

Supporting Information

Surface Engineered Colloidal Quantum Dots Toward Complete Green Process

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Synthesis of InP/ZnSe_xS_{1-x}/ZnS QDs

Materials. Indium acetate (In(ac)₃, 99.99 %), tris(trimethylsilyl)phosphine ((TMS)₃P, 99.9 %), zinc acetate (Zn(ac)₂, 99.99 %), selenium (Se, 99.9 %), sulfur (S, 99.9 %), oleic acid (OA, 99 %), n-trioctylphosphine (TOP, 99 %), and 1-octadecene (ODE, 99 %) were purchased from Uniam. All chemicals are used as received.

InP core synthesis. InP QDs were synthesized through the previously reported procedure with minor modifications.¹ All reactions were carried out under the inert atmosphere with the Schlenk line. A mixture of 3 mmol of In(ac)₃, 9 mmole of OA and 45 ml of ODE were degassed at 110 °C. After filling of the flask with argon, a mixture of 1.5 mmol of P(TMS)₃ and 3 ml of TOP was rapidly injected into the reaction flask to form a yellowish indium-phosphine complex. The flask was then heated to 260 °C to promote nucleation. After 1 hour reaction, the temperature decreased to room temperature to terminate the reaction. Synthesized InP QDs have the first excitonic peak around 460 nm. Larger InP cores were obtained by additional injection of indium and phosphine precursor. InP QDs were purified several times with precipitation/redispersion method.

InP/ZnSe_xS_{1-x} QDs. For InP/ZnSe_xS_{1-x} core/shell synthesis, 0.5 M Zn(OA)₂ in ODE stock solution and 2 M TOPSe and TOPS stock solution were prepared for cation and anion precursors of ZnSe_xS_{1-x} shell, respectively. A mixture of 10 ml of Zn(OA)₂ solution, 0.2 ml of TOPSe solution, 100 mg of InP cores and 15 ml of ODE were degassed at 110 °C, and filled up with argon. The temperature heated to 200 °C and an additional 0.7 ml of TOPSe and TOPS solution were injected. The flask was then heated up to 300 °C to proceed ZnSe_xS_{1-x} shell growth. The reaction time for the growth was fixed to 1 hour. An equivalent amount of Zn(OA)₂ and TOPS was injected to the flask to grow ZnS outermost shell. Synthesized green-emitting QDs were purified repeatedly *via*

precipitation/redispersion method. The use of larger InP cores with the same procedure for shell growth gives red-emitting InP/ZnSe_xS_{1-x} QDs.

Preparation of mono-color filter arrays

Carbon black dispersion (10 wt% in PMGEA) purchased from Dittotechnology (Korea) was mixed with photosensitive resins (*i.e.*, bisphenol A-ethoxylated diacrylate and dipropylene glycol diacrylate) followed by deposition on a glass substrate *via* doctor-blade coating. Then, it was exposed to UV light (i-line, 500 mJ/cm²) under photomask and rinsed by PGMEA to prepare finely patterned black matrix (BM). After baking of the prepared BM at 150 °C for 30 minutes, the 10 wt% of QD ink blended with the photosensitive resins was deposited with a drop velocity of 3 m/s, a drop frequency of 2 kHz, and a drop spacing of 200 μm at 35 °C. After jetting, the prepared color filter array was transferred to vacuum oven and dried for 30 minutes at 60 °C and then exposed to UV light (i-line, 30 mJ/cm²).

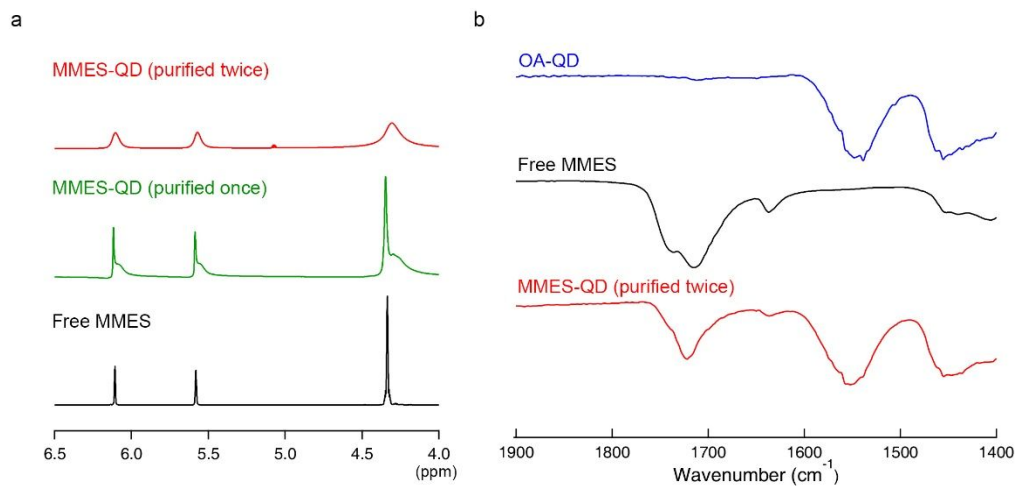


Figure S1. (a) ^1H -NMR spectra of MMES-QD upon the number of purification (twice: red, once: green) and free MMES (black) in CDCl_3 . (b) FT-IR spectra of OA-QDs (blue), free MMES (black) and MMES-QDs (red).

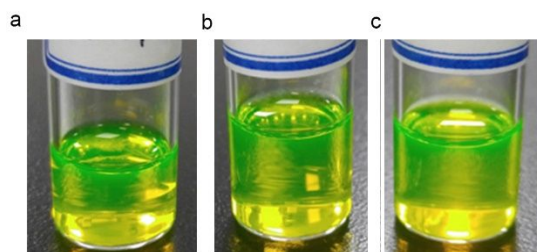


Figure S2. Photographs of carboxyethyl acrylate (CEA)-capped InP QDs in green solvents ((a) EtOH, (b) IPA, and (c) PGMEA).

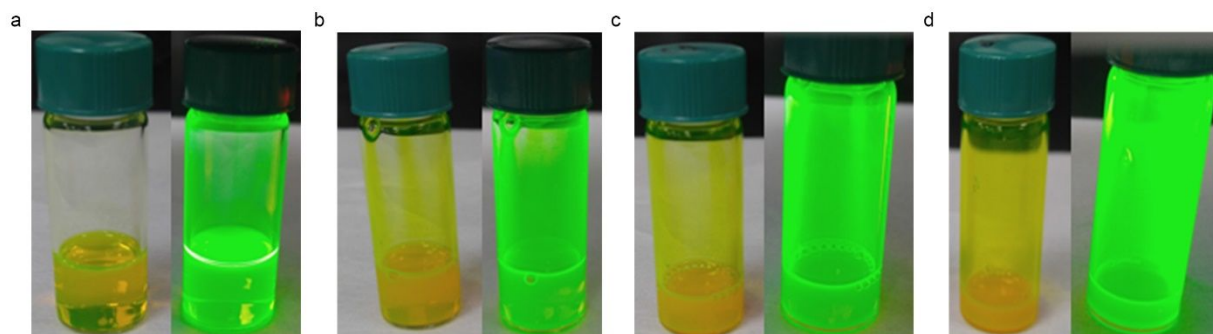


Figure S3. Photographs of MMES-QDs dispersed in PGMEA with concentration of (a) 50 mg/ml, (b) 150 mg/ml, (c) 250 mg/ml, and (d) 300 mg/ml.

Table S1. Calculated Z values of the mixtures with different ratio of PGMEA and DGMEA.

PGMEA : DGMEA (vol./vol.)	Density (g/ml)	Viscosity (cps)	Surface tension (dyn/cm)	Z
10:0	0.967	0.80	26.9	26.3
8:2	0.969	1.33	27.6	16.1
6:4	0.971	1.86	28.3	11.7
4:6	0.974	2.38	29.1	9.20
2:8	0.976	2.91	29.8	7.63
0:10	0.978	3.44	30.5	6.55

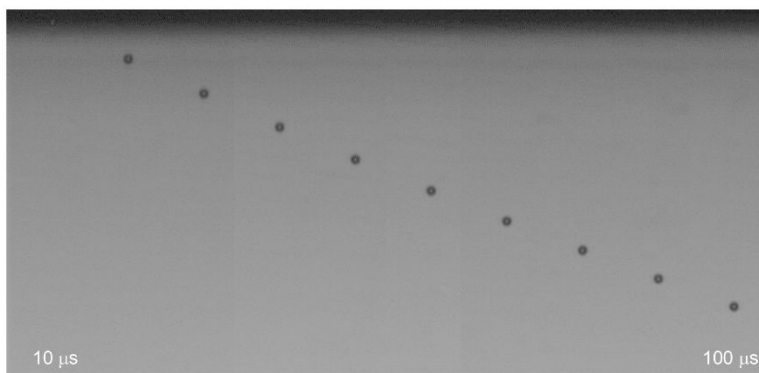


Figure S4. Sequentially captured images of an in-flight ink droplet dispersed in the mixed solvent of 40 % PGMEA and 60 % DGMEA from a cartridge-type nozzle. The time interval between two adjacent frames is 10 μ s.

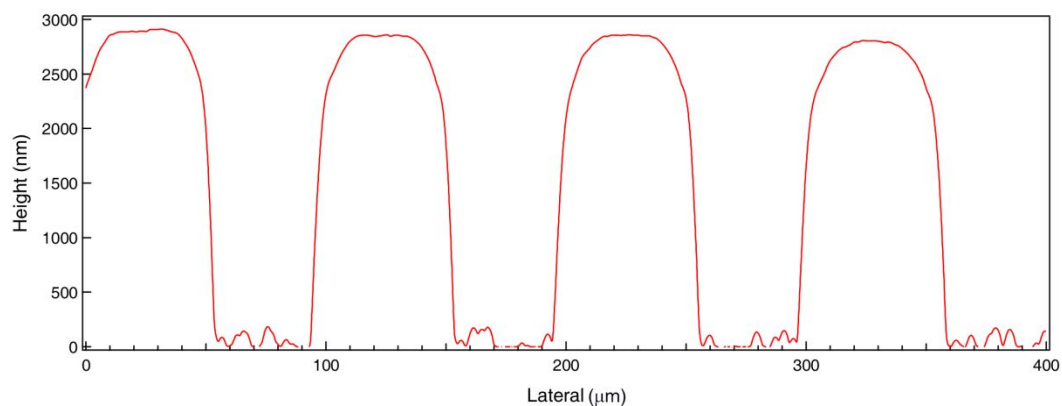


Figure S5. Surface profile of patterned MMES-QD films.

References

(1) Hahm, D.; Chang, J. H.; Jeong, B. G.; Park, P.; Kim, J.; Lee, S.; Choi, J.; Kim, W. D.; Rhee, S.; Lim, J., Design Principle for Bright, Robust, and Color-Pure InP/ZnSe_xS_{1-x}/ZnS Heterostructures. *Chem. Mater.* **2019**, *31*, 3476-3484.