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Directional Charge Transfer Mediated by Mid-Gap States: A Transient Absorption Spectroscopy Study of CdSe Quantum Dot/ β -Pb_{0.33}V₂O₅ Heterostructures

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Abstract

For solar energy conversion, not only must a semiconductor absorb incident solar radiation efficiently but also its photoexcited electron–hole pairs must further be separated and transported across interfaces. Charge transfer across interfaces requires consideration of both thermodynamic driving forces as well as the competing kinetics of multiple possible transfer, cooling, and recombination pathways. In this work, we demonstrate a novel strategy for extracting holes from photoexcited CdSe quantum dots (QDs) based on interfacing with β -Pb_{0.33}V₂O₅ nanowires that have strategically positioned mid-gap states derived from the intercalating Pb²⁺-ions. Unlike mid-gap states derived from defects or dopants, the states utilized here are derived from the intrinsic crystal structure and are thus homogeneously distributed across the material. CdSe/ β -Pb_{0.33}V₂O₅ heterostructures were assembled using two distinct methods: successive ionic layer adsorption and reaction (SILAR) and linker-assisted assembly (LAA). Transient absorption spectroscopy measurements indicate that electrons and holes can be transferred from the photoexcited CdSe QDs to the conduction and mid-gap states, respectively, of β -Pb_{0.33}V₂O₅ nanowires for both types of heterostructures. Holes were transferred on time scales less than 1 ps, whereas electrons were transferred more slowly on time scales of approximately 2 ps. In contrast, for analogous heterostructures consisting of CdSe QDs interfaced with V₂O₅ nanowires (wherein mid-gap states are absent), only electron transfer was observed. Interestingly, electron transfer was readily achieved for CdSe QDs interfaced with V₂O₅ nanowires by the SILAR method; however, for interfaces incorporating molecular linkers, electron transfer was observed only upon excitation at energies substantially greater than the band-gap absorption threshold of CdSe. Transient absorbance decay traces reveal longer exciton lifetimes (1–3 μ s) for CdSe/ β -Pb_{0.33}V₂O₅ heterostructures relative to bare β -Pb_{0.33}V₂O₅ nanowires (0.2–0.6 μ s); the difference is attributed to surface passivation of intrinsic surface defects in β -Pb_{0.33}V₂O₅ upon interfacing with CdSe (290 words).

Introduction

Harvesting sunlight and storing the energy of the absorbed photons in chemical bonds (in the form of

solar fuels) or by doing electrical work (as in photovoltaic devices) is critical to reducing our reliance on fossil fuels.¹⁻⁵ For effective solar energy conversion, a semiconductor must not only absorb a large portion of the incident solar radiation but the photoexcited electron–hole pairs must further be separated and transported across interfaces.^{2-3, 6-7} The kinetics of charge separation and transport are a critical consideration to mitigate the recombination or cooling of photogenerated charges.⁸⁻¹⁰ Achieving efficient charge transfer and separation across semiconductor interfaces is thus predicated on careful alignment of thermodynamic driving forces (which in turn depends on relative band alignments) and on the competing kinetics of directional charge transfer, cooling, and recombination pathways. The appropriate alignment of bands is a first and necessary criterion for achieving charge transfer.^{3, 7, 11} In many cases, a visible-light absorbing semiconductor is paired with a wide band gap semiconductor, and charge carriers

are injected into the latter upon photoexcitation of the former.^{1, 3, 5, 12-13} Simple binary semiconductors that have traditionally been studied for photovoltaics have clearly defined valence and conduction band (CB) edges separated by a bandgap and are difficult to reconfigure thereby establishing some immutable limitations on tunability of the thermodynamic driving force. A promising alternative is to strategically position electronic states in a semiconductor through the introduction of dopants or defect states.¹⁴⁻¹⁵ Mid-gap states are often defined by defects or surface traps.^{10, 16-18} In contrast, we have recently designed $\text{M}_x\text{V}_2\text{O}_5$ bronzes wherein the mid-gap states derive from stereoactive lone-pairs of post-transition-metal cations and are thus homogeneously distributed across the crystal.¹⁹ Here, we demonstrate that an intercalation-induced mid-gap state in $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ can mediate directional charge transfer of both electrons and holes from photoexcited CdSe quantum dots (QDs) to the CB and mid-gap-states of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$, respectively. The charge transfer dynamics are contrasted to those of CdSe QDs interfaced with V_2O_5 .

Several promising alternatives to traditional schemes of photoexcitation and charge separation within a semiconductor have been explored to increase the amount of solar energy absorbed and the efficiency with which it is converted to other energy forms.² Tandem solar cells, multi-junction cells, multiple

exciton generation, intermediate band solar cells, and hot-carrier solar cells are examples of different methods that demonstrate promise.^{1-4, 6, 20-23} Metal oxides have a long history of being used for a variety of applications due to their semiconducting nature. However, the very positive valence band (VB) edge potentials of a majority of metal oxide semiconductors limit their practical use in applications for harvesting solar energy. In previous work, we have found that ternary vanadium oxide bronzes (with the formula of $\beta\text{-M}_x\text{V}_2\text{O}_5$, where M is a post-transition-metal with a stereoactive lone pair and x is its stoichiometry) were found to possess mid-gap states slightly positive of the oxidation potential of water.¹⁵ This mid-gap state is not present in V_2O_5 , the parent oxide of the vanadium oxide bronze.²⁴ Initial density functional theory calculations predicting the presence of a mid-gap state have recently been experimentally verified using high-energy X-ray photoemission spectroscopy.^{14-15, 18} The energy positioning of the mid-gap state can be varied by choice of the intercalating cation, thereby providing a facile means for tuning the alignment of these levels with respect to other materials.¹⁸⁻¹⁹ The approximate relative energy positioning of this mid-gap state, along with the VB edge potential (E_V) and CB edge potential (E_C) of both $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ and V_2O_5 as well as CdSe are shown in Figure 1. This scheme suggests that upon photoexcitation of the CdSe QD (resulting in creation of a hole in the VB), hole transfer from the VB of the CdSe QD to the mid-gap state of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ is thermodynamically favorable, providing a driving force to extract the hole and ultimately to propagate it along the nanowire for solar fuel production. Indeed, in previous work, we have demonstrated the successful synthesis of CdSe/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures and experimentally verified substantial overlap of the CdSe VB edges with the mid-gap states of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ using high-energy X-ray photoemission spectroscopy.¹⁴ Such a heterostructure represents a readily reconfigurable platform wherein the VB edges of the QD can be modulated by compositional variation and size, whereas the energy positioning of the mid-gap state can be tuned by choice of the intercalating cation, thereby providing access to several routes for tuning the thermodynamic driving forces for charge transfer.

However, thermodynamic alignment of energy levels is but one part of the equation. As noted above, directional charge transfer needs to compete with back-electron transfer, charge recombination, and cooling pathways. Several studies have shown that the nature of the interface strongly affects the kinetics of charge transfer.²⁵⁻³⁰ Here, we seek to explore the kinetics of charge transfer in CdSe/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures using transient absorption spectroscopy as a function of the nature of the interface. Charge transfer dynamics are contrasted for heterostructures prepared *via* two distinct routes: linker-assisted assembly (LAA) and successive ionic layer adsorption and reaction (SILAR). LAA allows for more precise control over QD size and the separation between the two components, whereas SILAR facilitates direct contact between the QDs and the nanowires but does not allow for precise size control. The charge transfer kinetics for CdSe/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures are contrasted to those of CdSe/ V_2O_5 heterostructures to elucidate the role of the mid-gap states in facilitating charge transfer.

Experimental Section

Synthesis of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ and V_2O_5 Nanowires

$\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ nanowires were prepared using a one-step hydrothermal reaction as reported previously.¹⁵ Briefly, 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 copious amounts of water, and allowed to dry in air. The resulting nanowires were ca. 170 nm in diameter and spanned microns in length.¹⁵ V₂O₅ nanowires were prepared by the oxidation of hydrothermally grown V₃O₇·xH₂O nanowires as reported in previous work.³¹ The V₂O₅ nanowires were ca. 150-250 nm in diameter and spanned hundreds of microns in length.³¹

Synthesis of CdSe QDs

Cysteine-capped CdSe (Cys-CdSe) QDs were synthesized as reported previously.³² Briefly, the selenium precursor was prepared by refluxing an aqueous solution of Se powder and Na₂SO₃ overnight, and the cadmium precursor was an aqueous solution of 3CdSO₄·8H₂O 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 QDs, hereafter referred to as Cys-CdSe(sm) QDs, were purified by solvent–non-solvent (H₂O:MeOH, 3:1) washing to remove excess reagents. Larger Cys-CdSe (Cys-CdSe(lg)) QDs were synthesized and purified by the same procedure except that the cadmium precursor was heated to, and maintained at, 80°C for the duration of the reaction (2 h).

Functionalization of β -Pb_{0.33}V₂O₅ and V₂O₅ Nanowires with CdSe QDs by SILAR and LAA

CdSe was deposited onto β -Pb_{0.33}V₂O₅ nanowires *via* SILAR and LAA following our reported methods.¹⁴ In a single SILAR cycle, CdSe QDs were grown directly onto β -Pb_{0.33}V₂O₅ nanowires by sequentially mixing the nanowires with a 50 mM solution of Cd(NO₃)₂ in ethanol followed by a 50 mM solution of Na₂Se in ethanol. The nanowires were washed with ethanol following each mixing step in order to remove excess ions. This SILAR process was performed once (1x SILAR samples), three times (3x SILAR samples), or five times (5x SILAR samples) to vary the density of CdSe QDs on the surface of the nanowires. An analogous procedure was utilized to coat V₂O₅ nanowires with CdSe.

LAA was employed to prepare Cys-CdSe(sm)/ β -Pb_{0.33}V₂O₅ and Cys-CdSe(lg)/ β -Pb_{0.33}V₂O₅ heterostructures (and corresponding V₂O₅ heterostructures) in which cysteine acted as a bifunctional linker molecule. As reported in our previous work, cysteine bound preferentially to CdSe *via* the thiolate functional group and to β -Pb_{0.33}V₂O₅ through an electrostatic interaction between a positively charged, protonated amine group on cysteine and the negatively charged, hydroxylated surface of β -Pb_{0.33}V₂O₅ (or V₂O₅).¹⁴ In LAA, an aqueous dispersion of β -Pb_{0.33}V₂O₅ (or V₂O₅) nanowires 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 nanowires were recovered by centrifugation, rinsed with DI water to remove excess QDs, and subsequently dried at room temperature before characterization.

Preparation of Thin Films and Diffuse Reflectance Measurements

The nanowires and QD/nanowire heterostructures were immobilized onto glass microscope slides for diffuse reflectance and transient absorption measurements. Dispersions (20 mL) of β -Pb_{0.33}V₂O₅, V₂O₅, CdSe/ β -Pb_{0.33}V₂O₅, or CdSe/V₂O₅ in ethanol (1 mg/mL) were spray coated onto the substrate, forming

semi-transparent thin films. UV-Vis diffuse reflectance spectra of sample films were obtained with an Agilent 8453 diode array spectrophotometer equipped with a Labsphere RSA-HP-53 (Hewlett-Packard) reflectance accessory.

Spectroelectrochemistry Experiments

Spectroelectrochemical measurements were performed on $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ and V_2O_5 films to monitor changes in the absorption spectra upon oxidation or reduction. Films were prepared by spray coating nanowires onto fluorine-doped tin oxide (FTO)-coated glass slides. A one-compartment, three-electrode electrochemical cell configuration was used consisting of a thin film working electrode, a Pt mesh auxiliary electrode, and a saturated calomel (SCE) reference electrode. Electrochemical measurements were performed using a Princeton Applied Research (PAR) VersaSTAT 3 potentiostat. A quartz cuvette (1 cm path length) with a 24/40 ground glass joint connection was used as the cell, and the electrolyte consisted of 0.1 M tetrabutylammonium perchlorate (Alfa Aesar, electrochemical grade) in anhydrous acetonitrile (EMD). In order to avoid contamination with water the electrolyte solution was prepared in a glovebox and then brought out immediately before beginning the experiments. The cell was further purged with nitrogen to remove dissolved oxygen. The entire cell assembly was housed on the sample stage of spectrophotometer so that absorption spectra could be obtained while performing electrochemical measurements. For $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ films, either an oxidizing potential of +1.75 V (vs. SCE) or a reducing potential of -1.0 V (vs. SCE) was applied. In contrast, for V_2O_5 films, either an oxidizing potential of +1.5 V (vs. SCE) or a reducing potential of -0.25 V (vs. SCE) was applied. Absorption spectra of the oxidized or reduced films were obtained after applying a potential for 5 min. Separate films were used for the oxidation and reduction reactions in case any redox processes were irreversible. Ground state differential absorption spectra were computed by subtracting the absorption spectrum of the neutral sample from the absorption spectrum of the oxidized or reduced sample.

Transient Absorption Experiments

Transient absorption experiments were performed at the Advanced Optical Spectroscopy and Microscopy Facility in the Center for Functional Nanomaterials at Brookhaven National Laboratory (BNL). Ultra-fast transient absorption measurements were conducted using a commercial Ti:Sapphire amplified laser system (SpectraPhysics Spitfire Pro, 1 kHz repetition rate). Excitation light was generated using a commercial optical parametric amplifier (LightConversion). Supercontinuum probe light was generated by focusing the 800 nm fundamental into a sapphire disc. The probe light was split into signal and reference beams, both of which were detected on a shot-by-shot basis with fiber-coupled silicon (visible) or InGaAs (infrared) diode arrays. The pump-probe delay was controlled by means of a mechanical delay stage (Newport). Nanosecond transient absorption measurements were conducted using the same ultrafast pump pulses along with an electronically delayed supercontinuum light source with a sub-ns pulse duration (EOS, Ultrafast Systems). Transient absorption spectra were collected at pump wavelengths (λ_{pump}) of 360 nm, 425 nm, 490 nm, and 600 nm. Transient absorbance (TA) spectra presented in this manuscript were extracted from the data matrix by averaging ΔA values between 1.5 and 10 ns at each λ_{pump} . TA decay traces presented in this manuscript were extracted from the data matrix by averaging ΔA values over a given range of λ_{probe} at each delay time.

Results and Discussion

Ground-state Absorption Spectra of Unfunctionalized $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ and V_2O_5 Nanowires

Diffuse reflectance spectra of V_2O_5 and $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ films on glass slides are shown in Figure 2A. V_2O_5 displays an absorption onset at 580 nm with a steep rise in absorbance corresponding to bandgap excitation. $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ displays an absorption onset at 615 nm with a gradual increase in absorbance to approximately 540 nm, followed by a steep increase in absorbance, similar to V_2O_5 . The red-shifted absorption onset for $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ is assigned to the lower energy transition associated with excitation of an electron from the mid-gap state to CB states. A gradual increase in absorbance can be attributed to a convolution of mid-gap excitation and bandgap excitation. A broad absorption feature for the mid-gap excitation is not surprising owing to a broad energy range of the mid-gap states as opposed to a single discrete energy level. Based on previous high-energy X-ray photoemission studies and density functional theory calculations, the mid-gap state represents a filled anti-bonding state derived from the hybridization of Pb 6s and O 2p bands.¹⁸

Tauc plots are commonly employed to determine the optical bandgap of semiconductors by extrapolating the linear region to the abscissa.³³⁻³⁴ Tauc plots of $(\text{energy} \times \log(1/R))^2$ vs. energy, where R is reflectance, for V_2O_5 and $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ (insert, Figure 2A) accentuate the mid-gap excitation features. Both plots contain a linear region, associated with bandgap excitation, and a pronounced deviation from linearity at lower energies due to intrinsic localized absorptions derived from mid-gap states. An optical bandgap of ca. 2.4 eV was determined for both V_2O_5 and $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$. Closer examination of the non-linear region provides clear evidence of transitions involving the excitation of electrons from surface-localized and/or intercalative mid-gap states to the CB. The energy difference between the absorption onset and bandgap excitation can be interpreted as the difference between the highest-energy localized mid-gap states and the VB edge. Measured differences of 0.12 and 0.37 eV were obtained for V_2O_5 and $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$, respectively. Assuming no significant change in the distribution of localized surface states for $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ relative to V_2O_5 , the larger shift of the absorption onset relative to the band-gap excitation for $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ can be attributed to the presence of intercalative mid-gap states at even higher energies above the VB edge than surface-localized states.

Transient Absorption Spectra and Dynamics of Unfunctionalized $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ and V_2O_5 Nanowires

Transient absorption spectra were acquired to examine excited-state spectral features and exciton dynamics of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ and V_2O_5 nanowires. Films of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ and V_2O_5 were excited at 360 nm and probed from 425 nm to 900 nm. The excitation wavelength corresponds to an energy greater than the bandgap of both materials. Three-dimensional TA “color maps” of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ and V_2O_5 (Fig. 2B and 2C) reveal clear differences between the two samples, owing to the presence of mid-gap states in $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$. TA spectra (ΔA vs. wavelength) were extracted from the data matrix by averaging ΔA values between 1.5 ns and 10 ns at all probe wavelengths. The TA spectrum of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ (Fig. 3A) is characterized by two excited state absorption bands: a more intense band centered at ca. 510 nm and a less-intense and broad shoulder stretching from ca. 650 nm into the near IR, with a center at ca. 750 nm. The TA spectrum of V_2O_5 differs markedly, and is instead characterized by an intense bleach centered at ca. 430 nm and an absorption band centered at ca. 535 nm.

Figure 3. (A) TA spectrum of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ (a, green), TA spectrum of V_2O_5 (b, orange), and fit of spectrum (a) to a linear combination of oxidized and reduced $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ (c, black) as derived from spectroelectrochemical measurements. (B, C) TA decay traces and fits for $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ at $\lambda_{\text{probe}} = 510$ nm (a) and 750 nm (b) and for V_2O_5 at $\lambda_{\text{probe}} = 430$ nm (c) and 535 nm (d). For all data, $\lambda_{\text{pump}} = 360$ nm.

Spectroelectrochemical measurements were acquired to assist with the assignment of TA spectra. Ground-state absorption spectra of V_2O_5 and $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ films on FTO electrodes were acquired under the application of either an oxidizing or reducing potential. Absorbance difference spectra were generated by subtracting the absorbance spectrum of the neutral species from that of the oxidized or reduced species (Fig. S1 in Supporting Information). Oxidation of both V_2O_5 and $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ yielded a broad induced absorption band extending from <375 nm to ca. 675 nm. The oxidation of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ corresponds to the removal of electrons from filled mid-gap states that lie above the VB^{15, 18}; thus, we assign the induced absorption to the excitation of VB electrons into empty mid-gap states. For V_2O_5 , which has no intercalative mid-gap states, oxidation corresponds primarily to the removal of electrons from VB states. Therefore, the induced absorbance arises from the excitation of deep-VB electrons to the VB edge. Notably, the VB of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ is characterized by a pronounced Pb 6s—O2p bonding state that does not exist for V_2O_5 .¹⁸ Reduction of both V_2O_5 and $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ yielded a bleach of the band-gap absorption (Fig. S1), consistent with the Burstein-Moss effect.³⁵⁻³⁷ Reduction involves the filling of CB states,

effectively increasing the optical bandgap and blue-shifting the band-gap absorption onset. Reduced $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ also exhibited an induced absorption band extending from ca. 620 nm into the near IR. We assign this absorption to the excitation of electrons in the CB of reduced $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ to higher-energy states, consistent with established spectral assignments for reduced metal oxides.³⁶⁻³⁹

The spectroelectrochemical data were used to assign features in the TA spectra of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ and V_2O_5 . We assign the 510 nm absorption band in the TA spectrum of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$, which exhibits similar absorption maximum and spectral profile as the induced absorption band of oxidized $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$, to the excitation of an electron from the VB to empty mid-gap states. We assign the broad 750 nm absorption band, which is similar to the induced absorption band of reduced $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$, to the excitation of free CB electrons. Importantly, the TA spectrum of photoexcited $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ is well-modeled as a linear combination of the absorbance difference spectra associated with electrochemically reduced and oxidized $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ (Fig. 3A), supporting our interpretation of transient absorption bands as arising from the introduction of electrons into the CB and holes into the mid-gap states. For V_2O_5 , the bleach at 430 nm is assigned to a bleach of the ground state absorbance, as exhibited by reduced V_2O_5 . The absorption band at 535 nm, which is similar to the induced absorption band of oxidized V_2O_5 , is assigned to the excitation of electrons from deep within the VB to the VB edge.

TA decay traces for $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ and V_2O_5 were extracted from transient absorption data matrices by averaging ΔA values at a range of probe wavelengths for each delay time. Representative decay traces are shown in Figure 3B and 3C. TA decay traces were fit to multiexponential decay kinetics. The smallest number of individual decay lifetimes, τ_i , which resulted in the minimum χ^2 were used for each fit. All TA decay traces were modeled to biexponential decay kinetics (Eq. 1 with $i = 2$) except for the decay of the 510 nm absorption band of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$, for which triexponential decay kinetics (Eq. 1 with $i = 3$) yielded a substantially improved fit (on the basis of χ^2). Fitting parameters for all TA decay traces are listed in Tables S1-S3 (Supporting Information). V_2O_5 has previously exhibited multiexponential transient absorption decay kinetics due to the presence of distributions of electron and hole trap states that give rise to multiple trap-state recombination mechanisms.⁴⁰

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

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

TA decay traces reveal differences in kinetics for the various processes occurring in both samples. The decay traces (Fig. 3B and C) and the “color maps” (Fig. 2B and C) reveal clearly that excitons are longer-lived in $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ than in V_2O_5 . Long-lived excitons are advantageous for excited-state charge transfer because charge transfer can compete more effectively with electron-hole recombination. For ease of comparison and discussion of decay kinetics, amplitude-weighted average lifetimes ($\langle \tau \rangle$) were computed using Equation 2. For $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$, the 510 nm and 750 nm TA bands had $\langle \tau \rangle$ of $(2.3 \pm 0.1) \times 10^{-7}$ s and $(5.9 \pm 0.7) \times 10^{-7}$ s, respectively. For V_2O_5 , the 430 nm bleach and 535 nm TA band had average lifetimes of $(2.9 \pm 0.5) \times 10^{-7}$ s and $(7 \pm 2) \times 10^{-8}$ s, respectively. A first observation is that the transient absorption band of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ centered at 750 nm, assigned to excitation of electrons from the mid-gap states to states above the CB edge, is longer-lived than the bleach observed for V_2O_5 , suggesting

that the introduction of the mid-gap states (and the corresponding filled Pb 6s—O2p states in the VB) helps to increase the lifetime of the excited electron. A second key observation is that the absorption bands associated with the hole (510 nm band in $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ and 535 nm band in V_2O_5) decay more rapidly than the absorption bands associated with the electron (750 nm band in $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ and 430 nm bleach in V_2O_5). Finally, the hole is much longer lived in $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ than in V_2O_5 . This pronounced difference may arise from different spatial distributions of holes in the two compounds. The photogenerated holes in $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ reside in mid-gap states, which derive primarily from a Pb 6s—O 2p interaction and thus are localized on the intercalating Pb^{2+} -ions¹⁵; in contrast, the photogenerated hole in V_2O_5 is situated within the O 2p-derived VB on the V_2O_5 framework.⁴¹⁻⁴² For both structures, the electrons reside on V 3d states in the CB (the $3d_{xy}$ states are the lowest lying CB states).⁴¹⁻⁴² In other words, the electron—hole wave function overlap is expected to be greater for V_2O_5 where both charge carriers are localized on the V_2O_5 framework, whereas in $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$, the holes are located on the intercalants and the electrons reside on the V_2O_5 framework. This spatial separation is likely responsible for the longer exciton lifetimes observed for the latter.

Characterization of $\text{CdSe}/\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ and $\text{CdSe}/\text{V}_2\text{O}_5$ Heterostructures

Extensive structural characterization of SILAR-derived and LAA-derived (with Cys- $\text{CdSe}(\text{sm})$) $\text{CdSe}/\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures has been reported previously.¹⁴ Cys- $\text{CdSe}(\text{sm})$ QDs, with a narrow first excitonic absorption band centered at 423 nm, are not an optimal choice as solar light harvesters. In this work, we have prepared Cys- $\text{CdSe}(\text{lg})/\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ and Cys- $\text{CdSe}(\text{lg})/\text{V}_2\text{O}_5$ heterostructures using larger Cys- CdSe QDs, which offer greater overlap with the solar spectrum. An absorption spectrum of aqueous dispersed Cys- $\text{CdSe}(\text{lg})$ QDs (Fig. S2, Supporting Information) reveals an absorption onset at 580 nm with a first-excitonic maximum at 495 nm. Energy-dispersive X-ray spectra (EDS) of Cys- $\text{CdSe}(\text{lg})/\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ and Cys- $\text{CdSe}(\text{lg})/\text{V}_2\text{O}_5$ heterostructures (Fig. S3, Supporting Information) confirm the presence of Cd and Se on the nanowires. Average relative amounts of Cd, Se, Pb, and V have been calculated from five spectra, suggesting apparent molecular formulas of $\text{Cd}_{(0.4\pm0.1)}\text{Se}_{(0.3\pm0.1)}\text{Pb}_{(0.2\pm0.1)}\text{V}_2\text{O}_5$ and $\text{Cd}_{(0.3\pm)}\text{Se}_{(0.20.1\pm0.1)}\text{V}_2\text{O}_5$, respectively for the heterostructures incorporating Cys- $\text{CdSe}(\text{lg})$ QDs.

Transient Absorption Spectra and Dynamics of $\text{CdSe}/\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ and $\text{CdSe}/\text{V}_2\text{O}_5$ Heterostructures

$\text{CdSe}/\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures, synthesized using both LAA and SILAR methods, were characterized with transient absorption spectroscopy. Thin films of $\text{CdSe}/\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures were excited at 360 nm and 425 nm and probed from 425 nm to 900 nm. These pump wavelengths correspond to above-bandgap excitation for $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ and V_2O_5 and to excitation substantially above the bandgap for CdSe QDs (Fig. S2 in Supporting Information). TA spectra were compiled by averaging ΔA from 1.5 ns to 10 ns. Figure 4A and 4B show the results for the heterostructures excited at 360 nm pump wavelength. Interestingly, TA spectra of $\text{CdSe}/\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures are nearly identical to those of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ nanowires and consist of an intense transient absorption band centered at 500-550 nm and a less-intense and lower-energy absorption band extending into the near-IR. These spectra are notable for the absence of a bleach of the first excitonic transition of CdSe QDs, which is the well-established spectral signature of CdSe QDs on time scales greater than 10^{-9} s,⁴³⁻⁴⁵ and was the dominant feature of our measured TA spectrum of dispersed aqueous Cys- $\text{CdSe}(\text{lg})$ QDs (Fig. S4 in Supporting

Information). Thus, excitation of either CdSe QDs or $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ nanowires within the heterostructures yielded a TA spectrum associated with electron-hole pairs localized in the $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ nanowires. The most notable difference in the TA spectra of CdSe/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures relative to the bare $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ nanowires is that the spectra of heterostructures exhibit a substantial amplification

of the absorption bands. This enhanced amplitude (increased ΔA) suggests an increase in exciton concentration in the $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ nanowires arising from both hole and electron injection (exciton diffusion) from the CdSe QDs. In other words, apart from the native exciton population generated by direct excitation of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$, exciton diffusion from photoexcited CdSe QDs, which is thermodynamically favorable (Fig. 1), further increases the exciton population of underlying nanowires. This behavior is agnostic of the nature of the interfaces and is observed for both the LAA and SILAR heterostructures.

The higher-energy and more intense absorption band in the TA spectrum of 3x SILAR CdSe/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures (spectrum c in Fig. 4) is red-shifted relative to those of 1x SILAR CdSe/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures (spectrum b in Fig. 4) and $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ nanowires (spectrum a in Fig. 4). This apparent red-shift may have arisen from the increased contribution of the ground-state bleach of CdSe, since the 3x SILAR sample has a significantly higher ratio of CdSe QDs to $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ nanowires. If an appreciable fraction of QDs was not in direct contact with the nanowire surface, as observed previously¹⁴, then such QDs would probably not transfer charge carriers efficiently to the nanowires, resulting in some contribution of the excitonic bleach of CdSe to the overall measured TA spectrum.

TA spectra of CdSe/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures and bare $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ nanowires acquired with 425 nm excitation were also nearly identical but with higher ΔA values for the QD-coated samples. The amplified absorption bands associated with the nanowire-localized excitons can again be attributed to exciton diffusion from CdSe QDs to $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ nanowires.

TA spectra of CdSe/V₂O₅ heterostructures were collected as a set of control experiments. Hole transfer from CdSe to V₂O₅ is thermodynamically disfavored, whereas electron injection from photoexcited CdSe to V₂O₅ is feasible based on the relative energy positioning of the CB edges of CdSe and V₂O₅ (Fig. 1). Films of V₂O₅ and CdSe/V₂O₅ heterostructures were excited at 360 nm and 600 nm and probed between

425 nm and 900 nm, and TA spectra were compiled by averaging ΔA from 1.5 to 10 ns. The 5x SILAR CdSe/V₂O₅ heterostructures were chosen because the coverage of QDs on V₂O₅ nanowires was similar to the coverage of QDs on β -Pb_{0.33}V₂O₅ nanowires in 1x SILAR CdSe/ β -Pb_{0.33}V₂O₅ heterostructures, as verified by energy dispersive X-ray analysis.¹⁴ TA spectra of CdSe/V₂O₅ heterostructures differ significantly from the TA spectrum of V₂O₅ and furthermore exhibit substantial differences depending on the nature of the interface (Fig. 5). First, in TA spectra acquired with excitation at 360 nm (Fig. 5A, B), the CdSe/V₂O₅ heterostructures synthesized by both SILAR and LAA exhibit a transient absorption band centered at 525-545 nm, which is shifted and broadened significantly to long wavelengths relative to the 535-nm absorption band of V₂O₅. The band is less intense for CdSe/V₂O₅ heterostructures prepared by LAA than for those prepared by SILAR. Second, the transient absorption band of CdSe/V₂O₅ heterostructures is much more intense than that of V₂O₅ nanowires beyond 575 nm and extends into the near-IR. TA spectra of V₂O₅ nanowires and of Cys-CdSe(lg)/V₂O₅ heterostructures prepared by LAA were featureless when acquired with excitation at 600 nm (Fig. 5C, D), because 600 nm light is insufficiently energetic to excite the band-gap transition of V₂O₅ nanowires or Cys-CdSe(lg) QDs (Fig. S2). In contrast, the TA spectrum of 5x SILAR CdSe/V₂O₅ heterostructures, acquired with excitation at 600 nm, exhibits a long-wavelength absorption band similar to that observed upon excitation at 360 nm. This long-wavelength absorption band is noteworthy and facilitates spectral assignments. We attribute this feature, which extends to ca. 750 nm, to an absorption associated with trapped holes in CdSe QDs, consistent with reported assignments of TA spectra of oxidized CdSe QDs.⁴⁶ The presence of a trapped hole suggests that photoexcitation of the QDs is followed by electron transfer to V₂O₅, which is thermodynamically favorable (Fig. 1). Transfer of the photogenerated hole from CdSe to the VB of V₂O₅ is thermodynamically uphill (Fig. 1); thus, the hole apparently remains in the QD where it is confined in surface-localized trap states. The long-wavelength absorption band in the TA spectra of CdSe/V₂O₅ heterostructures acquired with 360 nm excitation (Fig.

5A, B) can thus also be similarly assigned. The shift of the TA band centered at 535 nm for V_2O_5 can now be assigned to an increased proportion of reduced V_2O_5 in the heterostructures as a result of electron transfer from the photoexcited QDs (Fig. S1). In addition, the superposition of a bleach from photoexcited QDs at probe wavelengths of 475-540 nm (Fig. S4) probably also contributed to the observed shift of the maximum of the net transient absorption centered at 525-545 nm. Since the 600 nm pump pulse was insufficiently energetic to excite Cys-CdSe(lg) QDs, it is not surprising that TA spectrum c in Figure 5D suggests no evidence for charge transfer. In contrast, the CdSe/ V_2O_5 heterostructures prepared by SILAR have a broader size distribution including larger nanocrystal sizes that likely allow for photoexcitation of a fraction of the QDs, enabling electron transfer to V_2O_5 and giving rise to the broad long-wavelength absorption associated with the hole in CdSe observed in Figure 5C. TA spectra acquired for these samples at pump wavelengths of 425 and 490 nm, both of which are more energetic than the band gap of CdSe QDs, are shown in Figure S5 in Supporting Information. The TA spectra of CdSe/ V_2O_5 heterostructures prepared by LAA and SILAR are markedly different. TA spectra for the SILAR-derived samples exhibit characteristic spectral signatures of electron transfer, whereas TA spectra of the LAA-derived samples are unmodified from that of V_2O_5 revealing the absence of electron transfer. These findings suggest that following excitation at 360 nm, hot electrons can be injected across the interfaces defined by the molecular linker but electrons excited to the CB edge are not energetic enough to diffuse across the interface. In contrast, electron transfer is observed following excitation at all pump wavelengths for the SILAR-derived interface.

TA decay traces of CdSe/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ samples pumped at 360 nm are shown in Figure 6. TA decay traces of the 510 nm absorption band were well-modeled with triexponential kinetics, and decay traces of the 750 nm band were well-modeled with biexponential kinetics. Tables S1 and S2 in the Supporting information list fitting parameters and calculated average lifetimes. Upon functionalization of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ with CdSe QDs *via* both SILAR and LAA deposition methods, values of $\langle\tau\rangle$ for both the 510 nm and 750 nm transient absorption

bands increased relative to uncoated $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$. For the 510 nm band, $\langle\tau\rangle$ increased by approximately 3-fold for SILAR-deposited CdSe/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$. LAA-derived samples exhibited greater increases in $\langle\tau\rangle$ of approximately 3.9- and 6.5-fold for Cys-CdSe(sm)/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ and Cys-CdSe(lg)/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures, respectively. The value of $\langle\tau\rangle$ for the 750 nm absorption band increased by

approximately 5-fold for CdSe/ β -Pb_{0.33}V₂O₅ prepared using both deposition methods. Observed increases in exciton lifetimes for CdSe/ β -Pb_{0.33}V₂O₅ are attributed to surface passivation of β -Pb_{0.33}V₂O₅ nanowires by the CdSe QDs and the elimination of surface trap states and trap state-mediated electron-hole recombination pathways.

TA decay traces of CdSe/V₂O₅ samples pumped at 360 nm are shown in Figure 7. All decay traces were well-modeled by biexponential kinetics; fitting parameters and average lifetimes are compiled in Table S3 in Supporting Information. Deposition of CdSe QDs onto V₂O₅ nanowires by both SILAR and LAA had minimal impact on the decay kinetics of the 440-nm bleach. Values of $\langle\tau\rangle$ for the bleach for CdSe/V₂O₅ heterostructures ranged from 70% to 150% of $\langle\tau\rangle$ for V₂O₅ nanowires. Deposition of CdSe had a somewhat greater impact on decay kinetics of the 535 nm absorption band. For SILAR-derived heterostructures, $\langle\tau\rangle$ for the absorption increased by approximately 3.3-fold relative to V₂O₅ nanowires. For LAA-derived CdSe/V₂O₅ heterostructures, $\langle\tau\rangle$ decreased by approximately 1.6-fold for Cys-CdSe(sm) and increased by approximately 2-fold for Cys-CdSe(lg). Similarly to the CdSe/ β -Pb_{0.33}V₂O₅ heterostructures, the increase of $\langle\tau\rangle$ upon SILAR deposition of CdSe or LAA of Cys-CdSe(lg) QDs may have arisen from passivation of surface trap states on V₂O₅ nanowires.

TA decay traces of the long-wavelength transient absorption band observed for both SILAR- and LAA-derived CdSe/V₂O₅ are shown in Figure 7C,D. As discussed earlier, the induced absorption observed exclusively for CdSe/V₂O₅ is assigned to trapped holes in oxidized CdSe QDs produced by the excited-state transfer of an electron from CdSe to V₂O₅.⁴⁶ Average lifetimes of $(1.0 \pm 0.8) \times 10^{-6}$ s, $(1.7 \pm 0.6) \times 10^{-7}$ s and $(2.7 \pm 0.7) \times 10^{-7}$ s were determined for this long-wavelength absorption band of 5x SILAR CdSe/V₂O₅, LAA-derived Cys-CdSe(sm)/V₂O₅, and LAA-derived Cys-CdSe(lg)/V₂O₅ heterostructures, respectively. This absorption band is longer-lived than the 535-nm absorption band of uncoated V₂O₅ $((7 \pm 2) \times 10^{-8}$ s) and the excitonic bleach of dispersed

Cys-CdSe(lg) QDs $((5.9 \pm 0.2) \times 10^{-8}$ s) (Fig. S4, Supporting Information), supporting our assignment of the

band to a charge-separated state. The lifetimes of the 535-nm absorption band of uncoated V_2O_5 and the bleach of dispersed Cys-CdSe(Ig) QDs are associated with a bound exciton. Charge-separated states are typically longer-lived than bound excitons as the spatial separation between electron and hole is greater resulting in diminished overlap of their respective wave functions.^{5, 12, 47}

Ultra-fast Dynamics

Ultra-fast transient absorption measurements were performed to examine exciton dynamics on a picosecond timescale and to directly observe charge-transfer processes. TA difference spectra for β - $Pb_{0.33}V_2O_5$, 3x SILAR CdSe/ β - $Pb_{0.33}V_2O_5$, and Cys-CdSe(Ig)/ β - $Pb_{0.33}V_2O_5$ were extracted at 1-ps intervals over the first 5 ps following excitation (Fig. 8). For β - $Pb_{0.33}V_2O_5$ nanowires, the transient absorption bands reached maximum amplitude within the instrument response time, as expected for TA signals derived from the direct photogeneration of an exciton in β - $Pb_{0.33}V_2O_5$. For 3x SILAR CdSe/ β - $Pb_{0.33}V_2O_5$ and Cys-CdSe(Ig)/ β - $Pb_{0.33}V_2O_5$, the shorter-wavelength band appears to be at full intensity within the temporal resolution of the measurement; however, a distinct progressive rise of ΔA amplitude in the longer-wavelength region of the absorption band is discernible. The growth of the absorption for 3x SILAR CdSe/ β - $Pb_{0.33}V_2O_5$ has been measured from approximately 525 to 650 nm, appearing as a broad growth of the entire longer-wavelength half of the absorption band. The rise in ΔA for Cys-CdSe(Ig)/ β - $Pb_{0.33}V_2O_5$ spanned a smaller wavelength range, from approximately 490 to 575 nm, with a local ΔA minimum at 535 nm in the TA spectra acquired at the shortest delay times of 1 and 5 ps.

The rise of ΔA across a specific spectral range, observed only upon interfacing with CdSe QDs, is logically attributed to contributions to the observed TA spectra from the decay of the bleach associated with the first excitonic ground-state absorption of the QDs. Considering that TA spectra of CdSe/ β - $Pb_{0.33}V_2O_5$ are

a combination of the signal from photoexcited β - $Pb_{0.33}V_2O_5$ and CdSe, the CdSe bleach can reasonably be expected to contribute to the total measured ΔA . Figure S4 (Supporting Information) depicts a TA spectrum and decay trace of Cys-CdSe(Ig) QDs dispersed in H_2O . A bleach of the ground-state absorption is observed, with an onset at 575 nm and a minimum at 516 nm and shoulder minimum at 445 nm, corresponding to the first and second excitonic bands, respectively.⁴³⁻⁴⁵ Indeed, the shape and position of the bleach are quite similar to the shape and position of the ΔA minimum observed in the TA spectrum of Cys-CdSe(Ig)/ β - $Pb_{0.33}V_2O_5$ (Fig. 8C) at short

delay times. As the CdSe bleach decays, its contribution to the total ΔA decreases and a net rise in ΔA is observed. It should be noted that a well-resolved bleach band was not observed in the TA spectrum of the SILAR-prepared sample due to a wide distribution of particle sizes inherent to the deposition method.²⁶ The broad rise in ΔA intensity observed is similar to what one would expect based on the ground-state absorbance of SILAR CdSe QDs on $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ as shown in Figure S2 of the supporting information.

Apart from the contribution from the CdSe bleach, the transient absorption band appears to be at maximal amplitude instantaneously for both CdSe/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ samples. As discussed earlier, this absorption band is associated with a hole located in the mid-gap states of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ nanowires and corresponds to excitation of an electron from deeper VB states. Therefore, we conclude that hole transfer from the VB of CdSe into the mid-gap states of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ must occur within the excitation pulse. If the hole transfer reaction were slower, one would expect the absorption band to grow as hole transfer occurred. In contrast, the time-resolvable decay of the first excitonic bleaches of CdSe(lg) and SILAR-derived CdSe QDs, suggests that the transfer of electrons to the CB of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ occurs more slowly than the transfer of holes to the mid-gap states. Ultra-fast TA decay traces (Fig. 8D) show the rise in ΔA associated with CdSe bleach decay. The rise in ΔA intensity can be fit to a single exponential function, and lifetimes of $(2.3 \pm 0.3) \times 10^{-12}$ s and $(1.8 \pm 0.1) \times 10^{-12}$ s are obtained for 3x SILAR CdSe/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ and Cys-CdSe(lg)/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$, respectively. These lifetimes can be attributed to the tail-end of electron transfer from the CB edges of photoexcited CdSe QDs into the CB edge of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$. Importantly, the bleach of free Cys-CdSe(lg) QDs, for which electron-hole recombination is the only deactivation pathway, decays with an average lifetime of $(5.9 \pm 0.2) \times 10^{-8}$ s. Thus, the vastly accelerated bleach decays for the CdSe/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ samples, which give rise to the time-resolvable growth of the net absorption, are entirely consistent with a mechanism in which rapid electron transfer competes with intra-QD electron-hole recombination.

Conclusions

Transient absorption spectroscopy measurements of CdSe/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures prepared by LAA and SILAR have provided compelling evidence that electrons and holes were transferred from photoexcited CdSe QDs into the CB and mid-gap states, respectively, of $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ nanowires. In stark contrast, for CdSe/ V_2O_5 heterostructures, only electron transfer from photoexcited QDs to CB states of V_2O_5 was observed. Ultra-fast transient absorption measurements of CdSe/ $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures suggest that holes were transferred more rapidly than electrons. The efficient extraction of holes from photoexcited CdSe QDs (as required for applications such as water oxidation) can thus be facilitated by the presence of mid-gap states derived from intercalative cations.

Distinctive electron transfer dynamics were observed for CdSe/ V_2O_5 heterostructures depending on the nature of the interface. Electron transfer from CdSe QDs to $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ nanowires occurred readily for heterostructures assembled *via* SILAR with direct interfaces; however, for heterostructures prepared by

LAA and interfaced using molecular linkers, electron transfer was observed only for hot electrons produced with excitation at energies significantly greater than the band-gap of CdSe.

The results presented here demonstrate that charge transfer from photoexcited CdSe QDs to β - $\text{Pb}_{0.33}\text{V}_2\text{O}_5$ nanowires can compete successfully with electron-hole recombination pathways, suggesting the feasibility of using intercalative mid-gap states as acceptors of photogenerated holes. Such an approach would represent a fundamentally distinct design principle for enhancing charge transfer across interfaces. Future work will focus on the development of CdSe/ β - $\text{Pb}_{0.33}\text{V}_2\text{O}_5$ hybrid photocathodes by incorporating an electron acceptor into the heterostructure, such that electron transfer to the acceptor might compete with electron injection into the CB of β - $\text{Pb}_{0.33}\text{V}_2\text{O}_5$.

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