ENGINEERING OF SEMICONDUCTOR NANOCOMPOSITES
FOR HARVESTING AND ROUTING OF OPTICAL ENERGY

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ABSTRACT

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The increasing demand for renewable energy sources requires a significant effort to be invested in the development of inexpensive and efficient light-harvesting materials. It is estimated that the usable portion of the solar energy is an order of magnitude greater than projected energy needs of the entire world in upcoming decades and most of the solar power is delivered at photon energies that are capable of driving photocatalytic hydrogen production or the reduction of carbon dioxide. Our ability to harvest these resources comes down to a number of technological challenges that are largely synthetic in nature. Among those, the design of materials that efficiently absorb solar light and convert its energy into long-lived charge separated states is of the key importance.

We addressed two crucial technology issues concerning composite nanomaterials application for photovoltaics (solar cells) and photocatalytic systems (water splitting):

(i) engineering of active-layer materials for hydrogen production systems and

(ii) development of a novel strategy for processing colloidal nanoparticles into highly photoconductive films for low-temperature production of high-efficiency solar cells.

We investigated the effect of hole localization on photocatalytic activity of Pt-tipped semiconductor nanocrystals. By tuning the energy alignment at the semiconductor-ligand interface, we demonstrate that hydrogen production on Pt sites is efficient only when electron-donating molecules are used for stabilizing semiconductor surfaces. These surfactants play
a crucial role in enabling an efficient and stable reduction of water by heterostructured nanocrystals as they fill vacancies in the valence band of the semiconductor domain, preventing its degradation.

Assembly of thin film devices from semiconductor nanocrystal (NC) “inks” has emerged as a cost-effective approach for the development of next generation light-harvesting materials with the potential to create a considerable technological impact on the solar cell industry. We explored a novel strategy for low-temperature (<150 °C) assembly of colloidal semiconductor nanocrystals into solid films, which resulted in the development of solar cells, processable entirely from solution. Specifically, the main accomplishments of this work included:

(i) hot-injection synthesis and assembly of copper zinc tin sulfide (CZTS) semiconductor NCs into solid films through spin-coating with consecutive ligand exchange,

(ii) optimization of the film morphology towards improving the carrier mobility, and

(iii) fabrication, characterization, and evolution of prototype solar cells comprising the developed morphology.

Improving the efficiency of prototype solar cells was achieved through material optimization (Cu2ZnSnS4 synthesis modification), adjustment of the thickness of functional solar cell layers, and study of ligand exchange and exhalation process. Light harvesting performance of fabricated cells comprising conductive transparent electrodes, CZTS/CdS film, and gold/palladium top contacts was routinely tested by measuring power conversion efficiency (PCE). We have also analyzed the oxidation stability of fabricated devices.
Homage to thee, O thou who risest in the horizon as Ra, passest over the sky, and every face watcheth thee,... and show thyself at dawn and at eventide day by day.

The Papyrus of Ani.

In The Book of the Dead;
British Museum Papyrus #9901;
translated by E. A. Wallis Budge.
To my grandparents: Rufina V. Kirsanova and Vladimir P. Katushkin

To my parents: Tatyana N. Kirsanova and Eduard O. Kirsanov

To my beloved husband: Alexander N. Nemchinov

To my brother: Konstantin E. Kirsanov
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INTRODUCTION

The research and development of molecular systems for catalytic production of solar fuels and environmental clean-up has been steadily growing ever since Fujishima and Honda demonstrated a successful photoelectrochemical decomposition of water on TiO$_2$ in 1972\cite{1}. Subsequently, several material strategies utilizing metal oxides have been introduced to drive catalytic reactions in the UV or blue portion of the solar spectrum. These methods have relied both on heterogeneous photocatalysis with oxide films and slurries\cite{2,3,4,5,6,7,8,9,10}, as well as modified oxide systems comprising noble metal/oxide composites\cite{11,12,13,14,15,16,17,18,19,20,21} and doped\cite{20,22,23,24,25,26,27} or carbonate-salt-assisted\cite{28,29} catalysts. But it wasn’t until 2001 that the first visible photocatalytic system utilizing In$_{1-x}$Ni$_x$TaO$_4$ semiconductor has been demonstrated to catalyze the water splitting reaction\cite{30}.

Over the last decade, the field of photocatalysis has witnessed a spur of activity\cite{31}, aided by the 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 photocatalytic materials beyond that of ultraviolet-primed TiO$_2$. Doping\cite{32,33,34,35} metal ion-implantation\cite{36,37,38,39,40}, modification of oxide surfaces with molecular or nanocrystals sensitizers\cite{41,42,43,44,45,46,47}, employment of alternative materials based on novel metal oxides\cite{48,49,50} and sulfide\cite{51,52,53,54,55,56,57} semiconductors, as well as semiconductor composites\cite{58,59,60,61,62,63,64} – have all been considered for driving catalysis in the visible and near-IR portions of the solar spectrum. Among these, sulfide semiconductors and their nanostructured composites are considered to be of particular interest since these materials allow harvesting a significant portion of visible light. It is expected that for the production of solar hydrogen to be commercially viable in the next decade\cite{48}, the quantum efficiency of water
splitting reaction should be at least 30% at 600 nm or near 75% in the CdS absorption edge ($\lambda \approx 460$ nm), which is a realistic target in light of the fact that the best photocatalysts based on nanostructured CdS show yields nearly on the par with this target value (Fig. 1).\textsuperscript{65,66,67} Despite these advances, the task of fabricating materials that can simultaneously exhibit efficient absorption, charge separation, and red/ox steps still poses tremendous challenges associated with such technical issues as “backward” charge recombination, side reactions, and material photocorrosion.

![Diagram](image)

**Figure 1.** Incident solar power obtained by integrating AM1.5 spectrum\textsuperscript{64}. Grey lines represent max power for devices with 5 and 25% of quantum efficiency. The red area shows the projected power levels obtainable with the hetero-epitaxial donor-acceptor-catalyst (HEDAC) technology.

Facing the problem of depleted sources of natural gas and oil, researchers are constantly looking for the technologies allowing the use of alternative energy sources. In connection with this topic, high-efficiency, low-cost, environmentally friendly second-generation solar cells are in great demand. Commercially used CIS (CuInSe\textsubscript{2}) and CIGS (CuIn\textsubscript{x}Ga\textsubscript{1-x}S(Se)\textsubscript{2})\textsuperscript{68,69,70} thin-film...
solar cells demonstrate fine stability\textsuperscript{71,72} and power conversion efficiencies up to 20\%\textsuperscript{73}, however rare elements used in these materials make them relatively expensive\textsuperscript{74,75}.

Development of Cu$_2$ZnSnS$_4$-based low-cost, non-toxic thin films for photovoltaic applications has become an attractive alternative\textsuperscript{76,77,78}. However, the power conversion efficiencies for this material have not yet been reported higher than 6.7\%\textsuperscript{79}, demanding further improvement. In this project, we develop a conceptually new technology for thin film deposition, allowing for the nanomaterials being absolved from long-chain organic ligands and solvents while having the quantum confinement preserved between the adjacent nanostructures.

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CHAPTER 1. THE ROLE OF HOLE LOCALIZATION IN SACRIFICIAL HYDROGEN PRODUCTION BY SEMICONDUCTOR-METAL HETEROSTRUCTURED NANOCRYSTALS

1.1 Introduction

Production of solar hydrogen through photocatalytic water splitting is a cost-effective strategy that can potentially compete with nonrenewable energy sources. The project seeks the development of active-layer materials, which enable spatially-extensive charge separation, long-term stability, and low processing costs, by exploring the cooperative effort of novel synthetic strategies and advanced spectroscopic investigation of material properties.

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. These nanoparticles are formed via coupling of several crystalline domains, each with its unique functionality into a composite nano-object that can drive an efficient separation of photoinduced charges, therefore precluding premature electron-hole recombination. Impressive photocatalytic activity of visible-range semiconductor/metal 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, including the visible-range absorbance of CdS and CdSe semiconductors and the existence of near-epitaxial bonds at the M-S domain interfaces, which promote fast injection of carriers into the metal catalyst. Moreover, the use of heterostructured CdSe/CdS nano-interfaces has been demonstrated to further 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.  

1.2 Benefits and Challenges

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, as compared to their oxide counterparts. Indeed, 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 light of the fact that for photocatalysts to be commercially viable, the cost of the produced H₂ should exceed the cost of Pt utilized as a catalytic domain of the structure, which puts a constrain on the minimal number of water splitting cycles that a single nanoparticle should perform before its irreversible degradation (\(>10^6-10^9\)). The use of sacrificial agents can facilitate the process of hole removal leading to the suppression of the photocorrosion, however, in order to be efficiently scavenged, the hole needs to be first promoted to the surface of the semiconductor domain. This issue is of central importance for nanoscale photocatalysts comprising heterostructured interfaces, such as CdSe/CdS or ZnSe/CdS. These S-S heterojunctions efficiently separate opposite charges suppressing their “backward” recombination, but lead to trapping of the hole in one of the NC domains, causing its decomposition as well as the degradation of the S/M interface. Consequently, the main thrust concerning the development of visible semiconductor photocatalysts is no longer centered on maximizing quantum efficiencies, since systems such as CdS/Pt and CdSe/CdS/Pt are already sufficiently robust in separating and storing photoinduced electrons to drive water reduction, but is shifted towards a more pressing issue concerning
the regeneration of the photoinduced hole, which hampers the production of H\textsubscript{2} via several mechanisms, including decomposition of the semiconductor, photocorrosion of the M/S interface, and the slowdown of the photocatalytic turnover cycle.

1.3 Accomplishments

Here we investigate the effect of hole localization on the sacrificial hydrogen production by ZnSe/CdS/Pt and ZnTe/CdS/Pt heterostructured nanorods comprising one metal (M) and two semiconductor (S\textsubscript{1}, S\textsubscript{2}) domains (see Fig. 2). The three components of the composite nanostructure are chosen to form a linear energy gradient, which drives photoinduced carriers to localize in non-adjacent parts of the nanorod, with holes residing in the S\textsubscript{1} and electrons in the M domains. The resulting spatially-extended localization of carriers helps suppressing the “backward” recombination of charges, leading to an efficient harvesting of visible photons through the injection of electrons into a Pt catalytic site.

In this work, tuning the localization of photoinduced holes in the S\textsubscript{1} domain of the nanorod was achieved by varying the energy level of the S\textsubscript{1} semiconductor material with respect to the HOMO level of the surface ligand. As shown in Fig. 2, when ZnSe material is incorporated as S\textsubscript{1} component of nanorod, photogenerated holes are driven to the surface of the structure due to exothermic electron transfer from HOMO level of hydrophilic ligand (mercaptpropionic acid (MPA) or mercaptoundecanoic acid (MUA)) to the valence band of the ZnSe material. Meanwhile, when ZnTe semiconductor is employed in lieu of ZnSe, for which the valence band energy lies above the ligand HOMO level, photoinduced holes remain trapped in the S\textsubscript{1} domain giving rise to a different mechanism of carrier decay. The two investigated nanorod morphologies, therefore, 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.

**Figure 2.** Electronic level diagram showing a relative alignment of excited state energies in ZnSe/CdS/Pt (a) and ZnTe/CdS/Pt (b) 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, which character 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 comparison of photocatalytic activity obtained with ZnSe/CdS/Pt and ZnTe/CdS/Pt composites revealed that hydrogen production on Pt site is efficient only when electron-donating molecules are used as surface ligands. These surfactants appear to be of key importance in enabling an 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. In particular, it is demonstrated that volumetric confinement of the photoinduced hole within the S_1 semiconductor domain (ZnTe/CdS/Pt) leads to a 10-fold suppression of H_2 production rate on Pt, as compared to a ZnSe/CdS/Pt system, for which holes are expelled to the surface of the structure and scavenged by methanol. The present experiments also demonstrate that degree
of charge separation in heterostructured nanocomposites (e.g. CdSe/CdS, or ZnSe/CdS and ZnTe/CdS) does not contribute significantly into rate of H₂ production since the transfer of photoinduced holes to the surface of the structure occurs at a substantially faster rate (τ < 1 ns) than “backwards” carrier recombination (τ ≈ 30-50 ns). Nevertheless, the use of photocatalytic nanocomposites that separate photoinduced charges across heterostructured interfaces may be an important factor in shielding the S/M boundary from oxidation by the photoinduced hole.

Perhaps, the most interesting outcome of the present study was the demonstration that semiconductor nanocomposites comprising electron-donating ligands degrade primarily via ligand desorption, with the minimal decomposition of the inorganic lattice. In particular, we show that the energy of oxidizing holes can be efficiently transferred to a ligand moiety, leaving the semiconductor domain intact. This allows re-charging “degraded” nanoparticles with fresh ligands whereby 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.91

1.4 Experimental Section

Synthesis of ZnSe/CdS/Pt colloidal nanocomposites was performed according to previously reported protocols89,90,92 using a four-step procedure. First, small-diameter ZnSe NCs were prepared using hot-injection methods, subsequently overcoated with a thin shell of CdS (∼3 monolayers) and finally 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.90 To fabricate ZnTe/CdS/Pt nanostructures, ZnTe seeds were first capped with a few monolayers (ML) of the CdSe shell, serving as a stress-relieve layer at the interface of ZnTe and CdS materials (ZnTe/CdS strain = 4.5%, and ZnTe/CdSe = 0.4%)93. 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 nanorods extensions and Pt tips proceeded according to the above-mentioned 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 provided in Appendix A.

1.5 Analysis and Discussion

Figure 3 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. 3a, 3e), exhibited a low dispersion of nanoparticles sizes (7% for ZnSe, 9% 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. 3b, 3f, 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 by the formation of characteristic nanorod-shaped nanoparticles (Figs. 3c, 3g) with aspect ratios ranging from 7 to 10. The average length of grown nanorods was estimated to be 20 nm with the standard length dispersion of 20%. Lastly, the deposition of Pt onto CdS nanorods of both nanomaterial systems resulted in the growth of 3-nm metal tips (Figs. 3d and 3h), forming primarily on one side of nanocomposites. Such anisotropic growth of Pt was first demonstrated by Mokati et al. and was attributed to the wurtzite crystalline structure of CdS nanorods that enables uneven rate of Pt nucleation on Cd- and S-rich nanorod facets.
The character of carrier localization in fabricated hetero-nanocomposites capped with hydrophobic ligands was substantiated by their respective optical properties. For ZnSe NCs, the growth of CdS shell was accompanied by the onset of the emission peak at $\lambda = 470$ nm (Fig. 4b), resulting from “spatially-indirect” recombination of carriers, $1S(e)_{\text{CdS}}-1S_{3/2}(h)_{\text{ZnSe}}$ in type II heterostructures.\textsuperscript{94,95,96} As was shown previously by ultrafast spectroscopy measurements,\textsuperscript{90,97,98} the existence of near-epitaxial associations at nanostructured interfaces of ZnSe and CdS materials promotes a fast separation of photoinduced changes with electron localizing in the CdS and holes in the ZnSe domain of the composite nanoparticle. The resulting charge separated state subsequently decays through a spatially-indirect radiative recombination process, distinguishable in the FL spectra as a red-shifted emission peak (Fig. 4b). Notably, the radiative lifetime

**Figure 3.** 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.
corresponding to this transition is typically an order of magnitude longer than that of binary semiconductor NCs, which is attributed 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. 4c), reflecting the delocalization-induced decrease in the energy of $1S_{\text{CdS}}$ electrons, associated with the rod morphology. The narrow bandwidth and the long radiative lifetimes ($\tau = 42$ ns, Fig. 5) of this emission peak provide additional evidence that the observed carrier decay originates predominantly from band edge excitons with no detectable contributions from trap states. 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 undergoes via spatially indirect transition, $1S(e)_{\text{CdS}} - 1S_{3/2}(h)_{\text{ZnSe}}$. 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 trapping of carriers at 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.
Figure 4. 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 a 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.
Figure 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).
Similar to ZnSe/CdS composites, 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)$_{\text{CdSe}}$-1S(h)$_{\text{ZnTe}}$ (Fig. 4f) and 1S(e)$_{\text{CdS}}$-1S(h)$_{\text{ZnTe}}$ (Fig. 4g) 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. 5) of 1S(e)$_{\text{CdS}}$-1S(h)$_{\text{ZnTe}}$ 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 a near-complete 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 arguably is just as critical to the ensuing decay dynamics, as the inter-domain alignment of electronic levels. Typically, surfaces of CdS nanostructures fabricated via hot-injection synthesis are capped with a combination of oleic acid (OA), tri-n-octylphosphine (TOP), and hexadecylamine (HDA) hydrophobic ligands, which all 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. 2), 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, in fact,
higher in energy than those of valence holes in a number of semiconductor NCs including small-diameter CdSe(S) and ZnSe(S) NCs,\textsuperscript{101} which explains a significant suppression of the FL emission in these materials following the OA→MPA ligand exchange.\textsuperscript{102} On the other hand, when the valence band of the semiconductor NC is located above the MPA HOMO level, the emission of NC-MPA complexes remains approximately the same upon ligand exchange. CdTe NCs provide a good example of the latter scenario, as the valence band of these nanoparticles (with a 4.2-nm diameter) is located 0.3 eV above that of MPA,\textsuperscript{101,103} resulting in highly emissive MPA-CdTe colloids, utilized for biological imaging applications.\textsuperscript{104}

The effect of surface ligands on electronic properties and carrier dynamics 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 molecules, which stabilize these nanocomposites in aqueous medium. According to the energy diagram in Fig. 2, 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 NRs. This hypothesis is confirmed by the FL measurements of MPA-capped nanocomposites, revealing that the emission of ZnSe/CdS NRs was completely quenched upon OA→MPA ligand exchange, while the emission of ZnTe/CdSe/CdS nanostructures remained the same (Fig. S1, Appendix A). The fact that the emission intensity of ZnTe-seeded NR was virtually unaffected by the OA→MPA 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, utilized copious surface chemistry. Furthermore, both nanoparticle types produced clear aqueous solutions that were stable for weeks in 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 MPA-capped ZnSe/CdS heterostructures. Indeed, according to Fig. 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 MPA. 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, we conclude that MPA(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-MPA systems, was estimated from the FL decay measurements to be 1.9 ns, however, the actual transfer time may be substantially shorter, as the FL intensity decay method often underestimates the charge transfer times in coupled NC systems.105

To understand the role of hole localization on the rate of hydrogen production, we compare the efficiency of water splitting reaction by ZnTe/CdS/Pt and ZnSe/CdS/Pt nanocomposite systems, corresponding to hole-confining and hole-delocalizing regimes, respectively. For H\(_2\) production experiments, both nanocomposites were capped with either MPA or MUA
ligands, dispersed in water/methanol (1:1) mixture, and subsequently degassed in a sealed cuvette with argon bubbling for 30 minutes. The reaction samples containing approximately 2 mg of nanocrystals in 10 mL of liquid were then illuminated using a filtered output of a 300 W Arc Xenon lamp (Oriel) through a fiber optic (Oriel) providing approximately 120 mW/cm² of spectrally integrated emission. The hydrogen gas was detected from the headspace and analyzed in a gas chromatograph (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 estimated from a calibration curve.

Figure 6a shows the integrated amount of produced H₂ versus irradiation time for ZnTe/CdS/Pt and ZnSe/CdS/Pt nanocomposites. In the first three hours of the reaction, the rate of H₂ 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, which expel the photoinduced hole to the surface. We note that surfaces of both nanocomposites are morphologically the same, such that the observed difference in the H₂ production rates can be attributed solely to the energetics of the seed nanoparticle (ZnSe, ZnTe). This result highlights an important role of surface ligands in hydrogen production by sulfide-based semiconductor nanoparticles. We expect 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 H₂ production on sulfide semiconductor-metal composites.
The lifespan of ZnSe/CdS/Pt photocatalysts observed under 120 mW/cm² illumination in H₂ production experiments averaged 4-5 hours (see Fig. 5), which is a 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.

Figure 6. (a). The rate of H₂ evolution from water on ZnSe/CdS/Pt hetero-epitaxial donor-acceptor-catalyst composites measured versus irradiation time (λ = 465 nm). (b). Photocatalytic reduction of methylene blue dye molecules by ZnSe/CdS/Au hetero-epitaxial donor-acceptor-catalyst nanocomposites (red) and CdS/Au (blue).
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, we have compared normalized absorbance profiles of “degraded” and freshly prepared nanocomposites (Fig. 7). According to Fig. 7a, 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 H2 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 an hour of the reaction, indicating possible formation of nanoparticle aggregates. This result was also consistent with Fourier transform infrared spectroscopy (FTIR) measurements of degraded samples, showing a noticeable decrease in the amount of MUA ligand on nanocomposite surfaces (see Fig. S4, Appendix A). Based on these observations, we propose that the suppression of H2 production on ZnSe/CdS/Pt observed in present experiments was caused primarily by the desorption of surface ligands and not the structural degradation of the semiconductor lattice.
The observed desorption of surface ligands, leading to 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 H$_2$ has resumed at a 30-50% level of the original rate. These experiments highlight an important fact: the inorganic domain of the nanorod-ligand system can be re-used even after the production of H$_2$ has stopped, simply by recharging the samples with fresh surface ligands.

Figure 7. Analysis of the 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 desorbs ceasing the hydrogen production.
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 nanocomposite-ligand photocatalysts will help answering these important questions.

1.6 Conclusion

In 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 ZnSe/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 \( \text{H}_2 \) 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 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 the homogeneous photocatalytic water reduction in the presence of sacrificial agents. In particular, we expect that the use of re-chargeable, electron-donating ligands may significantly improve the turnover numbers of photocatalytic composites utilizing charge-separating semiconductor hetero-interfaces.
References


CHAPTER 2. LOW-TEMPERATURE FABRICATION OF SOLUTION-PROCESSED COPPER ZINC TIN SULFIDE-BASED MULTI-JUNCTION SOLAR CELLS

2.1 Introduction

The increasing demand for renewable energy sources requires a significant effort to be invested in the development of inexpensive and efficient light-harvesting materials.\textsuperscript{109} Among those, colloidal semiconductor nanocrystals are emerging as a promising material class with the potential to produce a considerable technological impact on the solar cell industry. These expectations are mainly related to the unique ability of these colloids to combine the key optoelectronic properties of bulk semiconductors with the prospect for inexpensive solution-based device fabrication. Furthermore, the integration of semiconductor NCs in photovoltaic devices is further inspired by the possibility to tune the energy of nanocrystal charge carriers via nanoparticle size, which opens up a new degree of freedom for controlling charge flow rates at semiconductor/metal interfaces.

The potential for increasing the efficiency of solar energy production through the use of nanocrystal-based light harvesting schemes has been actively explored in the last decade via several photovoltaic architectures, including hybrid bulk heterojunction\textsuperscript{110,111,112,113,114,115,116,117,118,119,120,121,122,123,124}, all inorganic\textsuperscript{125,126,127,128,129,130}, Schottky barrier\textsuperscript{131,132,133,134,135,136,137}, and nanocrystal-sensitized\textsuperscript{138,139,140,141,142,143,144,145,146,147,148,149,150,151,152,153,154,155,156,157} solar cells, most of which successfully exploit the key advantages of nanoscopic semiconductors, such as size-tunable exciton energies and solution-phase device development. Nevertheless, the present-day performance of NC solar cells is still several times lower than the target value needed to effectively compete with the first and second generation photovoltaic devices.
The fundamental issue limiting the power conversion efficiency of NC solar cells concerns a poor electrical coupling between individual nanocrystals within solution-processed NC films that deliver photogenerated charges to electrodes. Since NCs are fabricated in via chemical routes, their surfaces become naturally encapsulated with a layer of organic ligands, which renders nanoparticle soluble and, simultaneously, serves as a protective barrier between electrical charges in NCs and their external environment. The presence of such organic shell, however, prevents an efficient coupling between colloidal NCs, leading to fairly short carrier diffusion lengths. As a result, the photoconductivity of ensuing NC solids remains below the corresponding values of bulk semiconductors, decreasing the efficiency of NC-based devices.

Several strategies for improving inter-NC coupling have been explored in the last few years, focusing for the most part on replacing the original bulky ligands on NC surfaces with shorter organic molecules or inorganic metal complexes. For example, binding or interlinking with short-chain dithiols, ethylenediamine, 3-mercaptopropionic acid (MPA), hydrazine, pyridine and metal chalcogenide ligands have all been considered for increasing the mobility of electrical charges in NC films.

We have developed the technique allowing low-temperature (below 150 °C) solution-processed fabrication of all-inorganic prototype heterojunction solar cells. An important advantage associated with this technique is the absence of any organic phase in resulting NC solids. This property is vital for solar-absorber materials, in view of expected thermal loads that photovoltaic panels will have to withstand in field conditions. It is well known that NC films interconnected with organic molecules (hydrazine, dithiols) while relatively efficient, are yet unlikely to endure an expected thermal impact for a minimum length of time that renders this technology cost-effective.
2.2 Materials and Methods

Single photovoltaic cell contained a network of donor-acceptor pairs (TiO₂, CdS and Cu₂ZnSnS₄) sandwiched between transparent conductive anode (ITO) and an Au/Pd electrode (cathode). Principal solar cell architecture and the photo of an actual cell are shown in Fig. 8.

![Solar cell architecture (a) and its physical appearance (b).](image)

The solar cell work function and energy diagram are explained in Fig. 9. Under solar irradiation, valence band electrons (showed by red arrows) in different semiconductor layers (TiO₂, CdS, and Cu₂ZnSnS₄) are being excited to conductive bands and undergo intersystem crossing to the energetically preferred ITO level. Holes (showed by blue arrows), in turn, are being collected on gold/palladium contacts.

The key steps for the film development included synthesis of Cu₂ZnSnS₄ NCs, solution-phase deposition of soluble NC precursors into films, replacement of original ligands on NC surfaces with easily volatile ligands and fusion of the film through ligand evaporation. Briefly, ITO-coated glass substrates were coated with 8 μm thick titanium dioxide layer (resulting from 0.07 mm thick titanium dioxide raw emulsion layer), annealed at 350°C for 15 min. to burn out the viscous agent (HPC), and consequently dip-coated with 8 monoatomic layers of Cd²⁺ and S²⁻ ions, which penetrated through the TiO₂ material. Substrates were then spin-coated with a layer of CZTS nanocrystals, sufficient for an appreciable
visible light absorption (>12 spin-coating layers, 20 μm thick film). At the same time, after the deposition of each 1-3 layers of CZTS colloidal NCs, high-boiling oleyamine ligands (boiling point 348-350°C) were exchanged with easily volatile 3-mercaptopropionic acid molecules (boiling point 110-111°C). The latter were evaporated at 120-140°C in argon atmosphere. Finally, 20 nm thick Au/Pd (60/40) contacts were vapor deposited with the use of shadow masks as structuring method. Gold/palladium has the same work function, but provides smaller grain size than gold alone. For detailed synthesis and solar cell fabrication description, refer to Appendix B.

![Energy diagram showing relative positions of band edges for the solar cell functional components.](image)

**Figure 9.** Energy diagram showing relative positions of band edges for the solar cell functional components.

Importantly, fabricated prototype solar cells are based on environmentally benign copper zinc tin sulfide heterostructures. All solar cell components are naturally occurring minerals (Fig. 10).
2.3 Morphological characteristics

High-resolution transmission electron microscopy measurements were carried out using a JEOL 311UHR instrument operated at 300 kV. Specimens were prepared by depositing a drop of nanocrystal chloroform solution onto a Formvar-coated copper grid and letting it dry in air. Figure 11a shows TEM image of Cu$_2$ZnSnS$_4$ quantum dots, after the size-selective separation of aggregated NCs. The average nanocrystal diameter is 10.9 nm with the standard deviation of size distribution 0.97 nm or 8.9%, as estimated by averaging the sizes of pronounced in TEM image nanocrystals using the AutoCAD 2012 application (Fig. 11b).

The morphology of a typical solar cell was demonstrated using scanning electron microscopy (SEM), shown in Fig. 12. As prepared cells were cut along the Au/Pd contacts, vapor-coated with carbon, to allow conductivity, in Denton BTT-IV Vacuum Evaporator (at $2 \times 10^{-5}$ Torr), and afterwards electrically grounded with copper tape (Electron Microscopy Sciences) to prevent the accumulation of electrostatic charge at the surface. Finally, samples were placed onto an SEM sample holder, and secondary electron imaging was obtained employing Hitachi S-2700 machine at high beam energies (20 kV).

Elemental analysis of the solar cell was demonstrated in energy-dispersive X-ray spectrometry (Fig. 13), using EDAX detector. ITO coating and Au/Pd contacts did not show well pronounced characteristic peaks due to insufficient for EDX resolution layers thickness.
Figure 12. SEM image of a prototype solar cell. CdS component is fully incorporated into the TiO₂ layer, forming 8 μm thick film. Cu₂ZnSnS₄ nanocrystals are being successfully merged onto its surface. However, several cracks in CZTS layer are clearly seen, possibly due to excessively rapid evaporation of MPA molecules, demanding further optimization of the technology, allowing for undisturbed ligands exhalation.

Figure 13. Energy-dispersive spectrometry of a solar cell. TiO₂, CdS, Cu₂ZnSnS₄ layers are recognized by the pronounced Ti, O, Cd, Cu, Zn, Sn, and S signature peaks. Si, Na, Ca and Al characteristic peaks are attributable to glass substrate and sample holder.
2.4 FTIR Measurements

To enable a low-temperature merging of NCs, the original high-boiling ligands on NC surfaces were exchanged with easily volatile molecules, which were consequently evaporated at various temperatures in order to study the ligands exhalation kinetics by monitoring the occurrence of vibration transitions of characteristic sp$^3$ C-H bonds on Fourier transform infrared spectra.

Initially, the FTIR pattern of 3-mercaptopropionic acid itself was measured (shown in red in Fig. 14). Moreover, a cell without CZTS layer was observed to obtain the reference of a solar cell characteristic spectrum free of MPA patterns (shown in white). Finally, MPA was added to that solar cell and another spectrum was measured (shown in pink).

Four solar cells were prepared with exactly the same technological steps, with each deposited CZTS layer being subsequently annealed at 70, 90, 120, and 170 °C. Even though pure MPA’s boiling point is 110-111 °C, the complete removal of these ligands was already achieved at 90 °C, which is likely due to the well-developed surface structure of the film, expediting the boiling process.

Nevertheless, higher annealing temperatures (up to 140 °C) promote smoother fusing of NCs, supporting stronger light-induced current generation (12 vs. 6 μA for the ligand exhalation temperature being increased from 90 to 120 °C) in a fabricated solar cell.
Figure 14. FTIR measurements showing obvious reduction in the intensity of vibrational transitions corresponding to MPA surface ligands, as the annealing temperature is being increased from 70° C to 90° C. Further increase in annealing temperatures demonstrates inappreciable difference in ligands exhalation.
2.5 Quantum Efficiency Measurements

Performance parameters of fabricated solar cells were determined from I/V curves, shown in Figure 15.

Figure 15. Light-induced current generation vs. applied inverse voltage characteristic curves comparison for the solar cells with different number of functional layers deposited and varying ligand exhalation temperatures. Second-order polynomial fitting curves were incorporated for the further quantum efficiency analysis.
Fill factor was calculated as follows:

\[ FF = \frac{P_{\text{max}}}{I_{sc} \cdot V_{oc}} \]

where \( I_{sc} \) is the short circuit current, \( V_{oc} \) – open current voltage, and \( P_{\text{max}} \) – the maximum power output observed from the solar cell (see Fig. 16), found by the Method of Iterations from the second-order fitting curve equations corresponding to each solar cell I/V characteristic.

Incident light intensity was measured by digital optical power and energy meter PM100D (Thorlabs) with a standard power sensor S120VC (Thorlabs), in order to find the power conversion efficiency:

\[ PCE = \frac{\text{Output power}}{\text{Input power}} = \frac{P_m \text{ (mW/cm}^2)}{\text{Light intensity (mW/cm}^2)} \]

where maximum power output was normalized by electrode’s active area.

Finally, the calculated solar cells characteristics were gathered in a comparison table, shown in Figure 17.
The strongest power output and power conversion efficiency were observed from the solar cells # 5 and 8, annealed at 160 and 120 °C, respectively. Higher annealing temperatures promoted higher voltage and more attractive fill factor parameters, however, lowered the PCE values.

Yet these measurements were conducted using a simplified cell architecture that may bear efficiency losses due to poor electrical contact of the top electrode, carrier trapping at remaining dangling bonds, and the contamination of NC films with residual organic material.

<table>
<thead>
<tr>
<th>Cell #</th>
<th>Anneal. temp. (°C)</th>
<th>CZTS deposition technique</th>
<th>Best performance</th>
<th>Pm (mW)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70</td>
<td>spin-coat</td>
<td>Voltage (mV)</td>
<td>Current (μA)</td>
<td>0.000382</td>
<td>14.1%</td>
</tr>
<tr>
<td>2</td>
<td>150</td>
<td>spin-coat</td>
<td>604</td>
<td>4.45</td>
<td>0.000574</td>
<td>25.1%</td>
</tr>
<tr>
<td>3</td>
<td>160</td>
<td>printed</td>
<td>509</td>
<td>8.33</td>
<td>0.001189</td>
<td>30.2%</td>
</tr>
<tr>
<td>4</td>
<td>160</td>
<td>spin-coat</td>
<td>286</td>
<td>22.19</td>
<td>0.001829</td>
<td>26.5%</td>
</tr>
<tr>
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<td>160</td>
<td>spin-coat</td>
<td>256</td>
<td>3.99</td>
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<td>27.5%</td>
</tr>
<tr>
<td>6</td>
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</tr>
<tr>
<td>7</td>
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<td>5.57</td>
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</tr>
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</tr>
</tbody>
</table>

**Figure 17.** Performance characteristics comparison table. Despite the fact that cell #1, annealed at 70 °C, demonstrated the highest voltage, it failed to show the appreciable fill factor and PCE. High voltage numbers might be due to the high resistance parameters, caused by the presence of residual ligands.
2.6 Longevity Observations

Poor oxidation stability of organically capped semiconductor NCs is believed to be the main issue preventing their utilization in heat-intensive applications, including solar cells. The use of inorganic capping on NC surfaces may thus provide a fundamental solution to the oxidation stability problem, as was recently demonstrated through the use of inorganic ligands comprising metal chalcogenide complexes\textsuperscript{169,170}.

Oxidation stability of fabricated devices, free of organic molecules, was examined by comparing the I/V curves measured on the day of solar cell preparation and weeks later. It was shown that the films preserve the same level of performance for more than a month. However, covering the films with the additional layer of penetrating semiconductor material would likely protect produced free electrons from being trapped at surface dangling bonds.

2.7 Conclusion

In this work, we have developed the low-temperature solution-processed solar cells preparation approach, allowing their fabrication at temperatures of 160 °C and below (excluding the process of hydroxypropyl cellulose burning at 300 °C, which is a necessary step in TiO\textsubscript{2} film preparation).

The fabricated devices are capable of absorbing the sun’s entire visible, near infrared, and short-wavelength infrared due to incorporation of the different-bandgap layers required to produce stacked multi-junction (TiO\textsubscript{2}, CdS, and Cu\textsubscript{2}ZnSnS\textsubscript{4} functional layers) solar cells.

Nevertheless, these devices require further optimization, including the search for different ligands, varying CZTS NCs size in order to spectrally tune the solar cell absorption spectrum via the quantum size effect, and investigation of thin film thickness effect on the performance parameters of fabricated solar cells.
References


2385–2393.


145–151.

363–369.


APPENDIX A. SUPPLEMENTARY INFORMATION FOR CHAPTER 1

Chemicals

Oleylamine (OLAM, tech., 70%, Aldrich), sulfur (99.999%, Acros), 1-octadecene (ODE, tech., 90%, Aldrich), cadmium oxide (CdO, 99.99%, Aldrich), oleic acid (OA, tech., 90%, Aldrich), tri-n-octylphosphine (TOP, 97%, Strem), tri-n-octylphosphine oxide (TOPO, 99%, Aldrich), n-octadecylphosphonic acid (ODPA, PCI Synthesis, 98%), n-hexylphosphonic acid (HPA, PCI Synthesis, 98%), hexadecylamine (HDA, tech., Fluke), 1,2-hexadecanediol (TCI), 11-mercaptoundecanoic acid (MUA, 95%, Aldrich), platinum (II) acetylacetonate (97%, Aldrich), tellurium powder (Te, 200 mesh, 99.8%, Aldrich), diethylzinc (Et$_2$Zn, 15% wt., 1.1 M solution in toluene, Aldrich), selenium powder (Se, 200 mesh, Acros), hexane (anhydrous, 95%, Aldrich), methanol (anhydrous, 99.8%, Aldrich), ethanol (anhydrous, 95%, Aldrich), acetone (tech., EMD Chemicals), tert-butanol (99.7%, Aldrich), and toluene (anhydrous, 99.8%, Aldrich) were used as purchased. All reactions were performed under argon atmosphere using the standard air free Schlenk technique unless otherwise stated. CdS nanorods (NRs) were synthesized using a seeded-type approach by introducing small-diameter seed NCs into the reaction mixture for nucleating the growth of CdS extensions. All reactions were carried out using standard air free techniques unless stated otherwise.

Synthesis of ZnSe and ZnTe Seeds

ZnSe NCs for seeding the growth of CdS nanorods were synthesized according to the procedure reported by Hines et al.$^{172}$ Briefly, 6.1 g of HDA was degassed at 125 °C with stirring for 30 minutes, switched to argon and heated to 310 °C. At this point, a selenium precursor prepared by dissolving 0.040 g of Se in 1.5 mL of TOP was injected into the reaction
flask. To initiate the NC growth, 0.72 mL of a 15% diethyl zinc solution (15% by wt. in toluene) mixed with 1 mL of degassed TOP was injected into the reaction flask at 270 °C and the mixture was kept at this temperature for the next 2 hours. After growth, the flask was cooled to 60 °C upon which 4 mL of BuOH and 3.5 mL of chloroform were added to precipitate NCs.

ZnTe seeds were synthesized according to a procedure described elsewhere. 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, OA (0.8 g) was mixed with ODE (3 g), degassed at 120 °C for ca. 30 min and switched to argon, upon which 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.

Growth of ZnSe/CdS Core/Shell Nanocrystals

For the growth of CdS shell onto ZnSe seeds, Cd precursor solution was prepared by dissolving 0.0308 g of CdO, 0.6 mL of OA, and 5.4 mL of ODE at 290 °C. Once clear solution was obtained, the mixture was allowed to cool down to room temperature. Similarly, sulfur solution was prepared by heating 0.0077 g of sulfur in ODE to 200 °C and cooling it down to room temperature. In a 3-neck flask, 1.5 g of ODA and 6.3 mL of ODE were mixed and degassed at 120 °C for ca. 30 minutes. After switching the flask to argon flow, 1 mL of colloidal ZnSe 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 ZnSe seeds for the shell growth procedure was determined by setting the absorbance of the NC solution at \( \lambda = 390 \) nm to 1.1 (as measured using a 1 mm thick cuvette). Once the temperature of the reaction mixture reached 240 °C, 1.5 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 \( \lambda \approx 450 \) nm and after 90 minutes, strong green emission (\( \lambda \approx 510 \) 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 acetone 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.

**Growth of 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 elsewhere.\(^{174}\) 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, \( \lambda = 473 \text{ nm} \), 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 \( \lambda = 690 \text{ nm} \) 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.

**Synthesis of CdS Nanorods**

Synthesis of heterostructured nanorods, using CdSe, ZnSe/CdS, and ZnTe/CdSe NC seeds, was carried out using a seeded-type growth, according to the procedure reported by Carbone et al.\(^{175}\) 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 toluene. The amount of CdSe, 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, (\( \lambda = 510 \text{ nm} \) for CdSe, \( \lambda = 450 \text{ nm} \) for ZnSe/CdS and \( \lambda = 680 \text{ nm} \) for ZnTe/CdSe) to 1.0, 1.0, and 0.1, respectively (as measured using a 1 mm thick cuvette). Separately, a mixture of CdO (0.060 g), 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 °C, 14 mL of ethanol was added and the content was centrifuged. The precipitate was subsequently re-dissolved in 2 mL of hexane and precipitated one more time using 8 mL of ethanol. The final product was stored in chloroform.

**Growth of Pt Tips on CdS Nanorods**

Platinum tips were grown onto the CdS NRs using a previously reported protocol. In a typical procedure, 0.2 mL of OLAC, 0.2 mL of OLAM, 43 mg of 1,2-hexadecanediol, and 10 mL of diphenyl ether were degassed at 80 °C in a three neck flask for one hour. Subsequently, the mixture was switched to argon and the temperature was raised to 200 °C, at which point, a mixture of hetero-nanorods (the 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 using methanol/chloroform (10:3) extraction and stored in chloroform.

**Ligand Exchange on Pt-Tipped CdS Nanorods**

The original hydrophobic ligands on Pt-tipped nanorods were exchanged with hydrophilic MUA or MPA molecules using a method reported by Costi et al. To this end, the solution of nanorods in chloroform (10-12 mL) was mixed with 10 mg of MUA (MUA). 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.

Characterization

UV-Vis absorption and photoluminescence (Fig. S1) spectra were recorded using Cary 50 Scan spectrophotometer, and 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 letting it dry in air. X-ray powder diffraction (XRD) measurements (Fig. S2) were carried out on a Scintag XDS 2000 X-ray powder diffractometer. FL lifetime measurements were performed using a time-correlated single photon counting setup utilizing SPC-630 single-photon counting PCI card (Becker & Hicke GmbH), picosecond diode laser operating at 400 nm, as an excitation source (Picoquant), and id50 avalanche photodiode (Quantique).

Figure S1. Emission spectra of ZnTe/CdSe/CdS nanorods capped with hydrophilic (black) and hydrophobic (red) ligands.
Figure S2. X-ray powder diffraction of ZnSe/CdS/Pt nanocomposites. The observed diffraction signal is primarily due to wurtzite CdS crystal lattice (shown in b), which is consistent with a greater fraction of the CdS phase in these nanocomposites.
Photochemical H₂ Evolution Measurements

1 mg of nanocomposites were dissolved 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 held in a 7 mL Pyrex round bottom flask was irradiated through with 300 W Arc Xenon lamp (Oriel) which output was water filtered and sent through a fiber optic (Oriel) to give 100 mW/cm² irradiation. The area of the beam was 1cm². Hydrogen was detected from the headspace by taking gas samples at different time intervals using a 100 µL gas tight 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). Number of H₂ moles was calculated from a calibration curve. CO₂ was detected as a byproduct of methanol oxidation, but not quantified.

Figure S3. Evolution of hydrogen production on CdSe/CdS/Pt nanocomposites.
**Figure S4.** 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.
References


Chemicals

Hydroxypropyl cellulose (HPC, average MW 80,000, powder, 20 mesh, 99%, Aldrich), acetic acid (glacial, 99%, EMD Chemicals), titanium dioxide powder (TiO$_2$, Degussa, P25), detergent powder (Alconox), cadmium acetate dihydrate (Acros, 98%), sodium sulfide nonahydrate (Na$_2$S·9H$_2$O, Alfa Aesar, 98.0% min.), oleyamine (OLAM, tech., 70%, Aldrich), sulfur (99.999%, Acros), copper (II) acetylacetone (99.99+, Aldrich), zinc acetate dihydrate (98+%, Acros), tin (II) chloride dihydrate (SnCl$_2$·2H$_2$O, 98%, Sigma-Aldrich), 3-mercapto-propionic acid (MPA, Alfa Aesar, 99%), gold/palladium target (Ladd Research, 60/40, 99.99%), chloroform (anhydrous, 99+%, Aldrich), methanol (MeOH, anhydrous, 99.8%, Aldrich), acetone (tech., EMD Chemicals), isopropanol (anhydr., 99.8+%, Acros), and octane (99.0%, Sigma-Aldrich) were used as received without any further purification. All procedures were performed in air atmosphere unless otherwise stated.

Preparation of TiO$_2$ Films

Titanium dioxide paste was prepared following the procedure previously described by Myahkostupov et al.$^{178}$ First, 2.0 g of HPC were dissolved in 10 mL of deionized water by slow stirring overnight until clear and viscose solution is achieved. Consequently, 0.4 mL of acetic acid and 1.2 mL of deionized water were mixed in a separate vial, and then 0.360 g of Degussa TiO$_2$ powder were added by small portions (ca. 0.05 g each) while constantly stirring. Finally, 0.9 mL of HPC solution was added and the mixture left for slow stirring overnight.

For the deposition of TiO$_2$ films, indium tin oxide (ITO)-coated 25x25 mm glass substrates (TEC15, 2.2 mm, Pilkington) were primarily cleaned, using the procedure reported elsewhere.$^{179}$
Substrates were thoroughly washed in detergent solution, rinsed by deionized water, methanol, acetone, then sonicated for 15 min. in isopropanol, and left to dry in air for 15 min.

Pre-fabricated TiO₂ emulsion was rolled over the clean ITO-coated glass substrates as described by reported by Takechi et al.⁶⁵. Films were dried in air and annealed for 10 min. at 300-320 °C.

CdS Chemical Bath Deposition

TiO₂-coated substrates were dip-coated with cadmium sulfide following the technique reported by Lee et al.¹⁸⁰ In a typical routine, 0.4253 g of cadmium acetate dihydrate were dissolved in 80 mL of methanol. TiO₂-coated films were kept in Cd precursor solution for 1 min., rinsed by methanol, then kept in a supersaturated solution of Na₂S·9H₂O (0.3842 g) in 80 mL of methanol for 1 min., and once again rinsed by methanol. Films were processed through cadmium-sulfur precursor solutions 8 times total and left to dry in air.

Synthesis of Cu₂ZnSnS₄ Nanocrystals

CZTS quantum dots were synthesized Cu-poor and Zn-rich, via a hot-injection procedure adapted from elsewhere.⁶⁵,¹⁸¹ Namely, 0.104 g of copper (II) acetylacetonate, 0.058 g of zinc acetate dihydrate, 0.036 g of tin (II) chloride dihydrate, 0.026 g of sulfur powder, and 8.0 mL of oleyamine were degassed under vacuum at room temperature for 30 min. and then exposed to argon using standard Schlenk technique. The mixture was kept at 110°C for 30 min. to remove water traces, then heated to 300°C and kept at this temperature while constantly stirring for 1 hour.

After the NCs growth, the synthesis was stopped by removing the heating mantle from under the reaction flask. Final product was purified using repeated solvent/non-solvent
(chloroform/ethanol) extraction, followed by a selective precipitation in ethanol in order to separate out large particles and agglomerates. Cleaned Cu$_2$ZnSnS$_4$ NCs were redispersed in chloroform and stored in dark under argon atmosphere.

CZTS Spin-Coating and Ligands Exchange

Spin-coating procedure was conducted in a glovebox under argon atmosphere, as described by Pattantyus-Abraham et al.$^{65}$ Concentrated CZTS colloidal solution in chloroform (1 mL of NCs solution in 4 mL of octane shows absorbance of 0.725 arbitrary units at 400 nm) was spin-coated over the TiO$_2$/CdS films at 650 rpm. Consequently, the original high-boiling ligands (oleylamine, b. p. 348-350°C) on Cu$_2$ZnSnS$_4$-coated thin films were exchanged with easily volatile MPA molecules (b. p. 110-111°C) using the method reported by Costi et al.$^{65}$

Namely, for each CZTS layer deposition, the following solutions were drop-counted, allowing each drop to dry completely on the film prior to depositing next portion of material: 5 drops (ca. 0.05 mL) of Cu$_2$ZnSnS$_4$ in chloroform, 5 drops (ca. 0.025 mL) of MPA:MeOH (1:9) solution substituting OLAM ligands, 10 drops (ca. 0.07 mL) of MeOH washing out the unbounded MPA ligands, and 10 drops (ca. 0.07 mL) of octane to rinse out the residue of methanol. Finally, films were heated up to 130 °C to allow MPA molecules exhalation.

Gold/Palladium Vapor Deposition

Lastly, the resulting CZTS-covered thin films were capped with gold/palladium (60/40) electrodes (20 nm thick), completing the cell assembly. Au/Pd contacts were vapor deposited under vacuum (0.04 Torr) in Polaron Sputter Coater SC510, using 1 mm thick molybdenum shadow mask with 16 holes, each 2.0 mm in diameter.
References


