enhance the power conversion efficiency (PCE) of quantum dot-sensitized solar cells, we have designed a method by introducing a hole transporting layer (HTL) of p-type CuS through partial cation exchange process in a postsynthetic ligand-assisted assembly of nanocrystals (NCs). High-quality CdSe and CdSe/CdS gradient alloy NCs were synthesized through colloidal method, and the charge carrier dynamics was monitored through ultrafast transient absorption measurements. A notable increase in the short-circuit current concomitant with the increase in open-circuit voltage and the fill factor led to 45% increment in PCE for CdSe-based solar cells upon formation of the CuS HTL. Electrochemical impedance spectroscopy further revealed that the CuS layer formation increases recombination resistance at the TiO2/NC/electrolyte interface, implying that interfacial recombination gets drastically reduced because of smooth hole transfer to the redox electrolyte. Utilizing the same approach for CdSSe alloy NCs, the highest PCE (4.03%) was obtained upon CuS layer formation compared to 3.26% PCE for the untreated one and 3.61% PCE with the conventional ZnS coating. Therefore, such strategies will help to overcome the kinetic barriers of hole transfer to electrolytes, which is one of the major obstacles of high-performance devices.

1. INTRODUCTION

Quantum dot-sensitized solar cells (QDSSCs) are promising candidates for 3rd generation solar cells because of their easy solution processability and low-cost fabrication technology, broad absorption spectra, high extinction coefficient, size, shape, and composition-tunable band gap, high photostability, and possibility of multiple exciton generation.1–5 However, till date, the QDSSC has reached about 13% efficiency which is way beyond the theoretical limits.1 In QDSSCs, exciton trapping and recombination are the major two processes that inhibit the charge carrier extraction, thus reducing their efficiency.1,2,3 Moreover, proper choice of the counter electrode and electrolyte is also very important and the use of the CuS or CuSe electrode along with a polysulfide electrolyte is well-accepted in the literature for QDSSCs.6–8 As for QD sensitizers, alloy nanocrystals (NCs) having excellent opto-electronic properties and photostability compared to their individual counterparts, improve solar cell performance. The alloy structure helps to absorb in a broader range and exhibits better charge separation.9–13 Therefore, the biggest challenge in QDSSCs is to control and reduce the unwanted exciton trapping and recombination at the TiO2/ QD/electrolyte interface, which is the focus of many recent investigations.12,14–19 In this regard, a passivating layer of a wide band gap semiconductor such as ZnS20–22 together with SiO2 has proved to be advantageous in improving the efficiency of the TiO2/QD/ZnS/SiO2 assembly.23–25

As discussed in the literature, one of the main limiting factors of the performance of QDSSCs is the hole transfer to the redox electrolyte which is orders of magnitude slower than the electron injection to TiO2.26–30 Previously, an inorganic capping layer has been used to facilitate hole transfer to the electrolyte from the NC valence band (VB).31–36 One of the limitations was the use of NCs grown by a successive ionic layer adsorption and reaction (SILAR) technique which suffers from corrosion of the device and limited control over NC size distribution, resulting in uncontrolled surface passivation and trap state density leading to poor solar cell performance.37–40

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Chapter 7

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This is to certify that Mr. Sourav Maiti of BARC, Mumbai has participated and delivered an Oral Presentation entitled "Exciton Dynamics in CdSe/PbSe Janus Hetero-nanocrystals" in DAE-BRNS Theme Meeting on Ultrafast Science-2016 (UFS-2016), held at Bhabha Atomic Research Centre, Mumbai, India during November 24-26, 2016.

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This is to certify that Mr. Sourav Maiti of BARC, Mumbai has participated and presented a poster entitled "Exciton dynamics and cyclic voltammetric studies with Cu-CdSe NCs" in DAE-BRNS Theme Meeting on Ultrafast Science-2016 (UFS-2016), held at Bhabha Atomic Research Centre, Mumbai, India during November 24-26, 2016.

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