

A general strategy for semiconductor quantum dot production

[Supplementary information]

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Experimental section

Materials

Sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$), lead acetate ($\text{C}_4\text{H}_6\text{O}_4\text{Pb} \cdot 3\text{H}_2\text{O}$), cadmium acetate ($\text{C}_4\text{H}_6\text{O}_4\text{Cd}$), copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), and anhydrous zinc acetate ($\text{C}_4\text{H}_6\text{O}_4\text{Zn}$) were purchased from Aladdin Industrial Corporation. Porous anodic alumina (PAA) (0.02 μm pore size) filter membranes were purchased from Whatman. N-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), and Tetraethyl orthosilicate (TEOS) were purchased from Shanghai Macklin Biochemical Co., Ltd. Tetrahydrofuran (THF), acetone, isopropanol (IPA), ethanol, and aqueous ammonia (25.0-28.0%) were purchased from Beijing Chemical Works. All of the materials were used as received. Deionized water was used in the experiments.

Synthesis of semiconductor bulk materials

Simple chemical precipitation was used for the synthesis of semiconductor bulk materials. Briefly, Na_2S was dissolved in water to prepare solution A (0.5 mol/L), and the metal precursor (such as $\text{C}_4\text{H}_6\text{O}_4\text{Pb}$, $\text{C}_4\text{H}_6\text{O}_4\text{Cd}$, CuCl_2 , FeCl_2 , and $\text{C}_4\text{H}_6\text{O}_4\text{Zn}$, etc.) was dissolved in water to prepare solution B (0.5 mol/L). Then, solution A was dropped to solution B with stoichiometric ratio of 1:1, resulting in immediate precipitation. After the complete precipitation, the precipitate was centrifuged (6000 rpm, 30 min) (Centrifuge, Z32 HK, HERMLE) and washed for several times. After drying, the semiconductor bulk materials (dried powders) were obtained.

Production of the QD dispersions and powders

The Stoeber process was used to synthesize monodisperse silica microspheres (approximately 450 nm in diameter).¹ The bulk materials (0.7 g), silica microspheres (7 g) and agate balls (70 g, 3mm in diameter) were put together in an agate jar for ball-milling (Planetary ball mill, QM-3SP04, Nanjing LaiBu Technology Industry Co., Ltd) at 500 rpm for 8 h. After ball-milling, the powder mixture was separated from the agate balls by the screen mesh (pore size 1 mm). The as-separated mixture was dispersed in single or mixed solvents (ethanol for PbS, NMP and IPA (volume ratio

1:1) for CdS, NMP and water (volume ratio 1:1) for CuS, and water for FeS and ZnS) with concentration of approximately 55 mg/mL (for PbS and CuS, 27.5 mg/mL) for sonication (Vibra-Cell Ultrasonic Liquid Processor, VCX800, SONICS) at 160 W for 5 h. After sonication, silica microspheres were removed by centrifugation at 1500 rpm for 30 min (for PbS, 1000 rpm for 30 min). The upper 2/3 liquid was vacuum-filtered through the PAA filter membrane (pore size is 0.02 μm). The filtrate was collected as the QD dispersions. By high-speed centrifugation (10000 rpm, 30 min), the QDs were precipitated from the initial dispersion. After drying, the QD powders were collected. By simple sonication (160 W, 1 h), the as-collected QD powders could be redispersed in a wide range of solvents (e.g., H₂O, ethanol, IPA, acetone, THF, DMF, NMP).

Fabrication of the QDs -PMMA hybrid thin films

The QDs-PMMA thin films were fabricated through solution processing. In brief, PMMA was dissolved in NMP to form highly concentrated solution A (150 mg/mL) (note that stirring and heating were required). Meanwhile, the QD powders were dispersed in NMP to form highly uniform dispersion B (5 mg/mL) (note that sonication was required). Solution A and dispersion B were mixed to satisfy the (desired) loading content and the (constant) total weight simultaneously (note that stirring and sonication were required). The mixture with known volume was dropped into a PTFE mold (a 8 μm thick polyimide film as the releasing layer). After removal of the solvent by heating at 70 °C overnight, the QDs-PMMA hybrid thin films were obtained.

Characterization

Scanning electron microscopy (SEM) images were acquired using a Hitachi SU8220 microscope. Transmission electron microscopy (TEM) images and high-resolution TEM (HRTEM) images were acquired using a FEI Tecnai G2 F20 U-TWIN microscope operated at 200 kV. Atomic force microscopy (AFM) images were acquired using a Bruker MultiMode 8 AFM using SCANASYST-AIR cantilevers with a nominal tip radius of 2 nm in a scanasyst mode. Zeta potential measurements were conducted using a Malvern Zetasizer Nano ZS analyzer. X-ray diffraction (XRD) patterns were recorded using D/Max-TTRIII (CBO) with Cu K α radiation ($\lambda =$

1.54056 Å). Raman spectra were recorded using a Renishaw inVia plus spectrometer with a 514 nm laser. X-ray photoelectron spectroscopy (XPS) measurements were conducted using an ESCALAB 250Xi electron spectrometer from VG Scientific with 300 W Al K α radiation. UV-vis-NIR absorption spectra were recorded using a Lambda 950 spectrophotometer from PerkinElmer. Photoluminescence (PL) measurements were conducted using a HORIBA Jobin Yvon NanoLog-TCSPC spectrofluorometer with varying excitation wavelengths. Nonlinear absorption measurements were performed with 100 fs pulses from a Coherent Astrella regenerative amplifier. The laser was operated at 800 nm wavelength with a pulse repetition rate of 1 kHz. All photographs were acquired with a digital camera.

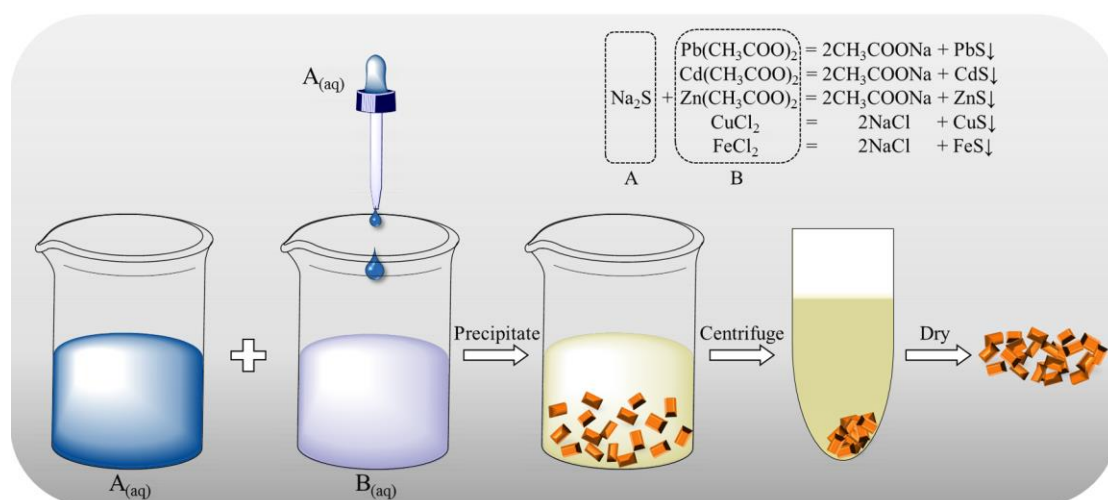


Figure S1. Schematic illustration of the synthesis of semiconductor bulk materials.

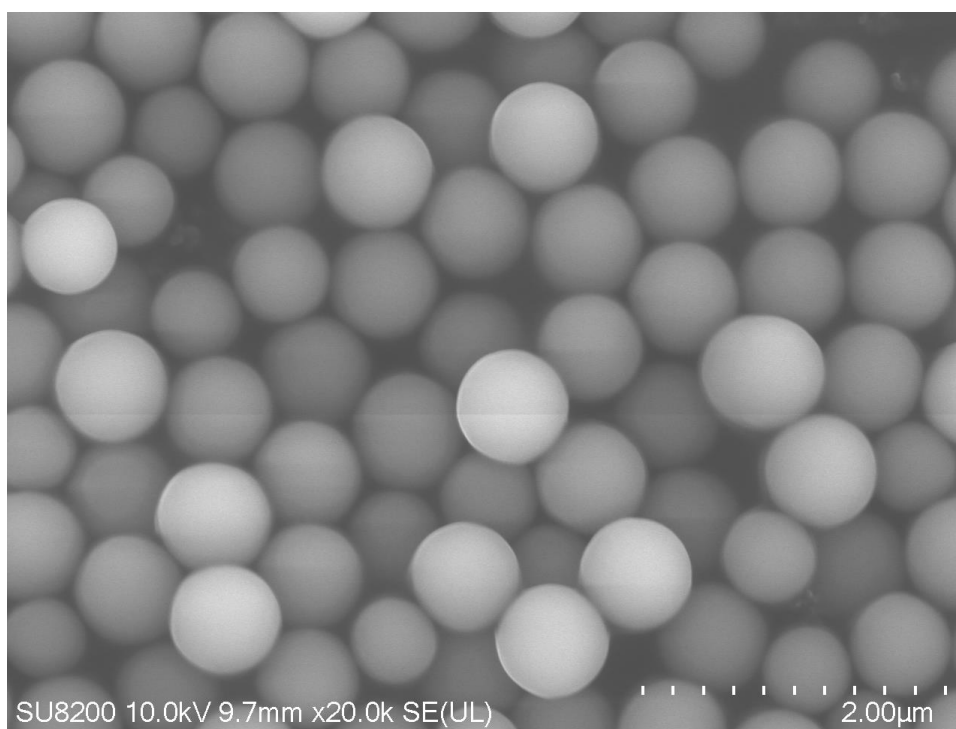


Figure S2. SEM image of the as-synthesized silica microspheres.

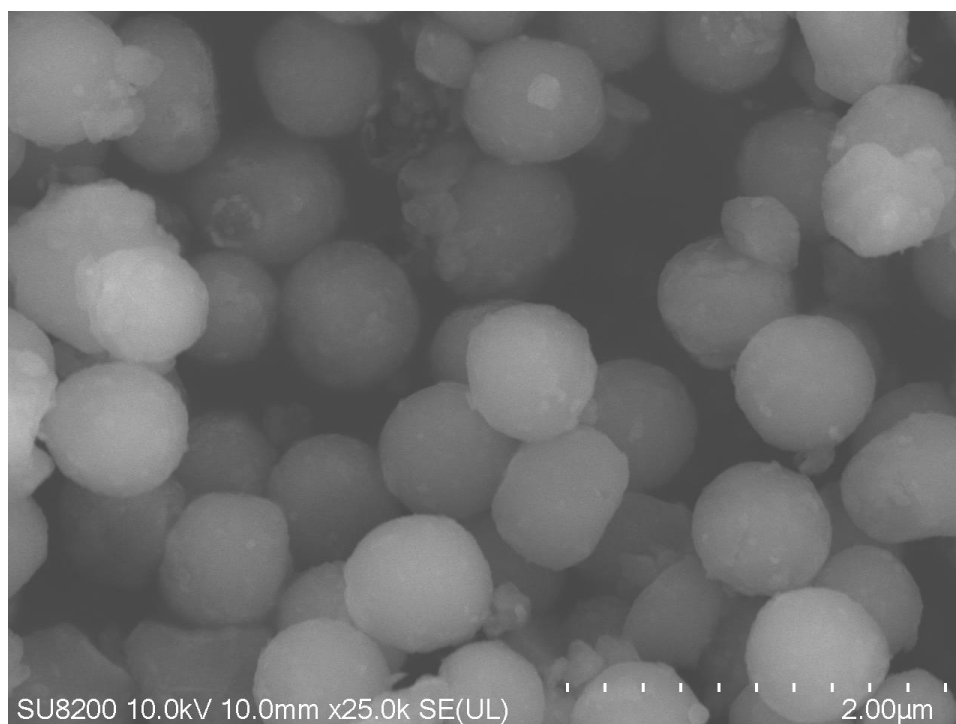


Figure S3. SEM image of the silica microspheres during ball-milling.

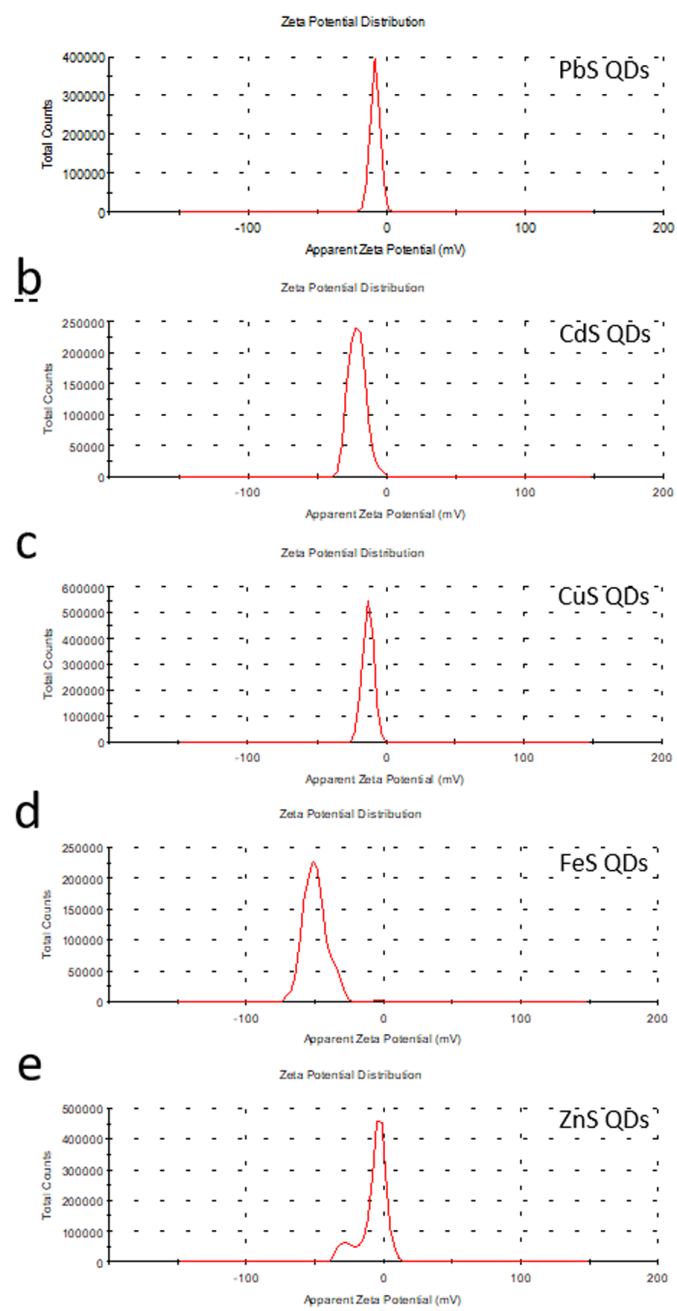


Figure S4. Zeta potentials of the QD aqueous dispersions. The concentration is fixed at 0.1 mg/mL.

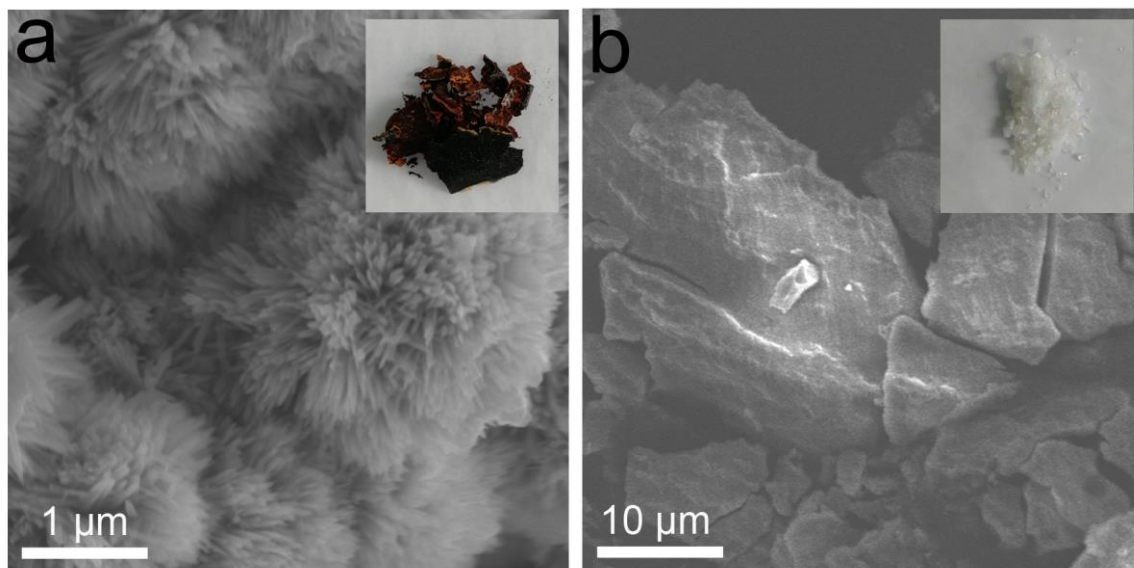


Figure S5. SEM images of FeS (a) and ZnS (b) bulk materials (insets showing the photographs of powders).

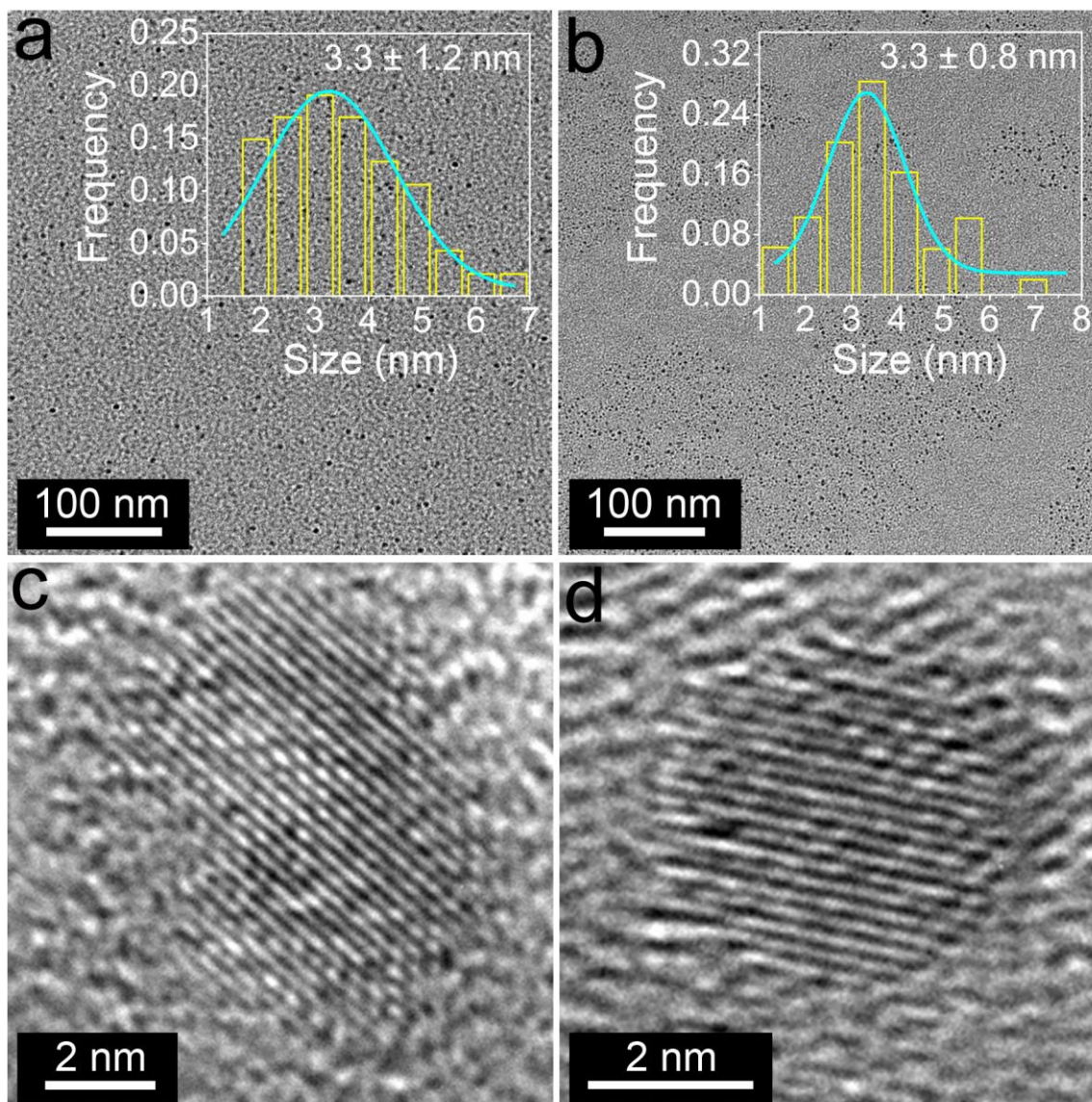


Figure S6. TEM images of FeS QDs (a) and ZnS QDs (b) (insets showing the size distributions). HRTEM images of FeS QDs (c) and ZnS QDs (d).

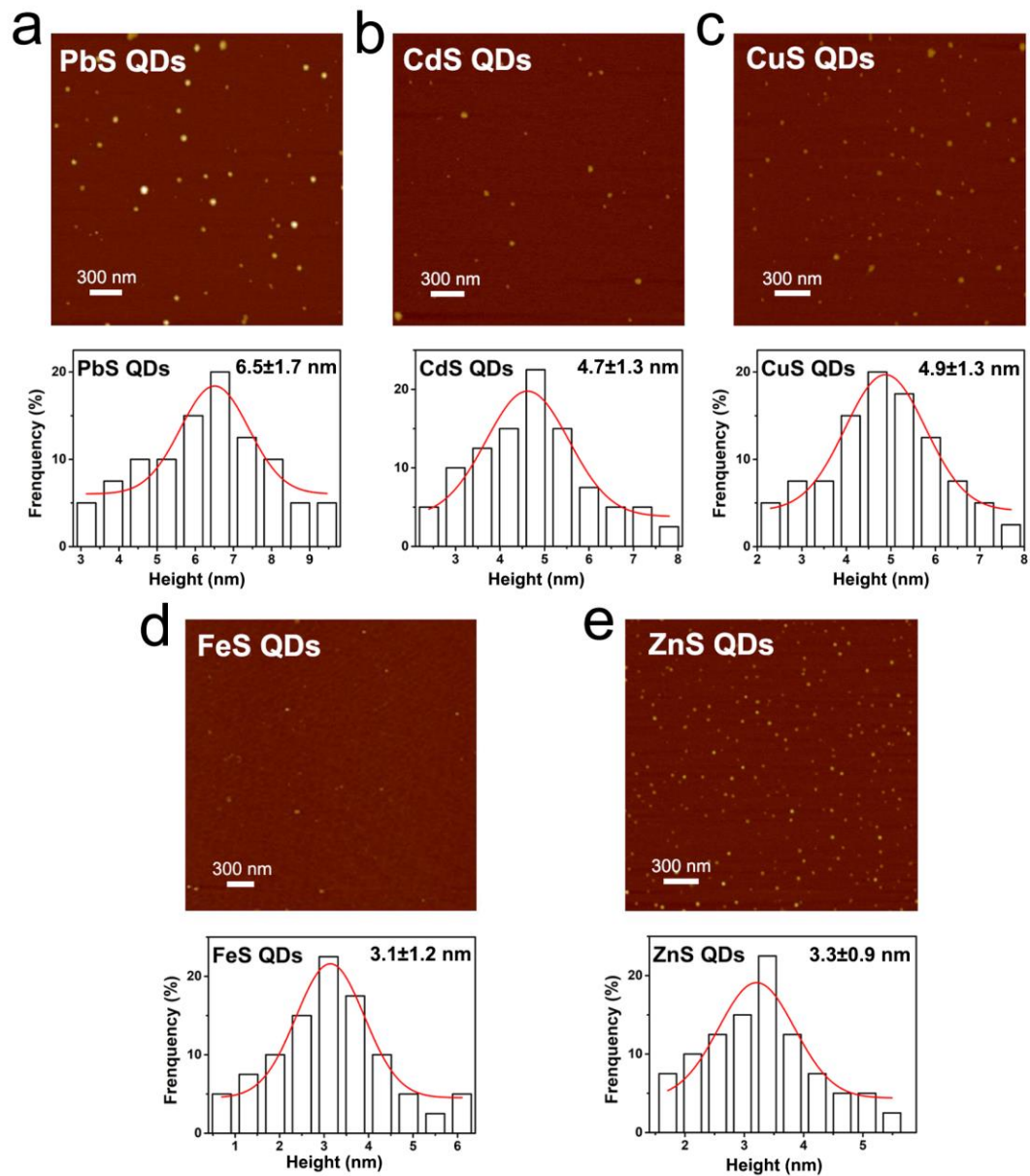


Figure S7. AFM images (top) and corresponding height distributions (bottom) of PbS QDs (a), CdS QDs (b), CuS QDs (c), FeS QDs (d), and ZnS QDs (e).

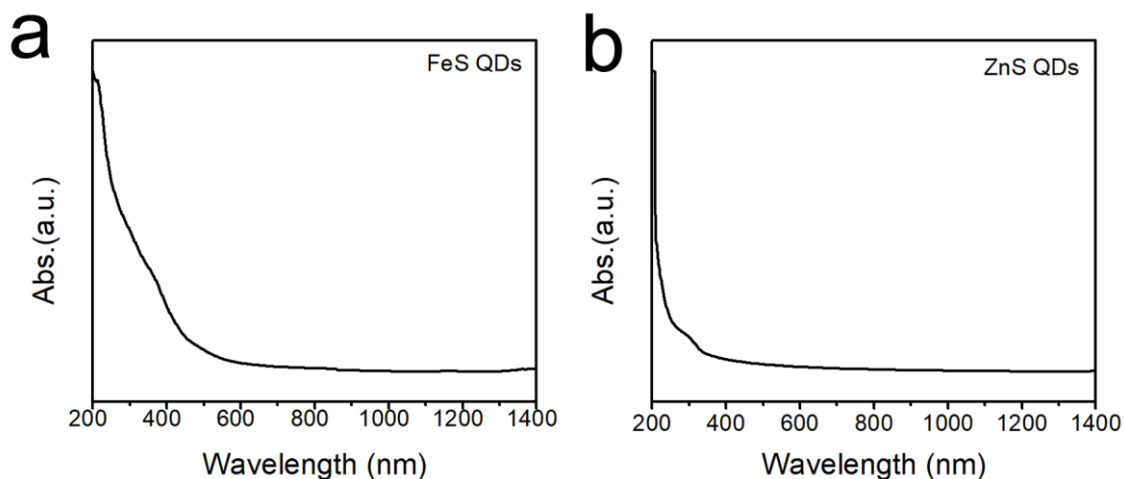


Figure S8. UV-vis-NIR absorption spectra of FeS QDs (a) and ZnS QDs (b).

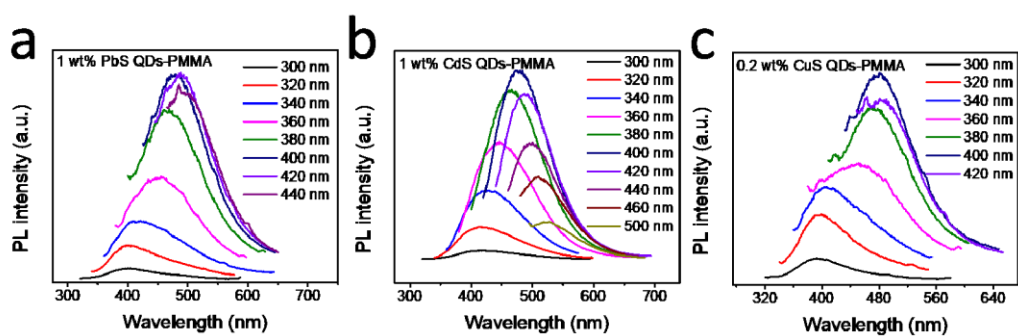


Figure S9. PL spectra of the QDs-PMMA thin films with varying excitation wavelengths.

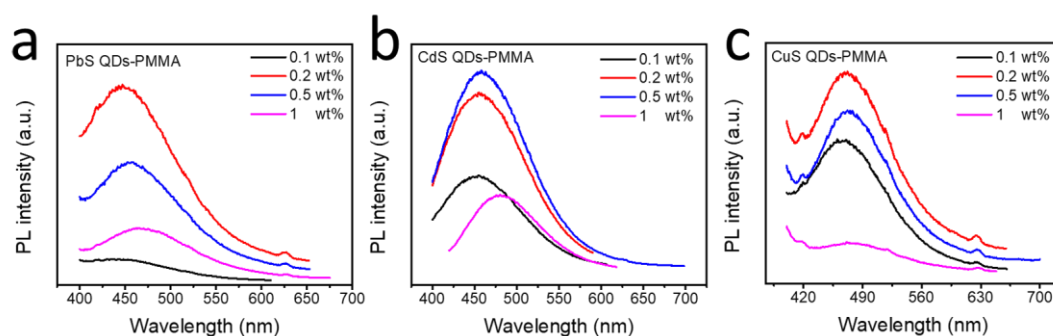


Figure S10. PL spectra of the QDs-PMMA thin films with varying loading contents.

The excitation wavelength was fixed at 360 nm.

Table S1. Comparison of the PL performances of CdS QDs prepared via different methods.

Method	Solvent	Diameter	Excitation wavelength	Emission wavelength	PLQY	PL lifetime	References
one-pot reaction	1-tetradecanol	4.9 nm	350 nm	452 nm	52 %	-	2
one-pot aqueous route	water	12.3 nm	360 nm	495 nm	-	15.9 ns	3
room-temperature solution synthesis	hexane	11.6 nm	-	500-675 nm	4.9 %	-	4
low-temperature aqueous route	water	2.1 nm	365 nm	500 nm	32 %	114 ns	5
biogenic synthesis	ethanol	3-5 nm	410 nm	670 nm	-	-	6
purchased	toluene	3.8 nm	375 nm	390 nm	-	5.34 ns	7
silica-assisted ball-milling and sonication-assisted solvent treatment	NMP	4.9 nm	440 nm	593 nm	-	11.4 ns	this work

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