**Probing structure-induced optical behavior in a new class of self-activated luminescent
0D/1D CaWO₄ metal oxide – CdSe nanocrystal composite heterostructures**

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Abstract: In this report, we synthesize and characterize the structural and optical properties of novel heterostructures composed of (i) semiconducting nanocrystalline CdSe quantum dot (QDs) coupled with (ii) both one and zero-dimensional (1D and 0D) motifs of self-activated luminescence CaWO_4 metal oxides. Specifically, ~ 4 nm CdSe QDs have been anchored onto (i) high-aspect ratio 1D nanowires, measuring ~ 230 nm in diameter and ~ 3 μm in length, as well as onto (ii) crystalline 0D nanoparticles (possessing an average diameter of ~ 80 nm) of CaWO_4 through the mediation of 3-mercaptopropionic acid (MPA) as a connecting linker. Composite formation was confirmed by complementary electron microscopy and spectroscopy (i.e. IR and Raman) data. In terms of luminescent properties, our results show that our 1D and 0D heterostructures evince photoluminescence (PL) quenching and shortened PL lifetimes of CaWO_4 as compared with unbound CaWO_4 . We propose that a photo-induced electron transfer process occurs from CaWO_4 to CdSe QDs, a scenario which has been confirmed by NEXAFS measurements and which highlights a decrease in the number of unoccupied orbitals in the conduction bands of CdSe QDs. By contrast, the PL signature and lifetimes of MPA-capped CdSe QDs within these heterostructures do not exhibit noticeable changes as compared with unbound MPA-capped CdSe QDs. The striking difference in optical behavior between CaWO_4 nanostructures and CdSe QDs within our heterostructures can be correlated with the relative positions of their conduction and valence energy band levels. In addition, the PL quenching behaviors for CaWO_4 within the heterostructure configuration were examined by systematically varying (i) the quantities and coverage densities of CdSe QDs as well as (ii) the intrinsic morphology (and by extension, the inherent crystallite size) of CaWO_4 itself.

Keywords: nanowire, luminescence, quantum dot, photoinduced charge transfer, synthesis.

Introduction

The family of AWO_4 compounds ($A = \text{Ca}, \text{Ba}, \text{Sr}$) has been extensively investigated both theoretically and experimentally as a result of their unique properties.¹⁻³ In particular, CaWO_4 is a material of special interest, because of its intriguing and superior luminescence properties as a ‘self-activated’ luminescent material, whose optical properties are defined to a large degree by its intrinsic structural properties.⁴⁻⁶ Specifically, upon UV excitation in the spectral range of 235-260 nm, a strong blue emission near 420 nm can be observed and can be attributed to electronic transitions associated with charge transfer between oxygen and tungstate moieties within the WO_4 group.^{2, 5, 7} In this light, CaWO_4 has been considered for potential applications including but not limited to phosphors, scintillators, optical fibers, optoelectronics, photocatalysts, and as host lattices for spin resonances.⁸⁻¹²

To date, various CaWO_4 possessing different morphologies, such as zero-dimensional (0D) nanocrystals as well as one-dimensional (1D) nanotubes and nanowires, have been successfully synthesized using a number of different methods, including sol-gel,¹³ molten-salt,¹⁴ hydrothermal,¹⁵ electrospinning,¹⁶ and microwave radiation protocols.¹⁷ Recently, our group has developed a modified template technique, enabling us to prepare crystalline 1D nanostructures associated with classes of diverse materials.¹⁸⁻²¹ Specifically, we have successfully prepared high-aspect-ratio, highly-crystalline, pure CaWO_4 nanowires using a reasonably simple solution-based U-tube protocol.²² Our methodology involves the use of the two arms of a glass U-tube apparatus to mediate a double-diffusion solution-based process under ambient conditions. Apart from its relative simplicity, flexibility, and generalizability, such a reaction can be run in one or two reaction steps in aqueous solvents, leading to high yields with little if any byproducts formed.

Nonetheless, it is evident that the behavior of individual nanostructures such as CaWO_4 can be subsequently altered and functionally tailored in unexpected ways through the formation of nanoscale heterostructures composed of different, distinctive, and complementary subunits. The key idea is that the properties of a composite whole can be favorably tuned so as acquire more interesting and compelling attributes as compared with its individual constituent components. For example, there are numerous reports of nanoscale heterostructures incorporating tungstate compounds, such as $\text{ZnWO}_4/\text{BiOI}$, $\text{Bi}_2\text{WO}_6/\text{TiO}_2$, $\text{CaWO}_4/\text{Bi}_2\text{WO}_6$, and SnO_2/WO_3 , which were generated with a goal towards developing novel photocatalytic and field emission properties.²³⁻²⁶ Moreover, our group and others have already coupled quantum dots (QDs), which are known to be effective highly luminescent materials because of their unique size-dependent absorption properties, with either carbon nanotubes, TiO_2 , or ZnO motifs in order to generate unique heterostructures, characterized by relevant and interesting charge transfer and transport properties for photovoltaic, photocatalytic, and light emitting diode applications, respectively.²⁷⁻³⁴

Most recently, QDs have been attached onto families of discrete and luminescent constituent materials including but not limited to various luminescent dyes as well as lanthanide (e.g. Eu and Tb) complexes. Examples of heterostructures created with the idea of coupling 2 or more complementary luminescent types of structures into 1 discrete whole include the formation of rare-earth doped inorganic materials, such as 0D CdSe QD – NaYF_4 : Yb, Er^{35} and CdTe QD – YVO_4 : Eu³⁶ nanocrystalline constructs as well as 1D CdS QD – LaPO_4 : Eu^{3+} core-shell nanowires.³⁷ These specific examples highlight the community's synthetic potential to combine and ultimately transform the optical properties of two subunits within the context of engineered nanoscale heterostructures.

Nevertheless, as is apparent from the previous systems constructed, when generating novel nanoscale QD-based heterostructures incorporating either chemically distinctive or structurally unique luminescent materials, the majority of the non-QD component subunits tend to consist of rare earth (i.e. Eu^{3+} , Tb^{3+} , Yb^{3+} , Sm^{3+} , Dy^{3+} , and Er^{3+})-activated/doped compounds. That is, the interesting optical properties of these particular materials derive primarily from the $4f$ - $4f$ transitions of the rare earth ion activators, which are not strongly affected by the host lattice itself and thereby give rise to comparable absorption and emission profiles, regardless of the host.³⁸ Therefore, the main optical characteristics of the resulting heterostructures emanate from predictable interactions between QDs and the rare earth ions.

In our group, we have sought to create more nuanced nanoscale architectures, coupling different morphological motifs in order to generate 0D-1D and 0D-3D composites in which size and morphology also play a role in determining the observed optoelectronic properties. In this vein, in terms of recent, relevant prior work, our group has reported on novel distinctive nanoscale heterostructures, comprised of 0D CdSe QDs attached onto either CePO_4 : Tb nanowires,³⁹ LaPO_4 : Eu 1D nanowires, or LaPO_4 : Eu 3D architectures.⁴⁰ In these composites, in addition to dopants, we treated structure, morphology, and chemical composition as reaction ‘variables’ with which to tailor and control optical behavior. That is, we could selectively ‘toggle’ between and otherwise purposely promote either energy or charge transfer processes by deliberately modulating localized chemical interactions amongst the constituent components of these discrete heterostructures.

Yet, to the best of our knowledge, all of the prior studies primarily rely on the use of external dopants to induce and promote interesting optical behavior within the composites. Therefore, the novelty and importance of this work is that we have created a new class of

distinctive heterostructures that incorporates 1D/0D self-activating metal oxide luminescent materials (which are intrinsically luminescent by virtue of their structure) coupled with 0D QDs (possessing size-dependent luminescent properties). In so doing, we have capitalized on an untapped area of parameter space by purposely utilizing the size and morphology dependence of the inherent energy bands as a means to better characterize and manipulate our system. Specifically, we have prepared 1D CaWO_4 nanowire - 0D CdSe QD heterostructures, wherein CdSe QDs have been successfully anchored onto the surfaces of high aspect-ratio, self-activated blue-emitting CaWO_4 nanowires in a process mediated with the use of a 3-mercaptoproponic acid (MPA) linking agent.

MPA represents a well-studied organic ligand that we have previously used to couple QDs with metal oxides and it consists of -SH and -COOH as terminal reactive end groups. Specifically, CdSe QDs easily and effectively adsorb SH due to the higher affinity of Cd-S and the unbound COOH groups in MPA can be reacted with the surfaces of metal oxide through favorable electrostatic interactions.³² In addition, we have successfully fabricated comparable 0D CaWO_4 nanoparticle – 0D CdSe QD architectures in an analogous manner in order to compare their luminescence properties with those of our novel 1D-based heterostructures. As readily adjustable variables, we have altered both QD coverage density onto the underlying CaWO_4 ‘template’ as well as the crystallite size of CaWO_4 itself.

In particular, we have characterized the optical absorption and photoluminescence (PL) emission spectra, in addition to the corresponding lifetimes of as-prepared nanoscale CaWO_4 – CdSe QD heterostructures. In so doing, we have observed PL quenching and shortened apparent lifetimes of both 0D and 1D CaWO_4 in our modified, engineered heterostructures as compared with unbound CaWO_4 . By contrast, we noted little if any significant change in the PL output and

lifetimes of CdSe QDs incorporated as part of our heterostructures. Moreover, the observed PL quenching data of our 0D CaWO_4 nanoparticles are more pronounced as compared with analogous 1D CaWO_4 nanowires within our nanoscale heterostructures. We propose therefore that the ‘aggregate’ of optical behavior, i.e. the PL quenching and the shortened PL lifetimes of CaWO_4 in our heterostructures, can be attributed to a photo-induced charge transfer process occurring from CaWO_4 to CdSe QDs.

In order to support our hypothesis, we have confirmed the presence of electron transfer from CaWO_4 to CdSe QDs within our heterostructure motif by probing the unoccupied states of the conduction band of CdSe QDs using near edge X-ray absorption fine structure analysis (NEXAFS). X-ray absorption spectroscopy has been used as a powerful tool to examine charge transfer in various composites (i.e. $\text{MoS}_2/\text{carbon}$ ⁴¹ as well as carbon nanotubes coupled with either ZrO_2 or SnO_2 ^{42, 43}) by providing information about the nature of unoccupied orbitals in the conduction band. As an example of the utility of this technique in analyzing nanoscale systems, Hamad et al.⁴⁴ have been able to observe electronic structural disorder in CdSe and InAs QDs, whereas Lee et al.⁴⁵ could probe the quantum confinement effect within CdSe QDs.

The differential optical behaviors of CaWO_4 and CdSe QDs as well as the more pronounced PL quenching of 0D CaWO_4 within our as-prepared heterostructures have been explained in the context of the inherent energy level alignments of both CaWO_4 and CdSe QDs. These particular considerations are crucial to determining not only the occurrence but also the corresponding efficiency of charge transfer between subunits in the heterostructure, which necessarily depend upon both (i) the QD coverage density onto CaWO_4 as well as (ii) the crystallite size of the CaWO_4 itself.

2. Experimental

2.1. Synthesis.

2.1.1. 1D structures of CaWO_4

A standard synthesis of 1D nanowires of CaWO_4 was performed, following our recently reported methods.²² In a typical ambient protocol, polycarbonate track-etched membranes, containing pore sizes measuring either 50 or 200 nm in diameter, were initially hydrated by immersion and sonication, and then mounted between the two half arms of a U-shaped tube. One of the two half-cells was filled with a 0.05 M $\text{Na}_2\text{WO}_4 \cdot 2 \text{H}_2\text{O}$ solution, while the other half-cell contained a solution generated from a 0.05 M $\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$ solution. We should note that each cell was filled simultaneously with an aqueous Ca^{2+} and WO_4^{2-} solution, respectively, so as to obtain a chemically uniform and homogeneous CaWO_4 material. The aqueous solutions within the 2 half cells of the system were then allowed to diffuse towards each other in an unperturbed manner for an incubation period of up to 24 h at room temperature.

To isolate products within the template pore channels themselves, the template membrane was gently abraded onto a smoothing stone, lubricated with mineral oil, and then sonicated for about 2 min in de-ionized water so as to ensure physical removal of unwanted particles on the external surface. The rinsed template was dried in air at 70°C before being ultimately dissolved with dichloromethane (DCM). As-prepared tungstate nanowires were later isolated from solution by washing and centrifugation steps involving DCM, followed by storage in methanol (MeOH).

2.1.2. 0D structures of CaWO_4

Zero-dimensional (0D) CaWO_4 nanoparticles were prepared using a modified hydrothermal protocol from the literature.¹⁵ Briefly, each dissolved cetyltrimethylammonium bromide (CTAB) solution, containing a mixture of 1 g of CTAB in 25 ml *n*-hexane and 1 ml of

1-pentanol, was added to two different solutions: one consisted of 260 mg of $\text{NaWO}_4 \cdot 2\text{H}_2\text{O}$ dissolved in 0.5 ml distilled, deionized (DI) water and the other was comprised of 130 mg of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved in 0.5 ml DI water so as to generate separate microemulsion solutions. Subsequently, these two microemulsion solutions were individually sonicated for 15 min, prior to mixing, and further sonicated for another 15 minutes. The final solution was transferred into a Teflon-lined stainless-steel autoclave (capacity of 50 mL) and sealed. The autoclave was subsequently oven heated to 140°C for 24 h, and cooled naturally to room temperature. As-prepared CaWO_4 nanoparticles were later isolated from solution by centrifugation upon washing with aliquots of water for 7 times in order to completely remove CTAB followed by drying in air.

2.1.3. CdSe QDs, MPA-capped QDs, and heterostructures of CdSe QD-1D/0D CaWO_4

Colloidal CdSe QDs were prepared using a modification of an existing literature protocol.⁴⁶ Briefly, 0.2 mmol CdO and 0.8 mmol of stearic acid were degassed at 150°C , and then heated under an Ar atmosphere in order to completely dissolve the precursors in a three-neck flask. Subsequently, 3.88 g each of trioctylphosphine oxide (TOPO) and hexadecylamine (HDA) were added to the flask, and the mixture was heated to 320°C . In parallel, in an air-sensitive glovebox environment, 2 mmol of Se were dissolved in tributylphosphine (TBP) in the presence of dioctylamine (DOA). The Se solution was then injected into the hot Cd precursor solution at 320°C , and subsequent QD growth was carried out at 270°C for 15 s. The mixture was later allowed to cool to room temperature, and was then washed with a solution of either MeOH or acetone, prior to further dissolution in hexane.

CdSe QDs capped with 3-mercaptopropionic acid (MPA), a mediating linker specifically chosen to connect between CdSe QDs and CaWO_4 in creating our heterostructures, were obtained through a ligand exchange reaction. In a typical experiment, 1 mmol of MPA ligand,

dissolved in 2 ml MeOH, was added dropwise to a suspension of as-prepared TOPO/HDA-capped CdSe QDs (0.04 mmol) in 4 ml of hexane with a molar concentration ratio of $[\text{Ligands}]/[\text{QDs}] = 25$, with stirring. The molar ratio of $[\text{Ligands}]/[\text{QD}]$ chosen herein is consistent with other reports for the effective promulgation of efficient ligand exchange from long alkyl chains to short thiol ligands.⁴⁷⁻⁴⁹ Under dark conditions, individual methanolic mixtures of the MPA were stirred for 30 min. After completion of the ligand exchange process in which the CdSe QDs in the hexane layer were transferred to and subsequently dissolved into the more polar MeOH layer, with the hexane layer becoming correspondingly clear (i.e. Figure S1), these ligand-exchanged QDs were later collected by centrifugation and washed with both ethanol and MeOH. The resulting QDs were finally re-dispersed in MeOH for future use and processing. A quantitative estimate of the degree of ligand exchange efficiency can be reasonably computed by monitoring the behavior of $-\text{CH}_3$ stretching modes associated with the various ligands by means of Fourier transform infrared spectroscopy. Our data indicate a high ligand exchange efficiency of $87 \pm 7\%$. Detailed protocols used to obtain ligand exchange efficiency values are described in the Supporting Information section

MPA-capped CdSe QDs were immobilized onto either 0D nanoparticles or 1D nanowires of CaWO_4 presumably through electrostatic interactions, in an analogous manner to previous reports of CdSe QDs attached onto various metal oxides, such as TiO_2 and ZnO .^{34, 50} For example, in a typical experiment, ~ 3 mg of CaWO_4 in 2 ml MeOH was added to 2 mg of MPA-capped CdSe QDs in 2 ml of MeOH. Thermogravimetric analysis (Figure S2) has suggested that these MPA-capped CdSe QDs consisted of 40 wt% of MPA and 60 wt% of CdSe QDs, whereas in the resulting, as-prepared heterostructures, we noted that both CaWO_4 0D nanoparticles and 1D nanowires possessed <5 wt% of molecular ligands on their outer surface. The resulting

solution was then sonicated for 10 min and stirred in the dark for 2 h in order to preserve the optical integrity of the CdSe QDs. These as-prepared heterostructures were subsequently washed with MeOH to remove unbound and merely physisorbed species, and ultimately these nanomaterials were re-dispersed in the same solvent, prior to further study.

2.2. Characterization.

Samples were (i) structurally characterized using a number of different complementary methodologies, including powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), high resolution TEM (HRTEM), and near edge X-ray absorption fine structure (NEXAFS), as well as (ii) optically probed using UV-visible spectroscopy, steady-state photoluminescence (PL) spectroscopy, and time-resolved fluorescence lifetime spectroscopy.

2.2.1. X-ray Diffraction.

Crystallographic and purity information on as-prepared CdSe QDs and CaWO_4 were initially obtained using a Rigaku Ultima III Diffractometer, operating in the Bragg configuration using $\text{Cu K}\alpha$ radiation (1.54 Å). Data were collected in a range from 15 to 62°, measured at a scanning rate of 1° per minute. To prepare as-generated QDs, 0D tungstate nanoparticles, and 1D tungstate nanowires for structural characterization, samples were rendered into slurries, i.e. in hexane for QDs and in ethanol for both 0D and 1D structures of CaWO_4 , respectively. Samples were subsequently sonicated for about 1 min, and then air-dried upon deposition onto glass slides.

2.2.2. Electron microscopy.

Low-magnification TEM images were obtained at an accelerating voltage of 120 kV on a JEOL JEM-1400 instrument, equipped with EDS mapping capabilities. HRTEM images coupled with complementary selected area electron diffraction (SAED) patterns were recorded using a JEOL JEM-3000F microscope equipped with a Gatan image filter (GIF) spectrometer operating at an accelerating voltage of 300 kV as well as on a JEOL 2100F analytical TEM instrument, equipped with a Gatan CCD camera and a Gatan HAADF detector, operating at an accelerating voltage of 200 kV. Specimens for all of these microscopy experiments were prepared by dispersing the as-prepared product in ethanol, sonicating for 2 min to ensure an adequate dispersion of the nanostructures, and evaporating one drop of the solution onto a 300 mesh Cu grid, coated with a lacey carbon film, for subsequent TEM and HRTEM analysis.

2.2.3. FTIR

FTIR spectra were collected on a Nexus 670 instrument (ThermoNicolet) equipped with a Smart Orbit diamond ATR accessory, a KBr beam splitter, and a DTGS KBr detector. As-prepared solid powder samples were placed onto the crystal surface, where data were taken with a reproducible pressure. A background correction in air was performed in the spectral range studied. FTIR data were typically recorded over the wavenumber range of 500–4000 cm^{-1} spanning the far-, mid-, and near IR regions, and were subsequently evaluated in terms of expected, characteristic absorption bands. Spectra were collected using the Omnic software with a spatial resolution of 1 cm^{-1} .

2.2.4. NEXAFS

Cd $M_{2,3}$ -edge and O K -edge NEXAFS spectra reported here were taken at the U7A NIST/DOW end station at the National Synchrotron Light Source at Brookhaven National Laboratory. The partial electron yield (PEY) signal was collected using a channeltron electron

multiplier with an adjustable entrance grid bias. A variable negative bias in the range of 20–200 V was applied to reject the extraneous background due to the presence of low-energy electrons. The use of different biases allowed for both top-surface and bulk (up to 10 nm) analyses. Data were recorded in a UHV chamber at room temperature, with an incident X-ray resolution of 0.2 eV. All spectra were processed through standard pre- and post-edge normalization methods. Additional experimental details can be found in previously published work.⁵¹⁻⁵⁴

2.2.5. Raman spectroscopy

Raman measurements using a Renishaw inVia confocal Raman microscope were performed using an experimental configuration consisting of a 100× objective lens, illuminated using either a 784 nm diode or a 514 nm Ar ion laser. The microscope was aligned by means of a computer-controlled motorized XYZ stage. Spectra were obtained at 1 cm⁻¹ resolution upon a 10 s exposure of the CCD detector possessing a 1800 line/mm grating in the wavenumber region between 100–1500 cm⁻¹. Data analysis of raw spectra was subsequently performed using Wire 4.0 software. Baselines were subtracted from all of the spectra presented, and individual spectra were normalized to the highest intensity of 1.

2.2.6. TGA

To provide for an estimate of nanoparticle concentrations, thermogravimetric analysis of the dried MPA-capped CdSe QDs as well as of 0D and 1D CaWO₄ nanostructures was performed using a TGA Q500 (TA Instruments) instrument. Isotherms were obtained by raising the temperature from 25 to 500°C at a rate of 5°C/min under a flow of ultra-dry high purity air, provided at a rate of 60 mL/min. The mass profiles revealed that the decomposition of the molecular ligands immobilized onto CdSe QDs as well as onto 0D and 1D CaWO₄ was essentially complete by 450°C.

2.2.7. UV-visible and fluorescence spectroscopy

Individual spectra were obtained for CdSe QDs, 0D nanoparticles of CaWO_4 , 1D nanowires of CaWO_4 , and associated heterostructures, all of which were individually sonicated for 2 min prior to data collection, so as to produce a homogeneous dispersion. Samples for PL spectra were dispersed in either MeOH or acetonitrile for MPA-capped CdSe QDs as well as for MPA-capped CdSe QD – CaWO_4 heterostructures. All of these materials were sonicated for 1 minute, prior to measurement.

Extinction spectra were collected on a PerkinElmer Lambda25 for samples suspended in acetonitrile, a solvent that exhibits high UV transmission. Fluorescence data were subsequently obtained at room temperature using a FluoroMax-4 spectrofluorimeter (Jobin Yvon) and an ISS PC1 photon counting spectrofluorimeter (ISS Inc., Champagne, IL) using excitation wavelengths of 260 nm and 460 nm, respectively. Photoluminescence intensity changes are discussed in terms of relative quenching due to the complex wavelength dependent emission features of the CaWO_4 . The corresponding fluorescence lifetimes for CdSe QDs were measured with a FluoroMax-4 spectrofluorimeter, equipped with an IBH NanoLED, emitting at 388 nm as an excitation source, and a NanoLED controller module, Fluorohub (Jobin Yvon), operating at 1 MHz. Decay data analysis was completed using the DAS6 software (Horiba Jobin Yvon IBH). Fluorescence lifetimes for CaWO_4 excited at 280 nm were measured using an ISS PC1 photon counting spectrofluorimeter (ISS Inc., Champagne, IL) using frequency-domain methods. Apparent lifetimes⁵⁵ have been determined from modulation measurements (τ_m) over a range of 10 kHz to 500 MHz and reported at the values where $\sim 50\%$ modulation is achieved (~ 50 kHz).

3. Results and Discussion

3.1. Structural Insights into CdSe QDs and CaWO₄ nanowires/nanoparticles

We note that the XRD patterns of as-prepared CdSe QDs can be reliably assigned to the reflection of a crystalline hexagonal wurtzite structure (JCPDS # 08-0459), as shown in Figure S3. The corresponding purity and crystallinity of (a) CaWO₄ nanowires, prepared by an ambient U-tube template-mediated synthesis, and of (b) CaWO₄ nanoparticles, synthesized by a modified hydrothermal protocol, were initially characterized using XRD. The XRD patterns suggest that the as-synthesized metal tungstate compound is composed of a single tetragonal scheelite structure with a space group of $I_{41/a}$, which agrees well with the JCPDS #72-1624 standard, as shown in Figure 1. The structure of CaWO₄, which represents the prototype of the scheelite incarnation of various materials such as MgWO₄, CaMoO₄, PbMoO₄, PbWO₄, YLiF₄, and high-pressure phases of DyVO₄, consists of Ca²⁺ ions and WO₄²⁻ groups with the corresponding coordination numbers of 8 for Ca²⁺ and 4 for W⁶⁺, as shown in Figure S4.^{56, 57} In addition, the constituent crystallite size, as estimated by the Debye-Scherrer formula, was found to be 37 nm for isolated 0D nanoparticles and 21 nm for individual polycrystalline samples composed of 200 nm and 50 nm-diameter nanowires.

The size, structure, and morphology of as-synthesized CaWO₄ nanowires and nanoparticles have been investigated using TEM. Typical lower and higher magnification TEM images of (i) nanowires prepared with the use of the 200 nm diameter template and of (ii) the corresponding nanoparticles are shown in Figure 2 A-B and C-D, respectively. On the basis of statistical measurements of several tens of nanowires and nanoparticles pertaining to each of our samples, our as-prepared larger diameter CaWO₄ nanowires measure on average 230 ± 30 nm in diameter with lengths of up to 3.07 ± 1.33 μ m and the average diameters of our as-prepared CaWO₄ nanoparticles were noted to be 72.8 ± 9.0 nm. Furthermore, we have successfully

synthesized CaWO_4 nanowires prepared with the use of smaller 50 nm diameter templates, and we found that these nanostructures possess an average diameter of 80 ± 9 nm with lengths of up to 2.16 ± 1.32 μm , as shown in Figure S5. The actual dimensions of our isolated nanowires reflect the inherent size heterogeneity of the channels associated with the commercial templates, from whence these one-dimensional nanostructures were derived.

3.2. Structural Characterization of 1D/0D CaWO_4 – CdSe QDs heterostructures

3.2.1. TEM, HRTEM, & EDS spectra and mapping

Figure 3 A-B and C-D highlight standard TEM and HRTEM images of CaWO_4 1D nanowire – MPA-capped CdSe QD and CaWO_4 0D nanoparticle – MPA-capped CdSe QD heterostructures, respectively. We were able to spatially discern distinctive regions wherein MPA-capped CdSe QDs were anchored and immobilized onto both the 0D and 1D CaWO_4 structures, as shown in Figure 3A and B. Moreover, the HRTEM images (Figure 3C and D) of individual MPA-capped CdSe QD – CaWO_4 heterostructures clearly suggest that highly crystalline CdSe QDs are indeed adjacent to and closely bound onto the outer surfaces of both CaWO_4 1D nanowires and 0D nanoparticles.

In addition, HRTEM revealed interlayer spacings, corresponding to the expected lattice parameters associated with the tetragonal scheelite structure of CaWO_4 and with the hexagonal structure of CdSe QDs, respectively. Specifically, 0.373 nm and 0.476 nm were in good agreement with the expected d spacings for the (100) and (101) lattice planes of CdSe QDs and CaWO_4 , respectively, within both the 1D nanowire and 0D nanoparticle-based heterostructures. The associated SAED pattern (insets to Figure 3C and D) revealed ‘less than ideal’ ring patterns, which might have likely originated from the overall polycrystallinity of the structures. Particular

features associated with the individual discrete diffraction patterns nevertheless could be specifically assigned either to CdSe QDs or to CaWO_4 nanostructures (1D and 0D), as indicated in the insets to Figures 3C and D, respectively.

From the standard TEM data, (i) the physical aggregation of QDs on the metal oxide surface and (ii) the poor differential contrast especially between the CdSe QD themselves and the external surfaces of the CaWO_4 nanowires and nanoparticles rendered it difficult to qualitatively and quantitatively determine the extent of coverage of QDs on the underlying 1D and 0D CaWO_4 templates. Hence, a detailed chemical analysis was carried out using energy-dispersive X-ray spectroscopy (EDS) in order to more precisely probe elemental composition throughout the heterostructures, so as to confirm the presence of CdSe QDs in our composites. Specifically, representative STEM images of typical (a) 1D 200 nm CaWO_4 nanowire-based and (b) 0D CaWO_4 nanoparticle-based heterostructures as well as their corresponding elemental maps are highlighted in Figure 4A-F and Figure 5A-F, respectively, and these data shed light on the spatial distributions of the various constituent elements associated with both QD and metal oxide species, i.e. Ca, W, O, Cd, and Se.

Importantly, in panels E and F of Figures 4 and 5, the locations of the Cd *L*-edge and the Se *K*-edge signals overlap and coincide reasonably well with those of the Ca *K*-edge, the W *L*-edge, and the O *K*-edge signals (Figure 4 and 5B, C, and D), thereby confirming that CdSe QDs are uniformly attached to and spatially distributed throughout the external surfaces of both CaWO_4 1D nanowire and 0D nanoparticle-based architectures. In order to further confirm and corroborate the qualitative coverage density estimated by EDS mapping data (Figure S6A and B), a more rigorous quantitative analysis to determine the actual coverage density of CdSe QDs on both 1D and 0D-based CaWO_4 structures was conducted.

In the associated Supporting Information section, we extensively describe our detailed reasoning and the mathematical protocol used to obtain both (i) our coverage values as well as (ii) the efficiency of the formation of our 0D/1D-tungstate-based heterostructures, using our relatively mild synthetic approach. From the results of our analysis, the efficiency of CaWO_4 -MPA-capped CdSe QD heterostructure formation using our synthetic protocol is $\sim 49\%$ in the presence of 1D tungstates and $\sim 38\%$ when using 0D tungstates. In addition, upon normalization to identical, external, exposed surface areas (i.e. 50 nm^2) of 1D and 0D structures, respectively, we calculated that approximately 17 QDs were attached onto 1D CaWO_4 nanowires, whereas only ~ 3 QDs were immobilized onto analogous 0D CaWO_4 nanoparticles under comparable reaction conditions, thereby suggesting that all other factors being equal, the numbers of attached CdSe QDs are slightly but perceptibly greater on the surfaces of 1D nanowire structures as compared with their 0D nanoparticulate counterparts.

3.2.2. FTIR analysis

The surface chemical bonding structure of the heterostructures has been confirmed by FTIR spectra, as shown in Figure 6. Specifically, the data in Figure 6A and B highlight the FT-IR spectra of CaWO_4 nanowires, CaWO_4 – MPA-capped CdSe QD heterostructures, and MPA-capped CdSe QDs, in the range of 4000-500 and 1800-600 cm^{-1} , respectively. The broad peak associated with the 1D CaWO_4 near 781 cm^{-1} corresponds to the anti-symmetric stretching vibrational mode originating from the W-O bond configuration in WO_4^{2-} tetrahedra, a finding which is consistent with other reports and with our parallel set of data on 0D CaWO_4 , shown in Figure S7.^{13, 16} In effect, AWO_4 -type scheelite oxides, possessing S4 site symmetry for the A and W atoms in particular, produce the main observed absorption bands in the region of 400–1000

cm^{-1} .^{16, 58} Hence, this vibrational analysis corroborates XRD results obtained for phase-pure CaWO_4 nanowires and nanoparticles.

On the other hand, the presence of the bands in MPA-capped CdSe QDs, which can be ascribed to C-H stretching modes, O-H stretching vibrations, carboxyl groups, and carboxylate species, have been monitored between 2800 and 3000 cm^{-1} , 3340 cm^{-1} , 1711 cm^{-1} , and 1550 - 1390 cm^{-1} , respectively. We should note that the absence of a distinctive S-H peak near the region of 2400 - 2500 cm^{-1} suggests that all ‘dangling’ thiol moieties associated with MPA are likely to be completely bound onto the surfaces of CdSe QDs.

In the more complex CaWO_4 – MPA-capped CdSe QD heterostructures, the IR spectra give rise to a number of specific peaks, which are invariably altered as compared with those associated with single, individual CaWO_4 and MPA-capped CdSe QD precursors. *First*, the C=O stretching vibration near 1711 cm^{-1} is absent. *Second*, carboxylate stretching modes near 1540 , 1426 , and 1396 cm^{-1} are shifted to 1546 , 1456 , and 1377 cm^{-1} , respectively (see Figure 6B). These data imply that the presence of either unbound COO^- or COOH moieties associated with MPA-capped CdSe QDs, which enable and facilitate attachment onto CaWO_4 . Therefore, the formation of CaWO_4 – MPA-capped CdSe QD nanoscale heterostructures likely follows the same mechanism previously reported to link and connect MPA-capped CdSe QDs with either TiO_2 or ZnO .^{34, 50} We should note that the position of the W-O stretching vibrational mode near 781 cm^{-1} is not significantly shifted within the heterostructures themselves (i.e. Figure 6B).

3.2.3. Raman spectroscopic study

In order to more thoroughly investigate the structural variation of the $[\text{WO}_4]$ group within CaWO_4 as compared with the corresponding heterostructure in more detail, we analyzed the Raman spectroscopy of both CaWO_4 and CaWO_4 – MPA-capped CdSe QD heterostructures.

CaWO₄ possessing a scheelite structure consists of isolated [WO₄] groups as tetrahedra within the crystal structure, as shown in Figure S4. Moreover, the strong covalent bonds intrinsic to the [WO₄]²⁻ group can be considered as distinctive structural elemental signatures, allowing us to obtain information about the structure of the crystal lattice as well as the presence of defects by analyzing specific variations in the Raman spectra (i.e. inhomogeneous splitting, peak shifts, and alterations in peak shapes).^{59, 60}

The respective Raman spectra of 1D CaWO₄ and of 1D CaWO₄ – MPA-capped CdSe QD heterostructures under irradiation at 785 nm are presented in Figure 7. Several phonon modes within Figure 7 can be ascribed to the vibrations of W-O bonds. Specifically, there are two types of optical phonon modes within the tungstate structure: (1) internal vibrational modes, which are associated with and localized in the [WO₄] group (i.e. ~330 cm⁻¹ for A_g(2) + B_g(2), ~400 cm⁻¹ for B_g(4), ~796 cm⁻¹ for E_g(2), ~839 cm⁻¹ for B_g(1), and 910 cm⁻¹ for A_g(1) modes, respectively) as well as (2) external vibrational modes (i.e. in the region <250 cm⁻¹, i.e. the B_g(1) and B_g(3) modes), accompanied by the deformation of the entire structure. The presence of these peaks is in accord with prior observations from previous studies of various tungstate structures.⁶¹⁻⁶⁴

As shown in Figure 7, most of the peak positions and intensities associated with both 1D CaWO₄ nanowire and the 1D CaWO₄ – MPA-capped CdSe QD heterostructure motifs are comparable. Moreover, we did not observe any significant variation in the line widths between the constituent CaWO₄ nanowires and their associated heterostructures. Specifically, the full width at half maximum for the A_g(1) and A_g(2) + B_g(2) modes for both 1D CaWO₄ and 1D CaWO₄ - MPA-capped CdSe QD heterostructures are approximately 14 and 18 cm⁻¹, respectively. However, interestingly, the A_g(1) mode (~910 cm⁻¹) and the A_g(2) + B_g(2) combination mode (~400 cm⁻¹) within as-prepared CaWO₄ – MPA-capped CdSe QD heterostructures exhibit

noticeable peak splitting into 910 and 936 cm^{-1} for the $A_g(1)$ band as well as 306 and 400 cm^{-1} for the $A_g(2) + B_g(2)$ combination mode. The splitting of the phonon mode can potentially be attributed to a local distortion of the WO_4 tetrahedra within the CaWO_4 crystals (i.e. a change in symmetry).⁵⁹

Furthermore, the internal vibrational modes, especially $A_g(1)$ and $A_g(2) + B_g(2)$, are sensitive to the local symmetry of the tetrahedron in the crystal and fluctuations in these vibrational modes are likely dependent on the nature of the dopants (i.e. $\text{CaWO}_4\text{:Nd}^{65}$) as well as the particle size of the nanocrystals.⁶⁶ Therefore, it is plausible that the local symmetry of the $[\text{WO}_4]$ group within the heterostructure is noticeably distorted and perceptibly perturbed when 0D CdSe QDs are anchored onto the 1D CaWO_4 nanowires, thereby resulting in the observed splitting and appearance of peaks located at 306 and 936 cm^{-1} .

Nonetheless, the overall structure of CaWO_4 appears not to be significantly altered, since the external vibrational modes (i.e. $B_g(1)$ and $B_g(3)$) of CaWO_4 are located in comparable positions to those of 1D CaWO_4 – MPA-capped CdSe QD heterostructures without any pronounced changes in the frequency ranges. This observation would presumably suggest that the inherent luminescent characteristics (i.e. the absorption and emission peaks) of CaWO_4 itself are not dramatically altered upon formation of the 1D CaWO_4 – MPA-capped CdSe QD heterostructures. We should also note that the extent of splitting of both the $A_g(1)$ and $A_g(2) + B_g(2)$ modes within unbound CaWO_4 is dependent upon the excitation wavelength and is dramatically reduced under visible light excitation (Figure S8).

3.3. Optical characterization of 1D/0D CaWO_4 - CdSe QD heterostructures

3.3.1. Absorption.

Figure 8 A and B display UV-visible extinction spectra of constituent 0D and 1D CaWO_4 nanostructures as well as of the resulting CdSe QD-metal oxide heterostructures, respectively. Control samples consisting of unbound MPA-capped CdSe QDs exhibit well-pronounced absorption peaks at ~ 565 nm, consistent with the excitonic absorption expected for QDs of this size (Figure 8). Indeed, the UV-visible spectra of both 0D and 1D based heterostructures suggest and reflect the presence of CdSe QDs on the CaWO_4 surface.

Specifically, the first exciton feature of CdSe QDs within the heterostructure is present in the extinction spectra of all of the heterostructures, appearing at ~ 565 nm (~ 2.2 eV) in MPA-capped CdSe QDs, for example (see arrows in insets to Figure 8 A and B). Nevertheless, the absorbance profile of CdSe QDs within 0D versus 1D CaWO_4 – MPA-capped CdSe QD heterostructures is less well defined. One explanation for this observation is that the overall concentrations and therefore the corresponding coverages of particulate CdSe QDs within the final, resulting 0D CaWO_4 – MPA-capped CdSe heterostructures are markedly quantitatively less than that in analogous 1D CaWO_4 – MPA-capped CdSe heterostructures, an assertion which would be consistent with our as-obtained EDS mapping results, which had been previously shown in Figures 4, 5, and S6.

3.3.2. Steady-state PL

The steady-state photoluminescence (PL) spectra of 1D/0D CaWO_4 – MPA-capped CdSe QD heterostructures are shown in Figure 9A and 9B. The PL spectrum exhibits a broad emission peak near 420 nm (~ 2.95 eV) attributable to CaWO_4 . The characteristic broad emission band of 0D/1D CaWO_4 near 420 nm (~ 2.95 eV) can be potentially assigned to the intrinsic emission of the CaWO_4 structure, which is due to the presence of charge transfer between oxygen and tungstate atoms within the anion complex WO_4^{2-} .⁴⁻⁶ Specifically, it is well

known that upon excitation from O_{2p} to W_{t2g} , the WO_4^{2-} groups effectively absorb ultraviolet irradiation within the $CaWO_4$ construct (i.e. Figures 8A, and 8B). In this excited state, the hole (on the oxygen) and the electron (on the tungsten) in WO_4^{2-} group are more likely to effectively form an exciton, due to their strong interactions, with the generation of a strong blue emission band near 420 nm (~ 2.95 eV).⁴⁻⁶

We should note that the defect-related emission attributable to typical structural defects, such as WO_3 Schottky defects and Mo^{3+} impurities,⁶⁷⁻⁷⁰ would normally be expected to be evident in the green-red spectral region. However, in our as-prepared 0D and 1D $CaWO_4$ nanostructures, we observed broad emission peaks near 420 nm and in effect, the broadness of the emission spectra of our as-prepared 1D and 0D $CaWO_4$ (i.e. FWHM ~ 130 nm) is comparable to what has been observed in prior reports (i.e. FWHM ~ 120 -140 nm).^{67, 71} Furthermore, there is no distinctive absorption feature (Figure 8) near 673 nm, which might have been potentially attributable to an oxygen vacancy.⁷² Therefore, it is much less likely that the observed emission of our 1D and 0D $CaWO_4$ herein originates from intrinsic structural defects and/or oxygen vacancies, as previously discussed. In addition, although the size of the $CaWO_4$ does not seem to induce spectral shifts,⁷³ both size and morphology have been shown to dictate relative emission intensities.⁷⁴ We should note that although both bare 0D and 1D $CaWO_4$ evinced differential absorption and emission behavior, especially with respect to intensities, these spectral data were actually obtained at identical sample concentrations, thereby insinuating a strong dependence on and highlighting the importance of surface quality.

Under identical excitation conditions at 260 nm (i.e. 4.78 eV), the emission intensity of the 0D/1D $CaWO_4$ – MPA-capped CdSe QD heterostructures is substantially reduced as compared with that of the corresponding 1D and 0D $CaWO_4$ ‘building blocks’ (Figure 9A).

Specifically, the 0D CaWO_4 -based heterostructures quench by a factor of 2.5, relative to bare CaWO_4 , and the analogous 1D CaWO_4 -based heterostructures quench by a factor of 2.2. Furthermore, in our 1D heterostructures, a reduction in the apparent lifetime from 1.3 μs for unbound CaWO_4 to 0.5 μs for the associated heterostructures (as determined from modulation data in frequency-domain measurements) has been observed, though the 0D heterostructures evinced less obvious changes.

Our data suggest that the PL quenching behavior of CaWO_4 within these QD-metal oxide heterostructures can be potentially experimentally controlled and functionally explained in light of two factors: (a) the coverage density of CdSe QDs on the underlying CaWO_4 template as well as (b) the intrinsic crystallite size of the CaWO_4 itself. *First*, (a) the PL quenching behavior of CaWO_4 appears to correlate with larger quantities of CdSe QDs bound onto CaWO_4 . Figure 9B highlights the emission spectra collected from 1D CaWO_4 – MPA-capped CdSe QD heterostructures, prepared using varying concentration ratios (i.e. $[\text{CdSe}]/[\text{CaWO}_4] = 0.5, 1, \text{ and } 1.5$) of CdSe QDs to 1D CaWO_4 and excited under 260 nm illumination. PL quenching of CaWO_4 is increasingly more evident in CaWO_4 - MPA-capped CdSe QD heterostructures prepared with ever larger and increasing quantities of CdSe QDs bound onto the underlying CaWO_4 template. In other words, the strong CaWO_4 emission at 420 nm appeared to be more effectively quenched by greater numbers of CdSe QDs bound onto CaWO_4 , i.e. with correspondingly higher concentration ratios of CdSe QDs relative to CaWO_4 from 0.5 to 1.5.

Second, (b) the PL quenching of CaWO_4 within CaWO_4 – MPA-capped CdSe QD heterostructures was observed to be more efficient and apparent with an intrinsically larger crystallite size of CaWO_4 . That is, we systematically analyzed the PL quenching behavior of 1D CaWO_4 within CaWO_4 - MPA-capped CdSe heterostructures as a function of the crystallite size

(*d*) of 1D CaWO₄. Specifically, we noted that a series of 1D CaWO₄ with increasing '*d*' = 21, 38, and 61 nm within CaWO₄-MPA-capped CdSe heterostructures quenches by a factor of 2.2, 2.7, and 3.95 greater than that relative to bare CaWO₄, respectively (Figure S9). Furthermore and potentially more interestingly, the PL quenching associated with 0D CaWO₄ (i.e. crystallite size of ~37 nm) is far more significant as compared with that of 1D CaWO₄ (i.e. crystallite size of ~21 nm) within our heterostructures despite the quantitatively lower QD surface coverage (i.e. a factor of 0.77, based on EDS mapping data) on the underlying 0D CaWO₄ 'template' as compared with the analogous 1D CaWO₄ framework (Figure 9A). We remark that all of these data had been normalized to the same concentration ratio of CdSe QDs to CaWO₄ of 1.

As discussed in Section 3.2.1, we should note that the efficiency associated with heterostructure formation is ~50% and ~40% for 1D and 0D CaWO₄-based composites, respectively. Therefore, we expect generally greater numbers of CdSe QDs attached onto 1D CaWO₄ as opposed to 0D CaWO₄ at identical [CdSe]/[CaWO₄] ratios. It is well known that the crystallite size inherently controls and is proportional to the PL quantum yield (PL QY) of luminescent materials.^{75, 76} Specifically, the crystallite size of 0D CaWO₄ (*d* ~37 nm) is larger than that of 1D CaWO₄ (*d* ~21 nm), thereby giving rise to the higher observed PL intensity of 0D CaWO₄ as compared with that of 1D CaWO₄, as shown in Figure 9A. Overall, these results indicate that though both size and coverage density represent key variables, the crystallite size is actually the more important parameter in terms of dictating the observed PL quenching behavior of CaWO₄ in our CaWO₄ – MPA-capped CdSe QD heterostructures.

Furthermore, luminescent materials possessing either higher PL output or PL QY can generate a large quantity of electrons and holes upon excitation. Therefore, increasing the number of excited charge carriers has the potential for allowing for a more efficient and effective

charge flow into neighboring acceptor materials, thereby resulting in a correspondingly more efficient PL quenching. This hypothesis is supported by previous reports on systems, such as QDs coupled with either ligand species, TiO_2 , or ZnO , respectively.⁷⁷⁻⁷⁹

Thus, we postulate that the cumulative effects of increased PL quenching and shortened lifetimes observed for the CaWO_4 within the heterostructure can be mainly attributed to charge transfer emanating from CaWO_4 to CdSe QDs. In terms of the inherent band offsets, the energy level of the conduction band edge (CB) of CaWO_4 is situated above that of CdSe QDs and MPA-ligand-coated CdSe QDs from the metal tungstate. In order to determine the nature of the trend for CaWO_4 emission quenching, the quenching behaviors for both the bare and associated heterostructured moieties were studied as a function of varying (i) quantities of CdSe QDs as well as (ii) the inherent CaWO_4 crystallite size (or morphology).

In order to examine the corresponding luminescent properties of CdSe QDs in heterostructure, the other key optically relevant species within our heterostructure, we collected PL spectra of 0D/1D CaWO_4 – MPA-capped CdSe QD heterostructures, excited at 460 nm irradiation (Figure 9C) as well as at 260 nm irradiation (Figure 9A). By contrast with the behavior of CaWO_4 in our heterostructure, there was no dramatic change observed in either the CdSe QD emission peak or its PL output within the heterostructure excited at 260 nm irradiation (Figure 9A). We should note that the PL signature of CdSe QDs within the heterostructures may overlap with the emission tails of CaWO_4 and hence, the measured total PL intensity associated with the CdSe QD peak within the heterostructures may in fact be smaller than it appears as compared with that of unbound CdSe QDs alone.

Under 460 nm excitation, the emission profile of only CdSe QDs can be obtained; the absorption of CaWO₄ is negligible due to the fact that the excitation energy at 460 nm is lower than that associated with the corresponding emission profile of CaWO₄ ($\lambda_{\text{em}} = 420$ nm). The PL intensity of unbound MPA-capped CdSe QDs is not noticeably altered in the profiles of CdSe QDs bound onto both 1D and 0D CaWO₄ structures, a finding which is also consistent with the emission profile obtained upon excitation at 380 nm irradiation (Figure S10). This assertion is confirmed by the emission decay behavior, shown in Figure 9D. Specifically, the emission decay curves of unbound CdSe QDs are not significantly different as compared with that of CdSe QDs incorporated as part of CaWO₄-based heterostructures. In fact, the average lifetimes of unbound MPA-capped CdSe QDs and of CdSe QDs immobilized within CaWO₄ – MPA-capped CdSe QD heterostructures are comparable ($\tau_{\text{av}} = 12.6 \pm 0.5$ ns), indicating there is no substantial evidence of charge transfer occurring from CdSe QDs to CaWO₄. Furthermore, we observed a similar trend with a mixture consisting of as-prepared CdSe QDs (prior to ligand exchange with MPA) physically mixed with CaWO₄, although the observed PL quenching of CaWO₄ within this sample mixture was less pronounced as compared with that noted in a chemically bound CaWO₄ - MPA-capped CdSe QD heterostructure (Figure S11).

To probe the photodegradation and photobleaching behaviors of the CdSe QDs within our CaWO₄ – MPA-capped CdSe QD heterostructures, we analyzed their optical properties (i.e. variation in the PL emission intensity and emission peak position) under UV irradiation as a function of irradiation time (Figure S12). Following prolonged UV irradiation of the CaWO₄ – MPA-capped CdSe QD heterostructures, we were able to observe a continuous shift in the emission wavelength accompanied by an overall decrease in emission intensity of CdSe QDs. Specifically, the emission wavelength is gradually blue-shifted from 580 nm (at 0 h of

illumination) to 547 nm (at 3 h of illumination). This emission wavelength blue-shift can be potentially attributed to irreversible photo-oxidation of CdSe QDs, and this type of scenario has already been discussed extensively in earlier studies.⁸⁰⁻⁸² Moreover, the PL emission intensity of CdSe QD exponentially decreases as a function of UV irradiation time with only 36% of the initial peak intensity preserved after 3 h of exposure time. We attribute the observed photobleaching of CdSe QDs within CaWO_4 – MPA-capped CdSe QD heterostructures to (1) the generation of non-radiative defect recombination sites during the photooxidation as well as to (2) the presence of electron transfer from the excited CaWO_4 into the conduction band of CdSe QDs under UV irradiation. A more detailed study of the photobleaching mechanism is beyond the scope of the current work.

We do note that it is still possible for energy transfer from CaWO_4 to CdSe QDs to take place under 260 nm excitation, since the spectral overlap between the emission of CaWO_4 ($\lambda_{\text{em}} = 420$ nm) and the absorption of MPA-capped CdSe QDs ($\lambda_{\text{abs}} = 400\text{-}565$ nm) is not negligible. However, the energy transfer efficiency would appear to be very low, since there is no distinctive difference between the emission intensity associated with unbound CdSe QDs and that of CdSe QDs bound within the heterostructure motif under 260 nm excitation (Figure 9A). To accurately determine in detail the role and behavior of photoinduced charge carriers emanating from CdSe QDs under 260 nm excitation, femtosecond transient absorption and time-resolved PL upconversion experiments will likely be needed in comprehensive future studies.

3.4. Data Interpretation in terms of Energy Level Alignments

To understand all of these experimental observations, the respective energy level alignments of CaWO_4 , MPA, and CdSe QDs need to be considered. In effect, Figure 10 shows

the schematic diagram of the energy levels associated with all of these species, i.e. CaWO_4 , MPA, and CdSe QDs. Recently, Longo et al. and others have studied and reported on the electronic level structure of bulk and nanocrystalline forms of CaWO_4 , based on the use of both experimental techniques (TEM and HRTEM) and *ab initio* theoretical calculations.^{6, 83} Based on this work, it is reasonable to assert that the conduction band (CB) of CaWO_4 (i.e. -1.4 eV relative to the vacuum level) is located above the corresponding CB of MPA (i.e. ~ 1.8 eV), the linking agent connecting CaWO_4 with CdSe QDs as well as the CB of CdSe QDs (i.e. -4.4 eV relative to the vacuum level⁵⁰). This scenario should therefore be conducive to inducing luminescence quenching as well as a diminution of the lifetime value of CaWO_4 within CaWO_4 - MPA-capped CdSe QD heterostructures as a result of electron transfer occurring from CaWO_4 to CdSe QDs, when the CaWO_4 motifs are optically excited, as shown in Figure 9A and 9B.

That is, it is energetically favorable for the excited electrons in the CB of CaWO_4 produced upon UV illumination (i.e. 260 nm) to flow into the corresponding CB of CdSe QDs in a non-radiative manner using MPA as a mediating linker, prior to the recombination of these excited electrons with the corresponding holes associated with CaWO_4 and the valence band (VB) of MPA. Conversely, under visible light (i.e. 460 nm) illumination, photoinduced holes generated in the CdSe QDs can readily and efficiently trap within the MPA linker, not only because of the relatively low electronegativity of thiols in MPA but also due to the correspondingly higher VB level of MPA (e.g. -5.5 eV⁸⁴) as compared with that of CdSe QDs (e.g. -6.1 eV). However, the photoinduced holes are not likely to flow into CaWO_4 due to the noticeably lower VB of CaWO_4 (e.g. -7.1 eV), thereby resulting in little if any reduction of the PL signal in CdSe QDs incorporated within heterostructure motifs, which is consistent with what we in fact observed.

3.5. Confirmation with NEXAFS Measurements

In order to further confirm the presence of electron transfer from CaWO_4 to MPA-capped CdSe QDs and thereby explain the PL quenching and shortened lifetimes of CaWO_4 within the heterostructure, we acquired the NEXAFS spectra of 1D CaWO_4 – MPA-capped 0D CdSe QD heterostructures as well as of MPA-capped CdSe QDs. Specifically, the NEXAFS spectra associated with the Cd $M_{2,3}$ edge of the 1D CaWO_4 – MPA-capped 0D CdSe QD heterostructures and with MPA-capped 0D CdSe QDs are shown in Figure 11A. The Cd $M_{2,3}$ edges can be used to probe the bottom of the CB in CdSe QDs, since both theory and calculation suggest that the bottom of the CB is predominantly composed of the Cd 5s state. Indeed, the Cd $M_{2,3}$ edges provide insight into the transition between the initial 3p state and the unoccupied 5s states, which follows typical dipole transition selection rules.⁴⁵

Interestingly, the partial electron yield (PEY) intensity of 1D CaWO_4 - MPA-capped CdSe 0D QD heterostructures in acquired Cd $M_{2,3}$ edge spectral data is noticeably reduced and the peak itself is shifted to lower photon energy as compared with that of MPA-capped CdSe QDs alone. Importantly, the PEY intensity is proportional to the unoccupied electronic density of states.⁸⁵⁻⁸⁷ Hence, the reduction in the number of unoccupied states associated with the CB in MPA-capped CdSe QDs within CaWO_4 - MPA-capped CdSe QD heterostructures as compared with the corresponding conduction band of unbound MPA-capped CdSe QDs (Figure 11 A) is suggestive of an increase in the number of electrons in the Cd 5s states (the CB of CdSe QDs) within the heterostructure, thereby providing for direct evidence of electron transfer occurring from CaWO_4 to CdSe QDs. Furthermore, a peak shift to lower photon energy within the heterostructure confirms that the CB associated with the CdSe QDs acts as an electron acceptor.

In general, the nature of the peak shift depends on the local chemical and electronic environment of the unpaired electron. A shift to higher binding energy likely signals the donation of electrons, whereas a shift to lower energy is more indicative of electron acceptor behavior.^{86, 88,}

⁸⁹ We should note that the reduction of the PEY intensity accompanied by a peak shift of MPA-capped CdSe QDs within the 0D CaWO₄ - MPA-capped CdSe 0D QD heterostructures is more pronounced than the analogous effects associated with 1D CaWO₄-based heterostructures. This overall observation implies that electron transfer from 0D CaWO₄ to MPA-capped 0D CdSe QDs is likely to be more efficient than that between the corresponding 1D CaWO₄ and 0D CdSe QDs, an assertion which is consistent with the optical PL data previously shown in Figure 9A.

O *K* edge NEXAFS spectra (Figure 11B) additionally support the idea of electron transfer from CaWO₄ to MPA-capped CdSe QDs. Specifically, peaks ‘b’ (532.1 eV) and ‘e’ (538.1 eV) correspond to the transition from the oxygen 1s to the π^* state of C=O and the σ^* state of C-O, respectively, with the peak intensity itself proportional to the unoccupied electronic density of states associated with the MPA ligands,⁸⁵⁻⁸⁷ consisting of SH (bound to CdSe) and of COOH (bound to CaWO₄) species. We find that the intensities of peak ‘b’ and ‘e’ are significantly reduced when the MPA ligands capped onto CdSe QDs are anchored onto CaWO₄ and that these intensities are further reduced for 0D CaWO₄-based heterostructures. Thus, we can infer that (a) MPA is likely acting as an electron acceptor within the heterostructure configuration, an idea consistent with the picture presented in Figure 10, and that (b) electron transfer from 0D CaWO₄ to MPA is likely more efficient than the corresponding process from 1D CaWO₄ to MPA.

We should note that the absence of the OH peak (i.e. peak ‘d’, 534.9 eV) within the heterostructure reveals that COOH groups were likely replaced by carboxylate groups due to the chemical generation of the heterostructure through the adsorption of COOH groups onto CaWO₄,

an assertion which is consistent with the FT-IR spectra (Figure 6). Furthermore, peaks ‘a’ (i.e. 530.7 eV for 1D and 530.2 eV for 0D), ‘c’ (i.e. 533.0 eV for 1D and 531.8 eV for 0D), and ‘f’ (i.e. 538.9 eV for 1D and 538.3 eV for 0D) can be assigned to transitions associated with $1s - e^*$ and $1s - t_2^*$ for W-O and $1s - 3d$ for Ca-O, respectively, associated with CaWO_4 . It is known that the O $2p$ states within W-O bond mainly affect the behavior of the valence band of CaWO_4 , as is apparent from complementary measurements and calculations.⁹⁰⁻⁹²

Hence, based on all of our data, it is reasonable to postulate that the PL quenching behavior coupled with the reduction in lifetimes of 1D/0D CaWO_4 within 1D/0D CaWO_4 - MPA-capped CdSe QD heterostructured composites can be viewed collectively as a consequence of electron transfer from CaWO_4 to CdSe QDs. It is still possible that energy transfer contributes to some extent by directly quenching a fraction of the photogenerated carriers within CaWO_4 . However, in order to determine its precise role and moreover, to quantify the relative contributions of charge versus energy transfer between CaWO_4 and CdSe QDs in the overall observed optical behavior, femtosecond transient absorption and time-resolved PL upconversion experiments will likely be needed in future studies.

4. Conclusions

Pre-formed CdSe semiconducting 0D nanocrystals ($d \sim 4$ nm) have been successfully attached onto self-activated luminescent CaWO_4 metal oxide (i) 1D nanowires, possessing very high-aspect ratios (i.e. ~ 230 nm in diameter and ~ 3 μm in length) and (ii) 0D nanoparticle ($d \sim 73$ nm) by means of electrostatic interaction between the ligands (MPA) bound to the CdSe QDs and the external surfaces of 1D/0D CaWO_4 structures. In so doing, we have created a new class of heterostructures by taking advantage of and functionally combining two distinctive types of

materials, whose intrinsically interesting individual optical behaviors primarily derive from their inherent structure, i.e. 0D QDs coupled with luminescent metal oxide tungstates. That is, by contrast with much of the prior literature, we are not relying on using dopants but rather on precisely tuning structural nuances of the constituent nanoscale components themselves to generate the ensuing novel optical characteristics of our resulting nanomaterials.

From a photophysical perspective, the resulting nanoscale 1D and 0D CaWO_4 – MPA-capped CdSe QDs heterostructures were found to display PL quenching and shortened lifetimes of 0D/1D CaWO_4 as compared with unbound CaWO_4 , due to photoexcited charge transfer occurring from CaWO_4 to CdSe QDs. This assertion has been confirmed using NEXAFS measurements as manifested in both (i) a reduction in the intensity of PEY at the conduction band of CdSe QDs along with (ii) a peak shift to lower photon energy, as compared with unbound QDs, based on studies of our heterostructure motifs. Conversely, there was no significant difference in the PL outputs and lifetimes of CdSe QDs incorporated within our as-prepared heterostructures as compared with unbound CdSe QDs.

This noticeable difference in optical behavior between CaWO_4 and CdSe QDs can be explained by the relative energy level alignment between CaWO_4 and CdSe QDs. Specifically, the CB of CaWO_4 is situated significantly higher than that of the corresponding CB levels of the MPA linker and that of CdSe QDs, thereby resulting in favorable electron transfer from CaWO_4 to CdSe QDs through the intermediary MPA agent. On the other hand, the VB of MPA-capped CdSe QDs is located noticeably above that of CaWO_4 , which is not necessarily ideal for photoinduced charge transfer from CdSe QDs to CaWO_4 .

Furthermore, PL quenching of CaWO_4 within our as-produced heterostructures is more pronounced and directly correlated with increasing amounts of CdSe QDs and with the larger

intrinsic crystallite size, associated with a higher PL QY, of CaWO_4 . Interestingly though, the observed PL quenching of 0D CaWO_4 is greater than that of 1D CaWO_4 within as-synthesized CaWO_4 – MPA-capped CdSe QD heterostructures, despite the slightly lower coverage and quantity of CdSe QDs attached and bound onto the underlying 0D versus 1D CaWO_4 templates. We ascribe such unexpected behavior mainly to the higher PL output and PL QY associated with the larger crystallite size of 0D CaWO_4 , which in turn generates more photoinduced charge carriers, thereby resulting in greater PL quenching as compared with the 1D CaWO_4 motif.

Overall, we propose that understanding and clearly delineating charge and energy transfer processes in our model CaWO_4 - CdSe QD heterostructures are fundamentally important for understanding the optoelectronic behavior of nanomaterial interfaces. Moreover, the implication of our studies is that we can enable not only the potential to design new types of photocatalytic architectures under various irradiation conditions but also the ability to tune the optoelectronic properties of nanomaterials for possible incorporation into functional nanoscale devices.

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Supporting Information Available

Additional structural characterization and lifetime data of our samples are presented.

This material is available free of charge via the Internet at <http://www.acs.org>.

Figure 1. (top to bottom) XRD patterns of as-prepared CaWO₄ nanoparticles (NP) as well as of 200 nm and 50 nm template-derived CaWO₄ nanowires (NW). The corresponding JCPDS No. 72-1624 database standard for bulk CaWO₄ is also shown as a comparison.

Figure 2. Representative TEM images at lower and higher magnifications of as-prepared CaWO_4 (A, C) 1D nanowires and (B, D) 0D nanoparticles, respectively.

Figure 3. Representative (A and B) TEM and (C and D) HRTEM images and corresponding SAED patterns (insets C and D), associated with the formation of CaWO₄ 1D/0D – MPA-capped CdSe QD heterostructures, respectively. Yellow circles in (A) and (B) highlight regions pertaining to CdSe QDs. In (C) and (D), ‘QD’ designates CdSe QDs reflections whereas ‘NW’ and ‘NP’ denote the corresponding CaWO₄ 1D nanowire and 0D nanoparticle reflections, respectively.

Figure 4. (A) Dark-field STEM image recorded on adjoining 1D CaWO_4 – MPA-capped CdSe QD nanoscale heterostructures. (B) – (F). Elemental EDS mapping of the same region of nanowires, highlighting the overlapping spatial chemical distribution of Ca (bright blue), W (blue), O (dark yellow), Cd (bright red), and Se (green-yellow), respectively. The scale bar is 2 μm in every image.

Figure 5. (A) Dark-field STEM image recorded on adjoining 0D CaWO_4 – MPA-capped CdSe QD nanoscale heterostructures. (B) – (F). Elemental EDS mapping of the same region of nanowires, highlighting the overlapping spatial chemical distribution of Ca (bright blue), W (blue), O (dark yellow), Cd (bright red), and Se (green-yellow), respectively. The scale bar is 200 nm in every image.

Figure 6. FT-IR spectra of (i) MPA-capped CdSe QDs, (ii) 1D CaWO_4 , and (iii) 1D CaWO_4 – MPA-capped CdSe QD heterostructures in the range of (A) 4000-500 cm^{-1} and (B) 1800-500 cm^{-1} .

Figure 7. Raman spectra of 1D CaWO_4 and of 1D CaWO_4 – MPA-capped CdSe 0D QD heterostructures, excited at 785 nm. Each spectra was normalized to a highest intensity of 1.

Figure 8. UV-visible spectra of (A) 0D CaWO₄ nanoparticles (NP), MPA-capped CdSe QDs, and 0D CaWO₄ NP – MPA-capped CdSe QD heterostructures, as well as of (B) 1D nanowires (NW) CaWO₄ and 1D CaWO₄ NW - MPA-capped CdSe QD heterostructures, respectively. The insets to (A) and (B) highlight the magnified spectral range near the absorption peak of MPA-capped CdSe QDs.

Figure 9. PL emission spectra of (A) CaWO₄ 0D nanoparticles (NP), CaWO₄ 1D nanowires (NW), MPA-capped CdSe QDs, 1D CaWO₄ – MPA-capped CdSe QD heterostructures, and 0D CaWO₄ – MPA-capped CdSe QD heterostructures, respectively, excited at 260 nm. Corresponding PL emission spectra of (B) 1D CaWO₄ – MPA-capped CdSe QD heterostructures prepared at various concentration ratios of [CdSe QDs] / [CaWO₄] (namely at 0.5, 1, and 1.5 respectively), excited at 260 nm. The 370 nm long wave path filter was used to obtain spectra shown in (A) and (B). PL emission spectra of (C) MPA-capped CdSe QDs, 1D CaWO₄ – MPA-capped CdSe QD heterostructures, 0D CaWO₄ – MPA-capped CdSe QD heterostructures, respectively, excited at 460 nm irradiation. (D) PL decay curves ($\lambda_{ex} = 388$ nm) associated with the excitonic emission of MPA-capped CdSe QDs, 1D CaWO₄ – MPA-capped CdSe QD heterostructures, and 0D CaWO₄ – MPA-capped CdSe QD heterostructures, respectively. Arrows in (A) and (B) indicate PL quenching behavior, attributed primarily to charge transfer processes occurring between CaWO₄ and CdSe QDs.

Figure 10. Electronic energy diagram of CaWO_4 – MPA–capped CdSe QD heterostructures and the corresponding charge transfer schematics in these materials. e^- = electron, h^+ = hole, E_g = band gap, CB = conduction band, and VB = valence band.

Figure 11. (A) Cd $M_{2,3}$ edge and (B) O K -edge partial electron yield spectra of both 1D/0D CaWO_4 – MPA-capped CdSe 0D QD heterostructures as well as of MPA-capped CdSe QDs, respectively. All of the spectra have been pre- and post-edge normalized.

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