Magic size InP and InAs clusters: synthesis, characterizations and shell growth

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Experimental section

Chemicals. Indium acetate (99.999%), tris(trimethylsilyl)phosphine (95%, $(TMS)_3P$), zinc oxide (99.999%), Bis(trimethylsilyl)sulfide ($(TMS)_2S$), 1-octadecene (90.0%) toluene (99% anhydrous), hexane (99%, anhydrous) and methanol (99.8%, anhydrous) were purchased from Sigma-Aldrich. Oleylamine (approximate C18 content 80-90%, OLA) was purchased from Acros. Trioctylphosphine (97%, TOP) was purchased from Strem chemicals. Bis(trimethylsilyl)selenide ($(TMS)_2Se$) was purchased from Gelest. Tris(trimethylsilyl) arsenide ($(TMS)_3As$) was synthesized as detailed in the literature.[1] All chemicals were used without further purification.

Preparation of zinc oleate-TOP solution (0.1 M). Zinc oxide (2mmol, 0.1628 g), oleic acid (4 ml) and TOP (16 ml) were mixed in a three neck flask. The mixture was degassed and refilled with Ar three times at room temperature and then heated to 110 °C. The mixture was kept at 110 °C under vacuum for 1 h to remove water. It was then heated to 300 °C and maintained at this temperature until all the zinc oxide was dissolved. Then the solution was cooled down to 120 °C, degassed for 2 h and then cooled to room temperature. The zinc oleate TOP solution (0.1 M) was kept in the glove box.

Synthesis of Magic Size Clusters (MSCs) and shell growth. All experiments were carried out using standard airless techniques: a vacuum/dry Ar gas Schleck line was used for synthesis and a nitrogen glove-box for storing and handling air- and moisture-sensitive chemicals.

(1). Synthesis of magic size InP nanoclusters. Indium acetate (0.9 mmol, 0.261 g), OLA (0.9 ml) and ODE (4.5 ml) were mixed in a three neck flask. The mixture was degassed and refilled with Ar three times at room temperature and then heated to 110 °C, and kept under vacuum for 1 h to remove the water in the reaction system. The indium acetate can be dissolved into OLA and ODE solution to form clear solution at 110 °C. Then heating was stopped and the system was cooled down to room temperature. At room temperature, 0.45 mmol $(TMS)_3P$ in 0.5 ml ODE solution was injected into the clear indium acetate stock solution. Following the injection, the mixture was heated at a rate of 2 °C/min. Aliquots were taken at different temperatures and reaction times to characterize the absorption.

(2). Synthesis of magic size InAs nanoclusters. The same synthetic route was used while employing the Arsenic precursor ($(TMS)_3As$) for InAs.

(3). Growth of ZnS shell on magic size InP nanoclusters. In the synthesis of the ZnS shell, the prepared zinc oleate-TOP solution (0.1 M) was selected as the zinc precursor, and $(TMS)_2S$-TOP solution (0.1 M) was used as the sulfur precursor. 1.8 ml solution from the synthesis of magic size InP nanoclusters with absorption at 365nm was dissolved into 7 ml TOP solution at 90 °C. The solution was degassed and vacuumed at 90 °C for 1 h. Then the calculated amounts of zinc and sulfur precursors for the first ZnS layer were injected into the flask at 90 °C, and the reaction was kept at 90 °C for 30 min to grow the first ZnS layer. For the second ZnS layer, the calculated amounts of zinc and sulfur precursors were injected at 90 °C, then the reaction was heated to 120 °C. The reaction was kept at 120 °C for 30 min to grow the second ZnS layer shell. For the third ZnS layer, the calculated amounts of zinc and sulfur precursors was injected at 120 °C, then the reaction was heated to 150 °C and kept at 150 °C for 30 min to grow the third ZnS layer shell. For the following layers of ZnS shell, we added the zinc and sulfur precursors at 150 °C, and the reaction was kept at 150 °C for 30 min to grow the ZnS shell.

The concentration of InP MSCs with absorption at 365nm in solution is $5.82*10^{-5}$ mmol/ml, the volume of InP MSCs is 8.6ml, the total amount of InP MSCs is $5.0*10^{-7}$ mmol. Based on the amount of InP MSCs core, and its estimated size, we calculate the amount of zinc and sulfur precursor for shell growth at each layer.

Table 1. The amount of zinc and sulfur precursor for each shell growth on InP MSCs. (The amount of InP MSCs is $5.0*10^{-7}$ mmol).

Layer	**Amount of core (mmol)**	**Volume of zinc oleate with 0.1M (ml)**	**Volume of $(TMS)_2S$ in TOP with 0.1M (ml)**
1ZnS	$5.0*10^{-7}$	0.30	0.30
2ZnS	$5.0*10^{-7}$	0.58	0.58
3ZnS	$5.0*10^{-7}$	0.96	0.96
4ZnS	$5.0*10^{-7}$	1.43	1.43
5ZnS	$5.0*10^{-7}$	2.00	2.00
6ZnS	$5.0*10^{-7}$	2.66	2.66
7ZnS	$5.0*10^{-7}$	3.41	3.41
8ZnS	$5.0*10^{-7}$	4.26	4.26
9ZnS	$5.0*10^{-7}$	5.21	5.21
10ZnS	$5.0*10^{-7}$	6.25	6.25
11ZnS	$5.0*10^{-7}$	7.38	7.38
12ZnS	$5.0*10^{-7}$	8.61	8.61
13ZnS	$5.0*10^{-7}$	9.93	9.93
14ZnS	$5.0*10^{-7}$	11.35	11.35
15ZnS	$5.0*10^{-7}$	12.87	12.87
16ZnS	$5.0*10^{-7}$	14.47	14.47
17ZnS	$5.0*10^{-7}$	16.18	16.18
18ZnS	$5.0*10^{-7}$	17.97	17.97
19ZnS	$5.0*10^{-7}$	19.86	19.86
20ZnS	$5.0*10^{-7}$	21.85	21.85
21ZnS	$5.0*10^{-7}$	23.93	23.93
22ZnS	$5.0*10^{-7}$	26.11	26.11
23ZnS	$5.0*10^{-7}$	28.38	28.38
24ZnS	$5.0*10^{-7}$	30.74	30.74
25ZnS	$5.0*10^{-7}$	33.20	33.20
		309.89(Total)	**309.89(Total)**

(4). Growth of ZnSe shell on magic size InP nanoclusters. The same synthetic route as described above for ZnS shell was used while employing the ($(TMS)_2Se$) for ZnSe shell growth.

The concentration of InP MSCs with absorption at 365nm in solution is $1.20*10^{-4}$ mmol/ml, the volume of InP MSCs is 3.0ml, the total of InP MSCs is $3.61*10^{-7}$ mmol. Based on the amount of InP MSCs core, we calculate the amount of zinc and sulfur precursor for shell growth.

Table 2. The amount of zinc and selenium precursor for each shell growth on InP MSCs. (The amount of InP MSCs is $3.61*10^{-7}$ mmol).

Layer	**Amount of core (mmol)**	**Volume of zinc oleate with 0.1M (ml)**	**Volume of $(TMS)_2Se$ in TOP with 0.1M (ml)**
1ZnSe	$3.61*10^{-7}$	0.29	0.29
2ZnSe	$3.61*10^{-7}$	0.66	0.66
3ZnSe	$3.61*10^{-7}$	1.17	1.17
4ZnSe	$3.61*10^{-7}$	1.83	1.83
5ZnSe	$3.61*10^{-7}$	2.63	2.63
		6.58 (Total)	**6.58 (Total)**

(5) Ligand exchange reaction. After the synthesis of InP MSCs with absorption at 365nm, the reaction solution was cooled down to room temperature. About 2.1ml of InP MSCs with OLA and OED solution was taken out and transferred to another flask. Then, 7.6ml of TOP was injected into the InP MSCs solution at room temperature. The mixture solution was stirred for 20 min for ligand exchange to TOP. After stirring, the InP MSCs with absorption at 365nm was precipitated via hexane and ethanol. The InP MSCs were purified with hexane and ethanol for three times.

Sample characterization.

Before of the measurements, all samples were purified with hexane and ethanol for three times.

UV−vis−NIR absorption spectroscopy was performed on a JASCO V-570 spectrometer using quartz cuvettes. Fluorescence emission and excitation were performed with a Varian Cary Eclipse fluorometer. Fluorescence lifetime measurements were performed using time-correlated single photon counting (TCSPC) using an Edinburgh Instruments FLS920 fluorometer with a TCC900 TCSPC card. Cuvettes containing solutions of InP/ZnS core/shell nanostructures were excited at a wavelength of 405 nm by an EPL-405 picosecond pulsed diode laser, with pulse width of 80 ps and repetition rate of 1 MHz.

X-ray powder diffraction (XRD) patterns were obtained using Cu Kα photons from a Phillips PW1830/40 diffractometer operated at 40 kV and 30 mA. Each sample was deposited as a thin layer on a low background-scattering quartz substrate.

Transmission electron microscopy (TEM) grids were prepared by depositing one drop of a solution of purified nanoparticles onto a standard carbon-coated grid. TEM was performed using a Tecnai G2 Spirit Twin T-12 transmission electron microscope with a LaB_6 filament running at an accelerating voltage of 120 KV.

FTIR measurements were carried out on a Fourier-transform infrared spectrophotometer (IRAffinity-1S, Shimadzu, Japan), which was used in conjunction with an attenuated total reflection (ATR) accessory (MIRacleTM, PIKE Technologies Inc., USA). The purified NCs were dissolved in hexane. For each measurement, 20ul of NCs in hexane solution was taken out and dropped on the sample holder.

The calculation of size of MSCs from XRD via the Debye-Scherrer equation

The Scherrer equation can be written as:

$$\tau = \frac{K\lambda}{\beta\cos\theta}$$

τ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size;

K is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite;

λ is the X-ray wavelength, λ = 1.54060 Å (in the case of CuKα1);

β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians. This quantity is also sometimes denoted as $\Delta(2\theta)$;

θ is the Bragg angle.

1. Calculation of size of InP MSCs

In the XRD of InP MSCs, there are two main diffraction peaks, the first diffraction peak at low angle is according to (111) plane. The second diffraction peak at high angle concludes diffraction from (200) and (311) planes, it is difficult to measure the β for (200) and (311) planes. We will select the diffraction peak from (111) plan to calculate the size of InP MSCs.

K=0.9

λ = 1.54060 Å

β=7.5*π/180=0.13095

2θ=27.76 degrees (diffraction peak from (111) plane)

τ_{InP}=0.9*1.54060/0.13095*cos13.88=10.9 Å

2. Calculation of InAs MSCs

In the XRD of InAs MSCs, there are two main diffraction peaks, the first diffraction peak at low angle is according to (111) plane. The second diffraction peak at high angle concludes diffraction from (200) and (311) planes, it is difficult to measure the β for (200) and (311) planes. We will select the diffraction peak from (111) plan to calculate the size of InAs MSCs.

K=0.9

λ = 1.54060 Å

β=8.1*π/180=0.14143

2θ=27.53 degrees (diffraction peak from (111) plane)

τ_{InAs}=0.9*1.54060/0.14143*cos13.765=10.1 Å

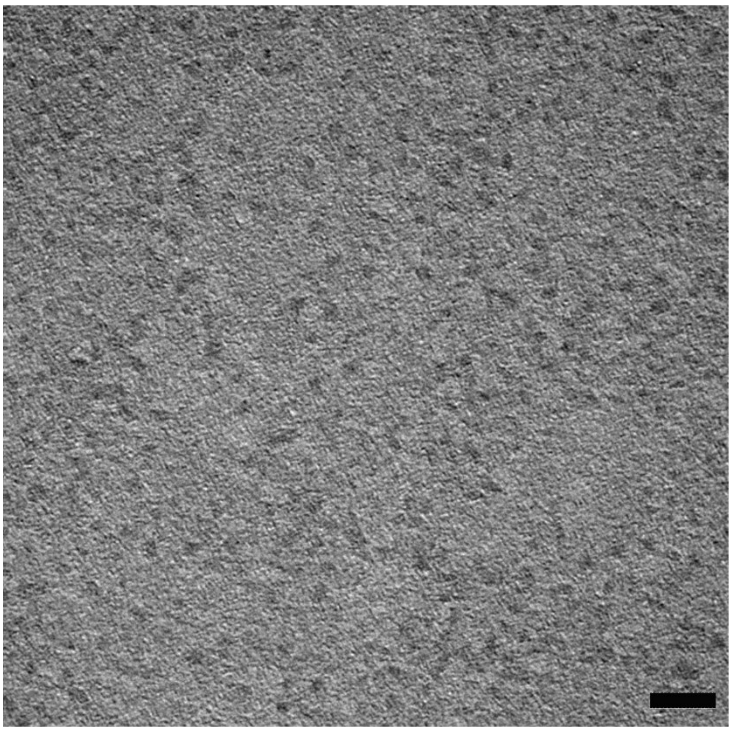

Figure S1. TEM image of InP nanoparticles produced from InP MSCs with absorption peak at 470nm, the scale is 10 nm.

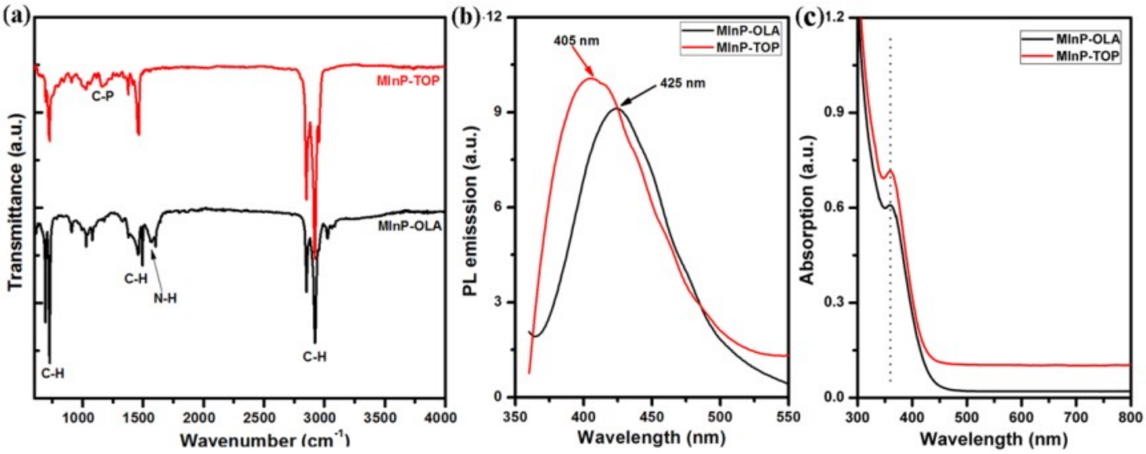

Figure S2. (a) Fourier transform infrared (FTIR) spectra of InP MSCs. The black and red lines give the transmittance spectra of InP MSCs with OLA and TOP as ligands, respectively. InP MSCs with OLA as ligand (black line): We can identify the stretching absorption of N-H at 1570cm^{-1}. InP MSCs with TOP as ligand: We identify the stretching absorption of C-P at 1210cm^{-1} , while the N-H stretch is absent. (b) Fluorescence emission spectra and (c) UV absorption spectra of InP MSCs with OLA as ligand (black line) and TOP as ligand (red line). The absorption peak of InP MCSs at 365nm is not changed with different ligand, however, there is a 20nm blue shift in the emission with TOP as ligand compared with OLA as ligand.

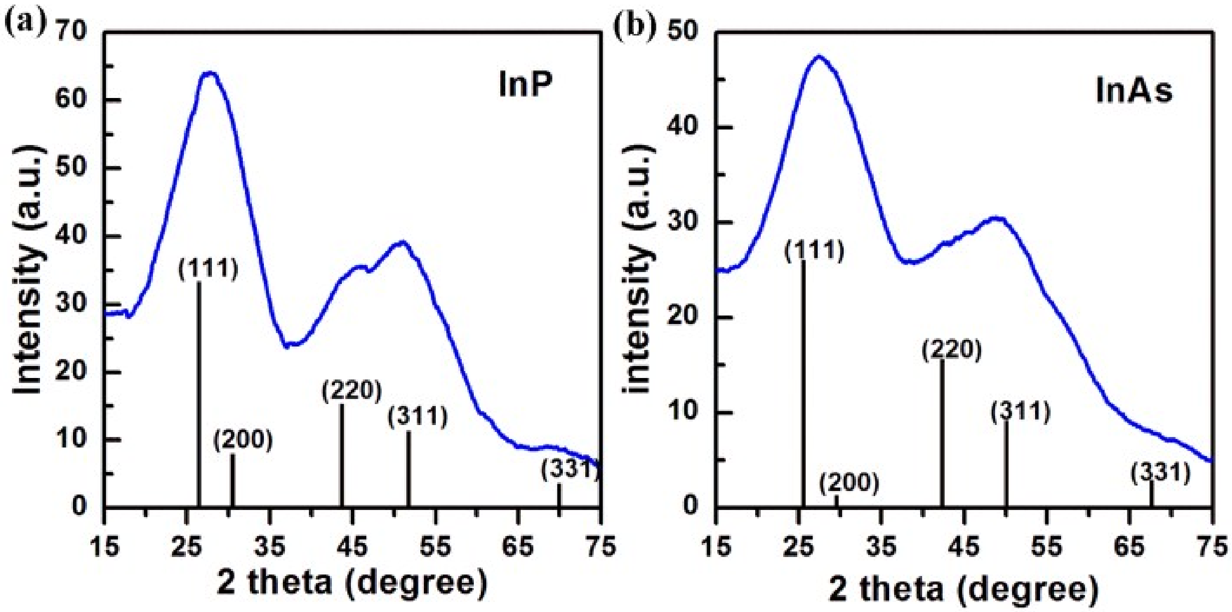

Fig.S3. (a) XRD pattern of the InP MSC with 365nm absorption peak. Solid lines indicate the diffraction peaks location for bulk InP with cubic zinc blende structure. (b) XRD pattern of the InAs MSC with 420nm absorption peak. Solid lines indicate the diffraction peaks location for bulk InAs with cubic zinc blende structure.

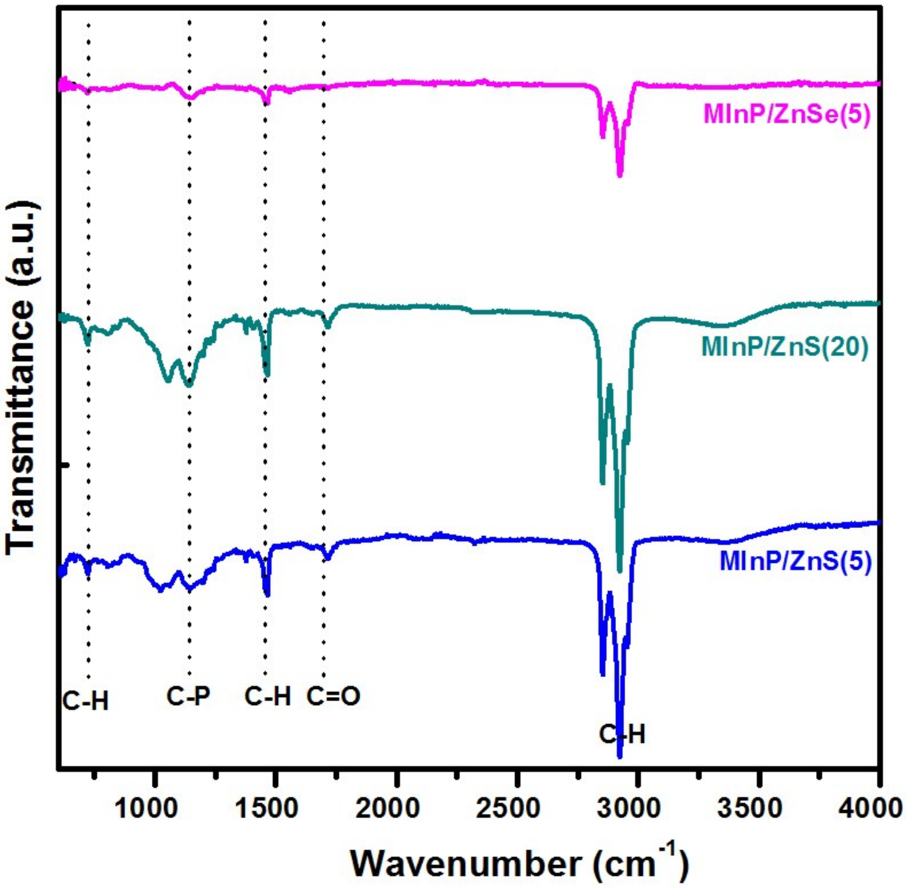

Figure S4. Fourier transform infrared (FTIR) spectra of surface ligands on InP/ZnS and InP/ZnSe core/shell nanostructures. We can see the absorption of C-P and C=O modes in InP/ZnS core/shell nanostructures. InP/ZnS NCs have the TOP and acid as mixture ligands. For InP/ZnSe NCs, we can detect the C-P binding only, indicating InP/ZnSe NCs have the TOP ligand only.

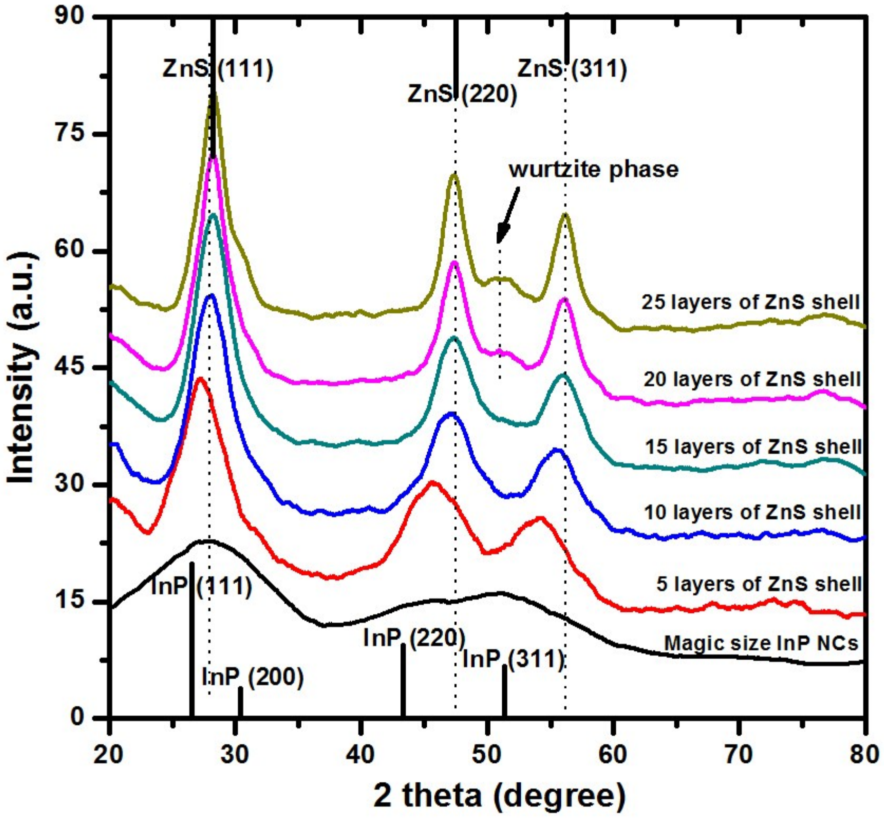

Figure S5. XRD patterns of InP/ZnS core/shell NCs with different number of ZnS layers. Stick spectra corresponding to the diffraction peaks of bulk ZnS and InP, are presented at the top and bottom, respectively.

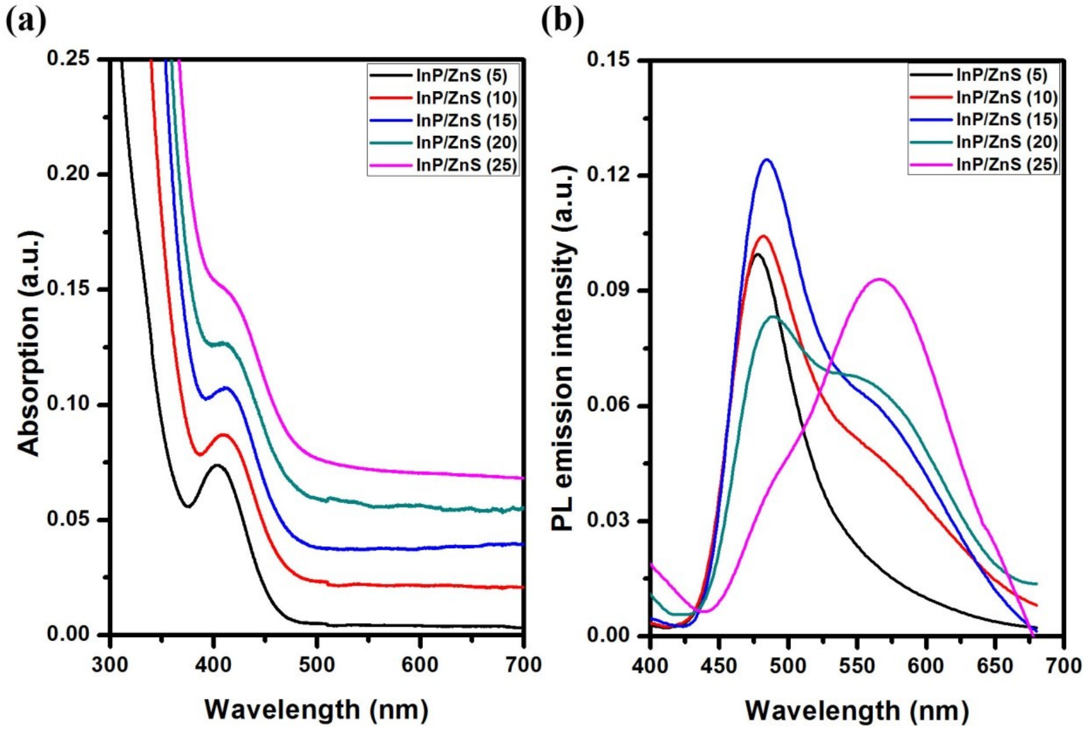

Figure S6. (a) UV-Vis absorption spectra of InP/ZnS core/shell NCs with 5 to 25 layers of ZnS shell, (b) fluorescence emission of InP/ZnS core/shell NCs with 5 to 25 layers of ZnS shell.

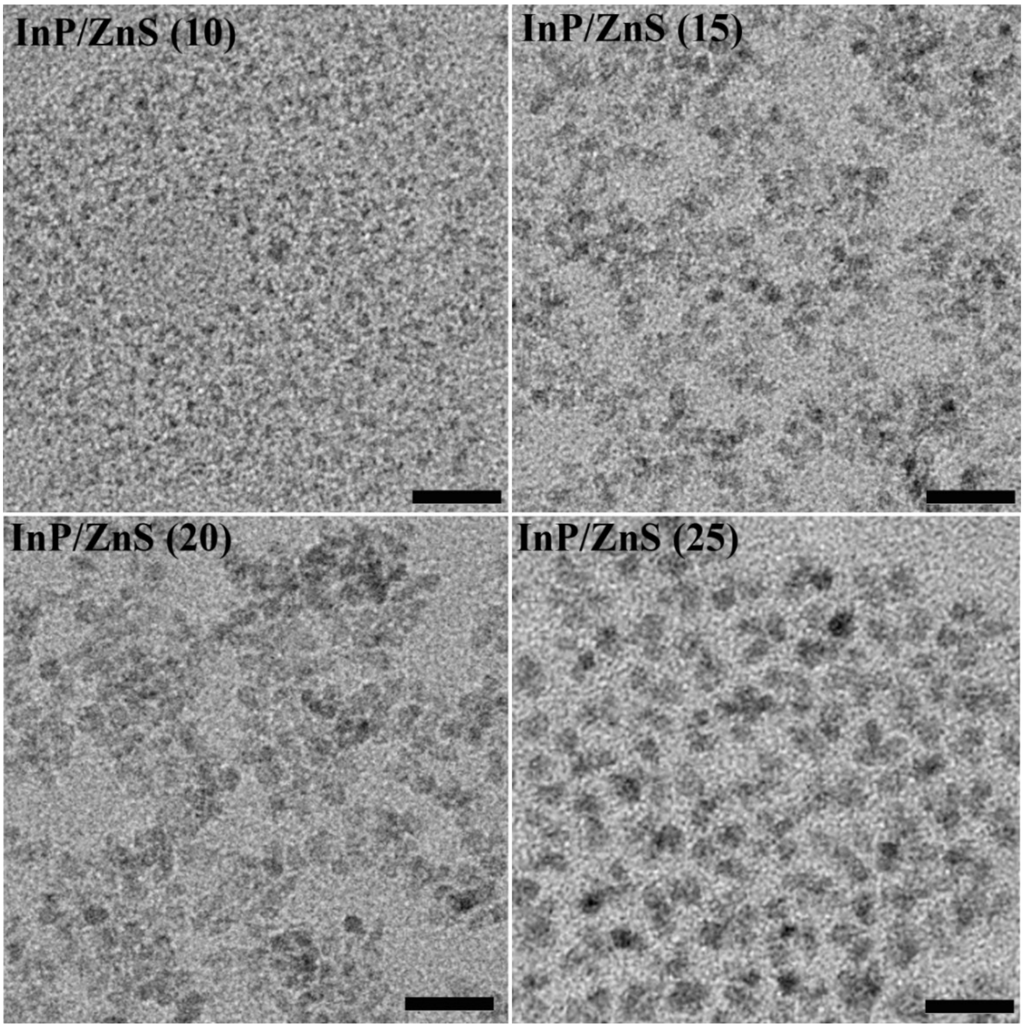

Figure S7. TEM images of InP/ZnS core/shell NCs with different layers of ZnS shell (indicated in parentheses), the scale bar is 20nm.The size of InP/ZnS NCs becomes bigger with more layers of ZnS shell. With 10 layers of ZnS shell, the InP/ZnS NCs are sphere-shape and size is 4.8nm. When we grew more layers of ZnS shell, the shape of NCs is not particles. In the end, the InP/ZnS NCs can grow to 9nm with 25 layers of ZnS shell.

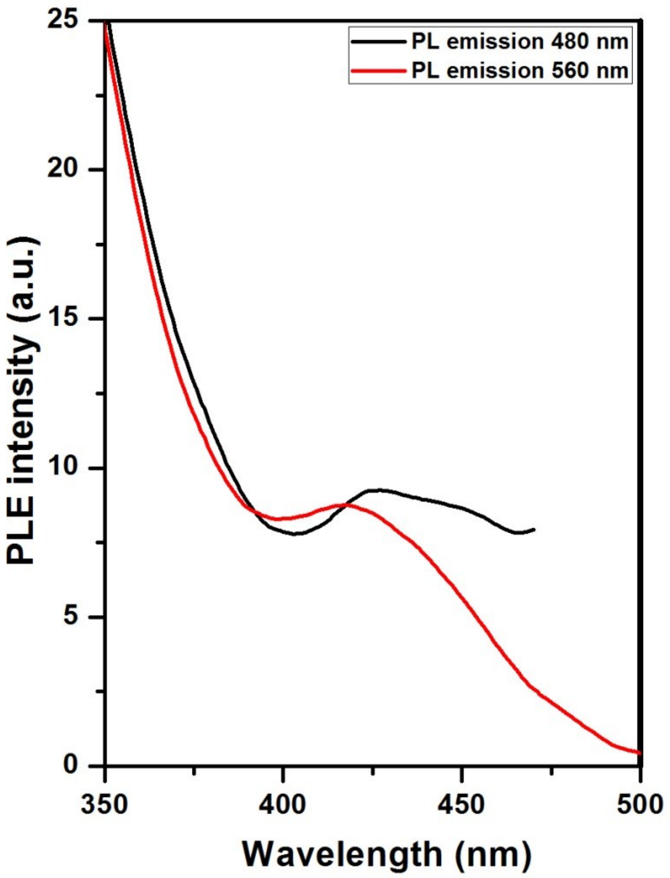

Figure S8. Photoluminescence excitation spectra of emission detected at 480nm and at 560nm for InP/ZnS NCs with 20 layers of ZnS shell.

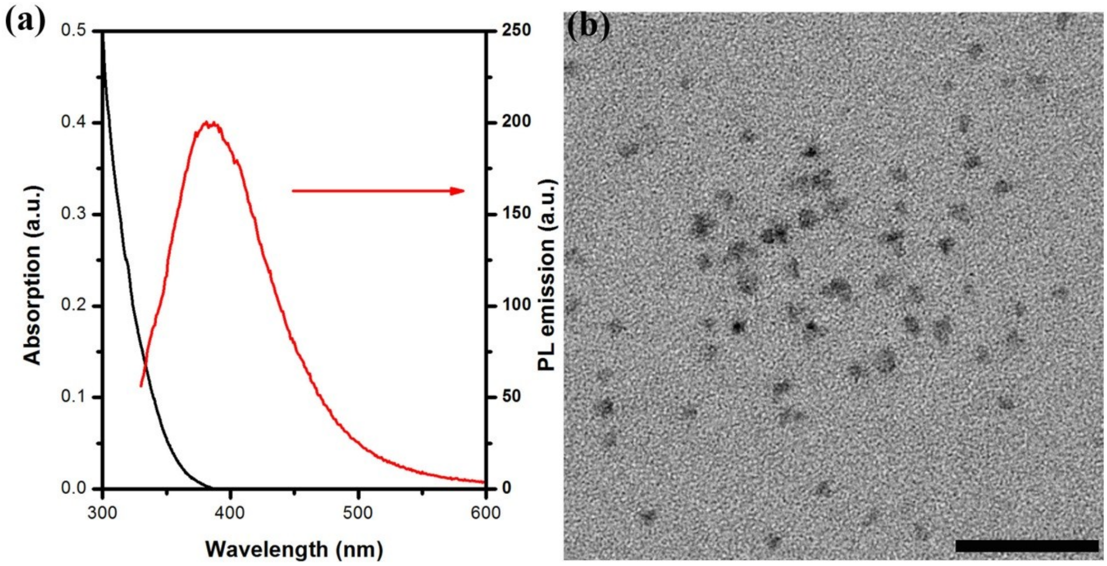

Figure S9. (a) UV-Vis absorption and fluorescence emission of ZnS nanoparticles prepared in a control reaction and (b) TEM images of the ZnS nanoparticles , scale bar is 20 nm.

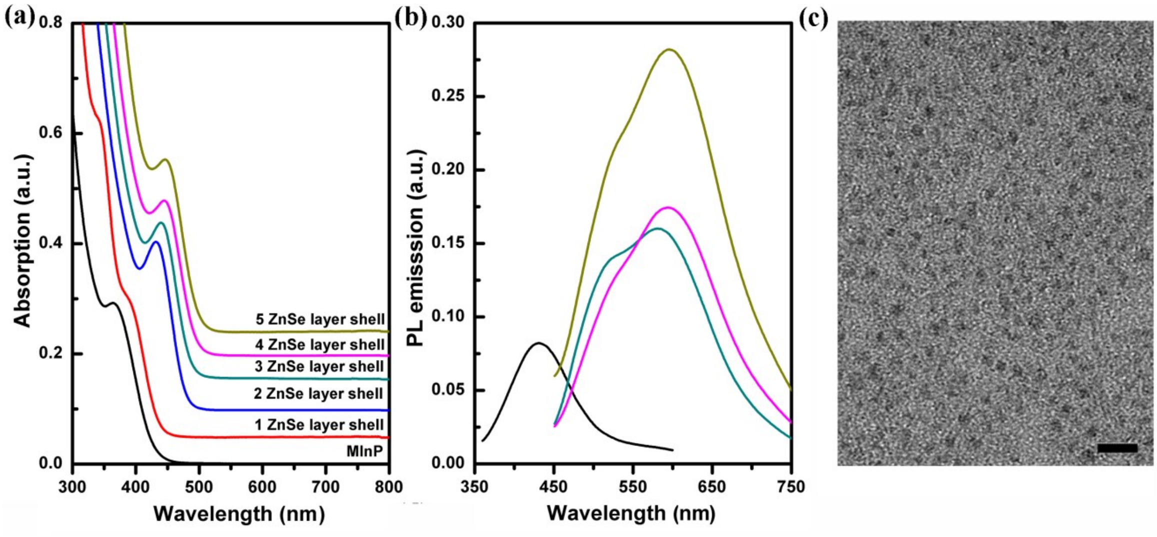

Figure S10. (a) UV-Vis absorption of the 365 nm InP MSC and of InP/ZnSe core/shell NCs with different number of layers of ZnSe, (b) fluorescence emission of InP/ZnSe core/shell NCs with different number of layers of ZnSe (color code same as in frame a), (c) TEM images of InP/ZnSe core/shell NCs with 5 layers of ZnS, scale bar is 10 nm.

References

1. G. Becker, G. Gutekunst and H. J. Wessley, *Zeitschrift für anorganische und allgemeine Chemie*, 1980, **462**, 113.