SYNTHESIS AND DYNAMICS OF PHOTOCATALYTIC TYPE-II ZNSE/CDS/PT METAL-SEMICONDUCTOR HETERONANOSTRUCTURES

Timothy F. O'Connor III

A Thesis
Submitted to the Graduate College of Bowling Green State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2012

Committee:
Dr. Mikhail Zamkov, Advisor
Dr. Lewis P. Fulcher
Dr. Liangfeng Sun
ABSTRACT

Advisor: Mikhail Zamkov

The following presents an analysis of the energetics of photocatalytic ZnSe/CdS/Pt metal-semiconductor heteronanorods capable of performing a sustained $\text{H}_2$ reduction reaction. The study begins with an investigation of the effects of charge carrier localization on the stability and efficiency of ZnSe/CdS/Pt. By switching the seed material of the dot-in-a-rod structure from ZnSe to ZnTe, the band edge alignment of the linear system can be altered from one that expels positive holes to the surface ligands of the structure to one that localizes holes in the semiconductor core, as is energetically favorable in the ZnTe seeded system. Positive holes that are not removed from the semiconductor domain are then available to oxidize the core, compromising the structure and photocatalytic capacity of the nanocrystal. In contrast, ZnSe seeded heteronanorods capable of removing chemically active holes pass this photodegradation on to the ligand moieties, destroying the inexpensive, organic surfactants rather than the nanostructure. Interestingly, it was found that fresh ligands can be reattached after the desorption of oxidized ligands, allowing for a larger turnover of photocatalytic cycles to be achieved.

After studying the effects of band edge energetics, a deeper analysis of the ultrafast charge carrier dynamics was undertaken to determine the time scales at which the three dominant charge transfer processes, namely, electron transfer from CdS to Pt, hole localization within ZnSe, and the subsequent hole transfer to the surface ligand, occur. The photocatalytic reaction rate is theorized to be limited by the slowest charge transfer mechanism, which was determined to be the removal of the hole from the semiconductor core by employing femtosecond transient absorption spectroscopy. These time resolved spectroscopic measurements yield a more
complete understanding of the energetic processes at work within the nanostructures and glean
insight as to methods of making more efficient photocatalytic nanoreactors.
I dedicate this thesis to those whom I love:

To the friends of my youth. I will wander far, but those years will always be near in my mind.

To my family, for making me feel welcome in this world.

To Sabrina and Sean, for being there for me over the years and sharing with me their confidence and their wisdom.

To my grandparents, David and Louise, for their faith in me, and Lila, for inspiring me.

To my sister, Christina, whom I am so proud of and happy for, as she continues her own journey.

To my parents, Timothy and Stephanie, for their guidance and for the unwavering support they have given me over the course of my life.

And to Josie Hug, who was with me through every step of this journey.
ACKNOWLEDGMENTS

I would like to thank those who have helped me grow and achieve:
My fellow lab and class mates, who have worked and learned alongside me. This would not have been possible without our cooperative efforts, with a special thanks to Erich, Geoff, and Tyler.

Dr. Haowen Xi, who has taught me to think of the world through inspiring new perspectives.

Dr. Lewis Fulcher, who instructed my first physics class at the university, after which I began my journey to become a physicist. Since then he has taught me everything I know about the classical universe.

And Dr. Mikhail Zamkov, for guiding my progress as a scientist and a researcher, giving me the opportunity to prepare an excellent future, and for being a brilliant advisor, an honorable colleague, and a true friend.

Thank you.
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INTRODUCTION

The increasing demand for renewable energy sources has provided the motivation for significant effort to be invested in the development of inexpensive and efficient light-harvesting materials.\(^1\) Of particular interest is the photocatalytic production of solar hydrogen from water and methanol, which allows for the conversion of sunlight directly into usable fuels. Photocatalytic hydrogen production is also a thermodynamically favorable process, as most of the solar power is delivered via photons that are energetically capable of driving the water splitting reaction (\(\lambda < 1100\) nm). Our ability to harvest these resources comes down to a number of technological challenges that are largely synthetic in nature. Among these challenges is the design of materials that efficiently absorb solar radiation and convert the photon energy into long-lived charge-separated states is of key importance.

Over the last decade, the field of photocatalysis has witnessed an escalation of activity, aided by significant advances in nanotechnology and nanofabrication of semiconductor and metal nanostructures, which resulted in the development of several successful strategies for extending the spectral range of photocatalysts beyond that of ultraviolet-primed TiO\(_2\). Doping,\(^2,3,4,5\) metal ion-implantation,\(^6,7,8,9,10\) modification of oxide surfaces with molecular or nanocrystal sensitizers,\(^11,12,13,14,15,16,17\) employment of alternative materials based on novel metal oxides\(^18,19,20\) and sulfide\(^21,22,23,24,25,26,27\) semiconductors, and semiconductor composites\(^28,29,30,31,32,33,34\) have all been considered for driving catalysis in the visible and near-IR regions of the solar spectrum. In particular, sulfide semiconductor-based photocatalysts have been receiving an increased amount of attention in past years, motivated in part by the excellent light-harvesting characteristics of materials such as ZnS and CdS. It is expected that for the production of solar hydrogen to be
commercially viable in the next decade,\textsuperscript{18} the quantum efficiency of water splitting reactions should be at least 30% at 600 nm wavelengths or near 75% at the CdS absorption edge ($\lambda \approx 460$ nm). This is a realistic target, considering that the best photocatalysts based on nanostructured CdS show yields nearly on the par with this target value.\textsuperscript{35,36,37} Despite these advances, the task of fabricating sulfide semiconductor composites that can simultaneously exhibit efficient absorption, charge separation, and red/ox steps still poses challenges due to technical issues, such as backward charge recombination, side reactions, and material photocorrosion.
CHAPTER I
THEORY AND BACKGROUND

1.1 Nanocrystals

Nanocrystals (NCs) are collections of matter of a single crystalline phase smaller than 100 nm in at least one dimension. As an extension of their incredibly small size these nanocrystals exhibit quantum effects, the extent of which can be adjusted simply by varying the size of the NC. These effects produce new properties in nanomaterials, unlike those of their bulk counterparts, which can be customized for a variety applications by controlling the size and shape of the NC. This increases their range of functionality, along with the low costs associated with creating such structures, makes metal and semiconductor NCs ideal candidates for new age optoelectronic devices.

Nanocrystals can be synthesized inexpensively via colloidal synthesis, which offers sufficient control over the morphology of the crystals. Through colloidal synthesis quantum dots (QDs), nanorods (NRs), nanocubes, nanopyramids, and other unique geometries can be achieved, each with their own characteristics. For instance, QDs offer three dimensional quantum confinement, while NRs of sufficient length confine particle wave functions in two dimensions, allowing them to spread out in the longer linear portion of the structure. By combining nanocrystals of different materials, more complex composite nanostructures, or heteronanocrystals, can be fabricated. Core/shell, dot in a rod, seeded tetrapod, and rod/metal tip structures are some common heteronanocrystals, and the regions at which the domains connect are referred to as heterojunctions. NC composites comprising dissimilar materials can have significantly different physical, electrical, and optical properties in adjacent domains of the same structure.
1.2 Semiconductor – Semiconductor Heterojunctions

Conjoining multiple semiconductor domains in a single nanocomposite provides a higher degree of customization in the development of unique optoelectronic materials. By judiciously choosing the initial domains and the geometry in which they are assembled, such heteronanocrystals can be made to offer superior control over the spatial distribution of charge carriers across material interfaces, in effect determining the overall functionality of the quantum system.

Conventionally, a heterojunction of two semiconductor materials can be classified as either type I, where both carriers are confined within the same semiconductor, or type II, where an electron and a hole are spatially separated in two different parts of the heterostructure. Due to highly stable emissions associated with nanocrystals in the first group\(^38,39,40\), their properties are readily utilized in applications that require a coupling of quantum dots to organic moieties, such as in hybrid LEDs\(^41,42,43\) or in vivo imaging\(^44,45\) where the use of single-phase nanocrystals typically causes an irreversible loss of fluorescence\(^46,47\) or severe blinking\(^48,49,50\). Heterostructures of the second group benefit from an efficient separation of charges between the core and the shell, which makes them useful in photovoltaic applications\(^51,52,53,54,55\), where spatial charge separation reduces an exciton dissociation potential, or QD-based lasers\(^56,57\), where an electric dipole of a photogenerated pair Stark-shifts the biexciton level resulting in a desirable linear light amplification regime.

One common feature, characteristic to above-mentioned carrier localization types is a straightforward correspondence between a quantum dot emission range and the energy spacing between the two closest band edges of the semiconductor materials that form the heterostructure. For both type I and type II heteronanocrystals, the energy of emitted photons is determined by
the energy difference between the closest zero-angular momentum states, 1S(e) and 1S (h), of the adjoined materials.

By choosing the sizes and materials of each domain in a heteronanostructure, a staggered alignment of the band edges at the interfaces of two materials can be achieved. This type of architecture is commonly referred to as a type II system. When an exciton is created within a type II nanostructure, the offset band gaps create a potential gradient, driving the electron and hole away from each other and spatially separating their wave functions. Due to a lesser degree of electron-hole overlap, type II systems generally have weaker fluorescence characteristics and longer emission lifetimes.

Type II systems will also experience a red-shift of the fluorescence peak relative to the emission of their constituents originating from the recombination taking place at the interface between materials, whereby electrons localized in the conduction band of one semiconductor will recombine with holes residing in the valence band of the other. This type of electron-hole recombination is also known as a “spatially indirect” recombination. The typical value of a Stokes shift in type II systems is thus dependent on the magnitude of the band edge offset, and can range from just a few nanometers for CdSe/CdTe nanocrystals to hundreds of nanometers for systems such as ZnSe/CdS or ZnTe/CdS.
1.3 Metal – Semiconductor Heterojunctions

Bulk heterojunctions of metal and semiconductor materials have long been of interest to fundamental science and device engineering due to the unique interaction of respective domains through the formation of the space-charge region, which gives rise to numerous technological applications including Schottky barrier solar cells, solid state lasers, light emitting diodes, and field effect transistors. Recent progress in synthetic methods of nanocomposite fabrication has extended the utility of metal-semiconductor heterojunctions to the nano realm, which has given rise to new opportunities for designing multifunctional materials with properties that cannot be obtained in the bulk phase. These hybrid nanocrystals attribute their properties not only to the size, shape, and configuration of the structure as a whole, but also to the unique interaction between the materials. These synergistic effects allow the nanostructures to function in ways well beyond the scope of their bulk and isolated individual forms. As a result of these advances, in the past decade a wide array of nanocomposite morphologies, including metal-core/semiconductor-shell heterostructures, metal-tipped semiconductor NCs, and organically non-epitaxially coupled metal-semiconductor composites have been proposed for manipulating energy at the nanoscale with potential application of these nanomaterials in areas of photovoltaics and solar fuel production, lasers, and Schottky detectors. Semiconductor domains decorated with metal tips on both sides have been proposed for use as electrical interconnects in nanoscale wiring applications, while semiconductors capped with a metal domain on one side can be harnessed as a charge separating unit in photovoltaic or photocatalytic composites.
1.4 Applications of Nanocrystals in Photocatalysis

As illustrated by a number of recent reports, the functionality of donor-acceptor heteronanocrystals can be greatly increased if one of the semiconductor components is appended with a metal nanoparticle. Such metal domains, fabricated from small-size gold or platinum nanocrystals, can serve the role of an electron sink, thus mimicking the action of a photocathode in photocatalytic or photovoltaic processes. The success of this methodology was exemplified in a number of experiments demonstrating that coupling of charge-separating CdSe/CdS or ZnSe/CdS heteronanocrystals to a small-diameter platinum nanoparticle can result in an efficient photocatalytic system capable of hydrogen production under visible radiation. In these studies a near-complete charge separation was achieved by using a dot-in-a-rod donor-acceptor morphology, for which electron-donating ZnSe or CdSe semiconductor quantum dots were used to seed the asymmetric growth of electron-accepting CdS nanorods appended with a Pt tip. Upon absorption of light, the resulting three-domain system promotes the dissociation of excitons by driving the transfer of photoinduced electrons first into the CdS and subsequently into the Pt domain, while forcing the photogenerated holes to localize within the ZnSe dot. The photocatalytic cycle is finally completed when both an electron and a hole exit the heteronanocrystal through the processes of proton reduction \((2H^+ + 2e \rightarrow H_2)\) and oxidation of the sacrificial agent (e.g. \(CH_3OH + 2h \rightarrow CH_2O+2H^+)\), respectively. Given the multi-step nature of this reaction, the upper limit of the \(H_2\) generation efficiency is expected to depend on the slowest of the three underlying processes, specifically, transfer of an electron to Pt, localization of a photoinduced hole in ZnSe, and transfer of a hole to the surface of the heteronanocrystal.
2.1 Colloidal Synthesis

2.1.1 ZnSe Nanocrystals

ZnSe NCs for seeding the growth of CdS nanorods were synthesized according to the procedure reported by Cozzoli et al.\textsuperscript{94} Briefly, 7.0 g of octadecylamine (ODA) was degassed at 130 °C with stirring for 90 minutes in a three-neck flask. After degassing, the solution was switched to argon and heated to 300 °C. (It is important to use a wide exhaust vent as ODA vapors will re-solidify at room temperature and clog narrow vents). At this point, a selenium precursor prepared by dissolving 0.063 g of Se in 2.4 mL of trioctylphosphine (TOP) through sonication under argon was injected into the reaction flask containing degassed ODA. The mixture was then re-heated to 300 °C. To initiate the NC growth, 1.0 mL of a 10% diethyl zinc (Et\textsubscript{2}Zn) solution (10% by wt. in hexane) was injected directly into the reaction flask and the temperature was allowed to stabilize at 265 °C and kept at this level for the duration of the reaction. The growth was stopped in approximately 5 min when the position of the absorbance edge in growing nanocrystals stopped red-shifting and “saturated” near λ=360 nm. Prolonged growth of nanocrystals sometimes resulted in the formation of nanorods, which was not the desired morphology for ZnSe. After the growth stage, the flask was cooled down to 60 °C, 20 mL of methanol was added, and the flask was reheated back to 60 °C. For the initial cleaning the mixture must be kept at above 55 °C prior to centrifuging to prevent the ODA from solidifying.
NCs were precipitated with methanol and re-dispersed in chloroform twice and stored in chloroform.

2.1.2 ZnTe Nanocrystals

ZnTe seeds were synthesized according to a procedure described in Ref. 2. To fabricate a Te precursor, 0.026 g of Te powder was mixed with 1 mL of degassed TOP and sonicated to get an optically clear solution. Subsequently, 1 mL of 1.1 M toluene solution of Et₂Zn was added to the Te solution and the mixture was stirred at room temperature. In the second flask, oleic acid (OA) (0.8 g) was mixed with 1-octadecene (ODE) (3 g), degassed at 120 °C for 30 min. The flask was then switched to an argon environment and the temperature was raised to 280 °C. At this point, the mixture of Zn and Te precursors was injected into the second flask. After 3 minutes of heating the flask was raised from the mantle and cooled in air. When the reaction mixture cooled down to 60 °C, 2 mL of hexane and 15 mL of ethanol was added. The mixture was then centrifuged at 5400 rpm for 10 minutes and the precipitate was washed one more time using hexane/ethanol extraction. The final product was stored in hexane.

2.1.3 ZnSe/CdS Core/Shell Nanocrystals

For the growth of CdS shells onto ZnSe seeds, a Cd precursor solution was prepared by dissolving 0.03 g of cadmium oxide (CdO), 0.6 mL of OA, and 5.4 mL of ODE at 290 °C under argon while stirring. Once a clear solution was obtained, the mixture was allowed to cool to room temperature. Similarly, a sulfur solution was prepared by heating 0.0077 g of sulfur in 6.0 mL of ODE to 200 °C under argon while stirring until clear and cooling to room temperature. In a 3-neck flask, 1.5 g of ODA and 6.3 mL of ODE were combined and degassed at 120 °C for 30 minutes. After switching
the flask to argon, 1 mL of ZnSe NC solution in chloroform, prepared in the first stage of the procedure were added into the mixture and the temperature was raised to 240 °C. The concentration of ZnSe seeds for the shell growth procedure was determined by setting the absorbance of the NC solution at the exciton shoulder (λ ≈ 360 nm) to 1.5 (as measured using a 1-mm-thick cuvette) – approximately half the amount of NCs fabricated in the first stage. Once the temperature of the reaction mixture reached 240 °C, 0.15 mL of the combined mixture of Cd and S precursor solutions was injected every 10 minutes. The growth of the CdS shell was monitored by measuring the NC emission. For instance, after the second injection, low-intensity red emission appeared due to CdS trap states. The continuous addition of precursors subsequently resulted in the onset of band gap emission at λ ≈ 450 nm, and after 90 minutes, strong green emission (λ ≈ 510-520 nm) was observed, at which point the reaction was stopped by raising the flask from the heating mantle. When the solution temperature reached 50 °C, 18 mL of ethanol was added to the flask and the solution was centrifuged to precipitate NCs, which were then re-dissolved in chloroform. After cleaning the NCs one more time, the precipitate was dissolved in chloroform and stored.

2.1.4 ZnTe/CdSe Core/Shell Nanocrystals

To improve the stability of ZnTe NCs, a thin shell of lattice-matched CdSe was grown onto ZnTe seeds using a procedure described in Ref. 3. In brief, 0.04 M Cd solution was made by dissolving 0.038 g of CdO in 0.6 mL of OA and 5.4 mL of ODE at 290 °C and cooling the mixture to room temperature. 0.04 M Se injection solution was made by dissolving 0.0187 g of Se powder in 6 mL TOP by sonication. Both the Cd and Se solutions were subsequently combined at room temperature. In another flask, a mixture of 1.5 g ODA and 6.3 mL ODE was degassed at ca.120 °C for 1 hour and subsequently switched to argon. At this point, 1 ml of
colloidal ZnTe NCs, grown in the first stage of the procedure were added into the mixture and the temperature was raised to 240 °C. The amount of ZnTe seeds for the shell growth step was determined by setting the absorbance of the NC solution at the excitonic peak, $\lambda = 473$ nm, to 1.2 (as measured using a 1-mm-thick cuvette). When the temperature reached 240 °C, 0.2 mL of Cd/Se mixture was injected every 10 minutes. The growth of core/shell NCs was monitored using steady-state fluorescence measurements. After the addition of a total of 1.2 mL of the Cd/Se mixture, a strong band gap emission at $\lambda = 690$ nm was observed and the reaction was stopped. When the solution temperature reached 50 °C, 16 mL of ethanol were added to the flask and the solution was centrifuged to precipitate NCs. After cleaning the NCs one more time, the precipitate was dissolved in chloroform and stored.

2.1.5 Seeded CdS Heteronanorods

Synthesis of heterostructured nanorods was carried out using a seeded-type growth, according to Carbone et.al.\textsuperscript{95} In a typical procedure, 0.120 g of S was dissolved in TOP (1.81 mL) at 200°C, and after cooling down to room temperature was mixed with 1 mL of nanocrystal seed solution in TOP. The amount of CdSe, ZnSe, ZnSe/CdS, and ZnTe/CdSe seeds for the nanorods growth step was determined by setting the absorbance of the NC solution at the excitonic peak, ($\lambda = 510$ nm for CdSe, $\lambda = 450$ nm for ZnSe/CdS and $\lambda = 680$ nm for ZnTe/CdSe) to 1.0, 1.0, 1.0 and 0.1, respectively (as measured using a 1-mm-thick cuvette). Separately, a mixture of CdO (0.060 g), trioctylphosphine oxide (TOPO) (3.0 g), ODPA (0.290 g), and HPA (0.080 g) in a 50mL 3-neck flask was exposed to vacuum at 150 °C for ca. 30 min. Subsequently, the system was switched to Ar flow and heated to 300 °C until the solution turned optically clear and colorless. At this point, 1.81 mL of TOP was added to the flask and the temperature was raised to 380 °C. The growth of nanorods was initiated
with a swift injection of nanocrystal seeds/sulfur mixture at 380 °C. After the temperature recovered to 350 °C, nanorods were allowed to grow for an additional 7-9 min at 350 °C, upon which the reaction was quenched by raising the flask from the mantle. When the temperature of the reaction mixture reached 60 ºC, 10 mL of chloroform was added and the contents were centrifuged. The supernatant was collected and the white precipitate was disposed of. The solution was then mixed with 20 mL ethanol and centrifuged again. The precipitate was subsequently re-dissolved in 2 mL of chloroform and precipitated one more time using 8 mL of ethanol. The final product was stored in chloroform.

2.1.6 Pt Tipped Heteronanorods

In a typical procedure, 0.2 mL of OA, 0.2 mL of oleylamine, 43 mg of 1,2-hexadecanediol, and 10 mL of diphenyl ether were degassed at 80 ºC in a three neck flask for one hour. Subsequently, the mixture was switched to argon and the temperature was raised to 200 ºC, at which point a mixture of heteronanorods (the entire amount fabricated in the previous step) in chloroform and 20 mg of platinum (II) acetylacetonate was injected. The reaction mixture was heated for 5-7 minutes, until the solution color turned black and the heat was removed from the flask. Pt-tipped nanorods were cleaned two times by precipitating with methanol/chloroform (10:3) mixture, designed to separate isolated Pt nanoparticles from Pt-tipped nanorods. 96

2.1.7 Ligand Exchange

The original hydrophobic ligands on Pt-tipped nanorods were exchanged with hydrophilic MUA or MPA molecules using a method reported by Costi et al. 89 To this end, the solution of nanorods in 10-12 ml of chloroform was mixed with 10 mg of mercaptoundecanoic acid (MUA)
(mercaptopropionic acid (MPA)). Subsequently, 4 mL of KOH solution (0.1 g KOH in 20 mL ultrapure water) was added and the mixture was vigorously shaken until nanorods were transferred into the aqueous phase. The latter was separated and extracted one more time using 2 mL of aqueous KOH. Finally, MUA-capped nanorods were precipitated with 10 mL of methanol and re-dissolved in 4 mL of ultrapure water.

2.2 Characterization

UV-vis absorption and photoluminescence spectra were recorded using a CARY 50 scan spectrophotometer and a Jobin Yvon Fluorolog FL3-11 fluorescence spectrophotometer. High resolution transmission electron microscopy measurements were carried out using JEOL 311UHR operated at 300 kV. Specimens were prepared by depositing a drop of nanoparticle solution in organic solvent onto a carbon-coated copper grid and allowing it to dry in air. X-ray powder diffraction (XRD) measurements were carried out on a Scintag XDS-2000 X-ray powder diffractometer. Fluorescence lifetime measurements were performed using a time-correlated single photon counting setup utilizing an SPC-630 single-photon counting PCI card (Becker & Hickle GmbH), a picosecond diode laser operating at 400 nm as an excitation source (Picoquant), and an id50 avalanche photodiode (Quantique).

2.3 \( \text{H}_2 \) Production Measurements

\( \text{H}_2 \) production measurements were performed by dissolving 1 mg of nanocomposites in 5 mL of the water:methanol mixture, 8:1 ratio by volume, and subsequently degassed with argon bubbling for 30 minutes. The sample solution was held in a 7-mL pyrex round bottom flask and irradiated through with 300W Arc Xenon lamp (Oriel), the output of which was water filtered.
and sent through a fiber optic cable (Oriel) to give 100 mW/cm² irradiation. The area of the beam was 1 cm². Hydrogen was detected from the headspace by taking gas samples at different time intervals using a 100 μL gastight syringe (Hamilton) followed by a gas chromatography analysis (Shimadzu GC-8A, argon carrier gas equipped with a 5 Å molecular sieve column (Restek) and thermal conductivity detector). The number of H₂ moles was calculated from a calibration curve. CO₂ was detected as a byproduct of methanol oxidation but not quantified.

2.4 Ultrafast Transient Absorption Spectroscopy Measurements

The laser system for transient absorption measurements was described in earlier reports. The set-up was based on a Ti: sapphire amplified laser system (Hurricane, Spectra Physics) operating at a repetition rate of 1 kHz/90-fs (fwhm) and delivering 800-nm laser pulses. The laser output was split into two components: one was directed to the TOPAS-C optical parametric amplifier to produce excitation pulses (120 fs @400 nm), and the second was focused onto a CaF₂ plate to generate a white-light-continuum for broad-band probe pulses (350-800 nm). All transient absorption data were corrected for the group velocity dispersion of the white-light continuum with an accuracy ± 25 fs by using the non-resonant ΔA signals from the neat solvent. The incident excitation pulse was attenuated before the sample position using appropriate neutral density filters to ensure the absence of solvent contribution due to non-linear pump absorption at time delays equal to or longer than Δτ = 500 fs. Linearity of the ΔA was verified by plotting the integrated bleach signal versus excitation pulse energy (400 nm pump, 0.4 - 4 μJ range, A= ~ 0.4 at excitation wavelength).
3.1 Introduction

One potentially rewarding strategy deployable for the production of solar fuels has been recently presented through the advances in the synthesis of CdS-based metal-semiconductor (M-S) nanocrystals (NCs). These nanoparticles are formed via coupling of several crystalline domains, each with its unique functionality, into a composite nanostructure that can efficiently drive the separation of photoinduced charges, thus precluding premature electron-hole recombination. Impressive photocatalytic activity of visible-range M-S composites utilizing CdSe/Au, CdS/Pt, CdS-PdX, and CdSe/CdS/Pt material systems has been observed in several recent experiments through water splitting and the reduction of organic dyes. The relative success of these methods was attributed to the two key factors of the composite architecture, the visible-range absorbance of CdS and CdSe semiconductors and the existence of epitaxial bonds at the M-S domain interfaces, which promotes a fast injection of carriers into the metal catalyst. Furthermore, the use of heterostructured CdSe/CdS nano-interfaces has been demonstrated to increase the quantum yield of hydrogen production through the spatial separation of charges in non-adjacent CdSe and Pt domains of CdSe/CdS/Pt nanocomposites.

At the present stage, the potential benefits of CdS-based photocatalysts associated with high efficiencies in the visible range and spatially extended separation of charges are compromised by the limited stability of these materials in comparison with their oxide counterparts. Sulfides are subject to rapid photocorrosion by oxidizing holes, which convert some of the excitation energy into chemical decomposition of the semiconductor into sulfur and metal ions. The stability
issue becomes even more important in the context of commercialization, where in order for photocatalysts to be commercially viable the cost of the H$_2$ produced should exceed the cost of platinum utilized as a catalytic domain of the structure. This puts a constraint on the minimum number of water splitting cycles that a single nanoparticle should perform before its irreversible degradation ($>10^6$-$10^9$)\textsuperscript{101}. The use of sacrificial agents can facilitate the process of hole removal and the suppression of photocorrosion, however in order to be efficiently scavenged the hole first needs to be promoted to the surface of the semiconductor domain. This issue is of central importance to nanoscale photocatalysts comprising heterostructured interfaces (e.g. CdSe/CdTe\textsuperscript{102,103}, CdSe/CdS\textsuperscript{95}, or ZnSe/CdS\textsuperscript{104,105}). These nanocomposites efficiently separate electron-hole pairs, preventing their “backward” recombination, but tend to trap holes in one of the NC domains, causing its decomposition as well as the degradation of the M/S interface\textsuperscript{93}. Consequently, the main challenge concerning the development of sulfide-based semiconductor photocatalysts is no longer associated with maximizing quantum efficiencies, which for systems such as CdS/Pt and CdSe/CdS/Pt already reach 80-90\%\textsuperscript{92}, but rather the more pressing issue of regenerating photoinduced holes that impede the production of H$_2$ via several mechanisms, including decomposition of the semiconductor, photocorrosion of the M/S interface, and rate restriction of the photocatalytic turnover cycle.

3.2 Results and Discussion

Here, the effect of hole localization on the sacrificial hydrogen production by ZnSe/CdS/Pt and ZnTe/CdS/Pt heterostructured nanorods composed of one metal (M) and two semiconductor ($S_1$, $S_2$) domains is analyzed (see Fig. 3.1). The three components of the composite nanostructure are chosen to form a linear energy gradient that drives photoinduced carriers to localize in non-
Figure 3.1 Electronic level diagram showing a relative alignment of excited state energies in (a) ZnSe/CdS/Pt and (b) ZnTe/CdS/Pt nanocomposites. Upon excitation, an electron-hole pair is efficiently separated at hetero-interfaces of the two semiconductor materials with electrons residing in the CdS and holes in the ZnSe(Te) domain of the structure. Subsequently, photoinduced holes undergo further localization, character of which is determined by the relative alignment of hole energies at the semiconductor-ligand interface. For instance, in the case of ZnSe-terminated nanorods, the photoinduced hole is accepted by the ligand molecule (MPA, MUA) and expelled to the surface of the composite nanoparticle; while for ZnTe-terminated nanorods, the hole is confined inside the semiconductor domain.

The resulting spatially-extended localization of carriers helps suppress the “backward” recombination of charges, leading to efficient harvesting of visible photons through the injection of electrons into the Pt catalytic site.

Tuning the localization of photoinduced holes in fabricated nanocomposites was achieved by varying the energy level of the S₁ semiconductor material with respect to the highest unoccupied molecular orbital (HOMO) level of the surface ligand. As shown in Fig. 3.1, when ZnSe material is incorporated as the S₁ component of the nanorod, photogenerated holes are driven to the surface of the structure due to exothermic electron transfer from the HOMO level of the hydrophilic ligand (mercaptopropionic acid (MPA) or mercaptoundecanoic acid (MUA)) to the valence band of the ZnSe material. However, when ZnTe semiconductor, for which the valence band energy lies above the ligand HOMO level, is employed photoinduced holes remain trapped in the S₁ domain giving rise to a different mechanism of carrier decay. Therefore, the two
nanorod morphologies investigated represent the two opposing cases of the hole localization pattern, corresponding to the surface (ZnSe/CdS/Pt) and volumetric (ZnTe/CdS/Pt) confinement of positive charges.

The comparison of photocatalytic activity in ZnSe/CdS/Pt and ZnTe/CdS/Pt nanocomposites revealed that hydrogen production on the Pt site is efficient only when electron-donating molecules are used as surface ligands. These surfactants are critical to the efficient and stable reduction of water by CdS-based nanocomposites as they fill the vacancy in the valence band of the semiconductor domain, preventing its degradation. It was observed that volumetric confinement of the photoinduced hole within the S₁ semiconductor domain (ZnTe/CdS/Pt) leads to a 30-fold suppression of H₂ production rate on Pt when compared to a ZnSe/CdS/Pt system, for which holes are expelled to the surface of the structure and scavenged by methanol.

Perhaps the most interesting outcome of the study was the demonstration that semiconductor nanocomposites utilizing electron-donating ligands degrade primarily via ligand desorption, with minimal decomposition of the inorganic lattice. It was shown that the energy of oxidizing holes can be efficiently transferred to a ligand moiety, leaving the semiconductor domain intact. This allows for recharging of “degraded” nanoparticles with fresh ligands, thus extending the lifespan of expensive inorganic materials (Pt), a task which cannot be easily achieved using homogeneous metallo-organic photocatalysts that tend to degrade irreversibly.106

Synthesis of ZnSe/CdS/Pt colloidal nanocomposites was performed according to previously reported protocols104,105,96 using a four-step procedure. Typically, small-diameter ZnSe NCs were prepared using hot-injection methods, overcoated with a thin shell of CdS (≈ 3 monolayers), and used to seed the growth of CdS nanorods, onto which Pt tips were deposited. The length of CdS nanorods was controlled by varying the amount of ZnSe seeds in the reaction flask.105 To
fabricate ZnTe/CdS/Pt nanostructures, ZnTe seeds were first capped with a few monolayers (ML) of the CdSe shell, serving as a stress-relief layer at the interface of ZnTe and CdS materials (ZnTe/CdS strain = 4.5%, and ZnTe/CdSe = 0.4%\(^{107}\)). The presence of CdSe shell has also helped passivating the surface of air-sensitive ZnTe, resulting in the enhancement of the band gap emission in ZnTe/CdSe core/shell NCs, as compared to that of bare ZnTe cores. Following the synthesis of ZnTe/CdSe seeds, the subsequent growth of CdS nanorod extensions and Pt tips proceeded according to the aforementioned protocol used for the growth of ZnSe/CdS/Pt heterostructures. Detailed procedures for the synthesis of ZnSe/CdS/Pt and ZnTe/CdS/Pt nanocomposites are discussed in Chapter 2: Synthesis and Experimental Apparatus.

Figure 3.2 shows several characteristic Transmission Electron Microscope (TEM) images of fabricated nanocomposites corresponding to the four consecutive stages of the growth protocol. ZnSe and ZnTe NC seeds, fabricated in the first step of the procedure (Figs. 3.2a, 3.2e) exhibited a low dispersion of nanoparticles sizes (6.8% for ZnSe, 8.4% for ZnTe) and were approximately round in shape, which gave rise to the formation of uniform ZnSe/CdS and ZnTe/CdSe core/shell composites in the second stage (Figs. 3.2b, 3.2f, respectively). For both structures, the shell was evenly distributed on the surface of core NCs, as was expected due to a relatively small strain at respective hetero-material interfaces (2.7% for ZnSe/CdS and 0.4% for ZnTe/CdSe). The subsequent growth of CdS extensions onto nanoparticle seeds was confirmed through the observation of characteristic nanorod-shaped specimens (Figs. 3.2c, 3.2g) with an average aspect ratio of 6.2. The average length of grown nanorods was estimated to be 25.5 nm, with a standard length dispersion of 11%. Lastly, the deposition of Pt onto CdS nanorods of both nanomaterial systems resulted in the growth of \(\approx\) 3-nm metal tips (Figs. 3.2d and 3.2h), forming primarily on one side of nanocomposites. Such anisotropic growth of Pt was first demonstrated by Mokari et
Figure 3.2. Transmission electron microscope (TEM) images of ZnSe/CdS/Pt and ZnTe/CdS/Pt nanocomposites corresponding to the four consecutive stages of the growth protocol. (a). ZnSe seed NCs. (b). ZnSe NCs with a few monolayers of the CdS shell. (c). ZnSe/CdS nanorods grown from ZnSe/CdS core/shell NCs. (d) ZnSe/CdS nanorods after Pt deposition. (e). ZnTe NCs. (f). ZnTe/CdSe core/shell NCs. (g). ZnTe/CdSe/CdS nanorods grown from ZnTe/CdSe seeds. (h). ZnTe/(CdSe)/CdS nanorods after Pt deposition.

al. and was attributed to the wurtzite crystalline structure of CdS nanorods that enables an uneven rate of Pt nucleation on Cd- and S-rich nanorod facets.

The character of carrier localization in fabricated heteronanocomposites capped with hydrophobic ligands was substantiated based on their respective optical properties. For ZnSe NCs, the growth of CdS shell was accompanied by the onset of the emission at $\lambda=490$ nm (Fig. 3.3b), resulting from the “spatially-indirect” recombination of carriers, $1S(e)_{\text{CdS}} \rightarrow 1S_{3/2}(h)_{\text{ZnSe}}$, a process which is commonly observed in type II semiconductor heteronanocrystals. As was previously demonstrated by ultrafast spectroscopy studies, the existence of epitaxial associations at ZnSe/CdS nanostructured interfaces promotes a fast separation of photoinduced charges with electrons localizing in the CdS domain and holes in the ZnSe domain of the composite nanoparticle. The resulting charge separated state proceeds to decay through a spatially-indirect radiative recombination, distinguishable in the FL spectra as a red-shifted
Figure 3.3 Optical properties of fabricated nanocomposites. (a). The absorbance of ZnSe NCs showing an excitonic feature at $\lambda = 390$ nm. Band-edge emission was not observed for these samples. (b). ZnSe NCs overcoated with a thin shell of CdS, for which the onset of type II carrier confinement regime is evidenced through red-shifted absorption ($\lambda \approx 475$ nm) and emission peaks ($\lambda \approx 490$ nm). (c). Emission and absorbance of ZnSe/CdS nanorods grown from ZnSe/CdS core/shell NCs. (d). Absorbance of ZnSe/CdS nanorods after Pt deposition. No emission was observed. (e)-(h). Emission and absorbance spectra associated with the four-step growth of ZnTe/CdS/CdS/Pt nanocomposites: (e). ZnTe NCs, (f). ZnTe/CdSe core/shell NCs, (g). ZnTe/CdSe/CdS nanorods grown from ZnTe/CdSe seeds, (h). ZnTe/(CdSe)/CdS nanorods after Pt deposition.
emission peak (Fig. 3.3b). The radiative lifetime corresponding to this transition is typically longer than that of binary semiconductor NCs, as expected due to a relatively small spatial overlap of carrier wave functions in type II systems. Upon growth of CdS extensions, the emission feature at \( \lambda = 470 \) nm further red-shifts to \( \lambda = 535 \) nm (Fig. 3.3c), reflecting the delocalization-induced decrease in the energy of 1S\(_{\text{CdS}}\) electrons associated with the nanorod morphology. Notably, the photon energy corresponding to this emission band is below the band gap energy of either ZnSe or CdS NCs, which further confirms that the recombination of carriers occurs via spatially-indirect transitions. Upon deposition of Pt tips, the emission of nanocomposites was quenched due to a combined effect of photoinduced charge transfer of electrons into M domains and the trapping of carriers at the CdS/Pt interface. The residual FL signal observed in nanoparticle samples after Pt deposition is believed to arise from those structures for which the Pt tip is either missing or too small to suppress radiative decay of CdS excitons. Growth of Pt tips has also resulted in the modification of the absorbance profile of ZnSe/CdS nanorods, distinguishable as an apparent widening of CdS excitonic features. This phenomenon was previously observed in Au/CdS composites and was attributed to the delocalization of the S electronic states into M domains.

Similar to ZnSe/CdS nanocomposites, the band edge alignment in ZnTe/CdS nanorods promotes spatial separation of photoinduced charges across the ZnTe/(CdSe)/CdS interface with electrons residing in CdS and holes in ZnTe domains of the structure. The formation of charge-separated excitons is manifested through the red-shifted emission of 1S(e)\(_{\text{CdSe}}\)\(\rightarrow\)1S(h)\(_{\text{ZnTe}}\) (Fig. 3.3f) and 1S(e)\(_{\text{CdS}}\)\(\rightarrow\)1S(h)\(_{\text{ZnTe}}\) (Fig. 3.3g) interfacial states with associated photon energies that fall below the band gap of either material. The spatial separation of charges in ZnTe/(CdSe)/CdS nanocomposites is also confirmed by the observation of increased radiative lifetimes (\(\tau = 59 \) ns,
Fig. 3.5) of $1S(e)_{CdS}-1S(h)_{ZnTe}$ excitons, which reflects the reduction in the spatial overlap of electron and hole wave functions. Similar to ZnSe/CdS heterostructures, the growth of Pt tips on ZnTe/CdS nanorods resulted in quenching of the emission.

In addition to interfacial morphology, another important factor affecting carrier localization in fabricated nanocomposites is the energetics of surface ligands, which are arguably just as crucial to the decay dynamics as the inter-domain alignment of electronic levels. Initially, surfaces of CdS nanostructures fabricated via hot-injection synthesis are typically capped with a combination of oleic acid (OA), tri-n-octylphosphine (TOP), and hexadecylamine (HDA) hydrophobic ligands, all of which provide a significant potential barrier to electrical charges in these nanostructures. As a result, charge carrier wavefunctions in as-prepared nanorods are confined inside the nanostructure with relatively low amplitudes on nanoparticle surfaces. The localization pattern of carriers in these structures, however, can undergo significant changes when hydrophobic ligands are replaced with hydrophilic MPA or MUA molecules. These ligands lower the potential barrier for photoinduced holes in the valence band (see Fig. 3.1), giving rise to the delocalization of charges or a transfer of holes to a ligand moiety. As was demonstrated by previous works, HOMO levels of MPA hydrophilic ligands are higher in energy than those of valence holes in a number of semiconductor NCs including small-diameter CdSe(S) and ZnSe(S) NCs\textsuperscript{113}. This explains the significant suppression of the FL emission in these materials following the OA→MPA ligand exchange.\textsuperscript{114} On the other hand, when the valence band of the semiconductor NC is located above the MPA HOMO level, the hole remains confined within the NC domain enabling the emission of NC-MPA complexes. The mechanism of the hole transfer in the semiconductor–ligand system has been well exemplified in the case of
CdTe NCs, in which the valence band lies 0.3 eV above that of MPA,\textsuperscript{113,115} resulting in an increased emission of these colloids upon OA→MPA ligand exchange.\textsuperscript{116}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{emission_spectra.png}
\caption{Emission spectra of ZnTe/CdSe/CdS nanorods capped with hydrophilic (black) and hydrophobic (red) ligands.}
\end{figure}

The effect of surface ligands on electronic properties of investigated heterostructures can be readily predicted from known energies of valence holes in ZnSe and ZnTe NCs and their relative positions with respect to the HOMO level of MPA and MUA hydrophilic ligands. According to the energy diagram in Fig. 3.1, MPA ligands are expected to scavenge holes from ZnSe, but not ZnTe core NCs, potentially leading to observable differences in the emission of ZnSe and ZnTe-seeded CdS NRs. This hypothesis was confirmed by the FL measurements of MUA-capped nanocomposites, revealing that the emission of ZnSe/CdS NRs was completely quenched upon OA→MUA ligand exchange, while the emission of ZnTe/CdSe/CdS nanostructures remained the virtually the same (Fig. 3.4). The fact that the emission intensity of ZnTe-seeded NR was virtually unaffected by the OA→MUA ligand exchange indicates that quenching of the emission
in ZnSe/CdS nanocomposites was not the result of nanoparticle aggregation or charge trapping on CdS surfaces, since both ZnSe- and ZnTe-based nanocomposites were prepared in the same manner, and therefore undergone copious surface treatment. Furthermore, both nanoparticle types produced clear aqueous solutions that were stable for weeks in the ambient environment, especially when longer-chain MUA molecules were used for stabilization, indicating that surfaces of these nanocomposites were adequately passivated. Therefore, the observed quenching of FL in MPA- or MUA-capped ZnSe/CdS heterostructures was attributed to the energetically favorable transfer of photoinduced holes to surface ligands.

FL lifetime measurements provide further evidence that the transfer of photoinduced holes is the dominant process contributing into quenching of emission in MUA-capped ZnSe/CdS heterostructures. According to Fig. 3.5a, the lifetime of interfacial excitons in ZnSe/CdS ($\lambda = 540$ nm) is reduced from 42.0 to 1.9 ns upon ligand exchange, indicating a fast depletion of charges in these nanoparticles, meanwhile, the FL lifetime of ZnTe-seeded NRs increases from 31 to 59 ns when OA ligands are replaced with MUA. Notably, the near-exponential shape of the FL decay trace in ZnSe/CdS NCs is consistent with a charge transfer-induced quenching of emission, since processes associated with poor passivation and carrier trapping usually contribute a non-exponential tail into the decay curve which may extend into a microsecond range. Based on these observations, the conclusion is made that MUA ligands efficiently remove photoinduced holes from ZnSe NCs while preventing the NC-to-ligand charge transfer in ZnTe-seeded NRs. The upper limit, associated with the hole transfer time in ZnSe-MUA systems, was estimated to be 1.9 ns, although, the actual transfer time could be substantially shorter than this value, since the FL intensity decay method often underestimates the charge transfer rates in coupled NC systems.
Figure 3.5 Summary of fluorescence lifetime measurements. (a). Comparison of the FL intensity decay traces observed for ZnSe/CdS (blue), ZnTe/CdSe/CdS (red) and CdSe/CdS (green) composite nanorods. Longer lifetimes correspond to a smaller spatial overlap between electron and hole wavefunctions in these structures. (b). Comparison of the FL lifetime of ZnSe/CdS nanorods capped with OA (blue) and MUA ligands (black). The dramatic decrease in the exciton lifetime upon OA→MUA ligand exchange is attributed to the transfer of photoinduced holes to MUA molecules. (c). FL lifetime of ZnTe/CdSe/CdS nanorods capped with OA (red) and MUA ligands (black).
In order to understand the role of hole localization on the rate of hydrogen production the efficiency of the water splitting reactions carried out in ZnTe/CdS/Pt and ZnSe/CdS/Pt nanocomposite systems, corresponding to hole-confining and hole-delocalizing regimes, respectively, were compared. For H\textsubscript{2} production experiments, both nanocomposites were capped with either MPA or MUA ligands, dispersed in water/methanol (8:1 by volume) mixture, and subsequently degassed in a sealed cuvette with argon bubbling for 30 minutes.

Figure 3.6a shows the integrated amount of produced H\textsubscript{2} versus irradiation time for ZnTe/CdS/Pt and ZnSe/CdS/Pt nanocomposites. In the first seven hours of the reaction the rate of H\textsubscript{2} generation on ZnSe/CdS/Pt nanoparticles is several orders of magnitude greater than that of ZnTe/CdS/Pt, indicating that the water splitting process is far more efficient on nanocomposites capable of expelling the photoinduced hole to the surface. Note that surfaces of both nanocomposites are morphologically the same, such that the observed difference in the H\textsubscript{2} production rates can be attributed solely to the energetics of the seed nanoparticle (ZnSe, ZnTe).

To provide further experimental support to this hypothesis, CdSe seeds, which are expected to donate holes to MUA ligands, were used in lieu of ZnSe in H\textsubscript{2} production tests. According to Figure 3.7, the rate of H\textsubscript{2} generation by CdSe/CdS/Pt nanocomposites was found to be nearly the same as in the case of ZnSe/CdS/Pt composites. These results highlight the important role of surface ligands in hydrogen production by sulfide-based semiconductor nanoparticles. It is expected that properly chosen ligands with corresponding HOMO energies designed to drive the photoinduced hole transfer from the semiconductor domain can be used to achieve additional improvements in the efficiency of H\textsubscript{2} production by sulfide semiconductor-metal composites.
Figure 3.6 (a). Evolution of hydrogen production on ZnSe/CdS/Pt (blue) and ZnTe/CdS/Pt (red) nanocomposites. The substantial difference in the amount of generated hydrogen between the two materials is attributed to the dynamics of photoinduced holes in the semiconductor-ligand system. (b). The hydrogen production is resumed upon recharging ZnSe/CdS/Pt nanoparticles with fresh MUA ligands. The $H_2$ production rate (the slope of the experimental curve) after addition of fresh ligands (8-12 hours) is approximately the same as prior to the initial degradation (0-8 hours).

Figure 3.7 Evolution of hydrogen production on CdSe/CdS/Pt nanocomposites.
The lifespan of ZnSe/CdS/Pt photocatalysts observed under 120 mW/cm$^2$ illumination in H$_2$ production experiments averaged 5-7 hours (see Fig. 3.6), which is within the typical range of degradation times observed for homogeneous photocatalytic systems based on metallo-organic compositions. The degradation of the latter has been the subject of many investigations and is attributed to the decomposition of some or all components of the photocatalytic assembly often accompanied by the decolorization of the solution. Conversely, the degradation mechanism associated with the present material system is not well known and is of a particular interest in view of the fact that oxidizing holes, deemed to cause the corrosion of sulfide semiconductors, are now driven away from the CdS/Pt interface and subsequently expelled to the surface of the structure.

To explain the mechanism of ZnSe/CdS/Pt degradation during the water splitting reaction, a comparison between normalized absorbance profiles of “degraded” and freshly prepared nanocomposites have been made. According to Fig. 3.8a, the shape of the ZnSe/CdS/Pt absorption after several hours of the water splitting reaction was nearly unchanged, with maximum differences in the profile of degraded and fresh nanoparticles not exceeding 0.1% across the visible range. The observation of such small changes suggests that structural decomposition of ZnSe/CdS/Pt nanorods was negligible, and therefore, unlikely to be the main cause for the observed suppression of H$_2$ production. While the morphology of ZnSe/CdS/Pt nanocomposites did not change as a result of the photocatalytic reaction, the solubility of these nanoparticles in aqueous solutions has decreased significantly. In contrast to fresh samples that were stable in water for several days, the “degraded” nanocomposites precipitated within hours of the reaction, indicating possible formation of nanoparticle aggregates. This result was also consistent with Fourier transform infrared spectroscopy (FTIR) measurements of degraded
Figure 3.8 Analysis of sample degradation. The absorbance of fresh (black) and degraded ZnSe/CdS/Pt (red) samples is compared in (b) and the associated difference is plotted in (a). The data indicates that the degradation of the inorganic lattice during water splitting is minimal. This is consistent with the fact that the energy of the oxidizing hole is transferred to ligands, which eventually desorb, ceasing the hydrogen production.

Figure 3.9 FTIR measurements showing the reduction in the intensity of vibrational transitions corresponding to MUA surface ligands, after the irradiation of ZnSe/CdS/Pt nanocomposites for 10 hours.
samples, showing a noticeable decrease in the amount of MUA ligand on nanocomposite surfaces (see Fig. 3.9). Based on these observations it is proposed that the suppression of H₂ production on ZnSe/CdS/Pt was caused primarily by the desorption of surface ligands and not the structural degradation of the semiconductor lattice.

The observed desorption of surface ligands, responsible for the loss of photocatalytic activity in ZnSe/CdS/Pt nanocomposites, can be attributed to their key role in removing photoinduced holes from the semiconductor, which exposes these molecules to oxidation. Notably, upon addition of fresh MUA molecules to “degraded” ZnSe/CdS/Pt nanorods, the production of H₂ was resumed at nearly 100% of the original rate (see Fig. 3.6b). These experiments highlight an important fact: the inorganic domain of the nanorod-ligand system can be re-used even after the production of H₂ has stopped, simply by recharging the samples with fresh surface ligands. It should be noted that the demonstrated recovery of photocatalytic properties upon recharging of MUA was tested only for the case of charge-separating nanocomposites that efficiently expel holes via surface ligands, whereas systems such as CdS/Pt may experience some decomposition of the S-M interface. Additional research into the dynamics of charge carriers in sulfide semiconductor-ligand photocatalysts will help answer these important questions.

3.3 Conclusion

The effect of hole localization on the photocatalytic activity of CdS-based heterostructured nanocomposites was investigated. The two nanoparticle morphologies, comprising Pt-tipped dot-in-a-rod ZnSe/CdS and ZnTe/CdS structures designed to efficiently separate photoinduced charges were used to simulate two different regimes of sacrificial water reduction, corresponding to the localization of holes inside (ZnTe/CdS/Pt) and on the surface (ZnSe/CdS/Pt) of the composite nanoparticle. It was found that the rate of H₂ production was substantially greater for
ZnSe/CdS/Pt nanocomposites that efficiently expel photoinduced holes to the surface of the structure via ZnSe-to-ligand charge transfer. The ability of surface ligands to accept oxidizing holes was also found to be crucial in preventing the degradation of the semiconductor-metal composites. In particular it was found that the energy carried by the hole was efficiently absorbed by the ligand/scavenger system leaving the structural integrity of the ZnSe/CdS/Pt nanoparticles intact. These findings highlight the importance of choosing proper energetics of the ligand-semiconductor system for improving both the efficiency and the stability of homogeneous photocatalytic water reduction in the presence of sacrificial agents. In particular, it is expected that the use of re-chargeable, electron-donating ligands may significantly improve the turnover numbers of photocatalytic composites utilizing charge-separating semiconductor hetero-interfaces.
CHAPTER IV

CHARGE CARRIER DYNAMICS

4.1 Introduction

Photoinduced charge separation represents an essential step in the process of solar energy conversion through photovoltaic or photocatalytic reactions. An ongoing search for an artificial system exhibiting such charge-separating capabilities has recently identified a promising approach, which relies on the integration of the two semiconductor domains with complimentary donor and acceptor functionalities into a single nanoscale reactor. When energetically optimized, the two domains of the resulting composite nanocrystal (NC) can promote fast and near-complete separation of excited charges across donor-acceptor interfaces with an overall effectiveness of charge transfer processes being facilitated by a direct, “heteroepitaxial” domain coupling as well as the relatively low exciton binding energy in semiconductor nanomaterials. Furthermore, an all-inorganic composition of such semiconductor nanocomposites ensures their compelling stability against the processes of photodecomposition by ultraviolet photons and thermal degradation in heat-intensive applications. Owing to these benefits, several types of donor-acceptor heteronanocrystals comprising CdSe/ZnSe, ZnSe/CdS, CdSe/CdS, CdSe/CdTe, and ZnTe/CdSe semiconductor combinations have been demonstrated in recent years as potential candidates for solar energy conversion. These studies have also made it clear that integrating composite nanocrystals into photovoltaic or photocatalytic schemes will require the development of novel, often intricate schemes for interfacing both the donor and acceptor components with charge-collecting moieties.
This study investigates the ultrafast dynamics of charge carriers in catalytically active ZnSe/CdS/Pt colloids comprising ZnSe/CdS dot-in-a-rod semiconductor nanocrystals appended with a small Pt tip. Using femtosecond transient absorption spectroscopy, the rates of the three steps involved in the photocatalytic cycle of proton reduction, electron transfer from CdS to Pt, hole localization within ZnSe, and the subsequent hole transfer to the MUA surface ligand, have been determined. An interesting outcome of these measurements was the observation of a fast and efficient sequence of charge-separating processes involved in the proton reduction cycle with the total system regeneration time of approximately 400 ps. In particular, it is shown that absorption of photons by the CdS domain triggers a fast exciton dissociation process (< 20 ps), during which an electron migrates into the Pt tip while a hole localizes in the ZnSe dot. The subsequent transfer of a hole towards photocatalytically active surface of the structure occurs at a substantially slower rate via tunneling to the surface ligand, where its energy is quenched through the methanol oxidation reaction.

It is expected that the efficiency of catalytic reactions performed by photoinduced charges in a ZnSe/CdS/Pt system is strongly correlated with the slowest stage of the photocatalytic process, namely, the transfer of a photoinduced hole to the surface of the semiconductor component (τ > 400 ps). While the dissociation of electron-hole pairs occurs within 20 ps, the semiconductor component (ZnSe/CdS) remains charged for 400 ps. The presence of the photoinduced hole in the ZnSe domain can impede the dissociation of secondary excitons, as can be expected due to the combined effect of electric field screening along the rod axis and the possibility of Auger decay from the trion state. Trapping of holes in the ZnSe domain can also lead to the photoinduced corrosion of the semiconductor lattice itself, which occurs via oxidative reaction: ZnSe + 2h^+ → 2Zn^{2+} + Se. This study analyzes the possible factors underlying the comparatively
slow hole transfer rate and discuss potential modifications of the heteronanocrystal morphology aimed to accelerate the hole exiting time.

4.2 Results and Discussion

A detailed description of the main steps involved in the preparation of ZnSe/CdS/Pt colloidal heteronanocrystals is provided in Chapter 2. In brief, synthesis was performed according to a previously reported four-step protocol. First, small-diameter ZnSe NCs were prepared using hot-injection routes and, in the second step, overcoated with a thin shell of CdS (≈ 1-3 monolayers). The resulting ZnSe/CdS core/shell heterostructures (or “bare” ZnSe NCs) were used as nanoparticle seeds for nucleating the growth of CdS nanorods. The length and the thickness of ZnSe/CdS nanorods were controlled by tuning the amount and the diameter of ZnSe/CdS seeds, respectively. In the final step, Pt tips were grown preferentially onto one of the CdS facets using to a methodology reported in Ref. 96.

Figure 1 shows several characteristic TEM images of fabricated heteronanocrystals corresponding to several successive stages of the ZnSe/CdS/Pt growth protocol. ZnSe NCs, fabricated in the first step of the procedure (Fig. 1e), were approximately 2.7 nm in diameter with an average size dispersion of 7%. To grow a CdS nanorod domain, either “bare” ZnSe or core/shell ZnSe/CdS NCs were used as nanoparticle seeds. Figures 1f and 1h illustrate the effect of an intermediate CdS shell on the ultimate shape of ZnSe/CdS nanorods. According to Fig. 1f, nucleation at ZnSe seeds promotes the growth of narrow-diameter ZnSe/CdS heteronanocrystals with a cylindrical symmetry.
Figure 1. Steady state absorption and emission spectra (a-d) of nanoparticles fabricated at intermediate stages during the 4-step synthesis of ZnSe/CdS/Pt heteronanocrystals. (a) ZnSe NCs (b) ZnSe/CdS nanorods grown from ZnSe NC seeds. (c) ZnSe/CdS nanorods after deposition of the Pt catalyst. (d) ZnSe/CdS nanorods grown from large-diameter ZnSe/CdS core shell NC seeds (e-h). The corresponding TEM images (e-h) are shown in the right panel of the figure.
Conversely, when nanorods are nucleated at large-diameter ZnSe/CdS core/shell NCs, the resulting heterostructures are tapered from the location of the original seed (see Fig. 1h). The average length of grown nanorods used in the spectroscopic measurements was 25.5 nm, with a standard length dispersion of 11%. Lastly, the deposition of Pt onto ZnSe/CdS heteronanocrystals resulted in the growth of ≈ 2-2.9-nm metal tips (Fig. 1g), forming primarily on one side of nanorods. Such anisotropic growth of Pt was first demonstrated by Mokari et al.\textsuperscript{96} and was attributed to the fact that the wurtzite crystalline structure of CdS promotes uneven rates of Pt nucleation on Cd- and S-rich nanorod facets. The elemental composition and crystallographic structure of ZnSe/CdS/Pt heteronanocrystals was analyzed using energy dispersive x-ray and x-ray powder diffraction methods, respectively.

![Figure 2](image-url). Energy dispersive x-ray (EDX) and X-ray powder diffraction (XRD) spectra of ZnSe/CdS/Pt heteronanocrystals.

The character of carrier localization in fabricated heteronanocrystals was substantiated based on their respective optical properties. For ZnSe NCs dispersed in chloroform, the absorption spectrum contained a sharp excitonic feature around $\lambda = 360$ nm, corresponding to the lowest energy 1S(e)-1S$_{3/2}$(h) transitions in these nanoparticles. No band gap emission was detected in
this case. The subsequent growth of CdS nanorods nucleated upon ZnSe seeds was accompanied by the onset of a strong absorbing transition at the CdS band edge (\( \lambda \approx 455 \text{ nm} \)) along with a smaller feature centered at \( \lambda = 525 \text{ nm} \), which corresponds to a “spatially-indirect” recombination of carriers, \( 1S_e(\text{CdS}) \leftrightarrow 1S_h(\text{ZnSe}) \), a process commonly observed in type II semiconductor heteronanocrystals.\(^{55,108,109}\) The position of the latter peak (marked with a red arrow in Fig. 1b) was found to correlate well with the “spatially-indirect” emission (red curve) in ZnSe/CdS nanorods, which was red-shifted by just a few nanometers from its corresponding absorbing transition. The inter-domain (CdS(e) → ZnSe(h)) character of the observed emission peak was consistent with both the low energy of corresponding photons, which fell below the band gap of both CdS and ZnSe semiconductor domains, as well as the relatively long radiative lifetime of the \( 1S_e(\text{CdS}) \rightarrow 1S_h(\text{ZnSe}) \) excited state, reflecting a weak spatial overlap of carriers residing in separated domains.

**Figure 3.** Fluorescence intensity decay of the spatially-indirect emission (\( \lambda = 525 \text{ nm} \)) in ZnSe/CdS/Pt heteronanocrystals capped with original hydrophobic ligands. Nanocrystals were kept in chloroform.
The ultrafast temporal dynamics of excited charge carriers in ZnSe/CdS/Pt heteronanocrystals was investigated using femtosecond transient absorption spectroscopy. This approach is rapidly becoming the method of choice for decoding the ultrafast behavior of excitons in multi-domain semiconductor heteronanocrystals, as a result of its competitive temporal resolution and the straightforward correspondence of the observed spectral (bleach) dynamics with electronic transitions in nanocrystals. In recent years both femtosecond and picosecond TA pump-probe spectroscopy have been used to measure the rates of exciton dissociation and the corresponding charge transfer times in a number of donor-acceptor heteronanocrystals, including CdSe/CdTe\(^{97, 111,132,133,134}\), CdSe/CdS\(^{135,136}\), ZnSe/CdS\(^{105,110,137}\), CdSe/ZnTe\(^{138}\), and CdTe/CdS\(^{139}\) systems. The primary outcome of these investigations was the demonstration of a fast transfer of photoinduced charges across semiconductor-semiconductor interfaces with typical transition times ranging from 300 fs to 100 ps. The exact transfer rate was found to be dependent both on the type of the charge carrier and the nature of the donor-acceptor interface. Despite a wealth of experimental reports on ultrafast electron phenomena in semiconductor heteronanocrystals, to date there have been no experimental accounts on the charge transfer dynamics in donor-acceptor heteronanocrystals appended with catalytically active domains, such as Pt nanoparticles.

Moreover, very little is even known about the effect of a metal tip on a single-phase semiconductor. For instance, it has been reported that metal-semiconductor colloids can trap both photoinduced carriers at hybrid interfaces, such as in the case of CdS nanorods capped with large-diameter Au domains\(^{90}\), or exhibit a very slow semiconductor to metal carrier injection as was reported in the case of ultralong nanorods\(^{140}\).

The structure of ZnSe/CdS/Pt heteronanocrystals selected for this study was chosen to be similar to the morphology of photocatalytically active nanocomposites reported earlier\(^{93,88}\).
Specifically, the size of the Pt domain was kept below 3 nm to suppress the unwanted trapping of photoinduced charges at metal-semiconductor interfaces. Such small-diameter Pt tips were previously shown to enable an efficient generation of H\textsubscript{2} by CdS/Pt composites with an associated quantum yield of up to 90\%\textsuperscript{92}. To better understand the unique role of each of the three domains (ZnSe, CdS, Pt) participating in the charge-separating process, transient absorption (TA) measurements were performed on three types of heterostructures, including Pt-tipped CdS nanorods, all-semiconductor ZnSe/CdS nanorods, and Pt-tipped ZnSe/CdS nanorods, as shown in Figures 4a, 2b, and 2c respectively. Note that the spectral distortions of TA traces associated with the Stark effect\textsuperscript{141} were not observed in these measurements due to the fairly low excitation intensities, corresponding to the linear power dependence regime. A negligible contribution of the Stark effect into the observed bleach dynamics was also consistent with the absence of a positive TA signal (ΔA > 0) at early probe times (τ < 2 ps). Finally, it is anticipated that the observed TA bleach is dominated by the contribution from photoinduced electrons, as expected\textsuperscript{142} due to comparatively low effective masses of these carriers in bulk CdS\textsuperscript{143,144}, as well as the high degeneracy of hole states in CdS NCs.

Figure 4a shows chirp-corrected transient absorption spectra resulting from the excitation of pure CdS NRs appended with a Pt tip (λ\textsubscript{exc} = 330 nm). A strong TA bleach (negative signal) centered at λ ≈ 455 nm is attributed to the excitation of the lowest-energy 1S(e)-1S\textsubscript{3/2}(h) transitions in the CdS domain. By measuring the recovery rate of this feature (Fig. 4d), the lifetime of excited carriers occupying 1S(e)-1S\textsubscript{3/2}(h) states in Pt-tipped CdS nanorods is determined to be 14 ps, which is considerably shorter than the lifetime of lowest-energy excitons in bare CdS (> 1000 ps\textsuperscript{90}) or ZnSe/CdS NRs (~ 900 ps, Fig. 4d). Such a dramatic decrease in the excited state lifetime is attributed to the transfer of excited electrons (and possibly holes) from
Figure 4. Transient absorption spectra of (a) – single-phase CdS nanorods appended with a Pt tip, (b) - ZnSe/CdS nanorods, (c) - ZnSe/CdS nanorods appended with a Pt nanoparticle. The main bleach signal at $\lambda = 455$ nm corresponds to the $1S_{\text{CdS}}(e) \rightarrow 1S_{\text{ZnSe}}(h)$ transition in CdS. The wavelength of the pump beam was set to 330 nm. (d) The temporal dynamics of the $1S_{3/2}(h)1S(e)$ bleach recovery for the three shown nanostructures. (e). Schematic representation of the electron transfer from the conduction band of the CdS domain into a Pt catalyst.

the CdS domain into the Pt tip as well as to the process of charge trapping on Pt islands that tend to form along the surface of CdS. The proposed charge transfer mechanism is consistent with the significant driving force for both carriers in CdS to fill the Fermi level states of Pt, and is supported by previous reports of fluorescence quenching in metal tipped semiconductors.\textsuperscript{145}
The increased rate of exciton dissociation caused by the presence of a Pt domain was also observed in the case of ZnSe/CdS/Pt heteronanocrystals (Fig. 4c). For the ZnSe-seeded structures, the recovery of the band-gap bleach in the CdS domain (λ=455 nm) occurred within 14 ps, which is substantially faster than the recovery of the corresponding bleach signal in bare ZnSe/CdS nanorods (τ = 0.9 ns). Similar to the case of CdS/Pt nanocrystals, the enhanced recovery rate was attributed to the transfer of photoinduced charges into the Pt domain. The difference in the exciton dissociation times between CdS/Pt (4 ps) and ZnSe/CdS/Pt (14 ps) NCs was ascribed to the difference in the sizes of Pt domains in each material, with average tip diameters being 2.9 and 2.2 nm in CdS/Pt and ZnSe/CdS/Pt, respectively. This assumption is supported by a recent study of carrier dynamics in Au-tipped CdS nanorods demonstrating that larger metal domains in a metal-semiconductor systems promote faster recovery of the 1S(e)-1S_{3/2}(h) bleach. Finally, in contrast to CdS/Pt structures, the TA spectra of ZnSe/CdS/Pt nanorods contained a second spectral bleach near λ = 525 nm, which was attributed to the 1S_{e}(CdS)-1S_{h}(ZnSe) spatially-indirect absorbing transitions. The presence of this feature in the TA spectra indicates an important role of the ZnSe domain in carrier dynamics of ZnSe/CdS/Pt heteronanocrystals despite a relatively small volume fraction of the ZnSe crystal phase in these nanoparticles (<3%).

Figure 4d summarizes the temporal evolution of the integrated 1S(e)-1S_{3/2}(h) bleach signals for the three types of investigated heteronanocrystals. As discussed above, the slowest recovery rate was observed for bare ZnSe/CdS nanorods, which indicates that in the absence of a metal domain both carriers tend to stay in one of the excited states of the semiconductor component. When the metal tip is present, the lifetime of 1S(e)-1S_{3/2}(h) excitons is decreased, as evidenced by a rapid decay of the TA bleach in CdS/Pt (blue) and ZnSe/CdS/Pt (red) NCs. Since the main
contribution into the TA bleach of CdS excitons comes from filling of 1S(e) states, the accelerated bleach recovery rate observed in Pt-tipped nanorods is likely the result of an electron transfer (CdS → Pt). The transfer of photoinduced holes into a metal tip could also play a role in depleting the excited state population, as can be inferred from the negative energy of the 1S(h) state with respect to the Pt Fermi level. However, this process does not contribute equally to the TA bleach signal and thus cannot be distinguished from the dominant electron transfer contribution. Based on the observed lifetime of 1S(e)-1S_{3/2}(h) excitons in all three structures, the transfer of photoinduced electrons must occur in less than 20 ps, with the exact charge transfer time being dependent on the size of Pt domain.

To understand the dynamics of photoinduced holes in ZnSe/CdS/Pt heteronanocrystals, we focus on the low energy TA feature (centered at λ=525 nm) that was previously identified as the spatially-indirect absorbing transition at the ZnSe/CdS interface (see the insert in Fig. 5b). When the wavelength of the excitation pulse is set to 400 nm, the direct excitation of band edge excitons in ZnSe is energetically inaccessible. The only transition contributing into the spatially-indirect TA bleach was then the inter-domain excitation of valence electrons occupying the ZnSe domain into the conduction band of CdS. One can expect that due to the subsequent CdS → Pt electron transfer, these inter-domain excitons will be quickly depleted. However, the temporal dynamics of the integrated bleach area shows a distinct rise at early probe times (τ < 2 ps). The delayed enhancement of the 1S_{h}(ZnSe)-1S_{c}(CdS) bleach amplitude strongly suggests that the carrier population in one of the involved states, either 1S_{h}(ZnSe) or 1S_{c}(CdS), is growing for several picoseconds after the excitation pulse. Since the excited electron state of CdS cannot be repopulated due to the lack of excited electrons with energies above that of 1S_{c}(CdS) (since λ_{pump} = 400 nm), the rise in the population of inter-band excitons was attributed to the energetically
Figure 5. (a). Recovery of the TA bleach for the two spectral bands in ZnSe/CdS/Pt nanorods associated with $1S_h(CdS) \rightarrow 1S_d(CdS)$ (green curve) and $1S_h(ZnSe) \rightarrow 1S_d(CdS)$ (red curve) transitions. (b). Steady state absorption spectra of ZnSe/CdS/Pt heteronanocrystals showing the onset of spatially indirect absorbing transition, $1S_h(ZnSe) \rightarrow 1S_d(CdS)$. (c). TA spectra of ZnSe/CdS/Pt nanorods highlighting the $1S_h(ZnSe) \rightarrow 1S_d(CdS)$ bleach near $\lambda=525$ nm. (d). TA spectra confirming the lack of the spatially indirect $1S_h(ZnSe) \rightarrow 1S_d(CdS)$ bleach in single-phase CdS nanorods appended with a Pt tip. (e). Temporal evolution of the TA bleach centered near the $1S_h(ZnSe) \rightarrow 1S_d(CdS)$ transition. The early-time increase in the bleach strength is attributed to a hole transfer from CdS into ZnSe (see text). (f). Schematic representation of the hole transfer process in ZnSe/CdS/Pt heteronanocrystals.
accessible transfer of photoinduced holes from $1S_h$(CdS) into $1S_h$(ZnSe) state. The transition of holes from CdS into ZnSe domain is exothermic and is expected to produce a delayed re-population of the ZnSe valence band, which in turn would result in the enhancement of the $1S_h$(ZnSe)$-1S_e$(CdS) bleach amplitude ($\lambda=525$ nm), as shown in Fig. 5e. It should be noted that a contribution of holes into $\Delta A$ is less than that of electrons, as expected due to high hole-to-electron effective mass ratios, but it is not zero. For instance, hole-induced bleaching of the above-the-pump-energy transition has been observed previously in CdSe/CdS heterostructured nanocrystals.\textsuperscript{135}

The transient absorption measurements indicate that the internal separation of photoinduced charges across the ZnSe/CdS/Pt nanorod occurs in less than 20 ps. Upon completion of this cycle, electrons become localized in the Pt tip and are ready to perform a catalytic function. Photoinduced holes, on the other hand, still remain confined within the ZnSe domain, which is catalytically inactive. Previous works have shown that the energy of the oxidizing hole can be effectively dissipated if it is expelled to the surface of the structures via a ligand-to-semiconductor electron transfer.\textsuperscript{93,146} Specifically, the use of hydrophilic MUA or 3-Mercaptopropionic acid (MPA) ligands facilitate the transfer of the hole to the surface where it is picked up by a scavenger, typically methanol.

The average time associated with the ZnSe-to-ligand hole transfer was determined from the measurements of the radiative decay of spatially-indirect excitons ($1S_e$(CdS) $\rightarrow$ $1S_h$(ZnSe)) in MUA-capped ZnSe/CdS nanorods. To insure that quenching of the emission occurs due to the removal of the valence hole from the ZnSe, and not due to the transfer of photoinduced electrons away from the conduction band of CdS, nanorods were not appended with a Pt tip. In this case
the radiative decay rate is determined primarily by two processes: a slow-rate radiative decay (or trapping) and a fast-rate transfer of holes to surface ligands. As a result, the lifetime of the spatially-indirect emission of MUA-capped ZnSe/CdS nanorods, $\tau_{\text{MUA}}$, provides an accurate estimate of the ZnSe-to-ligand hole transfer time, $\tau_{\text{ZnSe→MUA}}$, such that $\tau_{\text{ZnSe→MUA}} = \tau_{\text{MUA}}(1 + \tau_{\text{MUA}}/\tau_{\text{TOPO}})$. Figure 6 shows the FL intensity decay of MUA-capped ZnSe/CdS nanorods in water. The resulting emission lifetime of $\approx 400$ ps is two orders of magnitude shorter than that of a radiative decay of spatially-indirect excitons in TOPO-capped ZnSe/CdS (60 ns, see Fig. 3), such that the average time involved in the transfer of photoinduced holes to the MUA surface ligand is estimated to be $\tau \approx 400(1 + 0.4/60) \approx 403$ ps, assuming single-exponential decay associated with each of the two contributing processes. The hole transfer completes the charge-separating cycle since both the electron and the hole are now removed from the semiconductor component. Consequently, the ZnSe/CdS system becomes fully regenerated after $\approx 400$ ps following the absorption of a photon.

Figure 6. Fluorescence intensity decay of MUA-capped ZnSe/CdS nanorods (red circles) along with the instrument response time (blue curve). The observed lifetime of excited carriers is approximately equal to the average time associated with the transfer of holes from ZnSe to MUA.
Comparison of the three rates involved in the formation of the charge-separated state in ZnSe/CdS/Pt heteronanocrystals indicates that the slowest process limiting the entire catalytic cycle is the transfer of photoinduced holes to the semiconductor surface. Based on the observed dynamics of electrical charges, a potential direction for enhancing this rate through the morphological optimization of the ZnSe/CdS structure is proposed. Since the layer of CdS deposited over ZnSe seeds acts as a potential barrier to ZnSe-localized holes, the reduction of its thickness should promote an increased hole-to-ligand tunneling rate. In order to reduce the thickness of the CdS layer covering the surface of ZnSe, as-prepared ZnSe/CdS nanorods can be subjected to etching with a mild agent such as benzoyl peroxide, as was demonstrated previously with CdS NCs. While future work will be necessary to test this hypothesis, it is expected that such etching treatment may prove useful in exposing both acceptor (ZnSe) and donor (CdS) domains to external environment for a quicker charge regeneration.

4.3 Conclusion

Transient absorption spectroscopy was employed to investigate the ultrafast dynamics of photoinduced charges in ZnSe/CdS/Pt heterostructured nanocrystals comprising a charge-separating ZnSe/CdS semiconductor component appended with a Pt catalyst. Experimental data provide an accurate estimate of charge transfer rates associated with several sequential processes involved in the photocatalytic cycle of proton reduction. It is shown that the internal electron-hole separation across the ZnSe/CdS interface occurs within 4-14 ps with both electron and holes requiring approximately equal amounts of time for localizations in opposite ends of the structure. However, the charge-separating step makes only electrons available for a catalytic function while photoinduced holes still need to be advanced to the surface of the structure for sacrificial
regeneration. Such hole transfer was found to be relatively slow (> 400 ps) and is viewed here as the bottleneck of the catalytic cycle. Based on the structural analysis of ZnSe/CdS/Pt heteronanocrystals a general direction for the optimization of their morphology has been identified, which can potentially lead to the increased rate of hole transfer to the surface and the corresponding enhancement of the associated turnover frequency.
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