

Supporting Information

Two Step “Seed-Mediated” Synthetic Approach to Colloidal Indium Phosphide Quantum Dots with High-Purity Photo- and Electroluminescence

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1. Experimental

Chemicals. Indium acetate (99.99%), zinc acetate (99.99%), zinc stearate (Technical grade), sulfur (99.998%), selenium pellets (99.999%), oleic acid (90%) and 1-octadecene (90%, ODE) were purchased from Sigma-Aldrich. Tris(trimethylsilyl)-phosphine ((TMS)₃P) was purchased from SK Chemicals, Korea. Trioctylphosphine (97%, TOP) was purchased from Strem Chemicals. Hexane (HPLC grade) and isopropyl alcohol (HPLC grade) were purchased from Samchun Chemicals, Korea. All chemicals were used without further purification.

Preparation of 0.4 M zinc stearate in TOP. Zinc stearate (2.530 g) was dissolved in 10 mL of TOP at 150 °C inside a nitrogen glovebox.

Preparation of TOP-Se (1 M). Selenium pellets (0.789 g) were dissolved in 10 mL of TOP at room temperature (RT) inside a nitrogen glovebox.

Preparation of TOP-S (1 M). Sulfur (0.320 g) was dissolved in 10 mL of TOP at RT inside a nitrogen glovebox.

1.1 Preparation of Zn(In)-P complex: Indium acetate (1 mmol), zinc acetate (0.5 mmol) and oleic acid (4 mmol) were mixed with 10 mL of ODE in a 50 mL three-neck flask and fixed to a Schlenk line with a reflux condenser. The mixer was heated to 120 °C under vacuum for 12 h (vacuum level reaching 150 mTorr). Then, the flask was filled with N₂ and cooled to RT. Then, a solution containing 0.66 mmol of (TMS)₃P and 1 mL of TOP was quickly injected into the flask and stirred at RT for 60 min.

1.2 Synthesis of InP QD “seeds”: Indium acetate (0.15 mmol) and oleic acid (0.47 mmol) were mixed with 10 mL of ODE in a 50 mL three-neck flask and fixed to a Schlenk line with a reflux condenser. The mixer was heated to 130 °C under vacuum for 90 min (vacuum level reaching 150 mTorr). Then, the flask was refilled with N₂ and cooled to RT. Then, a solution containing 0.1 mmol of (TMS)₃P and 1 mL of TOP was quickly injected into the flask. Following the injection, the mixture was heated to 305 °C (15 °C/min) and kept at that temperature for 2 min before cooling to RT and transferred to N₂ filled glove box.

1.3 “Seed” mediated synthesis of larger InP QDs: 5 mL of the above prepared (Section 1.2) InP QD “seeds” were filtered with 0.2 µm PTFE syringe filter and mixed with 10 mL of dried ODE and heated to 280 °C. Then, the In(Zn)-P complex (Section 1.1) was loaded in a 10 mL syringe and fixed to a syringe pump and injected at a rate of 1mL/h (0.1 mmol/h based on indium concentration) to the hot ODE with InP “seeds”. The reaction was continued for 5 h to synthesis InP QDs of size around 4.5 nm.

1.4 Synthesis of red emitting InP/ZnSe/ZnS QDs (Em: 625 nm, fwhm: 39 nm): InP QDs with first excitonic peak around 570 nm were prepared following the procedure outlined in section 1.3. Then, the QDs were cooled to 150 °C and 1 mL of zinc stearate solution (0.4 M) was injected and kept at the same temperature for 30 mins. Then, 0.4 mL of 1M TOP-Se was injected

to the flask and maintained at 300 °C for 15 min. Next, 1.5 mL of zinc stearate was injected and after a 10 min wait, 0.6 mL of TOP-Se was injected and maintained at same temperature for 15 min. One more layer of ZnSe was coated using 2 mL of zinc stearate and 0.8 mL of TOP-Se. For the final ZnS shell, 2.5 mL of zinc stearate was added and after a 10 min wait, 0.5 mL of TOP-S was injected and maintained at 300 °C for 15 min. After cooling to RT, the QDs were precipitated with 50 mL of isopropyl alcohol and collected by centrifugation at 6000 rpm for 30 min. The QDs were washed one more time by dispersion in hexane followed by precipitation by addition of isopropyl alcohol and stored in hexane in a vial in a N₂ filled glovebox.

1.5 Fabrication of InP/ZnSe/ZnS based green and red QLEDs

The 25×25 mm patterned indium tin oxide (ITO)/glass substrates were cleaned by sonication sequentially in acetone, ethanol, and boiled isopropyl alcohol for 5 min. Subsequently, the ITO substrates were dried at 120 °C for 10 min in a conventional oven, followed by UV-ozone treatment for 900 s. The PEDOT:PSS (Clevios PVP A 4083) was then filtered with a 0.25 µm polypropylene (PP) filter and spin-coated at 4000 rpm for 40 s onto the ITO/glass substrates and annealing at 130 °C for 30 min as the hole injection layer. The thickness of PEDOT:PSS was 30 nm. 10 mg ml⁻¹ of poly(N,N'-bis-4-butylphenyl-N,N'-bisphenyl)benzidine (Poly-TPD) in chlorobenzene was then filtered with a 0.20 µm polytetrafluoroethylene (PTFE) filter and spin-coated at 5000 rpm for 40 s onto the 30-nm-thick PEDOT:PSS layer and annealing at 130 °C under N₂ atmosphere for 40 min as the hole transfer layer. The green and red InP/ZnSe/ZnS QD solution (2 mg ml⁻¹ in hexane) was then filtered with a 0.20 µm polytetrafluoroethylene (PTFE) filter and spin-coated at 3000 rpm for 40 s onto the 45-nm-thick poly-TPD layer and annealing at 90 °C under N₂ atmosphere for 30 min as the emitting layer. The thickness of the InP/ZnSe/ZnS QD was 1-2 monolayers. After the spin-coating process, 20-nm-thick 2,2',2'-(1,3,4-phenylene)-

tris[1-phenyl-1H-benzimidazole] (TPBi) as the electron transfer layer, 1-nm-thick LiF as the electron injection layer, and 100-nm-thick Al layers were thermally deposited under a base pressure of 1×10^{-6} Torr at a deposition rate of $0.5 \sim 0.7 \text{ Å s}^{-1}$ for TPBi, $0.1 \sim 0.2 \text{ Å s}^{-1}$ for LiF, and $4 \sim 5 \text{ Å s}^{-1}$ for Al layer, respectively. The overlapping area of the ITO and aluminum electrodes was approximately $2 \times 2 \text{ mm}^2$.

CHARACTERIZATION

UV-vis absorption spectroscopy. Absorbance spectra of the QDs dispersed in hexane were recorded in 1 cm path length quartz cuvettes using a Cary 5000 UV-vis-NIR (Agilent Technologies) spectrophotometer.

Photoluminescence (PL) spectroscopy and quantum yield measurement. PL spectra of QDs dispersed in toluene were recorded using a Cary Eclipse fluorescence spectrophotometer ($\lambda_{\text{exc}} = 400 \text{ nm}$).

PL Quantum Yield (QY): The quantum yields were measured by comparing the integrated PL intensities between primary dye solution and InP QDs at the same excitation wavelength using the following equation.

$$QY_{\text{QDs}} = QY_{\text{dye}} \times (I_{\text{QDs}}/I_{\text{dye}}) \times (A_{\text{dye}}/A_{\text{QDs}}) \times (\eta_{\text{QDs}}/\eta_{\text{dye}})^2$$

where, QY_{dye} and QY_{QDs} are the quantum yields of the standard dye and synthesized QDs, I is the integrated area of the PL spectrum, A is the absorbance value at excitation wavelength, and η is the refractive index of the solvent used. Coumarin 153, Rhodamine 101 inner salt and Rhodamine 6G were used as standard dye, depending on their PL wavelengths. The QDs and dye solutions were prepared in hexane and ethanol, respectively.

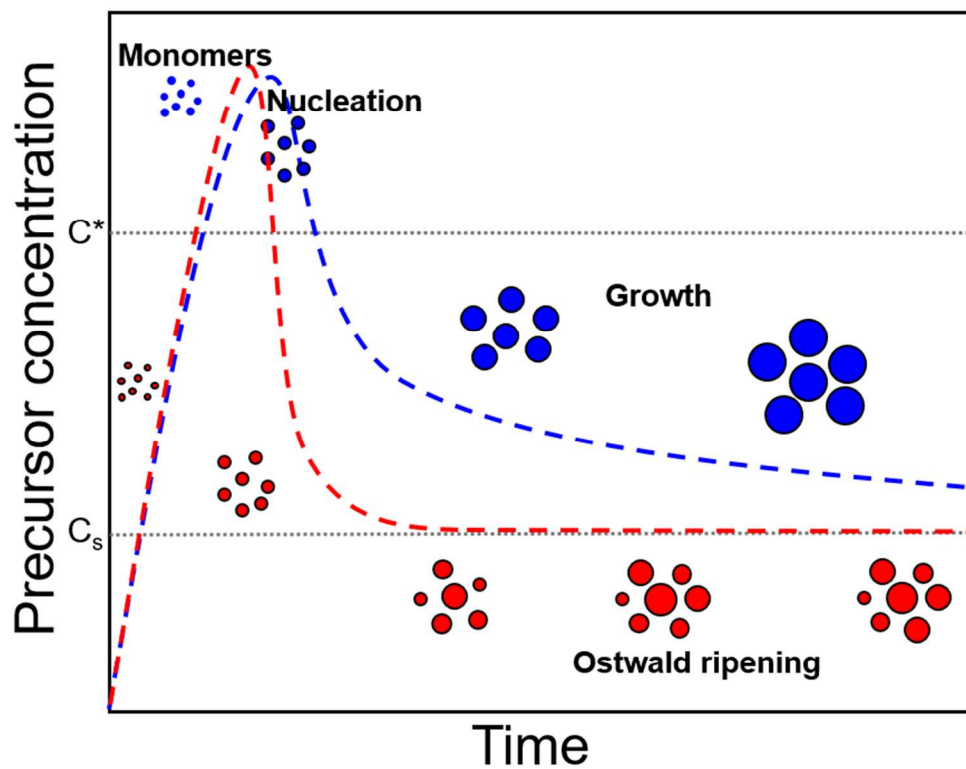
X-ray diffraction (XRD). X-ray diffraction patterns were obtained by using a Rigaku MiniFlex 600 diffractometer, equipped with a Cu K α X-ray source ($\lambda = 1.5418 \text{ \AA}$). Samples for XRD analysis were prepared by depositing (drop casting) the purified QDs dispersed in hexane on a glass substrate.

Transmission electron microscopy (TEM). TEM images were obtained using a Hitachi HF-3300 microscope operating at 300 kV. TEM samples were prepared by dropping the diluted QDs onto carbon coated 200 mesh copper grids.

X-ray photoelectron spectroscopy (XPS). XPS data were collected with a MultiLab ESCA 2000 spectrometer equipped with a monochromatic Al K α X-ray source and a concentric hemispherical analyzer. “Seed” InP QDs were purified using anhydrous isopropyl alcohol in a N₂ filled glovebox to avoid oxidation of the InP “seeds”.

¹H nuclear magnetic resonance (NMR): NMR sample were prepared samples by mixing In(Zn)- oleate and (TMS)₃P in benzene-d₆ at room temperature and measured using Bruker Avance III 400.

QLEDs characterization: The current density-voltage-luminance (J-V-L) characteristics of the devices were measured with a source measure unit system (Keithley 236), meanwhile the electroluminescence spectra and international commission on illumination (CIE) coordinates were obtained using a spectrophotometer (Konika Minolta CS-2000).



Scheme. S1 Schematic representation of Lamer Plot (Blue line) for the synthesis of monodisperse particles involving three different stages (i) monomer generation, (ii) nucleation and (iii) growth by the addition of monomers to the nucleated particles surface. Red line represents the monomers concentrations in various stages of typical InP QDs synthesis.

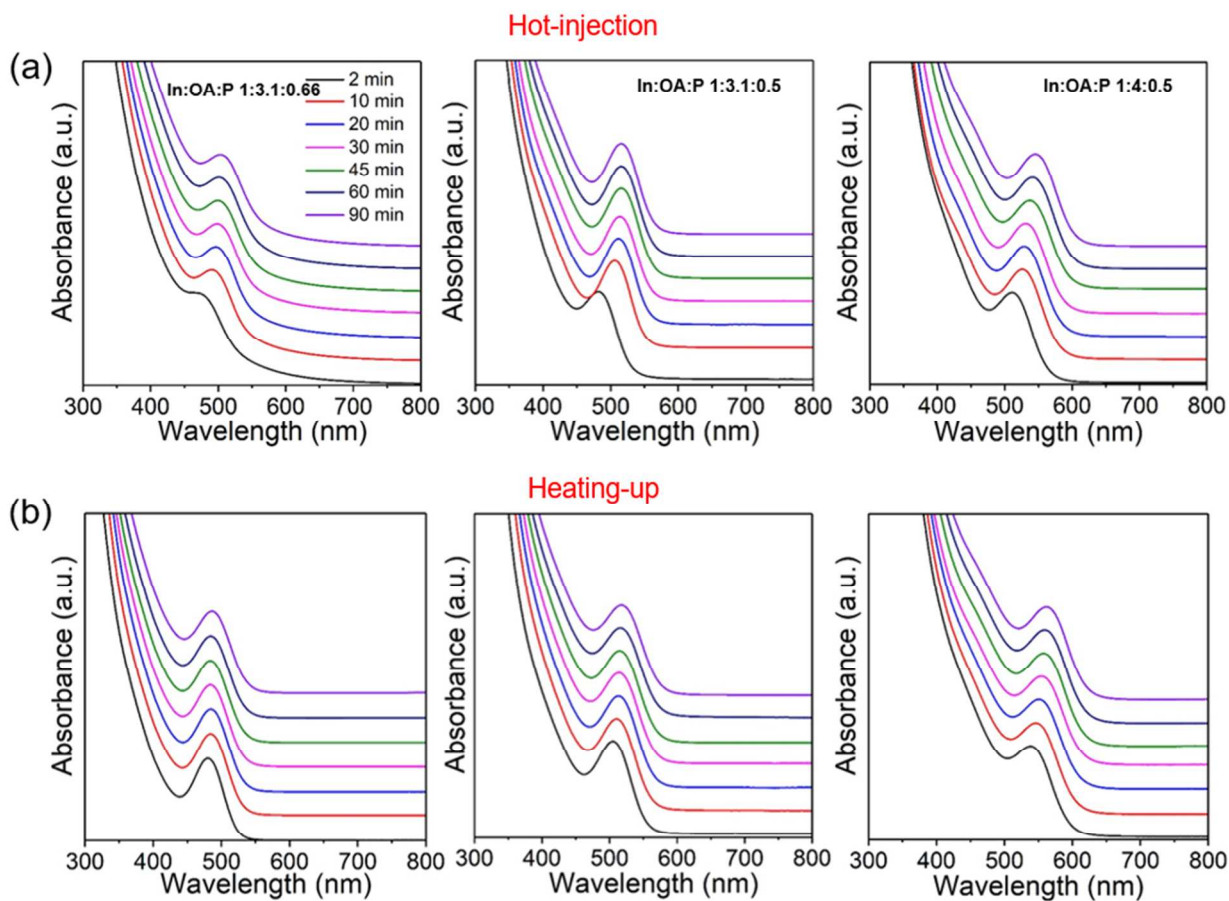


Figure. S1 Absorption spectra of InP QDs synthesized using (a) hot injection and (b) heating up methods with different synthetic conditions. In: Indium acetate, OA – Oleic acid and P – (TMS)₃P.

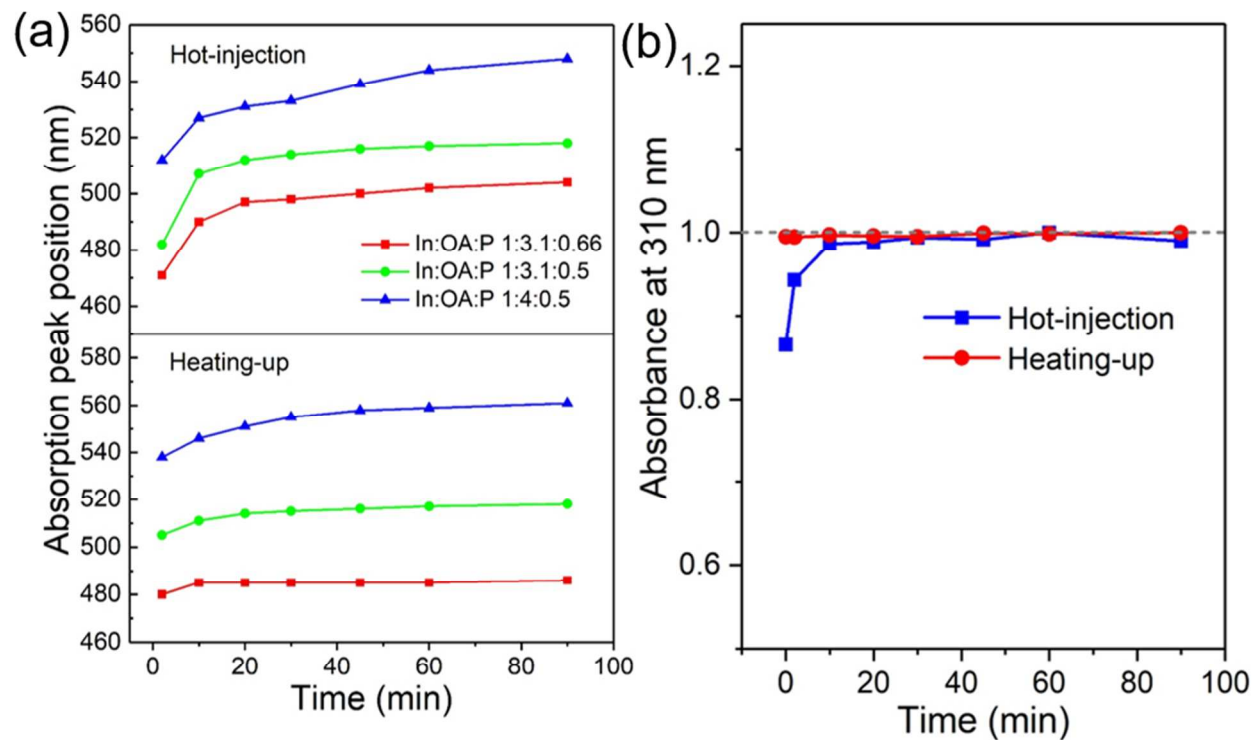


Figure. S2 Change in absorption peak position of InP QDs during hot-injection and heating-up methods (values were taken from Figure. S1). (b) Measured absorbance at 310 nm for the InP QDs synthesized using hot-injection and heating-up methods.

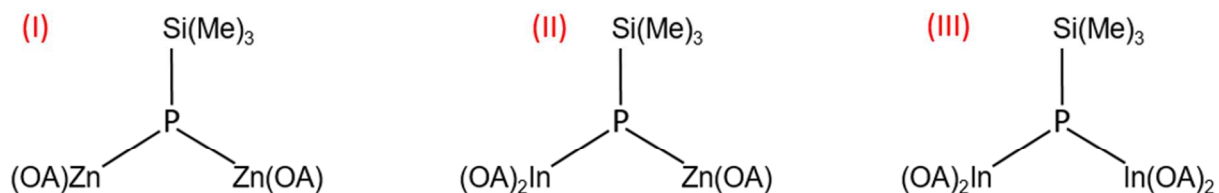


Figure. S3 Possible structures for Zn(In)-P complexes. Koh et al.¹ showed that in the presence of indium and zinc carboxylates, $(\text{TMS})_3\text{P}$ readily reacts with zinc and forms less reactive complex (I) rather than complex (II). In our synthesis method we employed Zn:P ratio of 1:1.32, assuming all the zinc converted to Zn-P complex (I), the excess $(\text{TMS})_3\text{P}$ could react with In carboxylate to produce complex (III). At this moment, we haven't characterized the complexes structure in the injection solution. We believe that the injection solution contains a mixture of complexes (I) to (III).

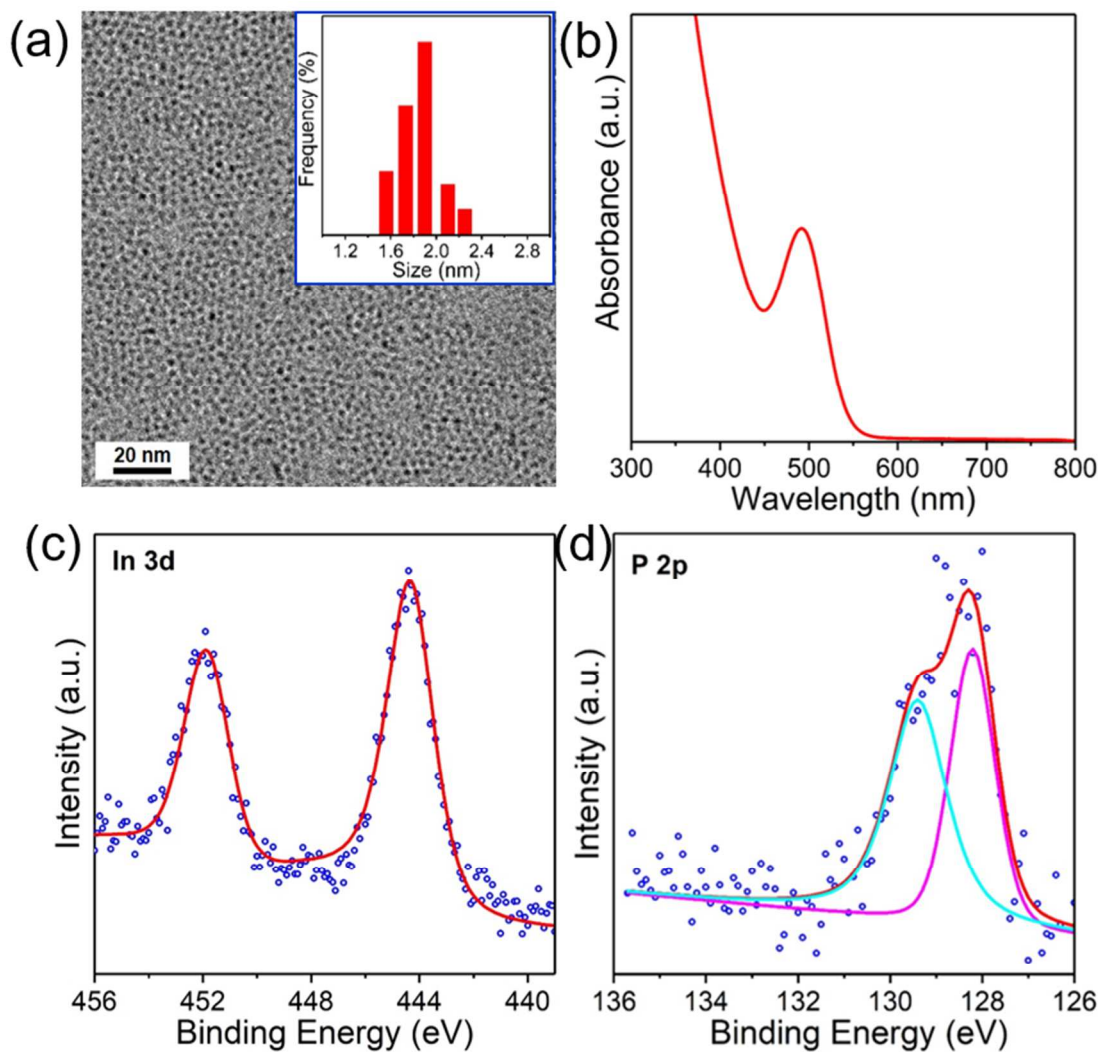


Figure. S4 Optical and structural characterization of InP "seed" QDs. (a) Absorption spectrum, (b) TEM image with size distribution histogram and (c and d) XPS spectra.

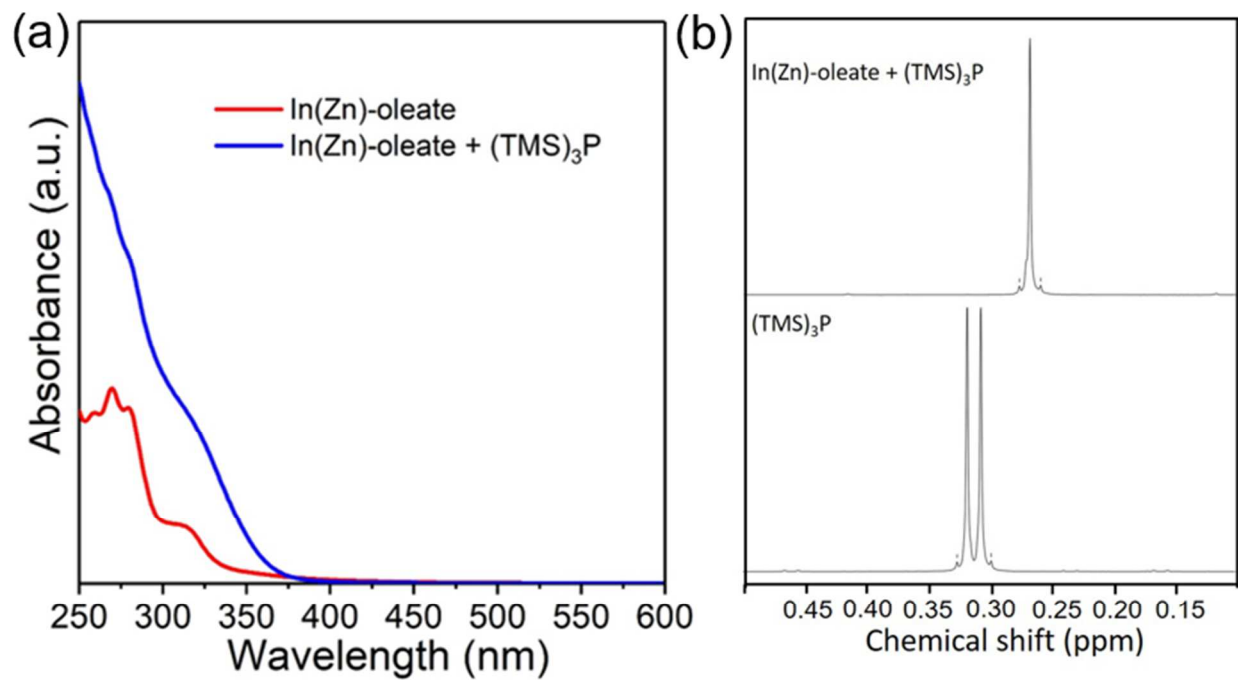


Figure. S5 (a) Absorption spectra of In(Zn)-oleate and Zn(In)-P complexes and (b) ¹H NMR spectra of (TMS)₃P and Zn(In)-P complex.

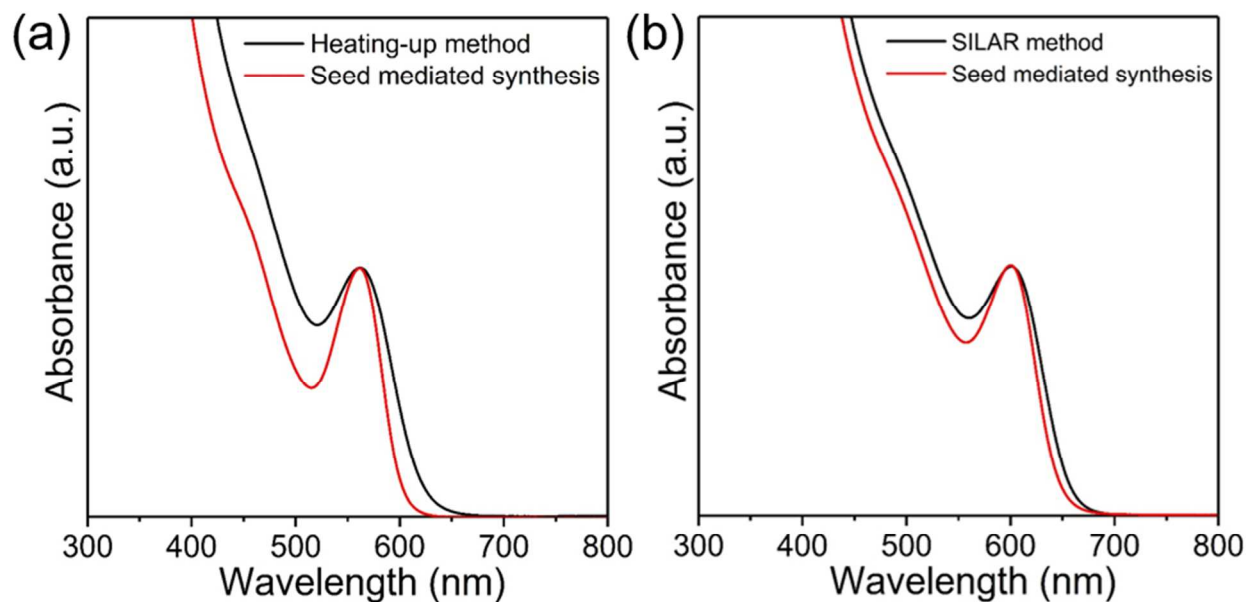


Figure. S6 Comparison of absorption spectra of InP QDs synthesized via (a) heating-up method and (b) SILAR method with our current “seed-mediated” two step synthesis. Absorption spectrum of heating-up method was taken from Figure. S1b and absorption spectrum of SILAR method was obtained by repeating SILAR method previously published by our group.²

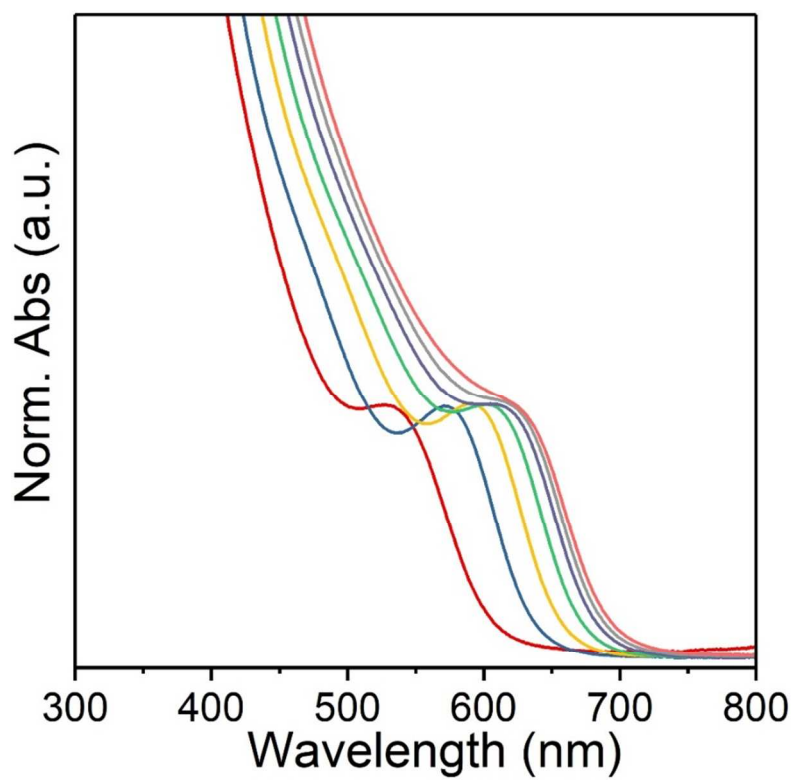


Figure. S7 Absorption spectra of InP QDs synthesized by directly injection Zn(In)-P complexes into hot ODE (without InP “seeds”).

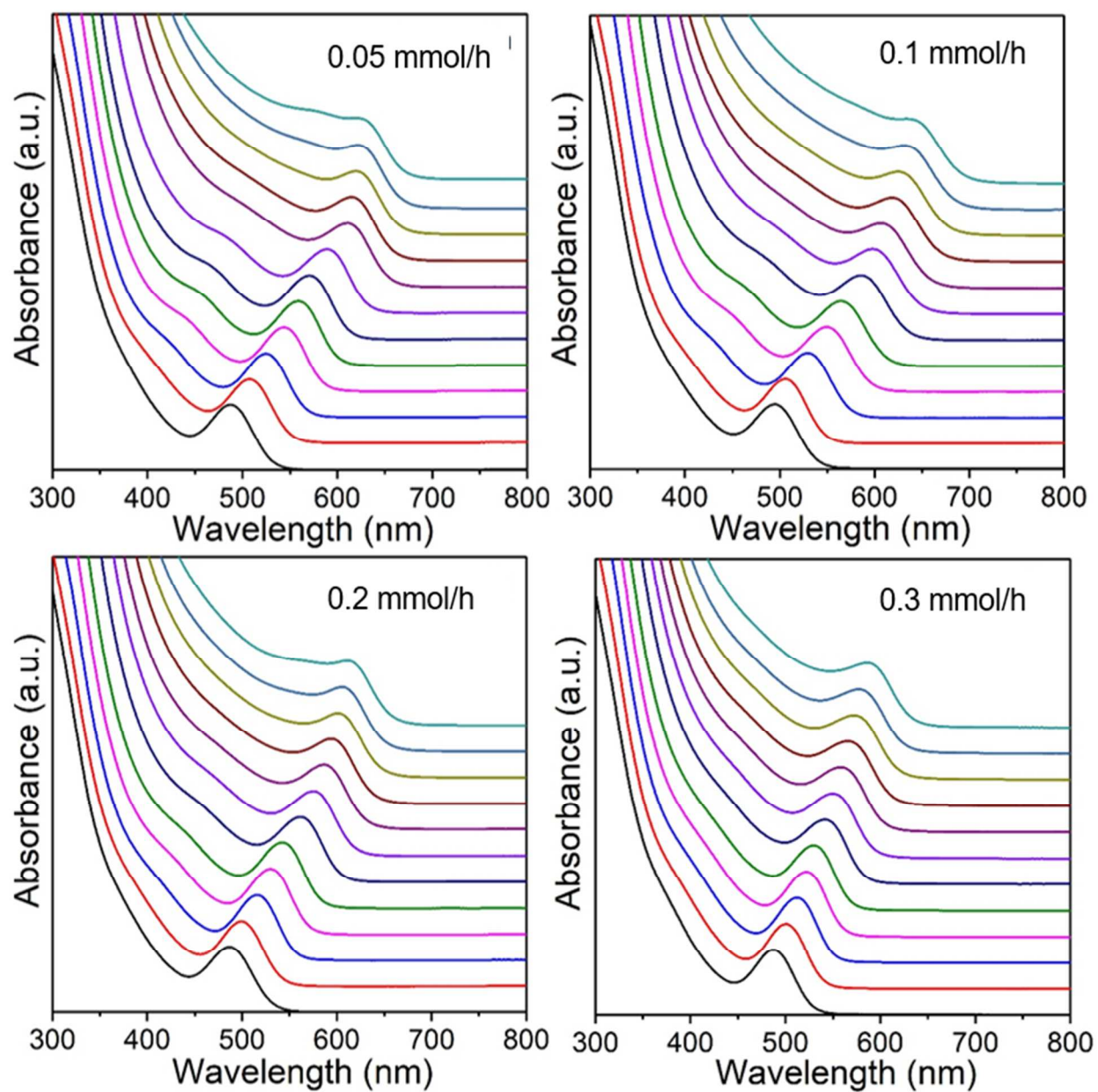


Figure. S8 Absorption spectra of InP QDs synthesized with different injection rates.

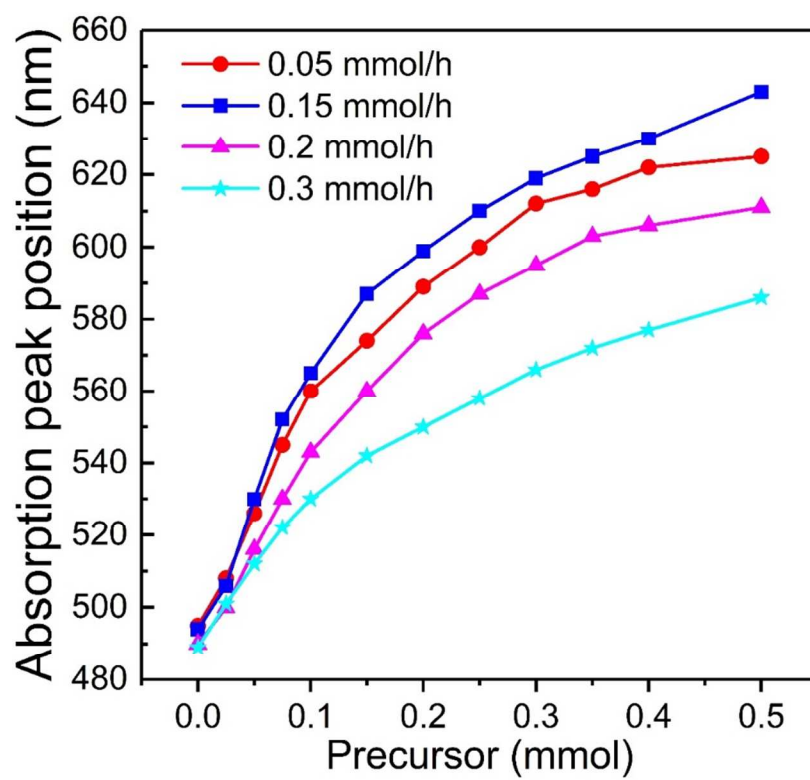


Figure. S9 Change in absorption peak position of InP QDs synthesized with different injection rates.

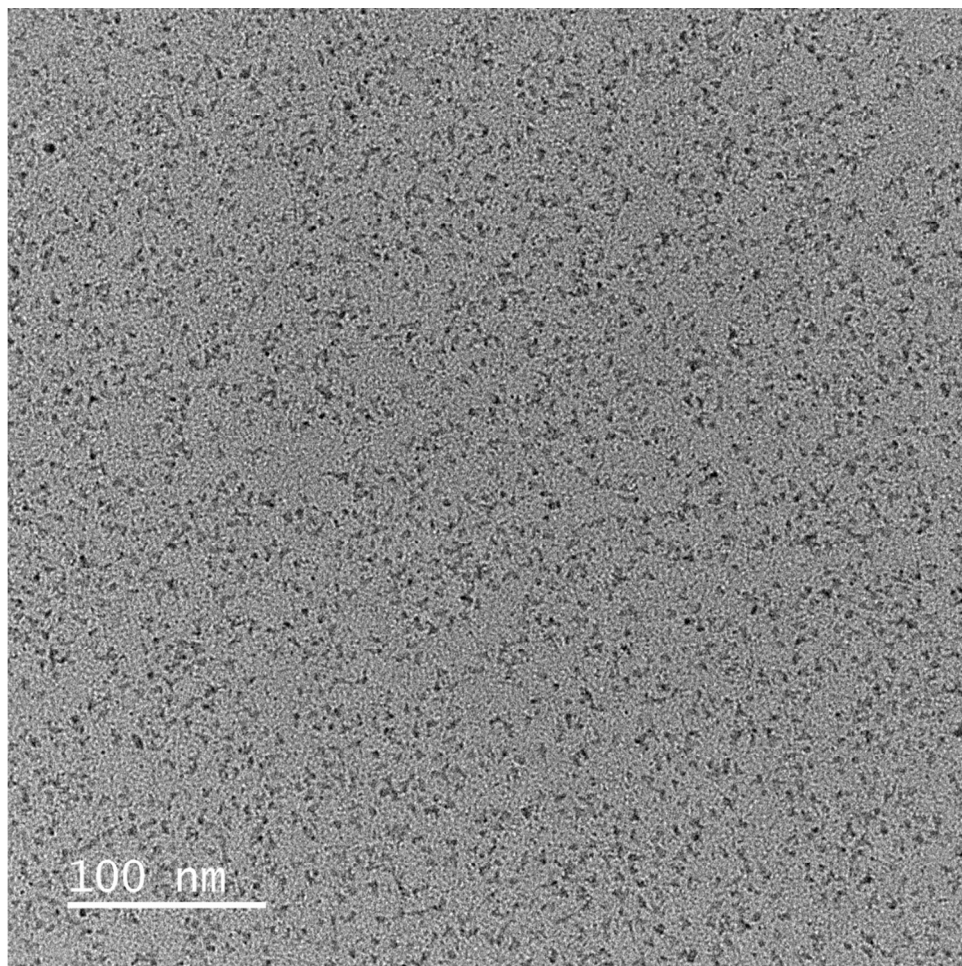


Figure. S10 TEM image of InP QDs synthesized at the injection rate of 0.3 mmol/h at 280 °C.

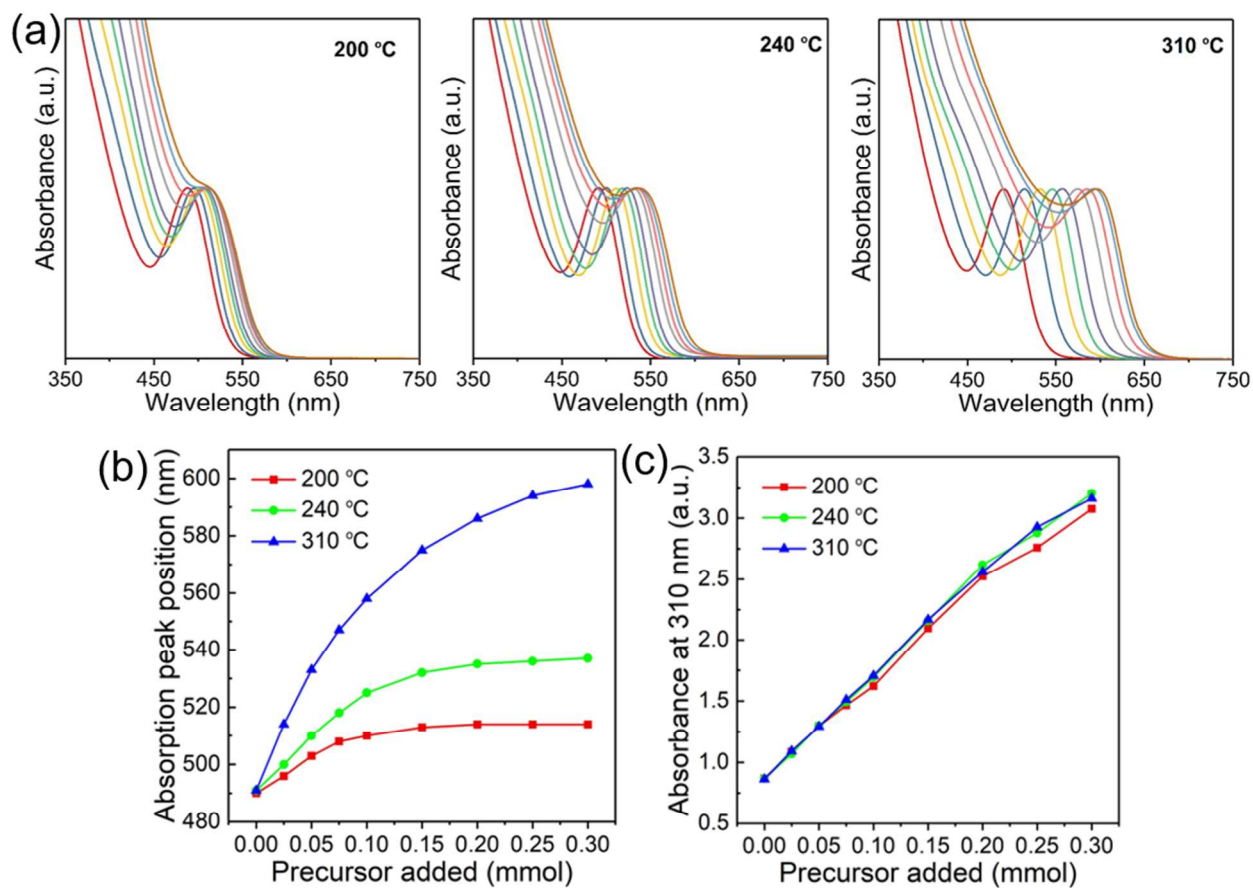


Figure. S11 (a) Absorption spectra (b) Change in absorption peak position and (c) absorbance at 310 nm of InP QDs synthesized at different injection temperature.

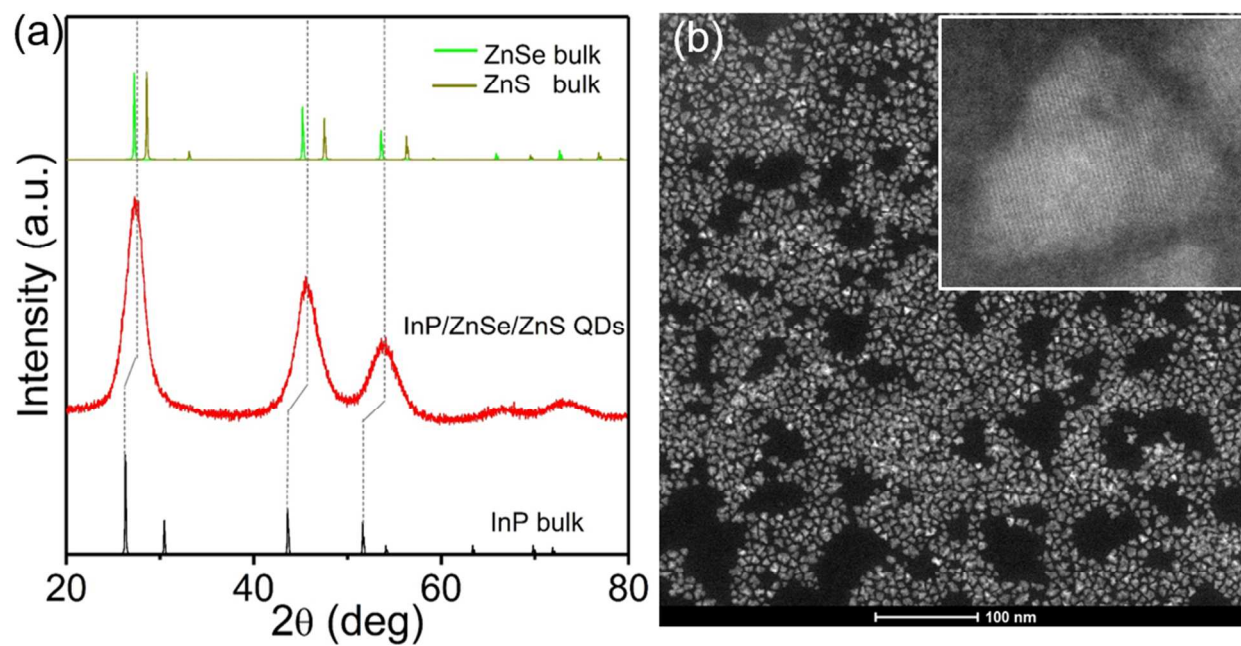


Figure.S12 (a) XRD pattern and (b) HAADF-STEM images of InP/ZnSe/ZnS QDs.

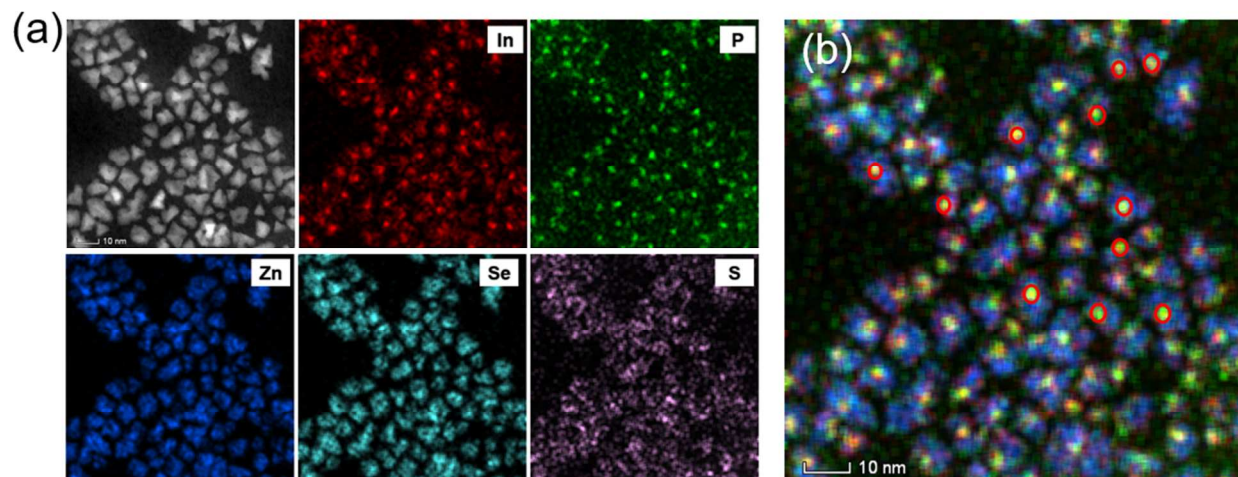


Figure. S13 (a) HAADF-STEM image and energy dispersive X-ray chemical map of core-shell InP/ZnSe/ZnS QDs. (b) Overlay image of In, P, Zn. Core InP is marked in red circle.

EDX elemental mapping data confirms the formation of thick ZnSe and thin ZnS outer shell. However, the shell materials were not uniformly coated over the core QDs, as evident from the shape and size inhomogeneity. In addition, the overlay chemical maps of In, P and Zn, shows that the core is not located at the center in most of the core-shell QDs. We attribute these observations to the non-spherical morphology of the core, which makes it difficult to coat the shell uniformly and not well optimized shell coating method. We believe that with further work on the shell coating method, it is possible to significantly decrease the emission FWHM as well as increase the QYs.

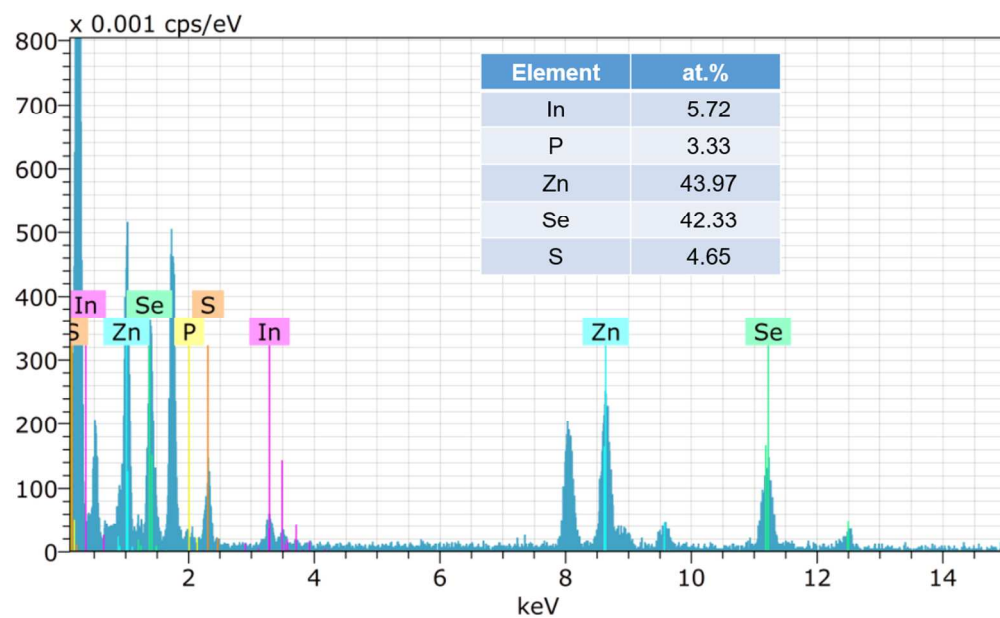


Figure. S14 EDX spectra of red emitting InP/ZnSe/ZnS QDs.

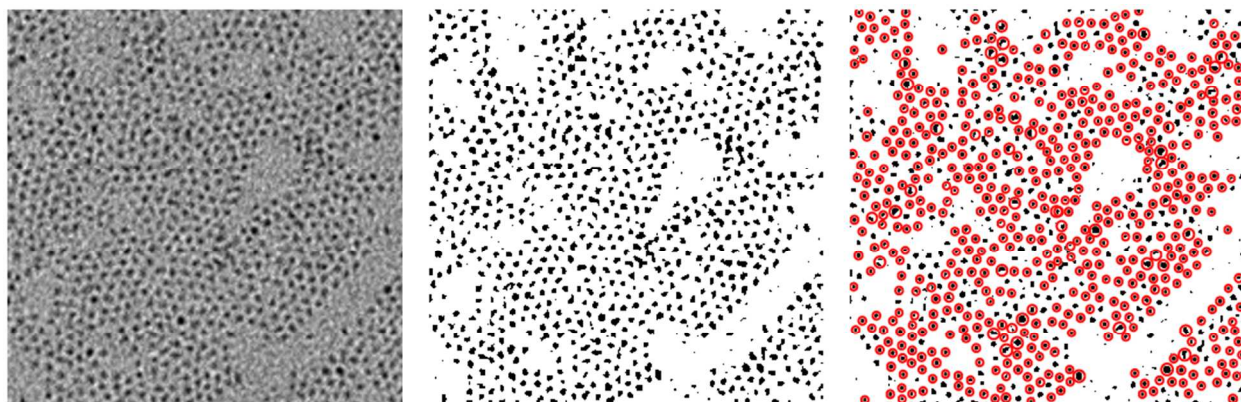


Figure. S15 Process to calculate the QDs' size distribution in Matlab. For the size distribution calculation, a script in Matlab was implemented. First of all, the original TEM image is converted into black and white and the equivalent in pixels of the scale bar is determined. Then, a function to detect circles is used and the radius of each particle approximated. Since the nanoparticles are not spherical, the final size was determined as a triangle inscribed in a circle. A representative sample of more than 500 nanoparticles were analyzed in this example.

Table S1. Comparison of EL peak position and FWHM values of InP based QLEDs

InP QDs	Device structure	EL peak position (nm)	EL FWHM (nm)	Ref
Green	ITO/PEDOT/PolyTPD/QDs /TPBI/LiF/Al	532	70	3
Green	ITO/ZnO/PFN/QDs /TCTA/MoO ₃ /Al	530	~65	4
Green	ITO/PEDOT/PolyTPD/QDs /TPBI/LiF/Al	555	56	5
Green	ITO/ZnMgO/InP- QDs/TcTa/NPB/HATCN/Al	545	>65	6
Green	ITO/PEDOT/PolyTPD/QDs /TPBI/LiF/Al	532	42	This work
Red	ITO/PEDOT/PVK or TFB/QDs/ZnO/Al	614-619	>65	7
Red	ITO/ZrO ₂ /QDs/TAPC/MoO ₃ /Al	600	74	8
Red	ITO/PEDOT/PolyTPD/QDs /TPBI/LiF/Al	628	50	This work

References:

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