

Supplementary Information

Deterministic Positioning of Few Aqueous Colloidal Quantum Dots

Muhammad Tegar Pambudi^{#,1,2,3}, Deepshikha Arora^{,#,2}, Xiao Liang⁴, Basudeb Sain^{2,5},
Anupama Sargur Ranganath², Matthew R. Chua¹, Cam Nhung Vu², Golnoush Zamiri², Md.
Abdur Rahman², Hilmi Volkan Demir^{*,4,6,7}, Joel K. W. Yang^{*,2}, Lu Ding^{*,1}*

[#]These authors made equal contributions to this work

¹Institute of Materials Research and Engineering (IMRE), Agency for Science, Technology and Research (A*STAR), 2 Fusionopolis Way, Innovis #08-03, Singapore 138634, Republic of Singapore

²Engineering Product Development, Singapore University of Technology and Design, Singapore 487372, Singapore

³School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798, Singapore

⁴LUMINOUS! Center of Excellence for Semiconductor Lighting and Displays, The Photonics Institute, School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798, Singapore

⁵Department of Atomic and Molecular Physics, Manipal Academy of Higher Education, Manipal, Karnataka 576104, India

⁶Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371

⁷UNAM-Institute of Materials Science and Nanotechnology, The National Nanotechnology Research Center, Department of Electrical and Electronics Engineering, Department of Physics, Bilkent University, Bilkent, Ankara, 06800, Turkey

*Corresponding Author

EXPERIMENTAL METHOD

Materials

Cadmium oxide (CdO) (99.9%), myristate acid (99%), zinc acetate [Zn(Ac)₂] (99.99%), 1-octadecene (ODE), selenium (Se) (99.99% trace metals basis), sulfur (S) (99.98% trace metals basis), oleic acid (OA) (90%), trioctylphosphine (TOP) (90%), 1-dodecanethiol (DDT) (98%), IGEPAL CO-520, tetraethyl orthosilicate (TEOS) (99.999%), ammonium hydroxide solution (28~30 wt%), cyclohexane, toluene, hexane, and ethanol were purchased from Sigma Aldrich.

Synthesis of Bare CdSe/CdS/Cd_xZn_{1-x}S QDs

Precursors for the synthesis of the QDs of 0.5 M Cd(OA)₂ and 0.5 M Zn(OA)₂ were prepared by dissolving the 100 mmol of CdO and Zn(Ac)₂ in solvent mixture of 100 mL of OA and 100 mL of ODE under Ar gas at 300 °C for 1 hour. The solutions of 2 M TOP-Se and 2 M TOP-S were prepared by dissolving 20 mmol of Se and S in 10 mL of TOP, respectively. CdSe/CdS/Cd_xZn_{1-x}S QDs were synthesized according to the procedures reported in the literature¹ with some modifications. Typically, 1 mmol of CdO, 3 mmol of myristate acid, and 15 mL of ODE were mixed in a three-neck flask and heated to 300 °C under Ar gas protection to form a clear solution. After that, 0.25 mL of 2 M TOP-Se was rapidly injected into the reaction flask to form CdSe core. After growing for 3 minutes, 1 mmol of DDT was added drop wisely within 1 min to initiate the medium CdS shell growth. After 30 min, 2 mL of 0.5 M Cd(OA)₂, 4 mL of 0.5 M Zn(OA)₂, and 1.5 mL of 2 M TOP-S were added into the reaction flask within 1 min for Zn_xCd_{1-x}S shelling and the reaction proceeded for 10 minutes. The final product with a PL peak at 640 nm and a near-unity

quantum yield of >99% was obtained after precipitation by ethanol and redispersion of the QDs in hexane.

Silica Coating of Bare QDs

The silica encapsulation of the bare QDs was carried out using a procedure adapted from our previous research². Briefly, 10 mL of cyclohexane and 1.2 g of IGEPAL CO-520 were mixed at room temperature. Subsequently, approximately 30 mg of the bare QDs is precipitated from hexane then dispersed in 300 μ L of toluene were introduced into the above mixture followed by 120 μ L of TEOS added and stirred continuously. After 20 minutes, the reaction was initiated by introducing 300 μ L of ammonium hydroxide solution, and the condensation was allowed to progress for 48 h. Then, the silica-coated QDs were separated from the microemulsion by adding 2 mL of ethanol, followed by centrifugation at 6000 rpm for 3 minutes. The resulting product, silica-coated QDs, was rinsed with ethanol and dispersed in 10 mL water for further use. See Supplementary Information for design consideration for silica-coated QDs used in this study.

Colloidal QDs Characterization

The PL spectra of the bare QDs and silica-coated QDs were measured from a spectrofluorophotometer (Shimadzu, RF-5301PC) with an excitation wavelength of 380 nm. The absorption spectra of the above QDs and silica-coated QDs were recorded by an ultraviolet-visible spectrophotometer (Shimadzu, UV-1800). The quantum yields of the above QDs and silica-coated QDs were recorded from an integrating sphere by calculating the ratio between the absolute emission and absorption photons. The TEM images of the above QDs and silica-coated QDs were

obtained using a transmission electron microscope (TEM, JEOL 2100F) with an acceleration voltage of 200 KV.

PMMA Template Fabrication

Si substrate was cleaned with O₂ RF plasma (JLS Designs) at 30 mT and 150 W for 30 seconds. The positive photoresist of polymethyl methacrylate (950 PMMA A2, MicroChem) was then spin-coated at 6000 rpm for 60 seconds for a thickness of around 60 nm and baked for 5 minutes at 180 °C. Electron beam lithography (Raith E-Line Plus) was performed to make circular hole array templates with various sizes. Finally, the template was developed in a cold 1:3 MIBK/IPA solution (Kayaku) for 1 minute with sonication, then blow-dried before cleaving into ~1x1 cm² substrate for deposition.

QDs Template-Assisted Deterministic Deposition

A setup of a 250 mL beaker with a 50 mL beaker placed upside-down inside and lid-closed with aluminum foil was used for saturated vapor deposition. A piece of glass slide was placed to provide a flat surface for the as-fabricated template. Ethanol was filled into the big beaker as the source of volatile solvent vapor. A total of 10 µL of aqueous QDs was drop-casted on the top of the template and left to dry for at least 12-24 hours. As the QDs drive into the hole, a thin film of QDs also forms on the top of the developed PMMA. The PMMA/QDs thin film was then lifted off with 4 hours of immersion in 70°C of acetone followed by 3 minutes of ultrasonication and blow-dried for further characterization. Statistical analysis used images taken from a field emission scanning electron microscope (FESEM, Jeol 7600F) with prior deposition of Pt/Pd layer by sputtering to avoid the charging effect.

Contact Angle Measurement

Substrates for static contact angle measurement with a goniometer (Kino) both at ambient and ethanol saturated vapor were prepared by spin coating PMMA A2 at 6000 rpm for 60 seconds, baked at 180°C for 5 minutes, then developed in a cold 1:3 MIBK/IPA solution for 1 minutes. A 2 μ L water droplet at room temperature was carefully dispensed on the surface of the substrate. The progression of contact angle was recorded at the rate of 2 frames per second. The Cast3 software used the Young-Laplace model to fit the curve of the droplet and calculate the contact angle. To observe the influence of the ethanol atmosphere, a 5 cm³ quartz container was filled with about 10-15 ml of ethanol. A sample was placed on a small pedestal in the quartz container sealed with a parafilm and let to equilibrate for several hours before measurement. A small hole was made on the parafilm to immediately dispense the water droplet on the surface of the sample and record the progression of the contact angle in the saturated ethanol atmosphere.

Photoluminescence Characterization of Deposited QDs

PL mapping was carried out using an inverted optical microscope (Nikon Ti-U) setup with a 488 nm continuous-wave laser pump (Omicron) and an objective lens (Nikon) with 50x magnification (0.55 NA) or 20x magnification (0.45 NA). The excitation laser was passed through a plano-convex lens (Thor Lab, $f = 300$ mm) to expand the beam and distribute the laser power. A dichroic mirror was used to filter the incident laser and PL signal at 640 nm. PL signal then being collected with a spectrometer (Andor SR-303i) at zeroth order diffraction with a single grating (150 gratings/mm) and blaze wavelength of 500 nm, coupled with electron-multiplier charged-coupled detector (EMCCD, Andor Newton 971). See the setup arrangement in **Figure S2**.

DESIGN CONSIDERATION FOR SILICA-COATED QUANTUM DOTS

Both QDs before and after silica-coating show a similar photoluminescence (PL) peak at 640 nm with absorbance below ~ 500 nm, while the average particle size is around ~ 10 nm and ~ 35 nm, respectively, for bare QDs and silica-coated QDs, see **Figure S1** for colloidal QDs characterization. It is worth mentioning that, here, the quantum yield of the silica-coated QDs still relatively high $>70\%$ where typically, the quantum yield of silica-coated QDs ranges from around $30\%-50\%$ in the literature³⁻⁶ as the ligand exchange process and the etching effects from ammonium hydroxide during silica encapsulation unavoidably generate trap states on the surfaces of the QDs. From the perspective of the QDs themselves, the significant drop in quantum yield on silica-coated QDs is attributed to the delocalization of the electron wavefunction due to the small offset between the conduction bands of CdSe and CdS, rendering the delocalized electrons highly sensitive to surface trap states. To improve the quantum yield of the final silica-coated QDs, here we added a thick $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ gradient shell on top of the CdSe/CdS as the outermost shell. The increased bandgap of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ not only effectively suppresses trap states on the QDs without silica coating, resulting in a near-unity quantum yield of over 99% , but also serves as an effective electron barrier, making the QDs less susceptible to surface trap states after silica coating. Therefore, it is possible to maintain the optical properties of the QDs with controllable high-yield deterministic patterning.

Table S1 Particles count data of deposited QDs on Si substrate. Counting was carried out from several SEM images of the same array on the same sample and summed up for each number of particles bin.

Hole Size (nm)	Sample ID	Particles Count							Sites Counted
		0	1	2	3	4	5	6	
130	#1	37	79	28	0	0	0	0	144
	#2	17	52	47	25	0	0	0	141
	#3	26	39	35	8	0	0	0	108
150	#1	22	66	65	19	2	0	0	174
	#2	8	20	38	28	11	3	0	108
	#3	15	33	8	11	3	2	0	72
170	#1	17	41	38	42	21	3	0	162
	#2	8	17	30	34	22	9	1	121
	#3	24	17	16	14	3	0	0	74
190	#1	9	26	42	42	54	23	26	222
	#2	7	15	44	37	31	25	8	167
	#3	11	16	11	5	4	1	0	48

Table S2 Count percentage for each hole size and sample.

Hole Size (nm)	Sample ID	Count Percentage (%)						
		0	1	2	3	4	5	6
130	#1	26	55	19	0	0	0	0
	#2	12	37	33	18	0	0	0
	#3	24	36	32	7	0	0	0
150	#1	13	38	37	11	1	0	0
	#2	7	19	35	26	10	3	0
	#3	21	46	11	15	4	3	0
170	#1	10	25	23	26	13	2	0
	#2	7	14	25	28	18	7	1
	#3	32	23	22	19	4	0	0
190	#1	4	12	19	19	24	10	12
	#2	4	9	26	22	19	15	5
	#3	23	33	23	10	8	2	0

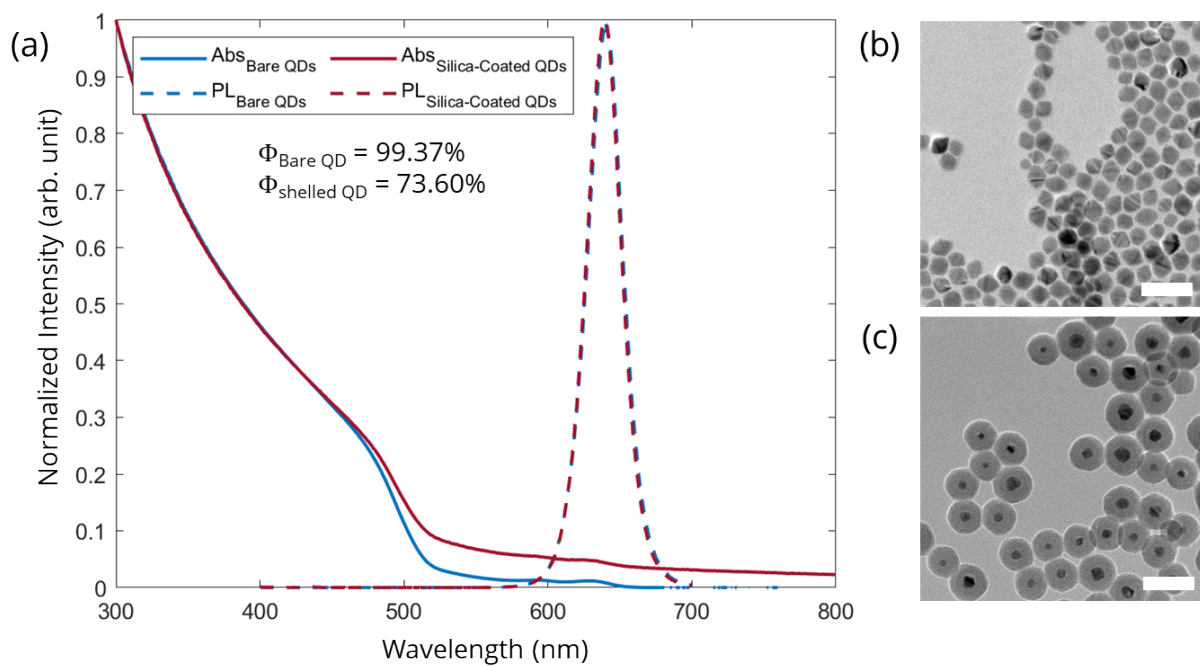


Figure S1. (a) Absorbance and PL spectra from CdSe/CdS Cd_xZn_{1-x}S QDs (bare QDs) and CdSe/CdS/Cd_xZn_{1-x}S@SiO₂ QDs (silica-coated QDs), PL peak at 640 nm. (b) TEM image from bare QD and (c) silica-coated QD, scale bar is 50 nm.

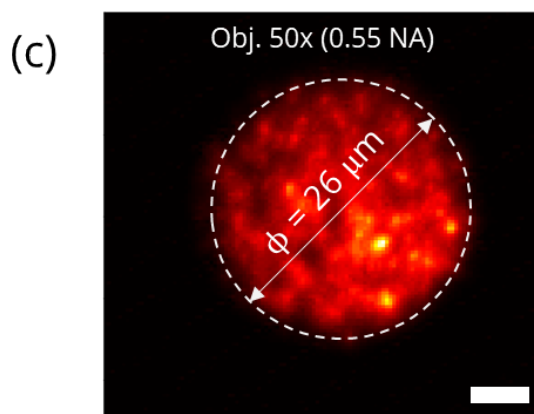
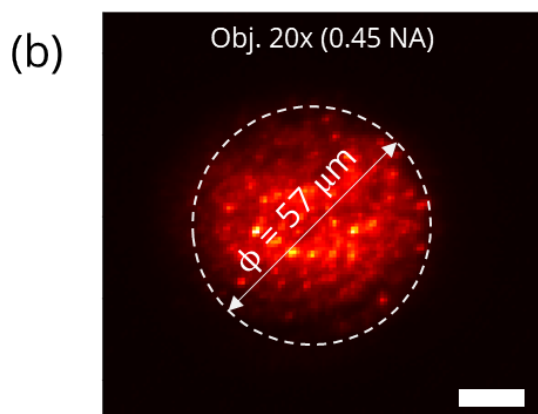
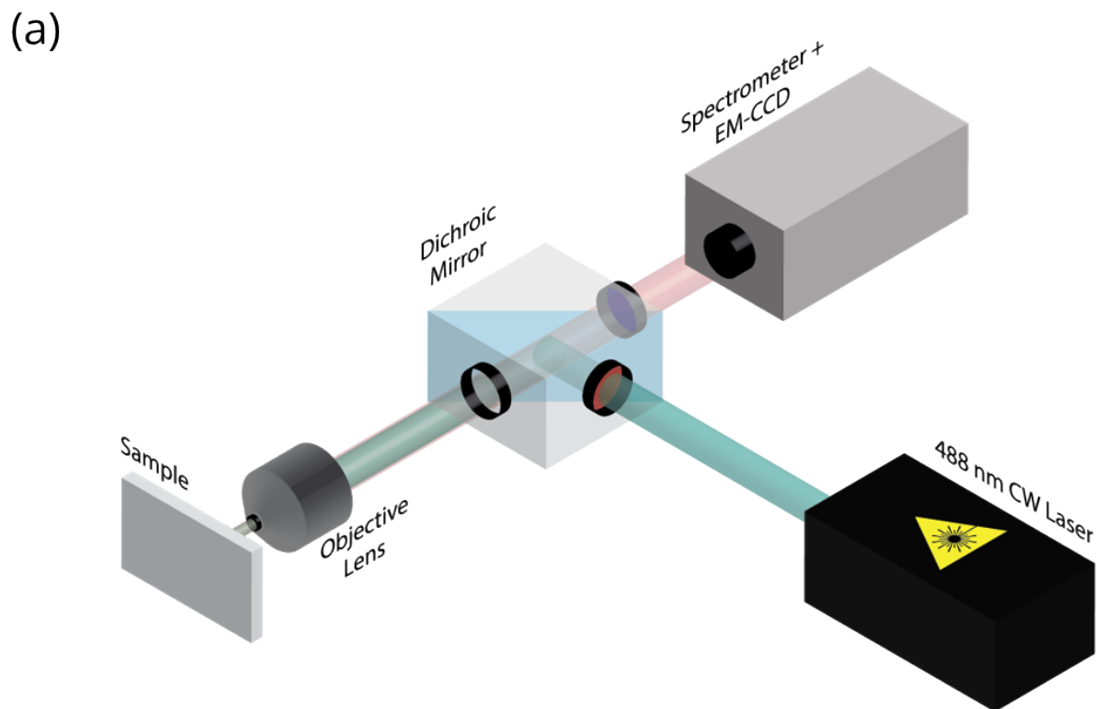


Figure S2. (a) PL measurement setup with 488 nm continuous-waves laser in an inverted optical microscope setup. (b) PL image from QDs thin film on Si substrate taken with 20x magnification (0.45 NA) and (c) 50x magnification (0.55 NA) objective lens.

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