Interface-modulated kinetic differentials in electron and hole transfer rates as a key design principle for redox photocatalysis by Sb<sub>2</sub>VO<sub>5</sub>/QD heterostructures

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ABSTRACT

The efficient conversion of solar energy to chemical energy represents a critical bottleneck to the energy transition. Photocatalytic splitting of water to generate solar fuels is a promising solution. Semiconductor quantum dots (QDs) are prime candidates for light-harvesting components of photocatalytic heterostructures, given their size-dependent photophysical properties and band-edge energies. A promising series of heterostructured photocatalysts interface QDs with transition-metal oxides which embed midgap electronic states derived from the stereochemically active electron lone pairs of p-block cations. Here, we examine the thermodynamic driving forces for charge separation in Sb$_2$VO$_5$/CdSe QD heterostructures, wherein a high density of Sb 5$s$-derived midgap states are prospective acceptors for photogenerated holes. Hard-x-ray valence band photoemission spectroscopy measurements of Sb$_2$VO$_5$/CdSe QD heterostructures were used to deduce thermodynamic driving forces for charge separation. Interfacial charge transfer dynamics in the heterostructures were examined as a function of the mode of interfacial connectivity, contrasting heterostructures with direct interfaces assembled by successive ion layer adsorption and reaction (SILAR) and interfaces comprising molecular bridges assembled by linker-assisted assembly (LAA). Transient absorption spectroscopy measurements indicate ultrafast (<2 ps) electron and hole transfer in SILAR-derived heterostructures, whereas LAA-derived heterostructures show orders of magnitude differentials in the kinetics of hole (<100 ps) and electron (~1 ns) transfer. The interface-modulated kinetic differentials in electron and hole transfer rates underpin the more effective charge separation, reduced charge recombination, and greater photocatalytic efficiency observed for the LAA-derived Sb$_2$VO$_5$/CdSe QD heterostructures.

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INTRODUCTION

Meeting the ambitious goals of the Paris Climate Accord to limit anthropogenic global warming to 1.5°C requires rapid acceleration of the energy transition. High-renewable pathways to combat climate change rely on the urgent replacement of fossil fuels with sustainable alternatives such as green hydrogen. Harvesting solar energy, an abundant and renewable source, and storing it in the energy-dense chemical bonds of hydrogen or other solar fuels represents an attractive route with clear benefits in terms of sustainability, carbon footprint, and distributed production as compared to current hydrogen production routes such as methane steam reformation. Photocatalysts that absorb sunlight, split water, and/or reduce CO$_2$ to liquid fuels are a central part of the puzzle. Yet,
FIG. 1. Mechanisms of assembly, modes of interfacial connectivity, and energetic offsets at Sb$_2$VO$_5$/CdSe interfaces. (a) Schematic representation of the SILAR and LAA modes for interfacing CdSe QDs with Sb$_2$VO$_5$ nanorods, showcasing the direct interface between QDs and Sb$_2$VO$_5$ (SILAR) and a cysteine molecular bridge interfacing CdSe QDs to Sb$_2$VO$_5$ nanorods (LAA) in the insets. (b) Energy diagram showing band edge positioning derived from HAXPES and DRS measurements. Timescales for hole and electron transfer processes are shown as derived from the TAS data discussed below. LPS denotes Sb 5s$^2$-derived lone pair states. (c) Valence-band HAXPES plots contrasting Sb$_2$VO$_5$, CdSe, and Sb$_2$VO$_5$/CdSe (SILAR 25×) acquired at an incident photon energy of 5 keV. (d) RedLine renderings contrasting the crystal structures of Sb$_2$VO$_5$ and M$_x$V$_2$O$_5$ (M = p-block cation). Interstitial sites occupied by p-block cations in the V$_2$O$_5$ framework are illustrated for the latter compound. The relatively lower stoichiometry of p-block cations in M$_x$V$_2$O$_5$ (0.33 in M$_x$V$_2$O$_5$) results in a lower density of lone-pair states. (e) Energy diagram depicting the valence and conduction band edges of $\beta$-Pb$_{0.33}$V$_2$O$_5$, $\beta$-Sn$_{0.23}$V$_2$O$_5$, Sb$_2$VO$_5$, and CdSe QDs.
According to previous work, the need to tune not just energy positioning but also the density of mid-gap states derived from p-block cations. A promising recent advance is the identification of a line compound, Sb\textsubscript{2}VO\textsubscript{5}, which has a distinctive electronic structure characterized by a high density of lone-pair states in proximity to the Fermi level [Fig. 1(d)].\textsuperscript{12,13} The midgap states of this compound are optimally positioned to facilitate excited-state hole transfer from the valence band edges of photoexcited II–VI QDs. The resulting Sb\textsubscript{2}VO\textsubscript{5}/QD photocatalysts catalyze both oxidative and reductive half-reactions, including oxygen reduction and hydrogen evolution, in photoelectrochemical cells, as well as in the form of dispersed photocatalysts.\textsuperscript{9}

Understanding and manipulating charge transfer kinetics at the interfaces of QDs is integral to advancing their role in redox photocatalysis. Charge transfer processes play a pivotal role in excited state reactivity, wherein they influence both reaction rates and yields. In this article, we complement hard x-ray photoemission spectroscopy (HXPES) studies of thermodynamic energy offsets in Sb\textsubscript{2}VO\textsubscript{5}/CdSe heterostructures with ultrafast transient absorption spectroscopy (TAS) studies of electron and hole transfer dynamics. In particular, we contrast the electron and hole transfer dynamics in Sb\textsubscript{2}VO\textsubscript{5}/QD heterostructures with two different modes of interfacial connectivity: (a) direct interfaces constructed using the successive ionic layer adsorption and reaction (SILAR) method and (b) molecular bridges connecting the individual components based on the linker-assisted assembly (LAA) method (Fig. 1).\textsuperscript{15} In the latter approach, cysteine (cys) is used as a molecular linker to tether the QDs to Sb\textsubscript{2}VO\textsubscript{5}. We specifically sought to understand the role of electron and hole transfer dynamics in mediating the previously reported improved photocatalytic function for LAA-derived heterostructures as compared to SILAR-based heterostructures.\textsuperscript{13}

### EXPERIMENTAL SECTION

#### Materials

Reagents were obtained from the following sources: (1) Alfa Aesar (CdO [99.998%], oleic acid (OA) [tech. 90%], and Cd(NO\textsubscript{3})\textsubscript{2} [98.5%]); (2) Millipore Sigma (selenium powder [99.9%], VO\textsubscript{2} [99.5%], tri-octylphosphine (TOP) [90%], L-cysteine (cys) [>97%], tetramethylammonium hydroxide pentahydrate (TMAH) [>97%], Sb\textsubscript{2}O\textsubscript{3} [99.9%, VO\textsubscript{2} [99%], SeO\textsubscript{2} [98%], and NaBH\textsubscript{4} [99%]); and (3) Acros Organics (1-octadecene (ODE) [tech. 90%], Methanol (MeOH), ethanol (EtOH), chloroform (CHCl\textsubscript{3}), and acetone were obtained from various commercial sources. Reagents and solvents were used as received.

#### Synthesis and characterization of Sb\textsubscript{2}VO\textsubscript{5}

Phase-pure Sb\textsubscript{2}VO\textsubscript{5} was prepared by a one-step solid-state reaction using equimolar amounts of VO\textsubscript{2} and Sb\textsubscript{2}O\textsubscript{3}, as described in previous work.\textsuperscript{11} Briefly, the precursor powders were mixed and ball-milled for 1 h with grinding beads in a Spex Sample Prep 8000D ball mill. The powder was then pressed into a pellet and transferred to a fused silica ampoule, which was sealed under vacuum and heated at a rate of 10°C/min to 700°C. The reaction mixture was held at this temperature for 24 h prior to cooling to room temperature. The resulting powders were mint green in color.
Synthesis and characterization of CdSe

Bulk CdSe was prepared via a precipitation reaction by preparing a Cd(NO$_3$)$_2$ precursor solution (ethanol, 50 mM) and a Na$_2$Se precursor solution was prepared by dissolving SeO$_2$ (0.4993 g) in ethanol under constant Ar flow. Se$^{2-}$ ions were obtained by adding NaBH$_4$ (0.3438 g) as a reducing agent and stirring for 1 h. The Cd(NO$_3$)$_2$ solution was added to the selenium precursor solution and the resulting CdSe was recovered via centrifugation and dried under constant N$_2$ flow. The resulting powder was red in color.

Synthesis and characterization of Sb$_2$VO$_5$/CdSe heterostructures by SILAR

Sb$_2$VO$_5$ rods were interfaced with CdSe QDs using the SILAR method in a glove bag under an argon atmosphere. Borosilicate glass slides (VWR, 76.2 × 25.4 × 1.2 mm$^3$) were first coated with the Sb$_2$VO$_5$ powder sample by sonicating 50 mg of Sb$_2$VO$_5$ in 15 ml of 2-propanol and drop casting the resulting dispersion onto the glass slides. The Sb$_2$VO$_5$-coated slides were then placed in an automated SILAR system (MTI, Model PTL-SC-6S-LD) designed to hold up to six solutions/dispersions. In each individual SILAR cycle, an Sb$_2$VO$_5$-coated slide was inserted into a Cd(NO$_3$)$_2$ precursor solution (ethanol, 90 mM) for 45 s, then washed with ethanol for 30 s, then immersed in a sodium selenide precursor solution (Na$_2$Se; ethanol, 90 mM) for 45 s, then washed again with ethanol to remove unreacted and loosely bound precursors. The Sb$_2$VO$_5$/QD heterostructures reported in this article were prepared by a total of 3, 15, or 25 sequential SILAR cycles (denoted as 5×, 15×, 25×).

Synthesis and characterization of Sb$_2$VO$_5$/CdSe heterostructures via LAA

The synthesis of LAA-derived Sb$_2$VO$_5$ heterostructures followed the method reported by Zaheer et al. Oleic acid (OA)-capped CdSe (OA-CdSe) QDs were first synthesized by preparing a Cd precursor solution of CdO (0.51 g, 4.0 mmol), ODE (70 ml, 0.22 mol), and OA (6.2 ml, 20 mmol). This mixture was deaerated under Ar (30 min) and heated to 250°C with constant stirring until it became a clear solution. In a separate flask, a selenium precursor was prepared under an inert, Ar-purged atmosphere by combining elemental selenium powder (0.1 g, 1.3 mmol), ODE (10 ml, 31 mmol), and TOP (0.6 ml, 1.3 mmol) and stirring until the mixture became clear (~1 h). The selenium precursor solution was quickly injected into the cadmium-containing solution and allowed to react for 1.5 min. The reaction was quenched by removing the heat source.

Preparation of Sb$_2$VO$_5$/CdSe heterostructure thin films for TAS

Glass microscope slides (VWR, 76.2 × 25.4 × 1.2 mm$^3$) were cleaned by ultrasonication in ethanol. Dispersions of Sb$_2$VO$_5$/CdSe heterostructures (10 mg), prepared by either SILAR or LAA, in ethanol (4 ml), were spray coated onto the glass slides held on a steel block surface on a hot plate held at 220°C using a Master Airbrush (Model 679) at a pressure of 60 lb/in.$^2$.

Transmission electron microscopy

High-resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) patterns were acquired using a FEI Tecnai G2 F20 field emission scanning electron microscope (FE-TEM) operated at 200 kV. Prior to imaging, the powder samples were dispersed in ethanol and drop-cast onto 300-mesh formvar-carbon films supported by copper grids (electron microscopy science). HRTEM images were analyzed using the Gatan Microscopy Suite software.

Scanning electron microscopy

SEM images were collected using a JEOL JSM-7500F FE-instrument, an ultrahigh-resolution field emission scanning electron microscope (FE-SEM) equipped with a high-brrightness conical FE gun and a low aberration conical objective lens. Sb$_2$VO$_5$ powder was spread on conductive carbon tape before imaging. Elemental maps were collected using the JEOL JSM-7500F FE-instrument equipped with a high-brrightness conical field-emission gun, a low aberration conical objective lens, and an Oxford energy dispersive spectroscopy (EDS) system.

Raman spectroscopy

Raman spectra were collected using a Horiba Scientific XploRA Plus confocal Raman microscope (Kyoto, Japan) mounted on an Olympus BX45F microscope body (Olympus Life Science, Tokyo, Japan) and equipped with a Horiba Syncrecy Peltier-cooled 1024 × 256 pixels CCD array detector. Spectra were collected for powders of bare Sb$_2$VO$_5$. SILAR-derived Sb$_2$VO$_5$/CdSe, and LAA-derived Sb$_2$VO$_5$/cysCdSe using a 532 nm laser, an Olympus LPMF20× objective lens, and a 1200 lines/mm grating. Powder samples were spread on carbon tape on a glass slide (VWR, 76.2 × 25.4 × 1.2 mm$^3$).

Hard x-ray photoemission spectroscopy

HAXPES measurements were performed at the National Institute of Standards and Technology (NIST) beamline SST-2 of the National Synchrotron Light Source II of Brookhaven National Laboratory. Measurements were performed at ~2 keV photon energy with a pass energy of 200 eV and a step size of 0.85 eV with the analyzer axis oriented parallel with the photoelectron polarization vector. HAXPES data at 5 keV were collected with a 500 eV energy filter. The higher excitation energy of HAXPES helps to alleviate deleterious charging issues that are ubiquitous in ultraviolet and soft x-ray photoelectron spectroscopy. Photon energies were selected.
using a double Si(111) crystal monochromator. The beam energy was aligned to the Fermi level of a silver foil before measurement.

**UV-vis spectroscopy**

Ground-state UV-vis absorbance of the dispersion of CdSe QDs was acquired with an Agilent 8453 diode array spectrophotometer within the 190–1100 nm range. QD-containing dispersion was housed in a four-sided quartz cuvette with a path length of 1 cm.

**Diffuse reflectance spectroscopy**

UV/vis diffuse reflectance measurements for bare Sb₂VO₅, SILAR-derived Sb₂VO₅/CdSe, and LAA-derived Sb₂VO₅/cysCdSe coated on glass slides were obtained with an Agilent 8453 diode array spectrophotometer equipped with a Labsphere SA-HP-53 reflectance accessory.

**Spectroelectrochemistry**

Spectroelectrochemical measurements were acquired for Sb₂VO₅ nanorods in colloidal suspension. Experiments were performed using a 7.5 g/l Sb₂VO₅ nanorod dispersion in anhydrous acetonitrile with 100 mM tetrabutylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte. Prior to experimentation, the cell was purged for 15 min with nitrogen to eliminate dissolved oxygen. The spectroelectrochemical cell, featuring a Pt honeycomb working electrode (Pine Research Instrumentation, USA), a Pt counter electrode, and an Ag/Ag⁺ reference electrode, had an optical path length of 1.7 mm. Spectroelectrochemical measurements were carried out using a spectrophotometer (AvaSpec-ULS2048 UV/Vis Spectrometer with a range of 200–1100 nm). This integrated system provided control over both the potentiostat (WaveDriver 40 DC Bipotentiostat, Pine Research Instrumentation, USA) and the spectrophotometer, ensuring synchronization of electrochemical and spectroscopic measurements. To investigate the electrochemical processes and changes in UV-vis absorption spectra, the potential was incrementally varied from 0 to 1.5 V (to oxidize Sb₂VO₅) or from 0 to −1.0 V (to reduce Sb₂VO₅) at 10 min intervals. Simultaneously, the absorbance changes were monitored in relation to the applied potential. The ΔA spectrum was generated by subtracting the UV-vis absorbance spectrum of neutral Sb₂VO₅ from the spectrum recorded at each potential.

**Transient absorption spectroscopy**

Transient absorption spectroscopy (TAS) data were acquired at the Center for Functional Nanomaterials of Brookhaven National Laboratory using a commercial broadband transient absorption spectrometer (Helios, Ultrafast Systems) with ~100 fs time resolution in a time window of 0–1.8 ns. Glass slides coated with thin films of Sb₂VO₅ nanorods or Sb₂VO₅/CdSe heterostructures were excited at 360 nm and probed using a white light continuum in the range of 425–700 nm. The same spectrometer was further configured to measure long-lived electronic and chemical species with sub-ns time resolution in a time window of 0–50 μs (EOS, Ultrafast Systems).

**RESULTS**

**Characterization of Sb₂VO₅/CdSe QD heterostructures**

Figure 1 contrasts the crystal structures of M₅V₂O₇ and Sb₂VO₅ and schematically illustrates the difference in interfacial connectivity between SILAR and LAA-derived heterostructures. The line compound Sb₂VO₅ provides a 6× increase in the concentration of p-block cations as compared to M₅V₂O₇ and, thus, yields a greater density of lone-pair-derived midgap states that can be used for hole extraction in heterostructures. The thiolate and amine functional groups of the cytinate dianion are known to coordinate with Cd⁺⁺ sites on the surfaces of the CdSe QDs, whereas the carboxylate moieties serve as a tether to the surfaces of the Sb₂VO₅ nanorods [Fig. 1(a)]. Variable-energy hard x-ray photoemission spectroscopy and diffuse reflectance spectroscopy [Figs. 1(c), S1, and S2] have been used to deduce the thermodynamic energy offsets shown in Fig. 1(b). Figure 1(c) contrasts valence band HAXPES spectra acquired at 5 keV for Sb₂VO₅, CdSe, and Sb₂VO₅/CdSe-SILAR (25×), whereas Fig. S2 compares valence band HAXPES spectra acquired at 2 and 5 keV for Sb₂VO₅, CdSe, and Sb₂VO₅/CdSe-SILAR (25×).

As-prepared Sb₂VO₅ nanorods, CdSe, and Sb₂VO₅ functionalized with CdSe QDs were investigated by HAXPES. The use of high-energy x-rays in synchrotron-based HAXPES yields emitted photoelectrons with higher kinetic energies and mean free paths, enabling the interrogation of bulk (and not just surface) electronic structure. Core-level HAXPES spectra for Sb₅Vo₅/CdSe/SILAR (25×) heterostructures were also compared to Sb₅Vo₅/CdSe-SILAR (25×) heterostructures. The valence band HAXPES spectra of bare Sb₂VO₅ measured at 2 and 5 keV. Both spectra exhibit three notable features at ~4.5, 7.5, and 13 eV. Based on intensity differences within energy-variant HAXPES data as well as previous density functional theory (DFT) calculations and Crystal Orbital Hamilton Population (COHP) analyses, these features can be assigned as Sb 5s–Oδ bonding (B) states (at 13 eV), V 3d–Oδ bonding (B) states that are predominantly Oδ in character (at 7.5 eV), and Sb 5s, 5p–Oδ lone pair states with predominantly anti-bonding (AB) characteristics (at 4.5 eV). The states with considerable 5s² lone pair character are notably enhanced at higher excitation energies.

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Difference spectra (Fig. S4), obtained by subtracting the valence band spectrum of pristine Sb$_2$VO$_5$ from the valence band of the Sb$_2$VO$_5$/CdSe heterostructure, yielded an onset energy of 2.14 eV for the heterostructure. The -0.26 meV increase in the onset value for the Sb$_2$VO$_5$/CdSe heterostructure is ascribed to the contributions of Se 4p states from the CdSe QDs, highlighted in orange in Fig. 1(c). This assignment is indeed corroborated by the HAXPES spectra of as-prepared CdSe QDs plotted in Fig. 1(c). The valence band spectra of both the functionalized and unfunctionalized materials measured at 2 keV yield a similar result [Fig. S2(b); see also the HAXPES spectra measured at 2 keV excitation for CdSe in Fig. S2(c)]. These results, along with the UV-vis and diffuse reflectance spectroscopy (DRS) results in Fig. S1, evidence a modification to the band edge if appropriate resonantly matched states are available.

Figures 2 and 3(a) show the electron microscopy characterization of SILAR-interfaced heterostructures of Sb$_2$VO$_5$ nanorods and CdSe QDs. Figure 2(a) shows a STEM image of Sb$_2$VO$_5$/CdSe heterostructures after 15 sequential SILAR cycles (15×), whereas Fig. 2(b) shows a HRTEM image where CdSe QDs are differentiated from Sb$_2$VO$_5$ nanorods based on SAED patterns in Figs. 2(d) and 2(f) and their respective lattice-resolved views in Figs. 2(c) and 2(e), respectively (indexed with reference to a previous Rietveld refinement of the powder x-ray diffraction pattern by Zaheer et al. for Sb$_2$VO$_5$ and to PDF No. 77-2307 for wurtzite CdSe). For 15× SILAR heterostructures, sub-monolayer coverage is observed, with individual QDs being the predominant species interfaced with the surfaces of the Sb$_2$VO$_5$ nanorods. Figure 2(g) shows a HRTEM image of Sb$_2$VO$_5$ and its respective SAED pattern in Fig. 2(h) indexed to the (200) plane of Sb$_2$VO$_5$ nanorods. The SEM image in Fig. 3(a) further shows CdSe QDs speckled along the surfaces of Sb$_2$VO$_5$ nanorods. The presence of Cd and Se is further corroborated by the EDS results in Fig. 3(b). Increasing the number of SILAR cycles results in continuous coverage, such that Sb$_2$VO$_5$ nanorods are entirely enrobed with agglomerated CdSe QDs. The analyses below will focus on 15× SILAR heterostructures with sub-monolayer coverage to examine charge transfer across Sb$_2$VO$_5$/CdSe QD interfaces without the complicating effects of additional pathways resulting from significant CdSe QD agglomeration. Extensive electron microscopy characterization of LAA-derived Sb$_2$VO$_5$/CdSe QD heterostructures has been reported in previous work.

![FIG. 2.](image-url)
Raman spectra shown in Figs. 3(c) and S5 show the emergence of the first LO mode of the LAA-derived Sb$_2$VO$_5$/CdSe heterostructure, which is assigned here with the help of spectroelectrochemistry, as plotted in Fig. S6. The Raman spectra of bare Sb$_2$VO$_5$ nanorods show greatly diminished but essentially featureless absorption at wavelengths beyond 425 nm and extending out to ~750 nm, which is consistent with previous reports. The first excitonic bleach persists until ~2 μs. An induced absorption feature centered at 509 nm emerges between the two bleach features beyond 2.3 μs; this absorption is attributable to a Stark-effect-induced shift of the interband excitonic transition of photoexcited CdSe relative to the ground state.

The TA spectrum of bare cysCdSe QDs contains a strong, long-lived first excitonic bleach centered around 575 nm and a weaker, shorter-lived second excitonic bleach centered around 470 nm, consistent with previous reports. The first excitonic bleach persists until ~2 μs. An induced absorption feature centered at 509 nm emerges between the two bleach features beyond 2.3 μs; this absorption is attributable to a Stark-effect-induced shift of the interband excitonic transition of photoexcited CdSe relative to the ground state.

The TA spectrum of bare Sb$_2$VO$_5$ nanorods exhibits a broad induced absorption at wavelengths beyond 425 nm and extending out to ~750 nm, which is concordant with the spectral signature of oxidized Sb$_2$VO$_5$ (reflective of low-energy transitions from states deeper in the valence band into empty states created upon photoexcitation near the valence band edge) measured by spectroelectrochemistry, as plotted in Fig. S6. In contrast, reduced Sb$_2$VO$_5$ shows greatly diminished but essentially featureless absorption across the visible region of the electromagnetic spectrum (Fig. S6).

The TA spectrum of SILAR-derived Sb$_2$VO$_5$/CdSe heterostructures exhibits a red-shift of the first excitonic bleach (centered at 665 nm) and second excitonic bleach (centered at 525 nm) features relative to the colloidally grown cystCdSe QDs, which is reflective of the larger size of the CdSe QDs prepared through 15× sequential immersion cycles. The first excitonic bleach reaches a maximum within ~197 fs (0.197 ps) [Fig. 6(a)], a greatly accelerated timescale when compared to the bare QDs. Indeed, this feature is fully recovered by 0.6 ps. Because the first excitonic bleach of chalcogenide QDs is sensitive primarily to excited electrons, the timescale and excited receiving states in charge acceptors. The energy offset diagram constructed based on HAXPES and DRS results in Fig. 1(b) illustrates the excellent overlap between Sb 5s$^2$-derived mid-gap states and the valence band of CdSe QDs. We used TAS to probe charge transfer dynamics within SILAR-derived and LAA-derived heterostructures. TAS is a powerful technique that provides invaluable insights into charge transfer dynamics in semiconductors and semiconductor heterostructures at ultrafast timescales. By utilizing short laser pulses to excite electronic excitations in a semiconductor, followed by a weak probe pulse at a specific delay time after the pump pulse, a time-dependent absorbance difference (ΔA) spectrum is derived. By changing the delay time between the pump and the probe and recording ΔA at each delay time, a ΔA profile is obtained as a function of time (ΔA(t)). The observed absorption changes correspond to photogenerated charge carriers and their migration and/or recombination, which are assigned here with the help of spectrophotometric chemical measurements in which absorption spectra are acquired upon electrochemical oxidation or reduction of a sample. Transient absorbance (TA) spectra were acquired as described in the experimental section. Samples for TAS were prepared by spray-coating glass slides with bare Sb$_2$VO$_5$ nanorods, SILAR-derived Sb$_2$VO$_5$/CdSe heterostructures, and LAA-derived Sb$_2$VO$_5$/cysCdSe heterostructures. TA spectra of colloidal dispersions of cysCdSe QDs with excitation at 360 nm, which excites both CdSe QDs and Sb$_2$VO$_5$ nanorods. “Color maps” depicting the temporal evolution of TA spectra are shown in Fig. 4; corresponding TA spectra at varying delay times are shown in Figs. 5 and 6.

The TA spectrum of bare cysCdSe QDs contains a strong, long-lived first excitonic bleach centered around 575 nm and a weaker, shorter-lived second excitonic bleach centered around 470 nm, consistent with previous reports. The first excitonic bleach persists until ~2 μs. An induced absorption feature centered at 509 nm emerges between the two bleach features beyond 2.3 μs; this absorption is attributable to a Stark-effect-induced shift of the interband excitonic transition of photoexcited CdSe relative to the ground state.

In semiconductor heterostructures, excited-state charge transfer involves the overlap of excited carrier states in charge donors and acceptors. Charge transfer dynamics in Sb$_2$VO$_5$/CdSe QD heterostructures is sensitive primarily to excited electrons, the timescale and excited receiving states in charge acceptors.

**FIG. 3.** Characterization of Sb$_2$VO$_5$/CdSe QD heterostructures prepared by SILAR. (a) SEM image of Sb$_2$VO$_5$ nanorods interfaced with CdSe QDs grown through 15× sequential SILAR cycles. (b) Integrated EDS spectra of Sb$_2$VO$_5$/CdSe heterostructures. (c) Raman spectra acquired for Sb$_2$VO$_5$ nanorods (black), for SILAR-derived Sb$_2$VO$_5$/CdSe heterostructure grown through 15× sequential cycles (red), and for LAA-derived Sb$_2$VO$_5$/cysCdSe heterostructure (blue). (d) Magnified view of Raman spectra highlighting the 1LO and 2LO bands of the CdSe QDs.

**Charge transfer dynamics in Sb$_2$VO$_5$/CdSe QD heterostructures**

In semiconductor heterostructures, excited-state charge transfer involves the overlap of excited carrier states in charge donors and acceptors. Charge transfer dynamics in Sb$_2$VO$_5$/CdSe QD heterostructures is sensitive primarily to excited electrons, the timescale and excited receiving states in charge acceptors.
FIG. 4. TA “Color maps” illustrating \( \Delta A \) across measured delay times and probe wavelengths for the following samples: (a) cisCdSe QDs showcasing the strong bleach centered around 560 nm extending out to microsecond timescales, (b) unfunctionalized Sb\(_2\)VO\(_5\) nanorods at picosecond timescales, (c) 15\( \times \) SILAR-interfaced Sb\(_2\)VO\(_5\)/CdSe QD heterostructures at picosecond timescales, (d) 15\( \times \) SILAR-interfaced Sb\(_2\)VO\(_5\)/CdSe QD heterostructures at microsecond timescales, (e) LAA-interfaced Sb\(_2\)VO\(_5\)/cisCdSe heterostructures at picosecond timescales, and (f) LAA-interfaced Sb\(_2\)VO\(_5\)/cisCdSe heterostructures at microsecond timescales. For all spectra, the excitation wavelength \( (\lambda_{\text{exc}}) \) was 360 nm.

The excitonic bleach of CdSe QDs are essentially unaffected by hole transfer.\(^{60}\)
FIG. 5. Transient absorption spectra of Sb$_2$VO$_5$/CdSe heterostructures and individual components. Transient absorption spectra at different delay times for (a) cysCdSe QDs at microsecond timescales, (b) unfunctionalized Sb$_2$VO$_5$ nanorods at picosecond timescales, (c) SILAR-derived Sb$_2$VO$_5$/CdSe QD heterostructures (15×) at picosecond timescales, (d) SILAR-derived Sb$_2$VO$_5$/CdSe QD heterostructures (15×) at microsecond timescales, (e) LAA-derived Sb$_2$VO$_5$/cysCdSe heterostructures at picosecond timescales, and (f) LAA-derived Sb$_2$VO$_5$/cysCdSe heterostructures at microsecond timescales. For all spectra, the excitation wavelength ($\lambda_{\text{exc}}$) was 360 nm.

FIG. 6. Transient absorption spectra of Sb$_2$VO$_5$/CdSe heterostructures at ultrafast (<0.5 ps) timescales. (a) TA spectra of SILAR-derived Sb$_2$VO$_5$/CdSe after 15 SILAR cycles show the maximum of the bleach at ∼197 fs. (b) TA spectra of LAA-derived Sb$_2$VO$_5$/cysCdSe show the maximum of the bleach at ∼448 fs. For both spectra, the excitation wavelength ($\lambda_{\text{exc}}$) was 360 nm.
slower electron transfer dynamics in Sb

not entirely decay through the entire 1.5 ns time range of the ultra-

relative to that of dispersed cysCdSe QDs and which indeed does

linked together by cys as a molecular linker, exhibits a strong first

the charge transfer dynamics. The TA spectrum of LAA-derived

modifying the mode of interfacial connectivity dramatically alters

the pronounced induced absorption band of SILAR-derived

Sb

the results provide strong evidence for interfacial charge separation

QDs decays after 2 ps and a prominent induced absorption band

absorption characteristic of electron–hole pairs that are longer lived

evolution of the bleach recovery into a long-lived induced broad

timescales of electron–hole transfers are initiated on comparable (<2 ps)

tethered by molecular linkers. Focusing on ultrafast timescales

ture electron-transfer dynamics and not just modification of the

heterostructures can be attributed to differences in heterostruc-

Analysis of TA decay dynamics [Fig. 7(b)] of this heterostruc-

The stimulated emission thus constrains the earliest times of hole

As such, the significant dif-

For the same two Sb

1.5 ns time window of the ultrafast measurement [Fig. 7(a) and Table

reaches a maximum at 5 ps and slowly decays. In comparison to

bare cysCdSe QDs, Sb

2

V

QD heterostructures also exhibit a broad tail of the bleach at wavelengths beyond the first excitonic

bleach (615–800 nm), which is attributed to stimulated emission.

After ~100 ps, a weak broad induced absorption band is observed

centered at ~600 nm, which is again the characteristic spectral

signature of oxidized Sb

2

V

QD heterostructures, which may arise from surface passivation upon SILAR deposition of chalcogenide QDs.33

Probing at longer timescales (into the microsecond range),

the pronounced induced absorption band of SILAR-derived

Sb

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CdSe QD heterostructures persists up to 2 µs (the end of the

measurement), reaching a maximum amplitude at ~5 ns. As such, the results provide strong evidence for interfacial charge separation

and the localization of holes in Sb

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. However, both electron

and hole transfers are initiated on comparable (<2 ps) picosecond
timescales. Figure 1(b) summarizes the ranges of timescales of
electron and hole transfer as deduced from initial observation of the
characteristic spectral signatures of electron and hole transfer.

For the same two Sb

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nanorods and CdSe QD components,

modifying the mode of interfacial connectivity dramatically alters

the charge transfer dynamics. The TA spectrum of LAA-derived Sb

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V

/cysCdSe heterostructures [Figs. 4(e), 4(f), 5(e), and 5(f)],

linked together by cys as a molecular linker, exhibits a strong first

excitonic bleach, which is red-shifted by 14–15 nm (52–58 meV)

to that of dispersed cysCdSe QDs and which indeed does not

entirely decay through the entire 1.5 ns time range of the ultra-

fast experiment. The persistence of this feature is indicative of much

slower electron transfer dynamics in Sb

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/CdSe QD heterostructures

tethered by molecular linkers. Focusing on ultrafast timescales

[Fig. 6(b)], the excitonic bleach reaches a maximum within ~448 fs

(0.448 ps) and begins to decay thereafter, indicating the initia-
tion of electron transfer. The second excitonic bleach from CdSe

QDs decays after 2 ps and a prominent induced absorption band

characteristic of CdSe QDs is visible at center at 525 nm, which

reaches a maximum at 5 ps and slowly decays. In comparison to

bare cysCdSe QDs, Sb

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/cysCdSe heterostructures also exhibit a broad tail of the bleach at wavelengths beyond the first excitonic

bleach (615–800 nm), which is attributed to stimulated emission.

After ~100 ps, a weak broad induced absorption band is observed

centered at ~600 nm, which is again the characteristic spectral

signature of oxidized Sb

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, reflective of hole transfer from photo-
toexcited CdSe QDs to the valence band of Sb

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. This induced absorption band exhibits diminished net absorption at wavelengths coincident with the excitonic bleach of cysCdSe (Fig. S7). The inset in Fig. 5(e) shows the emergence of this feature above the baseline. The stimulated emission thus constrains the earliest times of hole transfer that can be discerned in these experiments. Nevertheless, hole transfer denoted by the emergence of the induced absorption band is observed to be much more accelerated (<100 ps) as compared to bleach recovery denoting electron transfer (~1 ns). Consistent with this scenario, another induced absorption feature characteristic of the CdSe excitonic absorption is visible at shorter wavelengths (<475 nm), which reaches a maximum of 1 ps and decays by 1.5 ns. Analysis of the decay dynamics of the first excitonic bleach centered around 580 nm provides further evidence of the long-lived photoexcited state, which does not fully decay within the 1.5 ns time window of the ultrafast measurement [Fig. 7(a) and Table S1]. The strongly differentiated lifetimes of the excitonic bleaches for LAA- and SILAR-derived heterostructures are substantially modified as compared to the 60 ns excitonic bleach lifetimes measured for cys-capped colloidal CdSe QDs.33 As such, the significant differences in the rate of bleach decay for SILAR- vs LAA-derived heterostructures can be attributed to differences in heterostructure electron-transfer dynamics and not just modification of the QD environment from deposition onto a substrate. Indeed, comparing QD bleach lifetimes in related CdSe–linker–Pb

0.35

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2

QD and CdSe–linker–MoS

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heterostructures, the measured lifetimes show a strong dependence on linker length and connectivity, suggesting ligand-dependent rates of electron transfer, which are indeed further correlated with photocatalytic efficiencies.33

Probing the Sb

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/cysCdSe heterostructures at longer timescales, we observe a strong induced absorption feature that
reaches a maximum after 0.01 μs (10 ns) and slowly decays thereafter. The spectrum shows a weak, but unambiguously identifiable, induced absorption signal at the earliest times observed (1 ns). This feature is consistent with, and a continuation of, the induced absorption signal present toward the end of the ultrafast timescale measurements [Fig. S5(c)], providing evidence for effective charge-separation and a long-lived charge-separated state. As such, in the LAA-derived heterostructures, hole transfer proceeds on rapid <100 ps timescales, whereas the molecular bridges appear to considerably slow down electron transfer to ~1 ns timescales. Notably, TA spectra acquired on the longest time scales (≥2 μs) appear to contain a bleach at probe wavelengths below 450 nm, at shorter wavelengths than the onset of the induced absorption from oxidized Sb₂VO₅, attributable to reduced Sb₂VO₅ (Fig. S6) arising from electron transfer. We have previously reported that electron transfer from CdSe QDs to α-V₂O₅ nanowires gives rise to a similar bleach below 470 nm, attributable to reduced V₂O₅. Notably, in type-II CdSe/V₂O₅ heterostructures, in the absence of lone-pair-derived midgap electronic states, photogenerated holes remain localized on CdSe QDs even as photoexcited electrons are transferred to the conduction band of α-V₂O₅, thereby affording an excellent control heterostructure where hole transfer is entirely shutdown. Figure 1(b) summarizes the sharp kinetic differentiation of photogenerated electrons and holes in the LAA-derived structure, which stands in stark contrast to the directly interfaced SILAR structures.

**DISCUSSION**

Comparing TA spectra for both the SILAR-derived (15×) and LAA-derived Sb₂VO₅/CdSe QD heterostructures, both hole and electron transfer (initiation to termination) are greatly accelerated in the former heterostructures across direct interfaces, whereas in the latter heterostructures separated by a molecular linker, electron- and hole-transfer kinetics are differentiated significantly. While direct time-dependent density functional theory molecular dynamics (TD-DFT-MD) simulations of charge transfer explicitly considering time evolution of the electronic states as per |Ψ(t + Δt)⟩ = U(t + Δt, t)|Ψ(t)⟩ remain intractable owing to the large size of the Sb₂VO₅ unit cell and challenges in accurate treatment of electron correlation, model calculations on charge transfer dynamics from II–VI QDs to other semiconductors provide insight into operational mechanisms and possible origins of the observed difference in timescales as a function of the interfacial connectivity.29,30,65

In directly interfaced semiconductor heterostructures, such as the SILAR-derived Sb₂VO₅/cysCdSe heterostructures, interfacial charge transfer is mediated by the orbital mixing of excited carrier states in the donor and acceptor, which enables level coupling and engenders high charge transfer rates. Resonant matching of Sb 5s²-donor mid-gap states with photoexcited Se-centered hybrid valence band states of CdSe QDs can drive efficient and rapid excited-state charge separation even without an epitaxially matched interface, which is manifested experimentally here as the observed ultrafast hole transfer dynamics (including the transfer of energetic holes).30,32,66,67 Similarly, resonantly matched states across a broad range of energies likely also mediate facile electron transfer and enable relatively high charge transfer rates from photoexcited Cd-centered hybrid conduction band states (modified by quantum confinement) of the CdSe QDs to vanadium–oxygen hybrid conduction-band states of Sb₂VO₅.22

In contrast, for LAA-derived Sb₂VO₅/cysCdSe heterostructures, interfacial charge separation mechanisms (and rates) are strongly modified by the presence of a molecular linker. Zhang and co-workers predict based on TD-DFT simulations that deprotonated cysteine gives rise to delocalized quasi-metallic radical molecular orbitals that couple donor and acceptor excited electronic states and mediate through-ligand carrier transport. 19-21 Such radical molecular orbitals further renormalize the HOMO–LUMO gap. However, notably, while the predicted charge-transfer rates for molecular-bridged systems are substantially higher as compared to systems without ligand hybridization to both semiconductors, the rates are nevertheless diminished as compared to direct interfaces as a result of the greater donor–acceptor separation.21 This picture is indeed consistent with our recent observations comparing cys and a series of mercaptoalkanoic acid linkers, which show that electron-transfer dynamics in semiconductor heterostructures are tunable as a function of the length of the bridging ligands.22 TD-DFT simulations by Ciesler et al. indicate that the cys ligand’s density of states hybridizes with donor and acceptor surface states across a range of energies, which is key to the effective coupling of donor and acceptor excited electronic states.23 In addition to facilitating the coupling of electronic states, molecular linkers play a significant role in enhancing electron–phonon coupling, which enables rapid dissipation of carrier energy through the excitation of high-frequency molecular phonons associated with local vibrational modes of the ligand atoms.23 The charge transfer rates across molecularly bridged systems thus depend on (i) the effectiveness of the ligand in coupling donor and acceptor excited electronic states (which in turn depends on the mode of hybridization of the ligand density of states with the donor and acceptor), (ii) the interfacial dipole resulting from the photoexcited charge density, and (iii) the strength of electron–phonon coupling and the efficacy of phonon-aided charge transfer pathways.14,30,65 These effects can be vastly different for hole and electron transfer, providing a means of engendering differentials in electron and hole charge transfer rates as observed for LAA-derived Sb₂VO₅/CdSe QD heterostructures.

Differentials in electron and hole transfer rates and the lifetimes of charge-separated states have profound implications for photocatalytic performance. In previous work contrasting SILAR- and LAA-derived Sb₂VO₅/CdSe QD heterostructures as working electrodes in photoelectrochemical cells for oxygen reduction, oxidative photocurrents measured for LAA-derived heterostructures were (1.7 ± 0.9)-fold greater as compared to SILAR-derived heterostructures.18 Similarly, reductive photocurrents for LAA-derived heterostructures were (12.7 ± 0.3)-fold higher as compared to values measured for SILAR-derived heterostructures.32 By establishing a greater differential between hole and electron transfer kinetics and by dint of their longer-lived charge separated states, the LAA-derived heterostructures are able to slow the recombination of photogenerated holes and electrons. As such, the photogenerated carriers can be more effectively separated in real space and made available for redox reactions with solvated species in aqueous media. By slowing down electron transfer dynamics but still enabling ultrafast hole transfer, the LAA-derived heterostructures effectively separate photogenerated electron–hole pairs, thereby providing a
route for subsequent reduction and oxidation half-reactions to outcompete charge recombination.

CONCLUSIONS

Stereoelectronically active electron lone pairs of p-block cations provide a versatile design motif for precisely modulating the electronic structure of periodic solids. The energy dispersion and positioning of electronic states near the Fermi level are tunable through the choice of the p-block cation, crystal lattice, and cation stoichiometry. Lone-pair-derived states have attracted intense recent attention in photocatalysis, in part because of their ability to extract holes from photoexcited QDs at ultrafast timescales, which may provide a route to alleviate the longstanding problem of photoanodic corrosion. In this article, we have examined the thermodynamic energy offsets and charge transfer kinetics in a promising new class of semiconductor heterostructures comprising Sb$_2$VO$_5$ (exhibiting a high density of mid-gap states derived from stereoelectronically active Sb 5s$^2$ electrons) with CdSe QDs. Energy-variant HAXPES and DRS measurements allow for the delineation of thermodynamic energy offsets and driving forces for electron and hole transfer.

We have next examined charge transfer dynamics in Sb$_2$VO$_5$/CdSe QD heterostructures with staggered valence and conduction band edges as a function of interfacial connectivity, specifically contrasting direct interfaces with bridging molecular linkers. SILAR has been used to grow CdSe QDs directly onto the surfaces of Sb$_2$VO$_5$ nanorods, whereas cys is used as a linker to couple Sb$_2$VO$_5$ nanorods and CdSe QDs through hybridization of ligand states with semiconductor surfaces. In particular, thiolate and the amine functional groups of the cysteinate dianion coordinate to the Cd$^{2+}$ surface sites of CdSe QDs, whereas carboxylate moieties anchor cys onto the Sb$_2$VO$_5$ nanorods. Transient absorption spectroscopy measurements, interpreted with the aid of spectroelectrochemical measurements, provide evidence for ultrafast electron and hole transfer at <2 ps timescales in SILAR-derived Sb$_2$VO$_5$/CdSe QD heterostructures (15×) with a high-yield of charge-separated states. In contrast, LAA-derived Sb$_2$VO$_5$/CdSe QD heterostructures exhibit slower but still ultrafast hole transfer (<100 ps) but much more sluggish electron transfer (~1 ns) as a result of the increased interfacial distance. The initiation of both electron and hole transfer processes is also differentiated between SILAR- and LAA-derived heterostructures, as indicated by the initial growth dynamics of the excitonic bleach of CdSe. For SILAR-derived heterostructures, the first excitonic bleach reaches a maximum after ~197 fs, whereas for LAA-derived heterostructures, the first excitonic bleach reaches a maximum after ~448 fs. These TA dynamics at the earliest measurable time scales thus provide another indication of the difference in charge transfer kinetics arising from differences in interfacial connectivity between the CdSe QDs and the Sb$_2$VO$_5$ nanorods. The ultrafast measurements further indicate the transfer of non-thermalized charge carriers, which would account for efficient hole injection from deeper valence band states despite the modest (0.26 eV) thermodynamic barrier to hole injection inferred from HAXPES measurements of valence band edges. Based on TD-DFT simulations of charge transfer pathways reported in the literature, differentials in electron and hole transfer rates in ligand-bridged heterostructures are ascribed to differences in the effectiveness of ligand coupling of electronic states for electron and hole transfer and disparate efficacies of phonon-mediated charge transfer pathways. As such, the photogenerated carriers are more effectively separated in real space for the LAA-derived structures, wherein they can be available for redox reactions with solvated species in aqueous media.

Our spectroscopic results explain the substantially improved photoelectrochemical and photocatalytic function of LAA-derived heterostructures as compared to SILAR-derived heterostructures for both oxidative and reductive reactions, which results from more effective charge separation and slowing down of charge recombination by the cys linker. By slowing down electron transfer rates but still enabling ultrafast hole transfer through the introduction of a bridging ligand, the LAA-derived heterostructures efficiently separate charges in real space across the Sb$_2$VO$_5$ interface. The results provide a roadmap for the design of interfaces to precisely control electron–phonon coupling and electronic coupling of donor and acceptor excited electronic states and thereby deterministically modulate the kinetics of charge separation with a view toward enhancing the efficiency of photocatalytic processes. Future work will focus on implementing these design principles in multicomponent heterostructures embedding oxidative and reductive co-catalysts to effectively utilize the separated electrons and holes in redox catalysis.

SUPPLEMENTARY MATERIAL

The supplementary material includes UV-vis and DRS measurements of cysCdSe QDs, bare Sb$_2$VO$_5$/CdSe, and reproducible charge transfer measurements for Sb$_2$VO$_5$/CdSe heterostructures at different sequential cycles (10×, 15×, and 25×), spectroelectrochemical data for Sb$_2$VO$_5$/CdSe nanorods, as well as a table depicting the analysis of charge transfer kinetics using triexponential fits. Further information and requests for resources should be directed to and will be fulfilled by the lead contacts: David F. Watson and Sarbajit Banerjee.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

J.R.A. and K.E.G.-P. contributed equally to this work.

S.B. and D.F.W. directed the research. J.R.A., K.E.G.-P., D.F.W., and S.B. conceptualized and designed the experiments. J.R.A. synthesized Sb\textsubscript{2}V\textsubscript{2}O\textsubscript{8} to perform SILAR experiments to synthesize SILAR-derived Sb\textsubscript{2}V\textsubscript{2}O\textsubscript{8}/CdSe heterostructures, collected and analyzed SEM, EDS, and Raman spectroscopy. K.E.G.-P. synthesized LAA-derived Sb\textsubscript{2}V\textsubscript{2}O\textsubscript{8}/cySCs heterostructures, collected and analyzed UV-Vis and DRS data. A.R.G. collected and analyzed HAXPES data on bare Sb\textsubscript{2}V\textsubscript{2}O\textsubscript{8} and Sb\textsubscript{2}V\textsubscript{2}O\textsubscript{8}/CdSe heterostructures. U.W. acquired and analyzed spectroelectrochemical data. J.R.A., K.E.G.-P., and U.W. acquired and analyzed TA data. S.H. assisted in the analysis of the HAXPES data and collected and analyzed HAXPES data for bare CdSe. L.C. collected and analyzed TEM/hrTEM/hrTEM/SAED data. C.J. and C.W. assisted in setting up HAXPES experiments and data collection. D.A.F. assisted in the design of HAXPES experiments. J.R.A., K.E.G.-P., A.R.G., U.W., S.H., D.F.W., and S.B. contributed to writing the paper and the discussion of experimental results.

Jaime R. Ayala: Conceptualization (equal); Investigation (equal); Data curation (equal); Formal analysis (equal); Writing – original draft (equal); Writing – review & editing (equal). Karolína E. García-Pedraza: Conceptualization (equal); Investigation (equal); Data curation (equal); Formal analysis (equal); Writing – original draft (equal); Writing – review & editing (equal). Alice R. Giem: Data curation (equal); Formal analysis (equal); Methodology (equal). Udani Wijethunga: Conceptualization (equal); Investigation (equal); Data curation (equal); Formal analysis (equal); Writing – original draft (equal); Writing – review & editing (equal). Shruti Hariyani: Data curation (equal); Formal analysis (equal); Methodology (equal). Luis Carrillo: Data curation (equal); Formal analysis (equal); Methodology (equal). Cherno Jyaye: Formal analysis (equal); Investigation (equal); Visualization (equal). Conan Weiland: Formal analysis (equal); Investigation (equal). Daniel A. Fischer: Investigation (equal); Methodology (equal); Resources (equal). David F. Watson: Conceptualization (equal); Project administration (equal); Supervision (lead); Formal analysis (equal); Resources (equal); Writing – original draft (equal); Writing – review & editing (equal). Sarbjit Banerjee: Conceptualization (equal); Project administration (equal); Supervision (lead); Formal analysis (equal); Resources (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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