

Efficient Photocatalytic Hydrogen Generation from Ni Nanoparticle Decorated CdS Nanosheets

Maksym Zhukovskyi,* Pornthip Tongying, Halyna Yashan, Yuanxing Wang, and Masaru Kuno*

Department of Chemistry and Biochemistry, University of Notre Dame, 251 Nieuwland Science Hall, Notre Dame, Indiana 46556, United States

Supporting Information

ABSTRACT: High-quality, thickness-controlled CdS nanosheets (NSs) have been obtained through the thermal decomposition of cadmium diethyldithiocarbamate in octadecene. Ensembles with discrete thicknesses of 1.50, 1.80, and 2.16 nm have been made with corresponding lateral dimensions on the order of 90 nm \times 20 nm. These latter values make the 1–3 nm NSs the largest 2D CdS specimens made to date using colloidal chemistry. Associated Ni nanoparticle decorated counterparts have been made through the photodeposition of Ni onto NSs with an average nanoparticle diameter of 6 nm. Subsequent photocatalytic hydrogen generation measurements have compared the performance of CdS NSs with that of their Ni NP decorated counterparts in water/ ethanol mixtures. Apparent quantum yields as large as 25% have been seen for Ni NP decorated NSs with transient yields as large as 64% within the first 2 h of irradiation. Results from ensemble femtosecond transient differential absorption spectroscopy reveal



that the origin of this high efficiency stems from efficient electron transfer from CdS to Ni. In this regard, the CdS/Ni semiconductor/metal heterojunction acts to dissociate strongly bound excitons in CdS NSs, creating free carriers needed to carry out relevant reduction chemistries.

KEYWORDS: CdS, nanosheet, nickel, nanoparticle, charge separation, hydrogen generation

1. INTRODUCTION

Low-dimensional cadmium chalcogenides such as CdS quantum dots (QDs), nanorods (NRs), and nanowires (NWs) have been used extensively for photocatalytic hydrogen generation.^{1–11} This is due to their tunable band gaps, efficient absorption of visible light, large surface to volume ratios, and their favorable and tunable conduction/valence band energies.^{2,12,13} Corresponding heterostructures, designed to suppress charge recombination, have simultaneously been investigated. They include two- or three-component semiconductor/semiconductor (e.g., CdSe/CdS core/shell^{5,6} or dot-in-rod systems¹⁰), semiconductor/metal (e.g., CdS/Au,³ CdS/Pt,⁴ CdSe/CdS dot-in-rod/Pt^{9,10} and CdSe/CdS/Pt core/shell NWs⁶), and semiconductor/molecular heterostructures (e.g., CdSe/Ni-dihydrolipoic acid⁷ and CdS/[FeFe]-hydrogenase complexes⁸).

While 0D and 1D cadmium chalcogenide nanostructures have been widely investigated for use as photocatalysts,^{1–11} their 2D counterparts have only recently attracted attention in this regard due to new synthetic advances, enabling the production of high-quality, thickness-controlled NSs.^{14–20} Subsequent investigations have revealed the unique optical and electrical properties of 2D materials, which include their strong room-temperature excitonic resonances,¹⁴ their large absorption cross sections,¹⁵ high emission quantum yields, and large charge carrier mobilities.^{14,16} Consequently, 2D systems have quickly found use in light-emitting diodes,¹⁷ gas sensors,¹⁸ photodetectors,¹⁹ and field effect transistors.²⁰

Until now, though, the photocatalytic properties of 2D materials have not been investigated in any great detail,^{21–24} despite the aforementioned unique and intriguing photophysical properties. In what follows, we therefore investigate the use of atomically thin CdS nanosheets for photocatalytic hydrogen generation. We simultaneously investigate corresponding enhancements that arise due to the use of Ni nanoparticle cocatalysts. Of interest is how the large absorption efficiencies, room-temperature excitonic resonances, long lifetimes, and corresponding suppressed Auger responses²⁵ of CdS NSs affect their photocatalytic response.

2. EXPERIMENTAL SECTION

2.1. Materials. Cadmium diethyldithiocarbamate (CdDDTC, 99.5%) was purchased from BOC Science. 1-Octadecene (ODE, 90%) was purchased from Aldrich. Stearic acid (98%) was purchased from Alfa Aesar. Cadmium acetate dihydrate (CdAc₂, 98%) was purchased from Acros Organics. Methanol, ethanol, and toluene were purchased from Fisher Scientific and VWR. Unless otherwise noted, all chemicals were used as received.

2.2. Synthesis of 2.16 nm Thick CdS NSs. CdS NSs with 2.16 nm thickness were synthesized by combining the following in a three-neck flask: ODE (20 mL, 56.3 mmol), CdDDTC (41.1 mg, 0.1 mmol), stearic acid (29.0 mg, 0.1 mmol), and

Received: June 29, 2015

 $CdAc_2$ (81.6 mg, 0.3 mmol). The three-neck flask was then connected to a Schlenk line, whereupon its contents were dried and degassed at 65 °C for 30 min to remove any oxygen and water. When complete, the reaction mixture was back-filled with N₂ and was heated to 220 °C for 3 h with vigorous stirring. During this time, the initial translucent white slurry became clear and eventually turned yellow due to the formation of CdS NSs. Upon completion, the mixture was cooled to room temperature, whereupon 10 mL of toluene was added to dilute the ODE. CdS NSs were precipitated by adding 5 mL of methanol to this mixture and centrifuging the resulting suspension. Recovered sheets were washed with toluene and methanol three additional times before being stored in toluene.

Note that using CdDDTC alone in the reaction does not yield CdS NSs, given their 1:4 Cd:S stoichiometry. Additional CdAc₂ was therefore needed to supplement Cd in CdDDTC as well as to make the reaction Cd rich. CdDDTC does, however, play an important role in the NS synthesis in that on replacement by an equivalent amount of sodium diethyldithiocarbamate only spherical CdS nanoparticles were produced.

2.3. Synthesis of 1.50 and 1.80 nm Thick CdS NSs. To synthesize 1.50 nm (1.80 nm) NSs, 41.1 mg of CdDDTC (0.1 mmol), 72.5 mg of stearic acid (0.25 mmol), and 40.8 mg of CdAc₂ (0.15 mmol) (29.0 mg of stearic acid (0.1 mmol) and 54.4 mg of CdAc₂ (0.2 mmol)) were used. All other synthetic parameters/conditions were kept constant.

2.4. Sample Characterization. TEM samples were prepared by drop-casting dilute CdS NS toluene suspensions onto carbon-coated copper TEM grids (Ted Pella). NSs were analyzed with a JEOL JEM2011 TEM operating at 200 keV. XRD samples were prepared by depositing concentrated NS suspensions onto (0001) cut quartz substrates and allowing the suspension to dry under ambient conditions. Powder X-ray diffraction data (Cu K α radiation, $\lambda = 1.5418$ Å, D8 Advance Davinci, Bruker) were collected in 0.02° increments with a 10 s/step integration time.

To estimate NS thickness-dependent conduction band positions, voltammetry measurements were conducted. Electrochemical measurements were performed under dark conditions using a three-electrode cell with AgCl as a reference electrode, Pt as the counter electrode, and CdS NSs on FTO as the working electrode. Measurements were conducted in 0.1 M solutions of Na₂SO₄ under nitrogen. Potentials ranged from 0.2 to -2.0 V with a scan rate of 20 mV/s (Princeton Applied Research 2273). The NS conduction band potential was taken to be the peak potential for Cd²⁺ reduction in electrochemical scans.²

CdS NS concentrations were estimated using ICP-AES (PerkinElmer Optima 8000). Samples were prepared by precipitating 1 mL aliquots from a $\sim 1.3 \times 10^{-7}$ M NS stock suspension via centrifugation at 5000 rpm for 5 min. Supernatants were discarded and recovered NSs were dried under ambient conditions. They were then digested using 2 mL of aqua regia, whereupon 48 mL of 5% HNO₃ was added to produce samples suitable for ICP analysis. ICP elemental calibration curves were created using commercial standards with known concentrations.

UV-visible absorption spectra of CdS NSs suspended in toluene were recorded with a Jasco V-670 UV/visible/nearinfrared spectrophotometer coupled to a 60 mm integrating sphere. A 1 cm cuvette was used for all studies. Time correlated single photon counting (TCSPC) kinetics were acquired with a Jobin Yvon Fluorocube using 371 nm pulsed LED illumination (200 ps fwhm, 1 MHz repetition rate) with the NS emission at 442 nm detected with a fast photomultiplier tube (overall instrument time resolution of ~1 ns). For TDA measurements, NS samples were suspended in water/ethanol mixtures and were placed in a 2 mm path length cuvette. Optical densities (OD) were ~0.3 at the excitation wavelength (λ_{exc} = 387 nm).

Ultrafast TDA experiments were performed with a Clark MXR CPA 2010 laser system employing a fiber-based spectrometer. Experiments were conducted by exciting CdS and CdS/Ni NSs at 387 nm (3.20 eV) with ~150 fs pulses (pump fluence 10 μ J/cm²). Transient absorption spectra were subsequently acquired with a delayed, low-intensity white light continuum with wavelengths between 400 and 750 nm (3.10–1.65 eV). White light was generated by passing a fraction of the fundamental through a CaF₂ crystal.

2.5. Concerted Ni NP Photodeposition and Photocatalytic Hydrogen Generation Experiments. For photocatalytic H₂ generation measurements, CdS NSs were precipitated from 2 mL of a toluene stock suspension (approximate NS concentration 1.3×10^{-7} M) via centrifugation and were redispersed in 5 mL of ethanol. NSs were then precipitated a second time and again redispersed in 5 mL of ethanol. This precipitation/ethanol resuspension step was repeated three additional times to remove any residual toluene. Finally, NSs were resuspended in 5 mL of a 10%/90% water/ethanol mixture and purged with Ar to remove any oxygen.

In the case where Ni NPs were photodeposited onto NSs prior to photocatalytic H₂ generation measurements (discussed more fully in the Results and Discussion), CdS sheets were resuspended in 5 mL of a 10%/90% water/ethanol mixture containing NiSO₄ with concentrations ranging from 1.3×10^{-5} to 1.0×10^{-3} M. Solutions were then placed in quartz cells, purged with Ar to remove any oxygen, and irradiated with a 405 nm laser diode (Coherent Obis) for 30 min ($I_{exc} = 3.5 \text{ W/cm}^2$) to induce Ni NP photodeposition. Briefly, under laser excitation of CdS NSs, photogenerated excitons are created. The existence of defects means that some fraction of excitons will dissociate into component electrons and holes, whereupon subsequent surface trapping of electrons becomes possible. Such localized electrons can then reduce surface-adsorbed Ni²⁺ ions, leading to Ni nanoparticle formation.^{26,27} A corresponding yellow to greenish color change is observed, indicating Ni NP deposition.

For hydrogen generation measurements, all samples were excited with 405 nm light from the same laser used to photodeposit Ni. At given intervals, evolved gases were analyzed with a gas chromatograph (Thermo, Trace GC Ultra). For excitation intensity dependent measurements, Ni NPs were first deposited onto CdS NSs with a NiSO₄ concentration of 2.0×10^{-4} M (average resulting NP diameter 6 nm, coverage of one NP per NS). Following this, the 405 nm laser intensity was set to an $I_{\rm exc}$ value between 5 and 3.5 W/ cm². Hydrogen was then detected using gas chromatography at given intervals.

2.6. Polyethylenimine (PEI) Ligand Exchange. To conduct ligand exchange, CdS/Ni NSs were precipitated by centrifuging their toluene suspensions. A 4 mL ethanol solution of PEI (1.5 mM, MW 25000) was then added to the recovered sheets. The resulting suspension was stirred for 1 h. At this point, NSs were precipitated again via centrifugation, where-upon they were redispersed in water/ethanol mixtures with varying ratios of 10%/90%, 50%/50%, and 90%/10% (by



Figure 1. Low- and high-magnification TEM images of (a, c) CdS and (b, d) CdS/Ni NSs. Insets give the corresponding ensemble SAED images (a, b) and a high-resolution TEM image showing basal plane lattice fringes (top right in (c)) as well as a NS side view (bottom left in (c)). Ensemble EDXS spectra of 2.16 nm (e) CdS and (f) CdS/Ni NSs.

volume). All ligand exchange reactions were done under nitrogen in a glovebox to prevent Ni oxidation.

3. RESULTS AND DISCUSSION

3.1. Synthesis of CdS NSs. CdS NSs were synthesized through the thermal decomposition of cadmium diethyldithiocarbamate (CdDDTC) in octadecene. The approach is the first to use a single-source precursor in synthesizing cadmium chalcogenide NSs and complements existing approaches that involve the thermolysis of cadmium acetate (CdAc₂) in the presence of fatty acids and elemental sulfur.^{28–30} What results are CdS NSs with discrete thicknesses of 1.50, 1.80, and 2.16 nm and whose lateral dimensions are 90 nm \times 20 nm. These latter values make the produced CdS NSs the largest made to date using colloidal chemistry.

Briefly, a mixture of CdDDTC, cadmium acetate, and stearic acid in octadecene was degassed at 65 °C. Specific details regarding the amounts of each chemical used can be found in the Experimental Section. Thickness control was achieved by varying the cadmium acetate to stearic acid concentration ratio in preparations. Following degassing, the reaction vessel was back-filled with N₂ and was heated to 220 °C. The mixture was left at 220 °C for an additional 3 h. During this time, the mixture turned from clear to light yellow due to CdS NS formation. The resulting product was then isolated by centrifuging the suspension, followed by several toluene/ methanol washing steps to remove any excess surfactant.

Transmission electron microscopy (TEM) measurements of resulting 2.16 nm CdS NSs show that they possess lateral dimensions of $93(\pm 12) \times 15(\pm 2)$ nm (Figure 1a,c). Lateral sizing histograms as well as additional TEM micrographs can be found in Figures S1 and S2 in the Supporting Information. Their flexible, ultrathin nature is also evident in obtained TEM images through apparent rolling and twisting. Corresponding,



Figure 2. (a) Representative XRD powder patterns of 1.50, 1.80, and 2.16 nm thick CdS NSs. The JCPDS stick pattern for bulk zincblende CdS (JCPDS# 65-2887) is included for reference purposes. (b) UV/visible absorption and emission spectra of 1.50, 1.80, and 2.16 nm NSs. Asterisks denote absorption and emission contributions from thinner (minority) NS subpopulations within a given ensemble. (c) UV/visible absorption spectra of 2.16 nm CdS and CdS/Ni NSs. The inset gives CdS NS tail states highlighted on a semilogarithmic graph.

albeit rare, edge-on TEM images confirm the 2.16 nm thickness of the sheets. An example is shown in the inset of Figure 1c.

Tandem TEM-based ensemble SAED measurements reveal apparent (200), (222), and (400) diffraction rings (inset, Figure 1a) with associated *d* spacings of 0.294 nm (200), 0.170 nm (222), and 0.148 nm (400). High-resolution, basal plane images (inset, Figure 1c) further show that the sheets exhibit lattice spacings of ~0.34 nm, consistent with those from the (111) planes of zincblende (ZB) CdS. All experimental lattice parameters are larger than those found in bulk CdS. This discrepancy likely originates from lattice strain due to excess cadmium, terminating NS {100} basal planes.^{28,30} Energy dispersive X-ray spectroscopy (EDXS) analyses of the sheets (Figure 1e and Figure S3 in the Supporting Information) corroborate this conclusion by showing excess cadmium to sulfur ratios of 1.18(\pm 0.04), 1.18(\pm 0.06), and 1.16(\pm 0.07) for 1.50, 1.80, and 2.16 nm CdS NSs.

Corresponding 1.80 nm NSs possess similar rectangular shapes with associated lateral dimensions of $96(\pm 9) \times 21(\pm 3)$ nm. In contrast, 1.50 nm NSs exhibit irregular shapes, complicating an analysis of their exact lateral dimensions. TEM images of the 1.80 and 1.50 nm sheets and corresponding edge-on TEM images as well as associated lateral sizing histograms (where applicable) can be found in Figures S2, S4, and S5 of the Supporting Information.

Independent powder X-ray diffraction (XRD) measurements confirm that all CdS NSs adopt their cubic ZB lattice. Figure 2a illustrates XRD powder patterns acquired from 2.16, 1.80, and 1.50 nm NS ensembles. For 2.16 nm NSs, characteristic zincblende reflections are seen at 26.04° (111), 30.07° (200), 43.51° (220), 51.35° (311), and 63.32° (400) (JCPDS# 65-2887). Associated *d* spacings are 0.342, 0.297, 0.208, 0.178, and 0.147 nm. These values agree with aforementioned estimates from TEM-based SAED measurements. Similar reflections are seen for 1.80 and 1.50 nm NSs with corresponding *d* spacings that increase with decreasing NS thickness. This can again be attributed to lattice expansion, stemming from the presence of terminal basal plane Cd.^{28,30} Table S1 of the Supporting

Information summarizes all XRD-based CdS NS d spacings along with known bulk values.

To determine the conduction band positions of resulting NSs, electrochemical measurements were conducted as described in the Experimental Section. CdS NS electrodes were prepared by drop-casting samples onto fluorine doped tin oxide (FTO) substrates. After drying, electrodes were tested under dark conditions in 0.1 M Na₂SO₄ solutions (corresponding pH of 6.4). Resulting voltammetry scans show Cd²⁺ reduction peaks at -1.19 and -1.34 V vs the normal hydrogen electrode (NHE) for the 2.16 and 1.80 nm NSs (Figure S6 in the Supporting Information). These features are attributed to each ensemble's conduction band position given the lack of other reduction features in the scan and the similarity of these potentials to known conduction band positions for other cadmium chalcogenide nanostructures.^{2,31,32} No reduction features are seen for 1.50 nm NSs. This is consistent with previous observations in the case of small <2.6 nm diameter CdSe QDs,² where the lack of a reduction feature can be attributed to obscuration by electrode-related hydrogen evolution. Notably, the proton reduction Nernst potential of -0.38 eV versus NHE (dotted line, Figure S6) indicates that the 2.16 and 1.80 nm CdS NSs are suitable systems for photocatalytic hydrogen generation. Additional details about these electrochemical measurements/conduction band position estimates can be found in the Experimental Section.

3.2. Optical Characterization of CdS NSs. Ensemble absorption spectra of 2.16 nm thick CdS NSs show a characteristic band edge excitonic resonance at 433 nm (2.86 eV) (Figure 2b). Analogous absorption spectra are seen for 1.80 and 1.50 nm NSs, where the first excitonic transition shifts to the blue with decreasing NS thickness (Figure 2b). An apparent defect tail³³ also exists, decaying exponentially into the gap (inset, Figure 2c). The tail does not appear to be scattering related, since an integrating sphere, which accounts for scattering losses to the absorption, has been used.³⁴ Consequently, this represents the first observation of tail states in ultrathin CdS NSs. Plots illustrating analogous tails for 1.80

and 1.50 nm NSs can be found in the Figure S7 in the Supporting Information.

The peak absorption cross section of 2.16 nm NSs has been estimated using correlated TEM, UV/visible absorption spectroscopy, and inductively coupled plasma atomic emission spectroscopy (ICP-AES). The resulting cross section is $\sigma_{433 \text{ nm}} = 2.9 \times 10^{-13} \text{ cm}^2$ with an associated molar extinction coefficient of $7.5 \times 10^7 \text{ M}^{-1} \text{ cm}^{-1}$. Similar cross sections of $\sigma_{410 \text{ nm}} = 3.0 \times 10^{-13} \text{ cm}^2$ and $\sigma_{378 \text{ nm}} = 3.2 \times 10^{-13} \text{ cm}^2$ have been found for the 1.80 and 1.50 nm NSs. A summary of these σ values as well as details of their estimates can be found in the Supporting Information. Additional information about these ICP-AES measurements can also be found in the Experimental Section.

Band edge emission is seen from 2.16 nm NSs centered at 442 nm (2.81 eV) (Figure 2b). With decreasing NS thickness, this peak shifts to the blue and tracks the absorption. Emission maxima are therefore seen at 419 nm (2.96 eV) and 393 nm (3.16 eV) for 1.80 and 1.50 nm NSs, respectively. In all cases, dominant defect-related emission, centered between 530 and 570 nm (2.34–2.18 eV), corroborates the existence of tail states first seen in the NS linear absorption.

Complementary TCSPC measurements (Figure S8 in the Supporting Information) show that the 2.16 nm CdS NSs exhibit band edge emission decays that can be fit to triexponential decays. Corresponding time constants are $\tau_1 \approx 0.7$ ns (53.69% area based weight), $\tau_2 = 3.7$ ns (32.54% area based weight), and $\tau_3 = 26$ ns (13.77% area based weight). The fastest (τ_1) component is subsequently attributed to hole trapping, given similar time scales reported for exciton quenching due to hole trapping in CdSe nanoplatelets.³⁵ Next, since the TCSPC signal is sensitive to both electron and hole concentrations, the latter two ns decays suggest the existence of long-lived excitons within CdS NSs.

3.3. CdS/Ni Photocatalyst Preparation and Characterization. Many low-dimensional photocatalysts employ noble metals such as Pt to enhance their catalytic activity. This is because noble metals possess favorable Fermi levels, which enable them to act as effective electron acceptors while simultaneously enhancing charge separation efficiencies. Within the context of hydrogen generation, apparent quantum yields as large as ~10% have been seen for Pt NP decorated CdS NRs.¹⁰ Similar values on the order of 20% have been seen for Pt NP decorated CdSe/CdS dot-in-rod systems.⁹

Despite these large yields, the use of noble metals makes the large-scale use of these low-dimensional photocatalysts cost prohibitive. Consequently, Ni has been investigated as an alternative due to its low cost, earth abundance, and high catalytic activity. What results are high-efficiency photocatalysts, which include Ni nanoparticle decorated CdS NRs (53% apparent quantum yield for hydrogen generation in water/ ethanol mixtures¹¹), Ni NP decorated Cd_xZn_{1-x}S nanostructures (25% apparent quantum yield for hydrogen generation in sodium sulfite³⁶), Ni decorated CdS QDs (12.2% internal quantum yield for hydrogen generation in glycerol³⁷), and dihydrolipoic acid capped CdSe QDs coupled to Ni²⁺ (35% internal quantum yield for hydrogen generation in aqueous solutions containing ascorbic acid⁷).

Consequently, to produce Ni NP decorated CdS NSs in the current study, Ni was photodeposited onto NSs using NiSO₄. In these reactions and in all subsequent photocatalytic measurements, the thickest 2.16 nm NSs have been used, since they absorb further to the red than corresponding 1.80

and 1.50 nm NSs. Hence, they represent the most suitable system for creating a photocatalyst. Photodeposition was also chosen over a complementary thermal deposition approach, given the better adhesion known to result between semiconductors and surface-deposited metals.^{26,38}

In brief, the photodeposition procedure works by photoexciting CdS NS with visible light ($\lambda_{exc} = 405 \text{ nm}$, $I_{exc} = 3.5 \text{ W/}$ cm², 30 min exposure). This leads to exciton formation, whereupon the presence of surface traps results in exciton dissociation and subsequent electron trapping. These trapped electrons then reduce surface-adsorbed metal ions and lead to metal NP growth on NSs.^{26,27} Ni NP deposition onto CdS is favored by the NS conduction band position (determined by our prior electrochemical measurements) relative to the Ni²⁺/ Ni⁰ reduction potential of -0.23 V vs NHE.³⁹ A yellow to greenish color change is observed during photodeposition, indicating Ni NP nucleation and growth. Specific details of the photodeposition procedure can be found in the Experimental Section.

Figure 1b,d shows TEM images of resulting Ni NP decorated CdS NSs. An analysis of the images shows that $6(\pm 1)$ nm diameter Ni NPs have been deposited onto the NSs (specific conditions: [NiSO₄] = 2.0×10^{-4} M, $\lambda_{exc} = 405$ nm, $I_{exc} = 3.5$ W/cm²). Ensemble EDXS measurements corroborate the deposition of Ni NPs, indicating the presence of Ni in resulting CdS/Ni NS ensembles (Figure 1f).

In all cases, ensemble SAED measurements reveal that the deposited Ni NPs adopt their cubic form. This stems from the appearance of a diffraction ring that can be indexed to Ni's (200) reflection (inset, Figure 1b). Additional TEM images of 2.16 nm CdS NSs decorated with Ni NPs as well as associated Ni NP sizing histograms can be found in the Figures S9 and S10 in the Supporting Information.

To alter both the deposited Ni NP size as well as surface coverage, NiSO₄ concentrations were varied in succession from 1.3×10^{-5} to 1.0×10^{-3} M. Decreasing [NiSO₄] from 2.0×10^{-4} M to 1.3×10^{-5} M results in experimentally identical Ni NPs (average diameter $6(\pm 1)$ nm) being deposited onto the NSs. At low NiSO₄ concentrations, though, not all CdS NSs have Ni NPs deposited onto them (Figure S11 in the Supporting Information). Increasing the Ni salt concentration to 1.0×10^{-3} M, in contrast, results in larger Ni NPs (average diameter $10 (\pm 3)$ nm) being deposited onto the sheets. Figure S12 in the Supporting Information shows representative TEM images of these particles.

Following Ni NP deposition, slight changes to the absorption spectra of 2.16 nm CdS NSs are seen. Specifically, an apparent suppression of the excitonic resonance is seen as illustrated in Figure 2c. This observation is similar to that previously reported for CdSe NRs and tetrapods decorated with Au nanoparticles.²⁷ In those cases, suppression was attributed to the electronic mixing of states, affecting the strength of excitonic resonances.

NS emission intensities are likewise affected. Specifically, adding Ni NPs to the sheets leads to complete quenching of the emission, whether band edge or trap related (Figure S13 in the Supporting Information). This suggests good electronic contact between CdS and Ni due to either efficient charge transfer or energy transfer following photoexcitation. Subsequent hydrogen generation and corresponding transient differential absorption measurements, discussed below, suggest the former.

3.4. Photocatalytic Hydrogen Generation. At this point, hydrogen generation measurements were conducted on 2.16



Figure 3. Apparent hydrogen generation quantum yields from 2.16 nm CdS/Ni NSs at different (a) Ni²⁺ concentrations ($I_{exc} = 3.5 \text{ W/cm}^2$), (b) laser intensities, and (d) water to ethanol ratios, following ligand exchange. (c) Time-dependent hydrogen generation trajectory of CdS/Ni NSs under an incident excitation intensity of $I_{exc} = 13 \text{ mW/cm}^2$.

nm CdS and CdS/Ni NSs to investigate their photocatalytic properties. NS suspensions were purged with argon and were illuminated with the same 405 nm laser used to generate Ni NPs. Illumination times were set to 18 h. Effects of the incident light intensity were also tested by varying I_{exc} between 0.005 and 3.5 W/cm^2 as described below. A scheme illustrating the H₂ generation chemistry can be found in Figure S14 in the Supporting Information, wherein protons are obtained from both H₂O and ethanol with the letter also acting as a hole scavenger.^{40,41} In all cases, to quantify resulting H₂ generation efficiencies, gas chromatographic measurements were conducted on samples at given intervals during irradiation. From measured H₂ yields as well as the number of incident photons at a given excitation intensity, corresponding H₂ generation apparent quantum yields were calculated. Details of these quantum yield estimates can be found in the Supporting Information.

To investigate any Ni NP size influences on observed hydrogen generation efficiencies, NiSO4 concentrations used to deposit Ni NPs were varied between 1.3×10^{-5} and 1.0×10^{-3} M. The results of these measurements are summarized in Figure 3a. They show that hydrogen generation quantum yields $(\lambda_{\text{exc}} = 405 \text{ nm}, I_{\text{exc}} = 3.5 \text{ W/cm}^2, 18 \text{ h irradiation})$ increase from 0.34% to 4.14% with increasing [NiSO₄] between 1.3 \times 10^{-5} and 2.0 \times 10^{-4} M (corresponding NP diameter ${\sim}6$ nm in this range with surface coverages proportional to concentration and reaching a limit of one NP per NS). Beyond 2.0×10^{-4} M, however, quantum yields decrease, reaching a value of 0.69% for a corresponding NiSO₄ concentration of 1.0×10^{-3} M (corresponding Ni NP diameter ~10 nm). Although specific surface coverages in this regime are difficult to determine, the results empirically suggest that an optimal Ni NP size as well as surface coverage exists for effective hydrogen generation (i.e., 6 nm NP diameter, one NP per NS).⁴²

Next, excitation intensities in these H₂ generation measurements were tested to see their effect on apparent quantum yields. Excitation intensities were therefore varied in decreasing succession from $I_{exc} = 3500$ to $I_{exc} = 5 \text{ mW/cm}^2$ using CdS/Ni samples with empirically determined optimal Ni NP sizes and surface coverages. The lower intensity limit of 5 mW/cm² was dictated by the detection limit of the gas chromatograph. In each case, corresponding H₂ generation yields were measured after 18 h of irradiation.

Resulting apparent quantum yields were seen to increase from 4.14% ($I_{exc} = 3.5 \text{ W/cm}^2$) to 24.5% ($I_{exc} = 5 \text{ mW/cm}^2$) with an apparent maximum of 25.3% at $I_{exc} = 13 \text{ mW/cm}^2$. This observed quantum yield trend is summarized in Figure 3b and is consistent with prior studies on CdS/Ni NR photocatalysts where decreasing excitation intensities yielded larger apparent hydrogen generation quantum yields.¹¹ The behavior is attributed to differences in the kinetic order of native charge recombination versus chemical reduction processes.¹¹

Finally, the performance of CdS/Ni NSs was compared to that of their bare CdS NS counterparts ($I_{exc} = 13 \text{ mW/cm}^2$). Ni NP decorated NSs (~6 nm NP diameter) were seen to perform significantly better. In the former case, optimal apparent quantum yields of 25.3% were seen, whereas values of 0.95% were seen for CdS NSs. The observed enhancement has several origins and includes the presence of a metal/semiconductor heterojunction that aids charge separation,^{4,6,10} electron accumulation on the metal,^{43,44} and favorable proton affinities to Ni.⁴⁵ Together, a ~25-fold enhancement of hydrogen generation quantum yields results over that of bare CdS NSs. As a further point of contrast, despite the favorable Fermi level of Au, poor proton binding affinities,⁴⁵ and unfavorable Au electron discharge kinetics⁴³ lead to no apparent improvements in H₂ generation efficiencies for Au NP decorated CdSe nanowires.⁵ These results therefore suggest that CdS/Ni NS heterostructures represent a potentially useful high-efficiency hydrogen generation photocatalyst.

At this point, Figure 3c plots the measured hydrogen generation trajectory of an optimal CdS/Ni NS sample ([NiSO₄] = 2.0×10^{-4} M resulting in 6 nm Ni NPs, a coverage of ~1 NP per NS, and $I_{exc} = 13$ mW/cm²). Of note is that the H₂ generation rate changes during the reaction with larger rates seen at early times. In particular, the apparent quantum yield, measured after 2 h of irradiation, is ~64%, whereas in contrast after 18 h of irradiation the apparent quantum yield drops to 25.3%. Such temporal variations in hydrogen generation efficiencies have been seen before in Ni NP decorated CdS NRs, wherein initial hydrogen generation quantum yields of 53% were observed which later decreased to 20% after 80 h of irradiation.¹¹ We attribute these long time decreases in hydrogen generation yields to partial photocorrosion of both CdS⁴⁶ and Ni.⁴⁷

To improve the solubility of CdS/Ni NSs in aqueous solutions, we have additionally conducted ligand exchange to replace native stearate ligands with polyethylenimine (PEI), a long-chain polymer previously shown to aid the water solubilization of colloidal nanostructures.³ Details of these ligand exchange reactions have been provided in the Experimental Section. In this case, measured H₂ quantum yields under the same optimized reaction conditions used earlier ([NiSO₄] = 2.0×10^{-4} M resulting in 6 nm Ni NPs, a coverage of ~1 NP per NS, and $I_{exc} = 13 \text{ mW/cm}^2$ are seen to be lower by a factor of \sim 3. Observed apparent quantum yields are ~8% in comparison to ~25.3% before ligand exchange (Figure 3b vs Figure 3d). Near-identical apparent quantum yields are also seen for different water/ethanol mixtures, as illustrated in Figure 3d. We therefore speculate that this pre/ post ligand exchange difference arises due to unwanted charge recombination pathways which appear due to the exchange and which effectively compete with desired reduction chemistries. The hypothesis is corroborated by photoluminescence measurements on PEI passivated CdS NSs, where no emission is observed, whether band edge or trap related (Figure S13 in the Supporting Information).

3.5. Transient Differential Absorption Measurements. Finally, to better understand relevant charge recombination and relaxation processes in 2.16 nm CdS and CdS/Ni NSs during photocatalytic hydrogen generation, we have conducted transient differential absorption (TDA) spectroscopy under actual hydrogen generation conditions. TDA is an important spectroscopic technique in this regard, since it enables one to unravel the fate of photogenerated carriers in nanostructures. For low-dimensional cadmium chalcogenides, the TDA bleach signal predominantly reflects the response of electrons rather than holes due to their lighter effective mass.48-50 Consequently, by monitoring of the bleach dynamics of TDA spectra, electron localization and recombination kinetics can be studied. Specific details of these TDA measurements can be found in the Experimental Section. In all cases, experiments have been conducted with pump fluences in the linear regime to exclude kinetic contributions from multiexciton dynamics (Figure S15 in the Supporting Information).

Figure 4a shows that upon excitation of bare CdS NSs at 387 nm (corresponding pump fluence, 10 μ J/cm²) a band edge bleach appears within ~0.5 ps. The bleach maximum occurs at 442 nm and effectively corresponds to the lowest energy exciton transition in the NS absorption spectrum (Figure 2b). An associated bleach maximum at 442 nm is $|\Delta A|/A_{433} = 0.12$.



Figure 4. TDA spectra of 2.16 nm (a) CdS and (b) CdS/Ni NSs taken at different delays following excitation. Insets give comparisons of early time bleach kinetics at 442 and 457 nm for CdS and CdS/Ni NSs, respectively. (c) Band edge bleach kinetics for CdS and CdS/Ni NSs. In all cases, measurements involve exciting samples at λ_{exc} = 387 nm under equivalent pump fluences of 10 μ J/cm².

Interestingly, a bleach feature to the red side of the band edge also arises at 457 nm (2.71 eV) and is attributed to the existence of tail states. This is consistent with both the linear absorption and the accompanying trap related emission of CdS NSs between 530 and 570 nm (Figure 2b,c).

An analysis of the band edge bleach recovery kinetics in Figure 4c shows that decays can be fit to biexponential functions with time constants of $\tau_1 = 1.7$ ps (0.75% area based weight) and $\tau_2 = 232.6$ ps (99.25% area based weight). The fast decay component is attributed to ultrafast electron trapping into defects and is corroborated by the early time kinetics of the corresponding 457 nm bleach feature shown in the inset of Figure 4a. Namely, the 457 nm trap-related feature exhibits a short induction period before growth at the expense of the band edge bleach. Next, the slower τ_2 component is attributed to band edge exciton recombination, given experimentally observed exciton recombination time scales in CdS NRs less than 1 ns.⁵¹

Of note is that, at 1.5 ns, 29% of the initial bleach magnitude remains. This shows that long-lived electrons exist in CdS NSs. Analogous behavior has been seen in CdSe NSs with an associated decay constant of 10 ns or longer.²¹ The long-lived TDA bleach in CdS NSs therefore suggests that a sizable fraction of excitons do not trap or dissociate to undergo rapid charge recombination, despite the presence of apparent defectrelated tail states. At the same time, accompanying hydrogen generation experiments conducted on CdS NSs show low quantum yields of ~0.95%. This in turn suggests that, despite their long lifetimes, the strong binding energy of excitons in CdS NSs makes subsequent reduction chemistries prohibitive. Such large binding energies stem from dielectric contrast effects which arise in low-dimensional materials.⁵² In the case of CdSe NSs, this leads to exciton binding energies on the order of 300 meV.⁵³

Following Ni NP deposition, significant changes to the TDA response are seen. This is apparent in Figure 4b,c, where the band edge $|\Delta A|/A$ maximum decreases significantly to a value of $|\Delta A|/A_{433} = 0.078$. Corresponding bleach kinetics also become faster. In this regard, traces can be fit to triexponential decays with a significant shortening of all time constants. Namely, values of $\tau_1 = 0.39$ ps (0.7% area based weight), $\tau_2 = 4.11$ ps (3.6% area based weight), and $\tau_3 = 166$ ps (95.7% area based weight) are extracted, leading to only ~8% of the initial bleach magnitude remaining at 1.5 ns (Figure 4c).

Both the suppressed $|\Delta A|/A_{433}$ value as well as the faster decay kinetics are attributed to interactions between CdS and Ni. Possible processes include ultrafast energy transfer, an effect previously seen in Pt NP decorated CdSe NSs²¹ and ultrafast charge transfer from CdS to Ni. The latter scenario is supported by the above photocatalytic hydrogen generation measurements, wherein dramatic enhancements to experimental hydrogen generation quantum yields are seen. In this regard, efficient energy transfer should result in no enhancement, as it represents a parasitic loss process for excitations.

Consequently, we conclude that the presence of metal/ semiconductor heterojunctions in CdS/Ni NSs leads to the efficient dissociation of long-lived and strongly bound excitons. This, in turn, suggests that the combination of several intrinsic features of 2D CdS NSs, namely, their large absorption efficiencies, their strong exciton binding energies, and, more importantly, their long exciton lifetimes—all coupled to the presence of a metal/semiconductor heterojunction—results in efficient hydrogen generation.

4. CONCLUSION

In summary, we have synthesized high-quality, thicknesscontrolled, CdS NSs through the thermal decomposition of CdDDTC, a single-source precursor. Thicknesses between 1.50 and 2.16 nm have been produced with lateral dimensions larger than those currently made through the exclusive thermolysis of CdAc₂. Obtained conduction band potentials and absorption cross sections are useful not just within the context of photocatalytic applications described herein but also within the context of other energy-related applications. Corresponding Ni NP decorated NSs have been made through the photodeposition of Ni. Subsequent photocatalytic hydrogen generation measurements of both CdS and CdS/Ni NSs reveal long time apparent quantum yields as large as 25%. Ever larger yields, as high as 64%, have been seen during the initial stages of H₂ generation. Ensemble TDA spectroscopy illustrates that the improved photocatalytic efficiency of CdS/Ni NSs stems

from efficient electron transfer from CdS to Ni. The metal/ semiconductor heterojunction is thus critical in dissociating strongly bound excitons in 2D CdS NSs and introduces an effective pathway for creating free carriers needed to carry out relevant reduction chemistries.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b01812.

Low- and high-magnification TEM images of 1.50, 1.80, and 2.16 nm thick CdS NSs, lateral sizing histograms for 1.80 and 2.16 nm thick CdS NSs, ensemble EDXS spectra of 1.50 and 1.80 nm thick CdS NSs. Comparison of CdS NS d spacings obtained from ensemble XRD measurements along with known bulk values, electrochemical scans for 1.80 and 2.16 nm CdS NSs deposited on FTO, CdS NS tail states highlighted on a semilogarithmic plot, NS concentration and absorption cross section estimates, time-correlated single photon counting kinetics for 2.16 nm CdS NSs, TEM images and NP sizing histograms for Ni NPs deposited onto 2.16 nm CdS NSs using different NiSO₄ concentrations, emission spectra of 2.16 nm CdS, PEI passivated CdS, and CdS/ Ni NSs, schematic illustrating hydrogen generation from CdS/Ni composites in water/ethanol mixtures, apparent hydrogen generation quantum yield estimates, TDA spectra and integrated bleach feature areas for 2.16 nm CdS NSs obtained at different pump fluences (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: mzhukovs@nd.edu. *E-mail: mkuno@nd.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by the Army Research Office (W911NF-12-1-0578) and by the Center for Sustainable Energy at Notre Dame (ND Energy). P.T. thanks the Royal Thai Government Scholarship for financial support. We also thank the Notre Dame Integrated Imaging Facility (NDIIF) and the Notre Dame Radiation Laboratory for use of their facilities. Chemical analyses were conducted at the Center for Environmental Science and Technology (CEST) at the University of Notre Dame.

REFERENCES

(1) Sakamoto, M.; Xiong, A.; Kanakubo, R.; Ikeda, T.; Yoshinaga, T.; Maeda, K.; Domen, K.; Teranishi, T. *Chem. Lett.* **2012**, *41*, 1325– 1327.

(2) Zhao, J.; Holmes, M. A.; Osterloh, F. E. ACS Nano 2013, 7, 4316–4325.

(3) Ben-Shahar, Y.; Scotognella, F.; Waiskopf, N.; Kriegel, I.; Dal Conte, S.; Cerullo, G.; Banin, U. Small **2015**, *11*, 462–471.

(4) Berr, M.; Vaneski, A.; Susha, A. S.; Rodríguez-Fernández, J.; Döblinger, M.; Jäckel, F.; Rogach, A. L.; Feldmann, J. *Appl. Phys. Lett.* **2010**, *97*, 093108.

(5) Tongying, P.; Plashnitsa, V. V.; Petchsang, N.; Vietmeyer, F.; Ferraudi, G. J.; Krylova, G.; Kuno, M. J. Phys. Chem. Lett. **2012**, *3*, 3234–3240.

- (6) Tongying, P.; Vietmeyer, F.; Aleksiuk, D.; Ferraudi, G. J.; Krylova, G.; Kuno, M. *Nanoscale* **2014**, *6*, 4117–4124.
- (7) Han, Z.; Qiu, F.; Eisenberg, R.; Holland, P. L.; Krauss, T. D. Science **2012**, 338, 1321–1324.
- (8) Wilker, M. B.; Shinopoulos, K. E.; Brown, K. A.; Mulder, D. W.;
- King, P. W.; Dukovic, G. J. Am. Chem. Soc. 2014, 136, 4316-4324.

(9) Amirav, L.; Alivisatos, A. P. J. Phys. Chem. Lett. 2010, 1, 1051–1054.

- (10) Wu, K.; Chen, Z.; Lv, H.; Zhu, H.; Hill, C. L.; Lian, T. J. Am. Chem. Soc. 2014, 136, 7708–7716.
- (11) Simon, T.; Bouchonville, N.; Berr, M. J.; Vaneski, A.; Adrović,
- A.; Volbers, D.; Wyrwich, R.; Döblinger, M.; Susha, A. S.; Rogach, A. L.; Jäckel, F.; Stolarczyk, J. K.; Feldmann, J. Nat. Mater. 2014, 13,
- 1013–1018. (12) Vietmeyer, F.; McDonald, M.; Kuno, M. J. Phys. Chem. C 2012, 116. 12379–12396.
- (13) Alivisatos, A. P. Science 1996, 271, 933-937.
- (14) Tessier, M. D.; Mahler, B.; Nadal, B.; Heuclin, H.; Pedetti, S.; Dubertret, B. *Nano Lett.* **2013**, *13*, 3321–3328.
- (15) She, C.; Fedin, I.; Dolzhnikov, D. S.; Demortière, A.; Schaller, R. D.; Pelton, M.; Talapin, D. V. *Nano Lett.* **2014**, *14*, 2772–2777.
- (16) Ding, Y.; Singh, V.; Goodman, S. M.; Nagpal, P. J. Phys. Chem. Lett. 2014, 5, 4291-4297.
- (17) Chen, Z. Y.; Nadal, B.; Mahler, B.; Aubin, H.; Dubertret, B. Adv. Funct. Mater. 2014, 24, 295-302.
- (18) Lorenzon, M.; Christodoulou, S.; Vaccaro, G.; Pedrini, J.; Meinardi, F.; Moreels, I.; Brovelli, S. *Nat. Commun.* **2015**, *6*, 6434.
- (19) Lhuillier, E.; Robin, A.; Ithurria, S.; Aubin, H.; Dubertret, B. Nano Lett. 2014, 14, 2715–2719.
- (20) Lhuillier, E.; Pedetti, S.; Ithurria, S.; Heuclin, H.; Nadal, B.; Robin, A.; Patriarche, G.; Lequeux, N.; Dubertret, B. *ACS Nano* **2014**, 8. 3813–3820.
- (21) Wu, K.; Li, Q.; Du, Y.; Chen, Z.; Lian, T. Chem. Sci. 2015, 6, 1049-1054.
- (22) Wu, K.; Li, Q.; Jia, Y.; McBride, J. R.; Xie, Z.-X.; Lian, T. ACS Nano 2015, 9, 961–968.
- (23) Sigle, D. O.; Zhang, L.; Ithurria, S.; Dubertret, B.; Baumberg, J. J. J. Phys. Chem. Lett. **2015**, *6*, 1099–1103.
- (24) Voiry, D.; Yamaguchi, H.; Li, J.; Silva, R.; Alves, D. C. B.; Fujita, T.; Chen, M.; Asefa, T.; Shenoy, V. B.; Eda, G.; Chhowalla, M. *Nat. Mater.* **2013**, *12*, 850–855.
- (25) Baghani, E.; O'Leary, S. K.; Fedin, I.; Talapin, D. V.; Pelton, M. J. Phys. Chem. Lett. 2015, 6, 1032–1036.
- (26) Alemseghed, M. G.; Ruberu, T. P. A.; Vela, J. Chem. Mater. 2011, 23, 3571-3579.
- (27) Mokari, T.; Rothenberg, E.; Popov, I.; Costi, R.; Banin, U. Science **2004**, 304, 1787–1790.
- (28) Li, Z.; Qin, H.; Guzun, D.; Benamara, M.; Salamo, G.; Peng, X. Nano Res. **2012**, *5*, 337–351.
- (29) Bouet, C.; Mahler, B.; Nadal, B.; Abecassis, B.; Tessier, M. D.; Ithurria, S.; Xu, X.; Dubertret, B. *Chem. Mater.* **2013**, *25*, 639–645.
- (30) Li, Z.; Peng, X. J. Am. Chem. Soc. 2011, 133, 6578-6586.
 (31) Amelia, M.; Impellizzeri, S.; Monaco, S.; Yildiz, I.; Silvi, S.;
- (31) Antena, M.; Impenizzeri, S.; Monaco, S.; Hudz, F.; Shvi, S. Raymo, F. M.; Credi, A. ChemPhysChem **2011**, *12*, 2280–2288.
- (32) Poznyak, S. K.; Osipovich, N. P.; Shavel, A.; Talapin, D. V.; Gao, M.; Eychmüller, A.; Gaponik, N. *J. Phys. Chem. B* **2005**, *109*, 1094–1100.
- (33) Pan, A.; Liu, D.; Liu, R.; Wang, F.; Zhu, X.; Zou, B. Small 2005, 1, 980–983.
- (34) Bastin, J. A.; Mitchell, E. W. J.; Whitehouse, J. Br. J. Appl. Phys. 1959, 10, 412–416.
- (35) Kunneman, L. T.; Schins, J. M.; Pedetti, S.; Heuclin, H.; Grozema, F. C.; Houtepen, A. J.; Dubertret, B.; Siebbeles, L. D. A. *Nano Lett.* **2014**, *14*, 7039–7045.
- (36) Stroyuk, A. L.; Raevskaya, A. E.; Korzhak, A. V.; Kotenko, I. E.; Glebov, E. M.; Plyusnin, V. F.; Kuchmii, S. Ya. *Theor. Exp. Chem.* **2009**, *45*, 12–22.

- (37) Wang, J. J.; Li, Z. J.; Li, X. B.; Fan, X. B.; Meng, Q. Y.; Yu, S.; Li, C. B.; Li, J. X.; Tung, C. H.; Wu, L. Z. *ChemSusChem* **2014**, *7*, 1468–1475.
- (38) Bamwenda, G. R.; Tsubota, S.; Nakamura, T.; Haruta, M. J. Photochem. Photobiol., A **1995**, 89, 177–189.
- (39) Forouzan, F.; Richards, T. C.; Bard, A. J. J. Phys. Chem. 1996, 100, 18123-18127.
- (40) Korzhak, A. V.; Ermokhina, N. I.; Stroyuk, A. L.; Bukhtiyarov, V. K.; Raevskaya, A. E.; Litvin, V. I.; Kuchmiy, S. Y.; Ilyin, V. G.; Manorik, P. A. J. Photochem. Photobiol., A **2008**, 198, 126–134.
- (41) Lu, H.; Zhao, J.; Li, L.; Gong, L.; Zheng, J.; Zhang, L.; Wang, Z.; Zhang, J.; Zhu, Z. Energy Environ. Sci. 2011, 4, 3384-3388.
- (42) Nakibli, Y.; Kalisman, P.; Amirav, L. J. Phys. Chem. Lett. 2015, 6, 2265–2268.
- (43) Wood, A.; Giersig, M.; Mulvaney, P. J. Phys. Chem. B 2001, 105, 8810–8815.
- (44) Subramanian, V.; Wolf, E. E.; Kamat, P. V. J. Am. Chem. Soc. 2004, 126, 4943-4950.
- (45) Norskov, J. K.; Bligaard, T.; Logadottir, A.; Kitchin, J. R.; Chen,
- J. G.; Pandelov, S.; Stimming, U. J. Electrochem. Soc. 2005, 152, J23-J26.
- (46) Matsumoto, H.; Sakata, T.; Mori, H.; Yoneyama, H. J. Phys. Chem. 1996, 100, 13781-13785.
- (47) Zhang, L.; Liu, Q.; Aoki, T.; Crozier, P. A. J. Phys. Chem. C 2015, 119, 7207-7214.
- (48) Klimov, V. I. J. Phys. Chem. B 2000, 104, 6112-6123.
- (49) Puthussery, J.; Lan, A.; Kosel, T. H.; Kuno, M. ACS Nano 2008, 2, 357–367.
- (50) Zhukovskiy, M. A.; Stroyuk, A. L.; Shvalagin, V. V.; Smirnova, N. P.; Lytvyn, O. S.; Eremenko, A. M. J. Photochem. Photobiol., A 2009, 203, 137–144.
- (51) Wu, K.; Zhu, H.; Lian, T. *Acc. Chem. Res.* **2015**, *48*, 851–859. (52) Muljarov, E. A.; Zhukov, E. A.; Dneprovskii, V. S.; Masumoto, Y.
- Phys. Rev. B: Condens. Matter Mater. Phys. 2000, 62, 7420-7432.
- (53) Benchamekh, R.; Gippius, N. A.; Even, J.; Nestoklon, M. O.; Jancu, J.-M.; Ithurria, S.; Dubertret, B.; Efros, A. L.; Voisin, P. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2014**, *89*, 035307.