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Dot Heterostructures: Tuning Valence Band Edges
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Programming Interfacial Energetic Offsets and Charge Transfer in β -Pb_{0.33}V₂O₅/Quantum-Dot Heterostructures: Tuning Valence Band Edges to Overlap with Midgap States

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ABSTRACT

Semiconductor heterostructures for solar energy conversion interface light-harvesting semiconductor nanoparticles with wide-bandgap semiconductors that serve as charge acceptors. In such heterostructures, the kinetics of charge separation depend on the thermodynamic driving force, which is dictated by interfacial energetic offsets across the interface. A recently developed promising platform interfaces semiconductor quantum dots (QDs) with ternary vanadium oxides that have characteristic midgap states situated between the valence and conduction bands. Here, we have prepared CdS/ β -Pb_{0.33}V₂O₅ heterostructures *via* both linker-assisted assembly and surface precipitation and contrasted these to CdSe/ β -Pb_{0.33}V₂O₅ heterostructures prepared by the same methods. Increased valence band (VB) edge onsets in X-ray photoelectron spectra for CdS/ β -Pb_{0.33}V₂O₅ heterostructures relative to CdSe/ β -Pb_{0.33}V₂O₅ heterostructures suggest a positive shift in VB edge potential, and therefore an increased driving force for the photoinduced transfer of holes to the midgap state of β -Pb_{0.33}V₂O₅. This approach facilitates a ca. 0.40 eV decrease in the thermodynamic barrier for hole injection from the VB edge of QDs suggesting an important design parameter. Transient absorption spectroscopy experiments provide direct evidence of hole transfer from photoexcited CdS QDs to the midgap states of β -Pb_{0.33}V₂O₅ NWs along with electron transfer into the conduction band of the β -Pb_{0.33}V₂O₅ NWs. Hole transfer is substantially faster and occurs at <1 ps timescales whereas electron transfer requires 4–15 ps depending on the nature of the interface. The differentiated timescales of electron and hole transfer, which are furthermore tunable as a function of the mode of attachment of QDs to NWs, provide a vital design tool for designing architectures for solar energy conversion. More generally, the approach developed here suggests that interfacing semiconductor QDs with transition metal oxide NWs exhibiting intercalative midgap states yields a versatile platform

wherein thermodynamics and kinetics of charge transfer can be systematically modulated to improve the efficiency of charge separation across interfaces.

1. Introduction

Nanoscale semiconductor heterostructures are of tremendous interest for solar energy conversion owing primarily to the tunability of the bandgaps and band-edge potentials of semiconductors as a function of composition and size.¹⁻⁴ In a typical heterostructure configuration used for solar energy conversion, a light-harvesting semiconductor nanoparticle (excited-state charge donor) is interfaced with a wide-bandgap semiconductor (charge acceptor), and photogenerated charge carriers are transferred across the interface.⁵⁻⁷ To achieve efficient solar energy conversion, the separation of excited electrons and holes must occur more rapidly than excited-state relaxation; and subsequent charge-transport or redox photocatalytic steps must outcompete charge recombination. The kinetics of charge separation depend on the thermodynamic driving force, which is dictated by interfacial energetic offsets of electron-donating and accepting states. Consequently, the design of nanoscale semiconductor heterostructures for charge transfer and solar energy conversion requires careful consideration of interfacial energetic offsets.⁸⁻¹⁰ The tunability of electronic structure that is accessible in semiconductor quantum dots (QDs) provides a powerful adjustable parameter for achieving heterostructures with desired energetic offsets.^{1,11-12}

Recently, we demonstrated a promising tunable platform for light-harvesting and excited-state charge transfer derived from interfacing β - $\text{Pb}_{0.33}\text{V}_2\text{O}_5$ nanowires (NWs) with CdSe QDs.¹³⁻¹⁴ This platform exploits a distinctive feature in the electronic structure of ternary vanadium oxide bronzes: the presence of intrinsic midgap states, derived from the intercalating cations, that are

situated between the valence and conduction band edges.¹⁵⁻¹⁶ In the case of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$, midgap states are derived from Pb 6s-O 2p antibonding interactions.¹⁷⁻¹⁸ The energies and occupancies of these midgap states are tunable through the choice of intercalating cation and the cation stoichiometry.^{17,19} Since the intercalating cations are homogeneously incorporated within the quasi-1D crystal structure, such states constitute an integral part of the electronic structure and are quite distinct from midgap states derived from defects or dopants. Hard X-ray photoemission spectroscopy measurements revealed substantial energetic overlap between the midgap states of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ and valence-band states of CdSe, suggesting that the transfer of photogenerated holes from the valence band of CdSe into the midgap states of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ is possible as also verified by transient absorption spectroscopy experiments.¹³⁻¹⁴ However, the valence band edge of CdSe QDs was measured to lie ca. 0.7 eV higher in energy than the highest-energy midgap states of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs. Therefore, the transfer of thermalized holes at the valence band edge of CdSe QDs to the midgap states of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs was thermodynamically unfavorable.¹³

The size- and composition-dependent electronic structure of QDs is advantageous when designing heterostructures with desirable interfacial energetic offsets and tunable driving forces for excited-state charge transfer.^{2,5} In this article, we demonstrate that an improved driving force for hole transfer in QD/NW heterostructures is obtained by replacing CdSe QDs with CdS QDs of the appropriate dimensionality as light-harvesters and excited-state hole donors. The valence band edge of bulk CdS is ca. 0.5 eV lower in energy than that of bulk CdSe,²⁰⁻²¹ which provides a means for improving the energetic overlap of the valence-band states of QDs with midgap states of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs, thereby rendering such interfaces more suitable for excited-state charge separation and yielding heterostructures designed to optimally harvest solar radiation. Interfacial energetic offsets have been examined for heterostructures with distinctive sizes and modes of

attachment of CdS and CdSe QDs. Transient absorption spectroscopy measurements have further been used to dynamically resolve hole and electron transfer processes in these heterostructures and suggest that the midgap states of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs mediate hole transfer from photoexcited QDs at <1 ps timescales. The design concepts illustrated here underscore the programmability of charge transfer in heterostructures coupling QDs with NWs characterized by distinctive intercalative states.

2. Experimental Methods

2.1. Synthesis of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ nanowires

$\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs were prepared using a one-step hydrothermal reaction as previously reported.¹⁸ In brief, stoichiometric amounts of $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ and V_2O_5 were placed in a polytetrafluoroethylene-lined acid digestion vessel (Parr) along with 16 mL of deionized (DI) water. The vessel was sealed in an autoclave and heated to 250°C for 72 h. The product was isolated by vacuum filtration, washed with water, and allowed to dry in air.

2.2. Synthesis of Cysteinate-capped CdSe Quantum Dots

Cysteinate-capped CdSe QDs with average diameters less than 2 nm, hereafter referred to as Cys-CdSe(sm), were synthesized as previously reported.²² The selenium precursor was prepared by refluxing an aqueous solution of Se powder and Na_2SO_3 overnight, and the cadmium precursor was an aqueous solution of $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ and cysteine. The pH of the cadmium precursor was titrated to 12.5–13.0 with solid NaOH. The hot selenium precursor was added to the cadmium precursor and allowed to stir for 30 min. The resulting dispersions of Cys-CdSe(sm) QDs were purified by solvent/non-solvent ($\text{H}_2\text{O}/\text{MeOH}$, 3:1) washing to remove excess reagents. Cysteinate-capped CdSe QDs with greater average diameters, hereafter referred

to as Cys-CdSe(lg) QDs, were synthesized and purified by a similar procedure, differing only in that the cadmium precursor was heated to, and maintained at, 80°C for the duration of the experiment (2 h)²³.

2.3. Synthesis of Cysteinate-capped CdS Quantum Dots

Cysteinate-capped CdS QDs were prepared using a modification of the synthesis of Cys-CdSe(sm) QDs. A sulfur precursor solution was prepared by adding sodium thiosulfate (1.17 g, 7.41 mmol) to 25 mL DI water in a 50 mL round bottom flask and heating to reflux for 30 min. For QDs with relatively smaller average particle size, hereafter referred to as Cys-CdS(sm) QDs, the cadmium precursor was an aqueous solution (10.5 mL) of cadmium sulfate octahydrate (0.433 g, 1.69 mmol) and cysteine (1.02 g, 8.44 mmol). The pH of the solution was titrated to 12.5 - 13.0 with solid NaOH. The hot sodium thiosulfate solution (4.5 mL) was added to the cadmium precursor with stirring. The reaction was allowed to stir overnight (12-16 h) resulting in the formation of a cloudy, white suspension of flocculated Cys-CdS(sm) QDs. For QDs with relatively larger average particle size, hereafter referred to as Cys-CdS(lg) QDs, the cadmium precursor was an aqueous solution (21 mL) of cadmium sulfate octahydrate (0.866g, 3.38 mmol) and cysteine (2.05 g, 16.88 mmol). The pH of the solution was titrated to 12.5 - 13.0 with solid NaOH. The cadmium precursor was then heated to 80°C and the hot sodium thiosulfate solution (9 mL) was added with stirring. The reaction was allowed to continue heating for 4 h with stirring, resulting in the formation of a cloudy, yellow suspension of flocculated Cys-CdS(lg) QDs. Typical concentrations of cadmium, sulfur, and Cys in the reaction mixtures for both Cys-CdS(sm) and Cys-CdS(lg) were 113, 90, and 563 mM, respectively. Dispersions of both Cys-CdS(sm) and Cys-CdS(lg) QDs were purified by solvent/non-solvent washing to remove excess reagents. First, 5 mL of the flocculated QDs were centrifuged to isolate the QDs and the

supernatant was discarded. The pellet of QDs was then fully dispersed into 10 mL DI water resulting in a clear dispersion. Then, 30 mL of methanol was added to the dispersion of QDs, resulting in the flocculation of QDs. The flocculate was then centrifuged again to isolate the QDs, supernatant was discarded, and the QDs were redispersed into 10 mL DI water. This process was repeated once for a total of two purification cycles.

2.4. Successive Ionic Layer Adsorption and Reaction (SILAR) Assembly of CdSe/ β - $\text{Pb}_{0.33}\text{V}_2\text{O}_5$ and CdS/ β - $\text{Pb}_{0.33}\text{V}_2\text{O}_5$ Heterostructures

CdSe was deposited directly onto β - $\text{Pb}_{0.33}\text{V}_2\text{O}_5$ NWs via SILAR using a previously reported method.¹³ In a single SILAR cycle, CdSe QDs were grown directly onto β - $\text{Pb}_{0.33}\text{V}_2\text{O}_5$ NWs by sequentially mixing the NWs with a cadmium precursor solution ($\text{Cd}(\text{NO}_3)_2$ in ethanol), followed by a selenium precursor (Na_2Se in ethanol). The NWs were washed with ethanol following each mixing step to remove excess ions. CdS/ β - $\text{Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures were prepared using a modification of this procedure. A 50 mM solution of Na_2S was prepared by dissolving $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ in ethanol. Meanwhile, β - $\text{Pb}_{0.33}\text{V}_2\text{O}_5$ NWs (50 mg) were dispersed in 15 mL of ethanol, and a 100 mM solution of $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ was prepared in ethanol. All solutions and dispersions were placed in a glovebag filled with Ar gas. To begin the SILAR cycle, the dispersion of NWs was mixed with the $\text{Cd}(\text{NO}_3)_2$ solution, thus bringing the concentration of $\text{Cd}(\text{NO}_3)_2$ to 50 mM. The solution was stirred for 30 s, and the NWs were then removed through centrifugation at 6500 rpm for 90 s. Subsequently, the NWs were washed with 10 mL of ethanol for 30 s and centrifuged. Next, the NWs were mixed with the Na_2S solution for 30 s, centrifuged and isolated, and washed again with 10 mL of ethanol. This final washing step concludes one SILAR cycle.

2.5. Linker-assisted Assembly of Cys-CdSe/ β -Pb_{0.33}V₂O₅ Heterostructures

Cys-CdSe(sm)/ β -Pb_{0.33}V₂O₅ and Cys-CdSe(lg)/ β -Pb_{0.33}V₂O₅ heterostructures were prepared *via* LAA as reported previously.¹³ An aqueous dispersion of β -Pb_{0.33}V₂O₅ NWs was added to an aqueous dispersion of purified Cys-CdSe(sm) or Cys-CdSe(lg) QDs and allowed to equilibrate overnight (12–16 h). CdSe-functionalized NWs were recovered by centrifugation, rinsed with DI water to remove excess QDs, and dried at room temperature before characterization.

2.6. Linker-assisted Assembly of Cys-CdS/ β -Pb_{0.33}V₂O₅ Heterostructures

Cys-CdS/ β -Pb_{0.33}V₂O₅ heterostructures were prepared using a modification of the LAA method employed for formation of Cys-CdSe/ β -Pb_{0.33}V₂O₅ heterostructures. β -Pb_{0.33}V₂O₅ NWs (10 mg) were dispersed in DI water (10 mL) in a 20 mL scintillation vial. The dispersion was sonicated for 20 min to maximize the amount of dispersed NWs. An aqueous dispersion of either purified Cys-CdS(sm) QDs or purified Cys-CdS(lg) QDs (1 mL) was added to the dispersion of β -Pb_{0.33}V₂O₅ NWs and allowed to equilibrate overnight (12–16 h). Cys-CdS(sm)/ β -Pb_{0.33}V₂O₅ or Cys-CdS(lg)/ β -Pb_{0.33}V₂O₅ heterostructures were recovered *via* centrifugation and then rinsed with DI water to remove excess QDs. The heterostructures were dried at room temperature prior to characterization.

2.7. Characterization Methods and Instrumentation

Scanning electron microscopy (SEM) was performed using a JEOL JSM-7500F operated at 5 kV. Samples were prepared for SEM by spreading synthesized samples on carbon tape. High-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) measurements, and energy dispersive X-ray spectroscopy (EDS) were performed with a FEI Tecnai G2 F20 FE-TEM operated at 200 kV equipped with an EDAX Instruments EDS

detector. Samples were prepared for TEM by dispersing samples in ethanol and drop-casting onto carbon-coated copper grids. Raman spectra of solid-phase powders of SILAR CdS/ β - $\text{Pb}_{0.33}\text{V}_2\text{O}_5$ and Cys-CdS QDs were obtained with a Jobin-Yvon Horiba Labram HR800 instrument coupled to an Olympus BX41 microscope using the 514.5 nm laser excitation from an Ar-ion laser. Cys-CdS QDs were dispersed in water and drop-cast onto a gold-coated silicon pyramids to plasmonically enhance Raman signal. The preparation of substrates for surface enhanced Raman spectroscopy has been discussed in previous work.²⁴

X-ray photoemission spectroscopy (XPS) measurements were performed using a Phi VersaProbe 5000 system with a monochromated Al K α source and hemispherical analyzer at the Analytical and Diagnostics Laboratory (ADL) at Binghamton University. The valence band region was measured with a pass energy of 23.5 eV, and a flood gun was used to achieve charge neutralization. Valence band spectra were energy aligned to the Cd 4d peak at 11 eV.

Transient absorption (TA) measurements were acquired using a commercial Ti:sapphire amplified laser system (SpectraPhysics Spitfire Pro, 800 nm, 1 kHz repetition rate). Wavelength tunable pump pulses were generated in a commercial optical parametric amplifier (LightConversion). For femtosecond time delays, a supercontinuum probe beam (425—900 nm) was generated by focusing a fraction of the laser fundamental into a sapphire disc to generate supercontinuum probe light and was mechanically delayed (dynamic range of 3 ns) relative to the pump pulse. For longer probe times, a separate fibre based supercontinuum laser was used to generate the probe beam and was electronically delayed (dynamic range of > 20 μ s) relative to the pump pulse (Ultrafast Systems). TA decay traces were compiled by averaging ΔA values over a given range of probe wavelengths at each delay time.

3. Results and discussion

CdS/ β -Pb_{0.33}V₂O₅ heterostructures have been prepared using two distinct routes: linker-assisted assembly (LAA) and SILAR.¹³ Cys-CdS(sm) QDs with average diameters of ca. 2.6 nm and Cys-CdSe(lg) QDs with average diameters of ca. 3.8 nm, as determined from maxima of the first excitonic absorption bands,²⁵ were used for LAA. Cysteinate acts as a bifunctional linker molecule, preferentially binding to Cd²⁺ sites *via* the thiolate functional group and to β -Pb_{0.33}V₂O₅ through an electrostatic interaction between the positively charged, protonated amine of Cys and the negatively charged, hydroxylated surface of β -Pb_{0.33}V₂O₅.¹³ For SILAR-derived heterostructures, CdS QDs were grown directly onto β -Pb_{0.33}V₂O₅ NWs. In a single SILAR cycle, NWs were immersed first in a S²⁻ precursor solution then in a Cd²⁺ precursor solution. Multiple iterations of SILAR (1× and 3× are hereafter used to designate one and three cycles, respectively) allowed for tunability of the size of the QDs and their loading on the NWs.

3.1. Structural Characterization

The CdS/ β -Pb_{0.33}V₂O₅ heterostructures were characterized by electron microscopy, electron diffraction, and Raman spectroscopy (Figure 1). Transmission electron microscopy (TEM) images of 3× SILAR-derived CdS/ β -Pb_{0.33}V₂O₅ heterostructures reveal a continuous shell of QDs around the NWs (Figure 1A). TEM images of LAA-derived Cys-CdS(lg)/ β -Pb_{0.33}V₂O₅ heterostructures similarly reveal a continuous overlayer of Cys-CdS QDs with resolvable lattice fringes indexed to the separation between the (112) planes of wurtzite CdS (Joint Committee on Powder Diffraction Standards (JCPDS) #41-1049). Selected area electron diffraction (SAED) of Cys-CdS(lg)/ β -Pb_{0.33}V₂O₅ heterostructures yields a complex pattern with reflections from both β -Pb_{0.33}V₂O₅ and wurtzite CdS (Fig. 1E). The diffuse diffraction ring can be indexed to the (101)

plane of wurtzite CdS, consistent with our assignment of the lattice fringes observed in the TEM image. The other reflections are indexed to $\beta\text{-Pb}_{0.30}\text{V}_2\text{O}_5$ (JCPDS #41-1426).^{13,18} Energy-dispersive X-ray spectroscopy (EDS) spectra confirm the presence of Cd and S in the heterostructures (Figure S1 in Supporting Information), and this was further verified by X-ray photoelectron spectroscopy (XPS) survey scans. Scanning electron microscopy (SEM) images of SILAR- and LAA-derived heterostructures (Figure 1C and D) indicate speckled nanowires with homogeneous QD coverage along their entire lengths.

To further verify the phase assignment of CdS QDs, the SILAR-prepared heterostructures and dispersed Cys-CdS(sm) and Cys-CdS(lg) QDs were characterized by surface enhanced Raman spectroscopy (Figure 1F) by inclusion of the materials within pyramidal gold substrates.²⁴ Raman spectra of aqueous dispersions of Cys-CdS QDs exhibit a sharp, intense band at 300 cm^{-1} and a broader, less intense band at 600 cm^{-1} , which are assigned to the bulk longitudinal optical (LO) and second-order longitudinal optical (2LO) modes, respectively, of wurtzite CdS.²⁶ Raman spectra of SILAR-prepared CdS/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures reveal the emergence of both the LO and 2LO modes of wurtzite CdS overlapped with the characteristic modes of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$, which have been assigned previously.¹³ The CdS phonon modes are increased in relative intensity for the 3 $\times$ SILAR-derived heterostructures as compared to the 1 $\times$ SILAR-derived heterostructures, suggesting an increased thickness of the CdS QD overlayer with multiple SILAR iterations.¹³

3.2. Energetic Offsets: Thermodynamics of Hole Transfer in CdS/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$

Heterostructures

In order to measure the energetic offsets between the valence band edges of the QDs and the midgap states of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$, XPS measurements were performed as a function of the composition of QDs and their mode of attachment to the NWs. The valence band spectra of SILAR- and LAA-derived QD/NW heterostructures (overlaid with the spectrum of bare $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs) are shown in Figure 2A and B, respectively. The valence band spectrum of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs is characterized by a broad peak between 2 and 9 eV, which is derived primarily from O 2p non-bonding states.^{13,17-18} The lower photoelectron cross-section of Pb 6s compared to O 2p at Al K α energies precludes direct observation of midgap states in valence band XPS spectra. However, hard X-ray photoemission spectroscopy (HAXPES) measurements indicate a feature in the 1.8—3.6 eV range corresponding to Pb 6s—O 2p anti-bonding interactions that give rise to the midgap state.¹⁷ The energy dispersion of these states is denoted in Figures 2C and D by dashed vertical lines. To highlight changes in the electronic structure upon interfacing $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs with CdS QDs and to correct for Fermi level shifts, all valence band spectra were baseline-corrected, aligned, and normalized to the intensity of the O 2p nonbonding state at ca. 5 eV below an effective Fermi level (0 eV). Such an alignment enables the calculation of difference spectra and provides a gauge of the change in ionization potential since the primary O 2p feature is considered to be constant at a fixed ionization potential of ca. 8 eV below the vacuum level. We note that using this methodology, the Cd 4d semi-core level features for the coated samples in Figure 2 are at the same energy, which is consistent with the idea of a fixed ionization potential. For both LAA and SILAR-coated heterostructures, distinctive features emerge in close proximity of the energy levels demarcated as $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ midgap states as a result of S 3p and Se 4p contributions from the CdS and CdSe QDs, respectively. The Se 4p and S 3p features are much more clearly discernible at Al K α energies in contrast to HAXPES due to the

orbital cross-section variations between these photon energies.^{17,27} Difference spectra were obtained by subtracting the valence band spectrum of bare $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs from the spectrum of each QD/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructure. Such spectra are plotted in Figures 2C and D for SILAR- and LAA-prepared heterostructures, respectively, and allow for easier visualization of relative shifts in energetic offsets.

For the LAA samples that have approximately monolayer or sub-monolayer coverage of QDs, the Cd 4d levels are of comparable intensity for all of the samples (Figure 2B). The specific mode of attachment, which requires Cys to function as a bifunctional linker, limits the formation of thicker shells. In contrast, for the SILAR samples, the relatively greater thickness of the 3x samples as compared to the 1x samples is reflected in the stronger intensity of the Cd 4d core level feature observed in Figure 2A. The 3x SILAR CdSe/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures have a coating thickness intermediate between the 1x and 3x CdS/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ analogs. Numerical values of the valence band onsets were determined from intercepts of linear fits to the baseline and the low-energy part of the difference spectra as depicted in Figures 2E and F for LAA-prepared heterostructures comprising $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs interfaced with CdS(sm) and CdSe(sm) QDs, respectively.²⁸ Figure S2 of the Supporting Information shows fits obtained for LAA-prepared heterostructures comprising larger QDs as well as heterostructures prepared by SILAR. Since the differences in valence band onsets as a function of size are much smaller relative to the differences induced by changing the QD composition from CdSe to CdS (quantum confinement affects the conduction band edge to a much greater extent than the valence band edge), the valence band onsets have been averaged for the LAA and SILAR heterostructures in each case.²⁹⁻

³⁰ Table 1 summarizes these valence band edge values. Several findings are immediately apparent from analysis of the valence band spectra. First, both the difference spectra (Figures 2C

and D) and the extrapolated onset values (Table 1) indicate that the valence band onset of CdS QDs (1.32 ± 0.02 eV) is shifted to higher binding energies relative to CdSe QDs for LAA-prepared heterostructures (0.92 ± 0.01 eV). The observed increase in binding energy onset implies a more strongly bound state and can be directly correlated to the valence band edge of CdS (primarily S 3p in origin) being positioned at a relatively lower energy as compared to CdSe (primarily Se 4p in origin) on an energy scale where occupied states are negative and unoccupied states are positive with respect to a Fermi level of 0 eV. The relatively deeper valence band of CdS is a direct result of the higher electronegativity of sulfur, which consistent with Fajan's rules further yields a more ionic lattice with relatively less hybridization of S and Cd-derived states. A very similar trend is also noted for the SILAR CdS (1.32 ± 0.02 eV) and SILAR CdSe (0.94 ± 0.02 eV) samples (Fig. S2, Supporting Information). As evident in Figures 2C and D, an immediate consequence of the shift of the valence band to higher energies for CdS is a much improved overlap with the midgap states of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$.

Taking the intercept as a close approximation to the valence band onset, the valence band edge of Cys-CdS is shifted ca. 0.41 eV lower in energy than the Cys-CdSe valence band edge. Similarly, for SILAR-prepared heterostructures, there is a ca. 0.38 eV decrease in the valence band edge of CdS relative to CdSe. These experimentally determined differences in valence band edge energies of CdS and CdSe, for both SILAR- and LAA-prepared heterostructures, are in reasonable agreement with reported energy differences (ca. 0.5 eV) for the band edges of bulk CdS and CdSe.²⁰⁻²¹

The above discussion clearly indicates that the valence band edge of CdS QDs on $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs is lower in energy compared to CdSe QDs on the NWs, suggesting a decrease in the thermodynamic barrier to hole injection from the valence band edge of the QDs into the midgap

states of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$, as shown in Figure 3. The maximum thermodynamic barrier for the injection of thermalized holes from QDs to the midgap states of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ is estimated from the energy difference between the valence band edge of the QDs and the onset of the midgap states at ca. 1.8 eV. Thermodynamic barriers of ca. 0.47 eV and ca. 0.88 eV were estimated for hole injection from the band edges of Cys-CdS and Cys-CdSe QDs, respectively, suggesting a 0.40 eV decrease in the barrier for hole injection from CdS. Importantly, the shift of the valence band of CdS to lower energy than that of CdSe renders hole transfer to midgap states of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs thermodynamically favorable from a much greater fraction of states within the valence band.

3.3. Dynamics of Charge Transfer: Kinetic Considerations in the Design of Heterostructures

The design of semiconductor heterostructures for solar energy conversion necessitates not just optimal thermodynamics for directional charge transfer but also requires that the photoinduced charge transfer processes occur more rapidly than competing charge recombination pathways. In order to evaluate the timescales of these competing pathways, excited state charge carrier dynamics were investigated for the $\text{CdS}/\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures given that XPS measurements indicate that the valence band of these QDs is better overlapped with the midgap states of the NWs. TA spectroscopy experiments at picosecond timescales allow for a clear mapping of charge transfer processes within these heterostructures. The pump excitation wavelength of 360 nm (3.4 eV) used in these experiments corresponds to an above-bandgap excitation for both the CdS QDs (bandgap of 2.8 eV) and $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs (bandgap of 2.4 eV). TA spectra have been acquired in the wavelength range of 450–750 nm and 425–750 nm for thin films of SILAR- and LAA-derived CdS QD/NW heterostructures, respectively.

Figure 4 contrasts the TA spectra of unfunctionalized $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs as well as SILAR- and LAA-derived CdS QD/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs heterostructures. The spectra are extracted from the data matrix by averaging ΔA values at delay times between 1000 and 2500 ps. The following spectral features are distinguished in all three spectra: a transient bleach at 440–480 nm, an induced absorption band centered at 550–650 nm, and another lower energy induced absorption band at 650–750 nm. The spectral features have been assigned based on spectroelectrochemical studies of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs,¹⁴ which indicate that the TA spectrum for this material is captured well by a summation of spectra for electrochemically oxidized and reduced species. Considering unfunctionalized $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$,¹⁴ the intense 550–650 nm induced absorption band can be ascribed to the excitation of electrons from the valence band to empty midgap states (and is thus characteristic of a hole situated on the $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ framework).¹⁴ The lower energy 650–750 nm band can be attributed to the excitation of electrons from the conduction band to higher energy states in the conduction band (and is thus characteristic of a free electron in $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$). The bleach in the differential absorption spectra reflects the reduced oscillator strength of the bandgap absorption once an electron has been excited into the conduction band (bleach of ground state absorption). The spectra in Figure 4 are normalized to the transient bleach of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs in an attempt to contrast the spectral features of bare $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs with those of the CdS/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures. Both the LAA- and SILAR-derived QD/NW heterostructures exhibit an increased population of electrons and holes (but an otherwise very similar spectral profile) as compared to the bare $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ nanowires where the carrier density derives entirely from direct photoexcitation. The increased population of holes and electrons is attributed to charge transfer from the photoexcited CdS as schematically illustrated in Figure 3, wherein electrons are transferred from the photoexcited QDs to the conduction band of the $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$.

$\text{Pb}_{0.33}\text{V}_2\text{O}_5$ NWs, whereas holes are transferred to the midgap states of the $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs. This charge-transfer mechanism, and the transient absorption spectral features, are consistent with previously-reported results for $\text{CdSe}/\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures.¹⁴

To resolve the dynamics of electron and hole transfer, ultrafast transient absorption measurements were acquired on picosecond time scales for the LAA- and SILAR-derived $\text{CdS}/\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures and are shown in Figure 5. Ultrafast measurements for $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs are shown in Figure S3 (Supporting Information) and suggest that the transient absorption bands reach their maximum amplitude within the response time of the instrument, which is consistent with the assignment of these spectral features to electron–hole pairs generated by direct photoexcitation. The spectra for both the LAA and SILAR-derived samples evolve to the TA spectra observed in Figures 4 and S3. However, several additional features are discernible at earlier time scales and enable direct observation of interfacial charge transfer in these heterostructures. A pronounced bleach with a minimum at 455 nm is observed for LAA-derived Cys- $\text{CdS}/\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures; a similar bleach centered at 485 nm is observed for SILAR-derived $\text{CdS}/\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures. These features are attributed to the bleach of the first excitonic ground state absorption of the CdS QDs, consistent with the nanosecond-timescale TA spectrum of colloidal Cys-CdS QDs (Figure S4 in Supporting Information). The TA spectrum of aqueous dispersions of Cys-CdS(lg) QDs exhibits a long-lived bleach with an average lifetime of 230 ± 45 ns (Table S1, Supporting Information) centered at 440 nm with an onset at 462 nm (Figure S4A). Since both Cys-CdS QDs and $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs absorb at 360 nm, the TA spectra of the heterostructures can be reasonably assigned to the combination of the TA spectra of the individual components. The bleach derived from the CdS QDs recovers much more rapidly but at different timescales for the LAA- and SILAR-derived heterostructures until

only the blue-shifted characteristic bleach of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ remains (Figure 5). The bleach recovers with an average lifetime of 5.4 ± 1.1 ps for the LAA-derived Cys-CdS/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructure (Table S2). For the SILAR-derived CdS/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructure, the TA spectrum shows a bleach signal throughout the spectrum due to some contribution of instrument response to the TA signal, which precludes the reliable extraction of lifetimes. Nevertheless, it can be inferred from Figure 5A and 5C that the bleach corresponding to CdS QDs recovers to the blue-shifted bleach of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs within approximately 5 ps. Since the bleach feature in TA spectra of QDs is dominated by the electron population in the excited state,³¹⁻³³ the much more rapid decay of the bleach observed in QD/NW heterostructures as compared to the aqueous dispersion of Cys-CdS QDs can be reasonably assigned to electron transfer from CdS QDs to $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs. The red-shifted bleach observed for the SILAR QD/NW heterostructures is attributed to the larger size of these QDs. The greater barrier to electron injection observed for the LAA-derived heterostructures likely derives from the increased charge-transfer distance and relatively lower extent of electronic coupling (decreased overlap integrals) at these interfaces as compared to the directly coupled SILAR interfaces.³⁴⁻³⁵ The induced absorption band centered at 550–650 nm in Figure 5 approaches its maximum amplitude within the instrument response suggesting that hole transfer proceeds much faster, at <1 ps timescales, than electron transfer for both SILAR and LAA-derived heterostructures. Some modest growth of both the induced absorption bands is nevertheless still discernible over a few picoseconds in Figures 5A and B.

TA kinetic traces were extracted around the 440–470 nm bleach, the 550–650 nm absorption, and the 700–750 nm absorption band (Fig. 6). The decay of the bleach and the rises of the absorptions were fitted to multiexponential kinetics as per Equation 1:

$$\Delta A = \Delta A_0 + \sum_i C_i e^{(-\frac{t}{\tau_i})} \quad (1)$$

where ΔA is absorbance difference, ΔA_0 is the absorbance difference that the data approach at long timescales, C_i is a preexponential weighting factor, t is delay time, and τ_i is lifetime. The smallest number of individual lifetime components, τ_i , which resulted in the minimum χ^2 , were used for each fit. The decay curves corresponding to bleach and induced absorption features for aqueous dispersion of cysteinate-capped CdS QDs, LAA-derived CdS/ β -Pb_{0.33}V₂O₅ heterostructures, and SILAR-derived CdS/ β -Pb_{0.33}V₂O₅ heterostructures were fitted to either monoexponential kinetics ($i = 1$) or biexponential kinetics ($i = 2$). Decay curves for SILAR-derived CdS/ β -Pb_{0.33}V₂O₅ heterostructures could not be fitted accurately due to the highly variable bleach component observed at zero delay time, which is attributed to instrument response. The fitted parameters for the decay curves for various samples are tabulated in Tables S1 and S2 (Supporting Information). Amplitude-weighted average lifetimes ($\langle \tau \rangle$) were calculated using Equation 2:

$$\langle \tau \rangle = \frac{\sum_i C_i \tau_i}{\sum_i C_i} \quad (2)$$

The percentage of non-time-resolvable and time-resolvable growth of induced absorption bands, which provide indications of the percentages of hole-transfer events that occurred within our instrument response and on slower, resolvable, time scales, respectively, were estimated as $\Delta A_{\text{non-resolvable}}$ and $\Delta A_{\text{resolvable}}$:

$$\% \Delta A_{\text{non-resolvable}} = \frac{\Delta A_1}{\Delta A_2} \cdot 100 \quad (3)$$

$$\% \Delta A_{\text{resolvable}} = \frac{\Delta A_2 - \Delta A_1}{\Delta A_2} \cdot 100 = 100 - \% \Delta A_{\text{non-resolvable}} \quad (4)$$

where ΔA_1 and ΔA_2 are the absorbance differences at delay times of 0.8 ps (immediately after the initial sharp increase of apparent absorption attributable to instrument response) and 50 ps, respectively, for a given bleach or induced absorption band. The relevant delay times are indicated by dashed lines in Figure 6.

For the Cys-CdS(lg)/ β -Pb_{0.33}V₂O₅ heterostructures, values of % $\Delta A_{\text{non-resolvable}}$ for the 600 and 740 nm absorption bands were estimated to be 76.3% and 68.3%, respectively. This difference suggests that more holes were injected into the midgap states of β -Pb_{0.33}V₂O₅ NWs (the 550–650 nm induced absorption band is the characteristic signature of holes) from the photoexcited CdS QDs as compared to electrons into the conduction band of the NWs (the 740 nm induced absorption band is the characteristic spectral signature of electrons) within the instrument response time. The relative ease with which holes are transferred in these heterostructures and the ability to enhance the differential in the timescales of hole and electron transfer by insertion of molecular linkers suggests that the QD/NW heterostructures exploiting midgap states constitute a viable architecture for excited-state charge separation and photocatalysis.

Conclusions

We have synthesized CdS QD/ β -Pb_{0.33}V₂O₅ NW heterostructures through both SILAR and LAA methods. TEM and SEM images revealed a continuous shell of CdS QDs on the surface of β -Pb_{0.33}V₂O₅ NWs. SAED and Raman spectroscopy confirmed the wurtzite crystal structure of the CdS. XPS valence band measurements on CdS/ β -Pb_{0.33}V₂O₅ and CdSe/ β -Pb_{0.33}V₂O₅ have demonstrated that the valence band edge of CdS QDs is lower in energy relative to CdSe QDs, suggesting a ca. 0.4 eV decrease in the thermodynamic barrier for hole injection from the valence band edge of the QDs and a significant increase of the fraction of valence band states

that can inject holes into the NWs. Charge transfer within these heterostructures has been examined by TA spectroscopy, which provides direct evidence of hole transfer from photoexcited CdS QDs to the midgap states of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs along with electron transfer into the conduction band of the $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs. Hole transfer is substantially faster, with the majority occurring at <1 ps timescales, whereas completion of electron transfer requires ca. 4 ps for the SILAR-derived heterostructures and ca. 15 ps for the LAA-derived heterostructures. The disparate timescales of electron and hole transfer, and the tenability of the relative timescales as a function of the mode of attachment, provides a vital design tool for designing photocatalytic architectures to promote interfacial charge separation. The approach demonstrated here suggests that semiconductor QD/midgap-state NW architectures are a versatile platform wherein thermodynamics and kinetics of charge transfer can be systematically modulated to improve charge separation across interfaces.

FIGURES

Figure 1. (A) TEM image of 3× SILAR CdS/β-Pb_{0.33}V₂O₅; (B) TEM image of Cys-CdS(lg)/β-Pb_{0.33}V₂O₅ with the separation between the lattice planes indexed to wurtzite CdS; (C) SEM image of 3× SILAR CdS/β-Pb_{0.33}V₂O₅; (D) SEM image of Cys-CdS(lg)/β-Pb_{0.33}V₂O₅; (E) SAED of Cys-CdS(lg)/β-Pb_{0.33}V₂O₅ indexed to the wurtzite phase of CdS (JCPDS #41-1049) and β-Pb_{0.33}V₂O₅ (JCPDS #41-1426); (F) Raman spectra of NWs, dispersed Cys-CdS QDs, and SILAR-derived heterostructures acquired with 514.5 nm excitation from an Ar-ion laser.

Figure 2. Legend: **1.** β -Pb_{0.33}V₂O₅; **2.** 1× SILAR CdS/ β -Pb_{0.33}V₂O₅; **3.** 3× SILAR CdS/ β -Pb_{0.33}V₂O₅; **4.** 3× SILAR CdSe/ β -Pb_{0.33}V₂O₅; **5.** Cys-CdS(lg)/ β -Pb_{0.33}V₂O₅; **6.** Cys-CdS(sm)/ β -Pb_{0.33}V₂O₅; **7.** Cys-CdSe(lg)/ β -Pb_{0.33}V₂O₅; **8.** Cys-CdSe(sm)/ β -Pb_{0.33}V₂O₅. (A) Valence band spectra of QD/ β -Pb_{0.33}V₂O₅ SILAR heterostructures; (B) Valence band spectra of QD/ β -Pb_{0.33}V₂O₅ LAA heterostructures; (C) Difference spectra of SILAR-derived heterostructures; (D) Difference spectra of LAA-derived heterostructures; (E) Difference spectrum of LAA Cys-CdS(sm)/ β -Pb_{0.33}V₂O₅ with linear fits and extrapolated valence band edge value; (F) Difference spectrum, of LAA Cys-CdSe(sm)/ β -Pb_{0.33}V₂O₅ with linear fits and extrapolated valence band edge value. Dashed vertical lines in C and D denote the energy dispersion of the midgap states of NWs.

Figure 3. Schematic indicating the relative positioning of the valence band and conduction band edges of Cys-CdSe *versus* Cys-CdS as deduced from XPS measurements, as well as the timescales for electron and hole transfer from photoexcited CdS QDs into the midgap states and CB of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$, respectively, as obtained from TA spectroscopy experiments.

Figure 4. TA spectra of unfunctionalized $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ NWs (black), 3 $\times$ SILAR CdS/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures (blue), and Cys-CdS $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures (red) acquired at $\lambda_{\text{pump}} = 360$ nm. The spectra are averaged for delay times in the interval 1000–2500 ps.

Figure 5. TA spectra of (A) 3x SILAR CdS/ β -Pb_{0.33}V₂O₅ and (B) Cys-CdS β -Pb_{0.33}V₂O₅ and 2D TA color maps of (C) 3x SILAR CdS/ β -Pb_{0.33}V₂O₅ and (D) Cys-CdS β -Pb_{0.33}V₂O₅, indicating ΔA in the 0–50 ps range for probe wavelengths in the range of 425–850 nm with $\lambda_{\text{pump}} = 360$ nm.

Figure 6. TA decay traces and multiple exponential fits measured for LAA-derived QD/NW heterostructures at different probe wavelengths of 455 (biexponential), 600 (monoexponential), and 740 nm (monoexponential) with $\lambda_{\text{pump}} = 360$ nm.

Table 1 Experimentally determined valence band onsets for CdSe/ β -Pb_{0.33}V₂O₅ heterostructures

Sample	Valence Band Edge (eV)
LAA Cys-CdS/ β -Pb _{0.33} V ₂ O ₅	1.33±0.02
SILAR CdS/ β -Pb _{0.33} V ₂ O ₅	1.32±0.02
LAA Cys-CdSe/ β -Pb _{0.33} V ₂ O ₅	0.92±0.01
SILAR CdSe/ β -Pb _{0.33} V ₂ O ₅	0.94±0.02

Supporting Information. EDS spectra and XPS difference spectra of LAA- and SILAR-derived CdS QD/ β -Pb_{0.33}V₂O₅ NW heterostructures, TA spectra and corresponding 3D TA color map of bare β -Pb_{0.33}V₂O₅ NWs, TA spectrum and decay kinetic fit of colloidal CdS QDs, and kinetic fitting parameter and average lifetime for colloidal CdS QD and LAA-derived CdS QD/ β -Pb_{0.33}V₂O₅ NW heterostructure.

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Notes

The authors declares no competing financial interest

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ABBREVIATIONS

NWs, nanowires; QDs, quantum dots; Cys, cysteine; CB, conduction band; VB, valence band; SILAR, successive ion layer adsorption reaction; LAA, linker-assisted approach, lg, large; sm, small; TA, transient absorption;

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