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Supporting Information for "Morphology and dopant-dependent optical characteristics of novel composite 1D and 3D-based heterostructures of CdSe nanocrystals and LaPO₄: Re (Re = Eu, Ce, Tb) metal phosphate nanowires"

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Figure S1. XRD patterns of as-prepared CdSe QDs (top, black) and the corresponding JCPDS No. 08-0459 database standard for bulk CdSe (bottom, red).



Figure S2. FT-IR spectra of LaPO₄: Eu nanostructures, possessing different morphologies and processed at varying post-annealing temperatures.



Figure S3. Representative lower magnification SEM image of LaPO₄: Eu 3D urchin-like architectures.



Figure S4. Representative SEM images of LaPO₄: Eu heterostructures, prepared by solution-precipitation protocols in the presence of varying molar precursor ratios of La/P, set at (A) 0.5, (B) 0.75, (C) 1, and (D) 1.5. Reaction times for all samples shown were held constant at 2 h.



Figure S5. Representative TEM images of LaPO₄: Eu fabricated using a solutionprecipitation approach in the presence of (A) 3-mercaptopropioic acid and (B) 11mercaptoundecanoic acid, respectively.



Lsec: 171.1 0 Cnts 0.000 keV Det: Apollo XLT SUTW Det Reso



Figure S6. EDS spectra and quantitative elemental analysis data for AET-capped CdSe-LaPO₄: Eu (A) 3D urchin-like and (B) 1D nanowire-based heterostructures.

Calculation of coverage density of CdSe QDs on 1D and 3D LaPO₄ structures

The number of anchored dots on either the single LaPO₄ nanowire or 3D structures can be estimated by the following Equation S1.

$$\frac{W_{LaPO_4}}{W_{LaPO_4} + nW_{CdSe}} \approx wt\% \text{ of } LaPO_4 \text{ in heterostructure (S1)}$$

wherein W_{LaPO4} = weight of either a single LaPO₄ nanowire or 3D LaPO₄ heterostructure, W_{CdSe} = weight of a CdSe QD, n = the number of QDs attached onto the underlying LaPO₄, and *wt% of LaPO₄ in heterostructure* are all obtained either directly or indirectly by examining the results of the EDS spectrum and corresponding EDS mapping.

Based on the EDS spectrum, the 3D-based heterostructures consist of nearly 92.3 wt % for LaPO₄: Eu, and 7.7 wt% for CdSe QDs (Figure S6A). The volume of one 3Dbased heterostructure of LaPO₄: Eu is 5.1×10^{-14} cm³ (with $r_{3D-LaPO4:Eu} \sim 230$ nm, as obtained by TEM analysis), assuming that the 3D structure can be visualized as a perfect sphere. Hence, the weight of a single 3D LaPO₄ is equal to 2.63×10^{-13} g (assuming a density of LaPO₄ = 4.19 g/cm³)¹. On the other hand, the volume of a single CdSe QD is 5.03×10^{-20} cm³ (with $r_{CdSe} \sim 2.29$ nm, as obtained by TEM). Assuming the density of CdSe is equal to 5.82 g/cm³, the as-obtained weight of a single CdSe QD is 2.93×10^{-19} g. Hence, from all of these weight values, we calculate that the number of quantum dots ('*n*') attached onto a single discrete 3D LaPO₄: Eu structure is estimated to be 6.1×10^4 QDs, according to Equation S1.

Based on the EDS spectrum, the 1D-based heterostructures consist of nearly 97.5 wt % for LaPO₄: Eu and 2.5 wt% for CdSe QDs (Figure S6B). By analogy, assuming a 1D nanowire can be represented as a very thin rectangular tube with a thickness of 1 nm, the corresponding volume of 1D LaPO₄: Eu can be computed to be 8.03×10^{-18} cm³,

based on a nanowire length of \sim 1100 nm and corresponding width of 7.3 nm, as determined from TEM data. Therefore, using equation S1, we were able to calculate that \sim 2.94 QDs are attached onto a single individual 1D LaPO₄: Eu nanowire.

In order to reasonably compare coverage densities, we need to normalize for the same volume of 1D and 3D heterostructures incorporating LaPO₄: Eu. Since the volume of 1D LaPO₄: Eu ($8.03 \times 10^{-18} \text{ cm}^3$) is nearly four orders of magnitude smaller than that of the corresponding 3D structure ($5.17 \times 10^{-14} \text{ cm}^3$), upon normalization to identical volumes (i.e. to (100 nm)³) of 1D and 3D structures, we calculated that 1193 QDs (e. g. ($6.1 \times 10^4 \times (100 \text{ nm})^3/((5.17 \times 10^{-14} \text{ cm}^3))$) were attached onto 3D LaPO₄ urchin-like structures, whereas only 367 QDs (e. g. ($2.94 \times (100 \text{ nm})^3/((8.03 \times 10^{-18} \text{ cm}^3))$) were immobilized onto analogous 1D LaPO₄ nanowires under comparable reaction conditions.



Figure S7. FT-IR spectra of LaPO₄: Eu 1D nanowire structures, AET capped CdSe QDs, and CdSe QD-LaPO₄: Eu 1D nanowire heterostructures.



Figure S8. UV-visible spectra of AET capped CdSe QDs, LaPO₄: Eu 3D urchin-like structures, 1D LaPO₄: Eu nanowires, AET capped CdSe QD - LaPO₄: Eu 3D urchin-like heterostructures, and AET capped CdSe QD - LaPO₄: Eu 1D nanowire-based heterostructures.



Figure S9. PL emission spectra of AET capped CdSe QDs, normalized LaPO₄: Eu, AET capped CdSe QD - LaPO₄: Eu 3D urchin-like heterostructures, and AET capped CdSe QD - LaPO₄: Eu 1D nanowire-based heterostructures within the magnified region of 650-750 nm under 380 nm excitation.

Table S1. Kinetic parameters and emission decay analysis associated with CdSe QDs, CdSe QD-LaPO₄: Eu 1D-nanowire heterostructures, CdSe QD-LaPO₄ 3D-based heterostructures, CdSe QD-LaPO₄: Eu 3D-based heterostructures, CdSe QD-LaPO₄: Ce 3D based heterostructures, and CdSe QD-LaPO₄: Tb 3D-based heterostructures.

	т ₁ (ns)	T ₂ (ns)	т _з (ns)	a1	a	a ₃	T _{av} (ns)	X ²
CdSe QDs	5.146	23.82	1.133	0.044	0.0041	0.1634	7.3	1.19
CdSe QD-1D LaPO₄: Eu	3.63	20.8	0.699	0.021	0.0011	0.2633	3.2	1.18
CdSe QD-3D LaPO₄: Eu	4.22	23.0	0.8615	0.034	0.0022	0.217	5.1	1.21
CdSe QD-3D LaPO₄: Ce	2.893	18.4	0.542	0.0075	0.0003	0.18	1.8	1.06
CdSe QD-3D LaPO₄: Tb	4.32	20.5	0.9183	0.0396	0.0033	0.1751	5.7	1.20
CdSe QD-3D LaPO ₄	3.21	13.95	0.756	0.0266	0.0013	0.2248	2.4	1.16

Tri-exponential decay kinetics were noted to be satisfactory for the determination of emission lifetimes (τ_i). These values were then used to estimate the corresponding average lifetimes (τ_{av} (or $\langle t \rangle$)) associated with the CdSe emission decay, using the following Equations S2 and S3.^{2, 3}

> $F(t) = a_1 \exp\left(-\frac{t}{\tau_1}\right) + a_2 \exp\left(-\frac{t}{\tau_2}\right) + a_3 \exp\left(-\frac{t}{\tau_3}\right)$ Equation S2 $\left\langle t\right\rangle = \frac{\sum a_i \tau_i^2}{\sum a_i \tau_i}$

Equation S3

References

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