

Supporting Information for

**'Probing Charge Transfer in a Novel Class of Luminescent
Perovskite-Based Heterostructures Composed
of Quantum Dots Bound to RE-Activated CaTiO₃ Phosphors'**

Crystal S. Lewis¹, Haiqing Liu¹, Jinkyu Han², Lei Wang¹,

Shiyu Yue¹, Nicholas A. Brennan¹, and Stanislaus S. Wong^{1,2*}

¹Department of Chemistry, State University of New York at Stony Brook,
Stony Brook, NY 11794-3400

²Condensed Matter of Physics and Materials Sciences Department,
Brookhaven National Laboratory, Building 480; Upton, NY 11973

*To whom correspondence should be addressed.

Email: Stanislaus.wong@stonybrook.edu; sswong@bnl.gov

Phone: 631-632-1703; 631-344-3178

#	Precursors (Ratio is 1: 1 unless otherwise noted)	Titanium Precursor	Temp (°C)	Surfactant (mL)	Time (hr)	Cooling Rate (°C/min)	Product (composition, morphology, size)
Molten Salt Method							
<i>(Titanium precursor): Pr doped sample</i>							
A	Calcium Oxalate and TiO ₂	P25 TiO ₂	820	No surfactant	3.5	Natural cooling	
B	Calcium Oxalate and TiO ₂	P25 TiO ₂	820	No surfactant	3.5	Quenched	Avg. Diam.: Increased cubic morphology
C	Calcium Oxalate and TiO ₂	P25 TiO ₂	820	NP-9 (1.75 mL)	3.5	Natural cooling	Avg. Diameters: 54 ± 13 nm 50% cubes vs. 50% spheres – Pure CaTiO ₃
D	Calcium Oxalate and TiO ₂	P25 TiO ₂	820	NP-9 (2.33 mL)	3.5	Natural cooling	Pure CaTiO ₃
E	Calcium Oxalate and TiO ₂	P25 TiO ₂	820	Triton X- 100	3.5	Natural cooling	Pure CaTiO ₃
F	Calcium Oxalate and Bulk TiO ₂	Bulk TiO ₂	820	Triton X- 100	3.5	Natural cooling	Average Diameters: 210 ± 22 nm 100% Roughened particles – Pure CaTiO ₃
G	Calcium oxalate and TiO ₂	P25 TiO ₂	820	Triton X- 100	3.5	Natural cooling	Pure CaTiO ₃
H	Calcium Oxalate and TiO ₂	5 nm TiO ₂ NPs	820	NP-9	3.5	Natural cooling	Avg. Diameters: 56 ± 33 nm 30% cubes vs. 70% particles – Pure CaTiO ₃
<i>Eu doped sample</i>							
1	Calcium Oxalate and 2% Europium Nitrate	Bulk TiO ₂	820	Triton X- 100	3.5	Natural cooling	Average Diameters: 210 ± 32 nm 100% Roughened particles – Pure CaTiO ₃
2	Calcium Oxalate and 4% Europium Nitrate	Bulk TiO ₂	820	Triton X- 100	3.5	Natural cooling	Average Diameters: 220 ± 26 nm 100% Roughened particles – Pure CaTiO ₃

3	Calcium Oxalate and 6% Europium Nitrate	Bulk TiO ₂	820	Triton X-100	3.5	Natural cooling	Average Diameters: 290 ± 35 nm 100% Roughened particles – Pure CaTiO ₃
Hydrothermal Method							
#	Precursor Ratios (1M NaOH unless otherwise noted)	Ti precursor	Temp. (C)	Surfactant	Time	Cooling	Product (composition, morphology, size)
F	0.25 Ca(OH) ₂ Stock Solution	Ti foil	130	No surfactant	4	Natural cooling	Avg. Diameters: 278 ± 87 nm Large aggregates of CaTiO ₃ -- with TiO ₂ and CaO ₄ impurities
G	0.5 M CaCl ₂ – 30 mL for 4 hours	Ti foil	180	No surfactant	4	Natural cooling	Avg. Diameters: 178 ± 87 nm Cubes - No CaTiO ₃ -- with TiO ₂ and CaO ₄ impurities – Irreproducible!!
H	0.5M CaCl ₂ – 10 mL		180	No surfactant	4	Natural cooling	Avg. Diam.: 500 ± 154 nm Microspheres with CaO ₄ impurity-- without HCl wash
I	0.25 CaCl ₂ – 10 mL		180	No surfactant	4	Natural cooling	Avg. Diam.: 380 ± 140 nm Microspheres with reduced intensity of CaO ₄ impurities-- without HCl wash
J	0.25 CaCl ₂ – 10 mL		180	No surfactant	10	Natural cooling	Avg. Diam.: 500 ± 45 nm Microspheres with reduced intensity of CaO ₄ impurities-- without HCl wash

Table S1. Detailed reaction parameters and product descriptions for all reactions conducted using both the molten salt and hydrothermal methods for preparing Pr doped-CaTiO₃ micron-scale spheres.

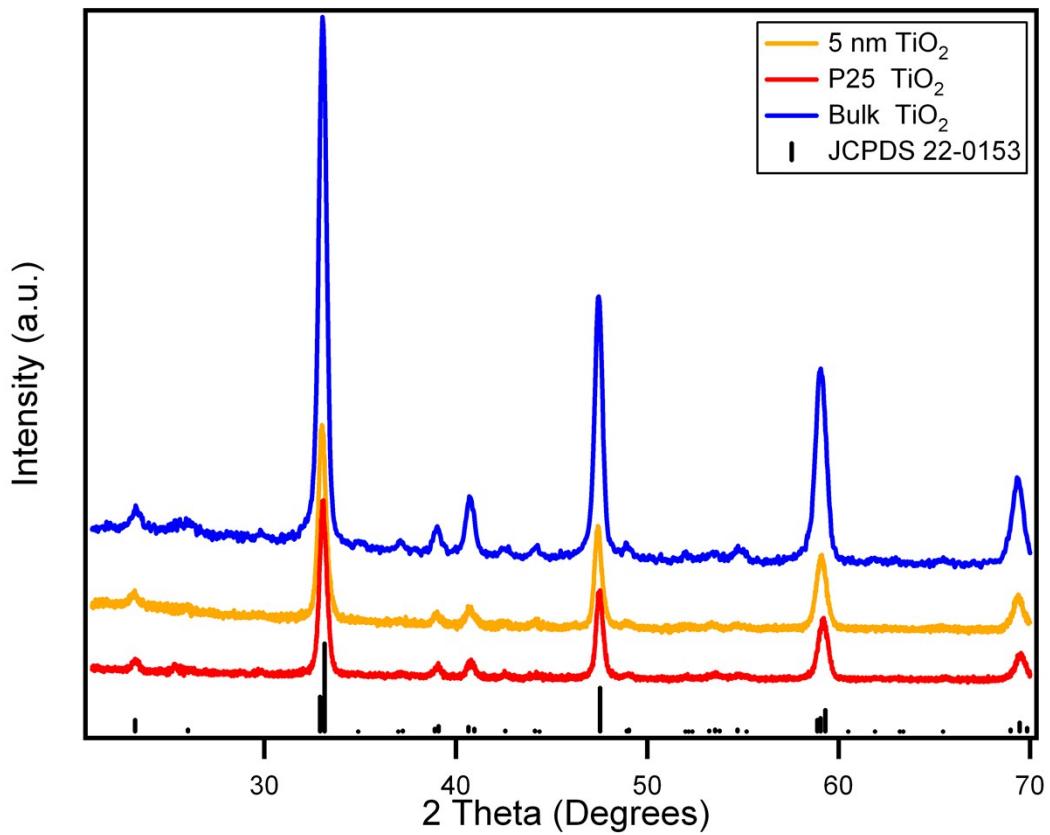


Figure S1. XRD results for samples, prepared using the molten salt method with various titanium precursors.

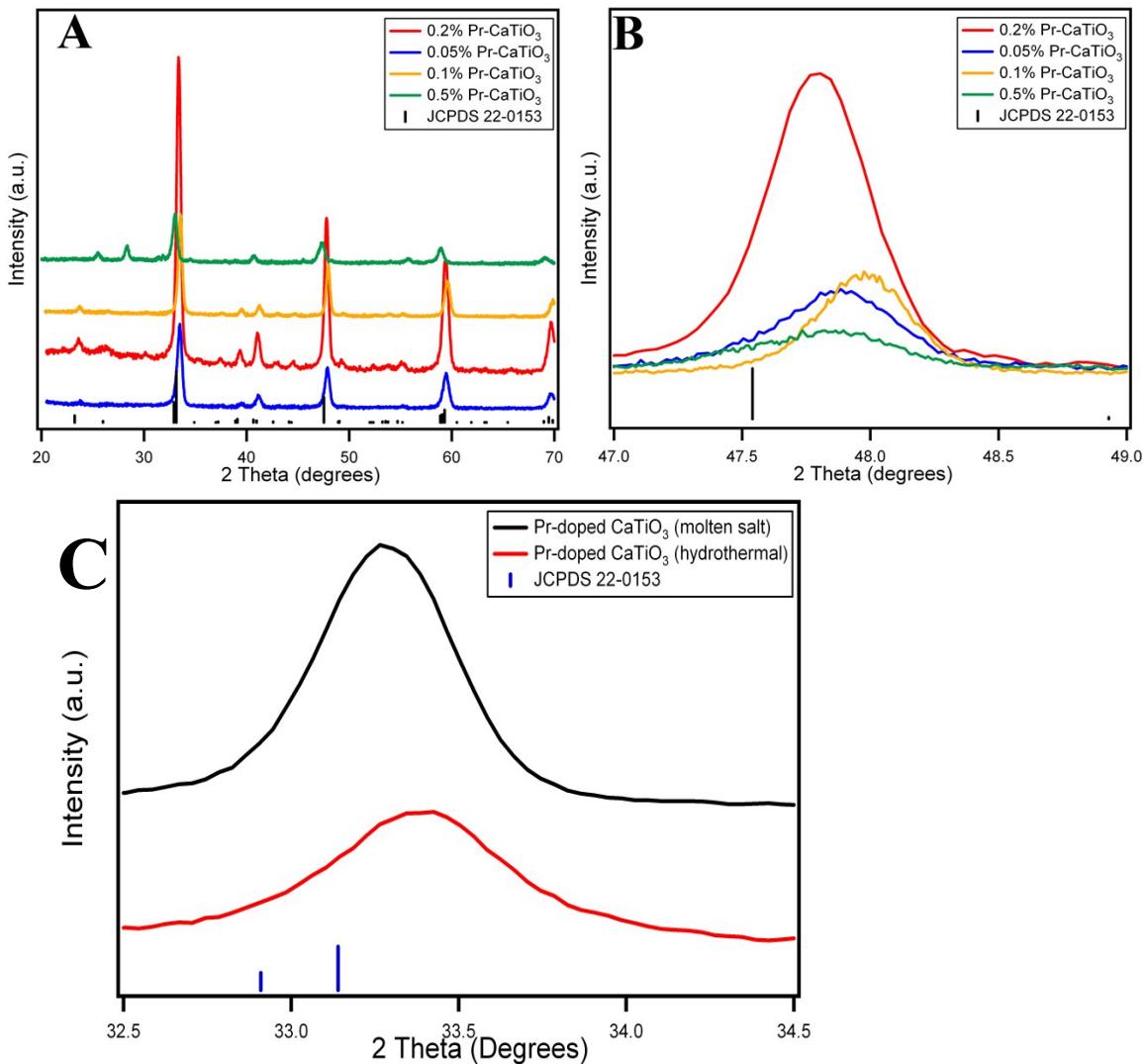


Figure S2. X-Ray Diffraction patterns of (A) 0.2%, 0.05%, 0.1%, and 0.5% Pr-doped CaTiO₃; associated peak shifts (B) for a signal centered at a 2θ value of ~47 degrees; as well as peaks shifts (C) for the molten salt-prepared (black) and hydrothermally-generated (red) 0.2% Pr-doped CaTiO₃ samples, centered at a 2θ value of ~33 degrees.

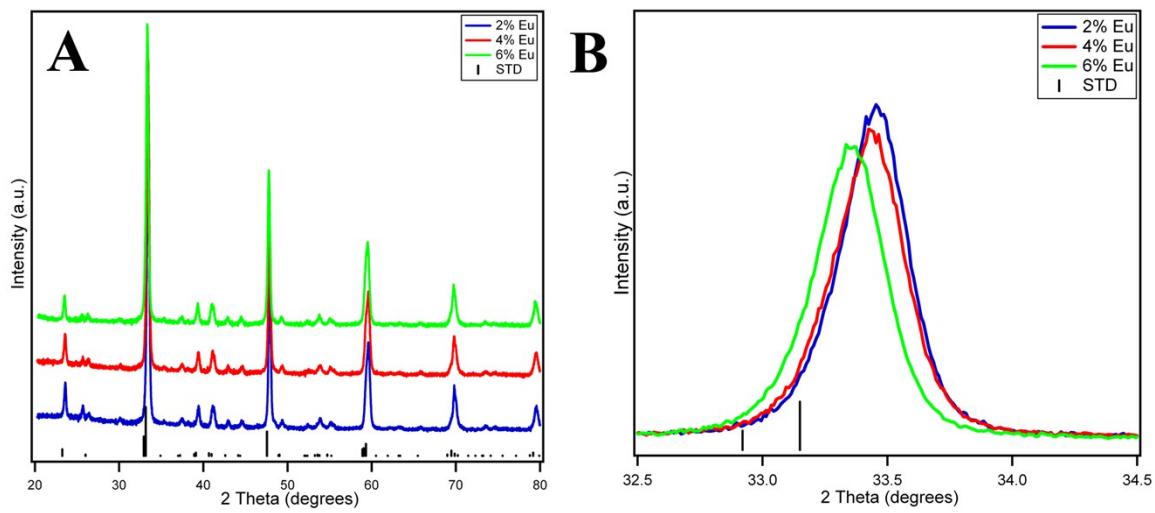


Figure S3. X-Ray Diffraction patterns of (A) 0.2%, 0.05%, 0.1%, and 0.5% Eu-doped CaTiO_3 and associated peak shifts for a signal centered at a 2θ of ~ 33 degrees.

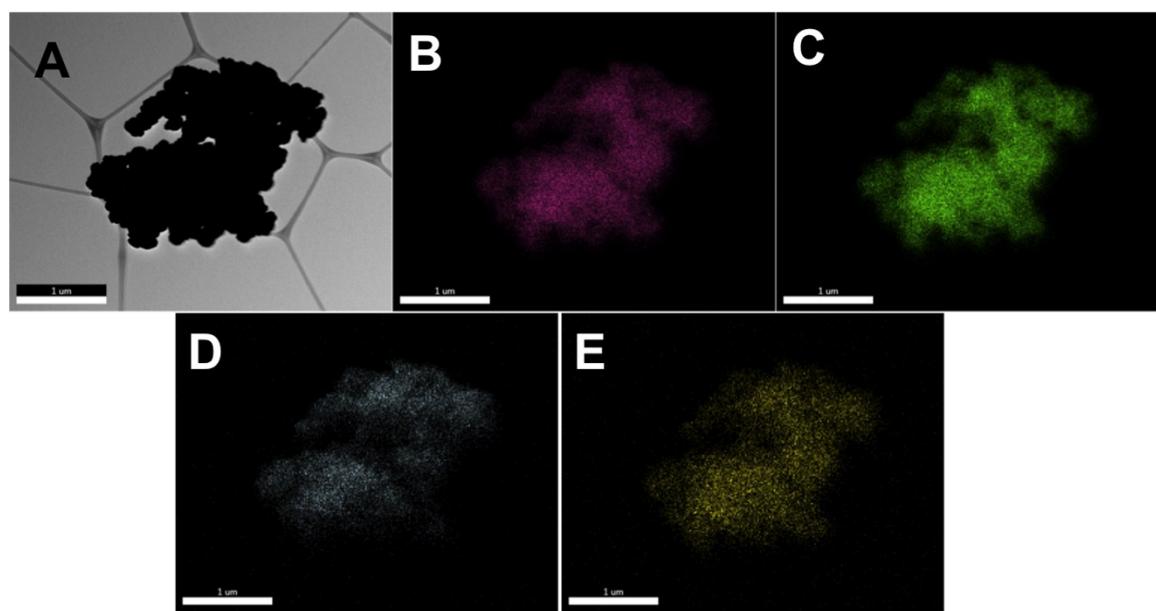


Figure S4. (A) Dark-field STEM image of CdSe QDs anchored onto CaTiO₃: Pr heterostructures. Elemental mapping of the same region, as measured by energy dispersive X-ray spectroscopy, highlighting the spatial elemental distribution of (B) Ca, (C) Ti, (D) O, and (E) Pr, respectively. Scale bar is 1 μm for each image.

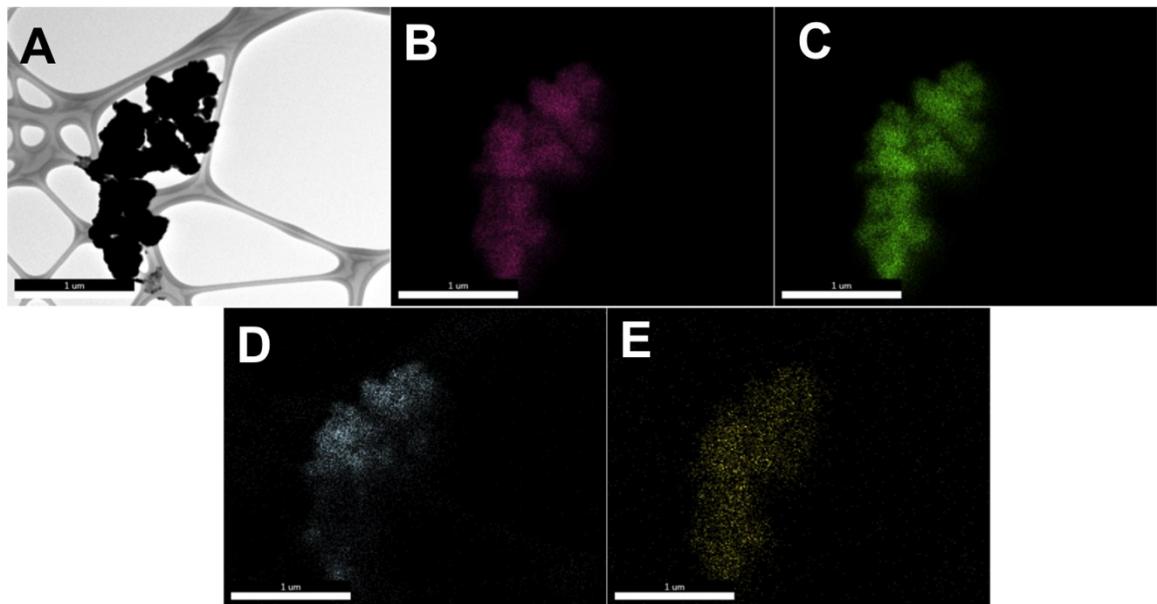


Figure S5. (A) Dark-field STEM image of CdSe QDs anchored onto CaTiO_3 : Eu heterostructures. Elemental mapping of the same region, as measured by energy dispersive X-ray spectroscopy, highlighting the spatial elemental distribution of (B) Ca, (C) Ti, (D) O, and (E) Eu, respectively. Scale bar is 1 μm for each image.

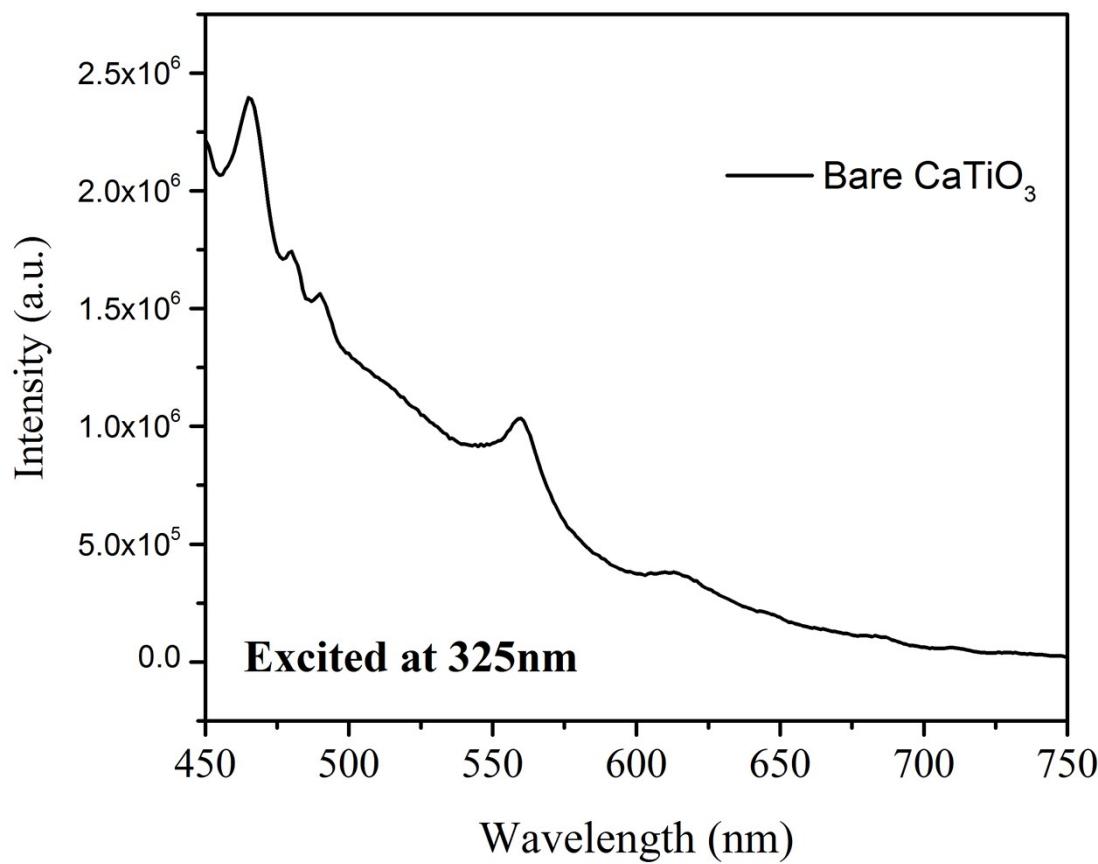


Figure S6. Photoluminescence emission profile of bare CaTiO_3 .

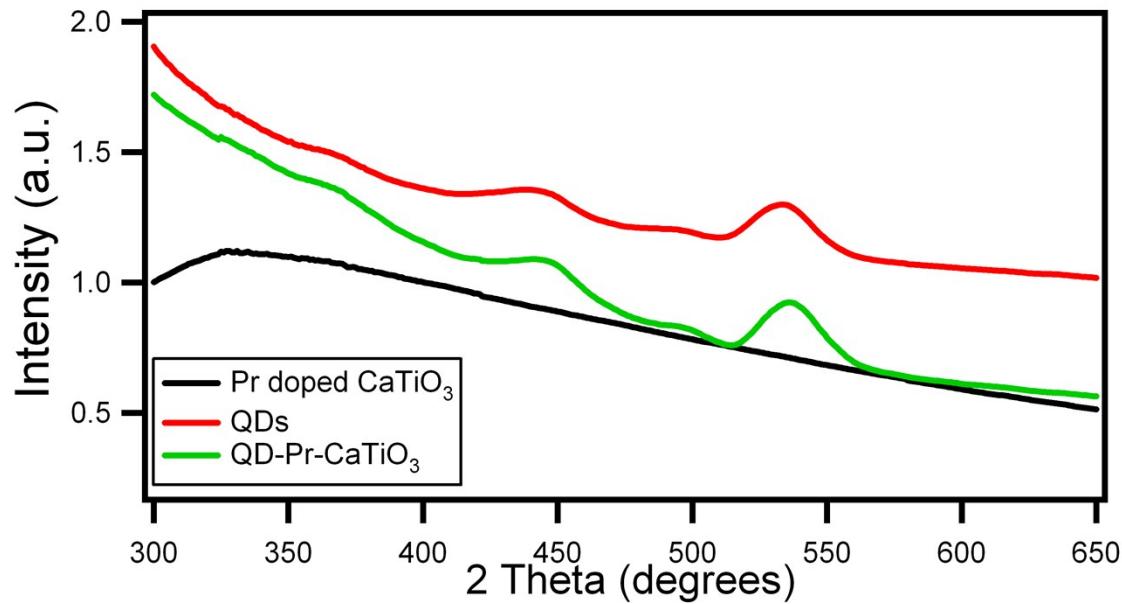


Figure S7. UV-visible spectra of Pr doped CaTiO₃, bare CdSe QDs, and Pr-doped CaTiO₃ structures, decorated with CdSe QDs.

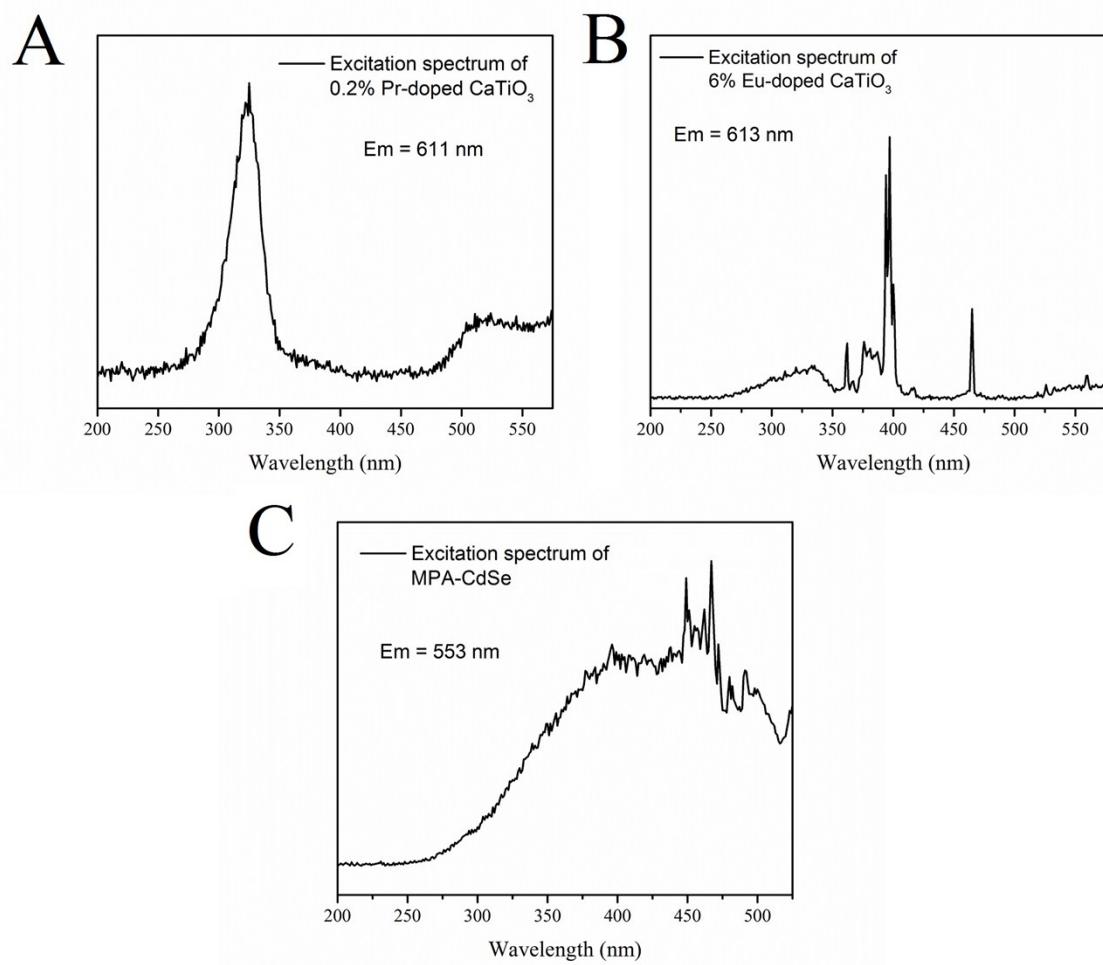


Figure S8. Excitation spectra of Pr-doped CaTiO_3 , Eu-doped CaTiO_3 , and MPA-capped CdSe QDs. Emission data were acquired at their respective emission peak positions.

Table S2. BET surface area analysis of as-prepared samples of lanthanide ion-doped CaTiO₃

Name	Surface Area (m ² /g)
Pr-CaTiO ₃ : MSS (molten salt syn.) method	8.79
Pr-CaTiO ₃ : Hydrothermal method	51.9
Eu-CaTiO ₃ : MSS (molten salt syn.) method	9.56