

Temporal evolutions of the photoluminescence quantum yields of colloidal InP, InAs and their core/shell nanocrystals

Jianbing Zhang,^{a, b} Rong Li,^a Weipeng Sun,^a Qi Wang,^a Xiangshui Miao,^{a, b} and Daoli Zhang^{a, b, *}

^a School of Optical and Electronic Information, Huazhong University of Science and Technology, No. 1037 Luoyu Road, Hongshan District, Wuhan City, Hubei Province, 430074, P. R. China. Electronic mail: zhang_daoli@hust.edu.cn

^b Wuhan National Laboratory for Optoelectronics, 1037 Luoyu Road, Hongshan District, Wuhan City, Hubei Province, 430074, P. R. China

E-mail: zhang_daoli@hust.edu.cn

Experimental details

Synthesis of InAs, InAs/ZnSe and InAs/ZnSe/ZnS nanocrystals: InAs nanocrystals were synthesized according to ref [25]. Typically, 0.3 mmol InAc₃ was mixed with 0.9 mmol myristic acid (MA) and 8 mL 1-octadecene (ODE) in a three neck flask. The mixture was flushed with Ar, and was heated to 220 °C under Ar atmosphere. In another container, 0.15 mmol Zn₃As₂ powder was divided into two parts (0.05 and 0.1 mmol). Firstly, the 0.05 mmol Zn₃As₂ reacted with HCl, about 10 min later, excess HCl was injected into the 0.1 mmol partition. Then the generated AsH₃ was bubbled into the hot In precursor under Ar flow through a drying tube containing P₂O₅. The growth of InAs nanocrystals was controlled in 20-30 min. InAs-zinc stearate nanocrystals were synthesized similarly except 0.3 mmol zinc stearate was added along with In source. For the growth of ZnSe shell, the temperature of the reaction solution was dropped down to ~130 °C after the formation of InAs-zinc stearate nanocrystals, then 0.3 mL 1 M TOPSe (Se powder dissolved in trioctylphosphine) was added. After that, the reaction mixture was heated to 220 °C very slowly, and maintained at the temperature for 1 hour. For the synthesis of InAs/ZnSe/ZnS nanocrystals, InAs-zinc stearate nanocrystals were synthesized at 240 °C in the presence of 0.6 mmol zinc stearate. Then a layer of ZnSe shell was formed according to the above method. And then a ZnS

shell was formed using the same method with that of ZnSe shell except dodecanethiol (DDT) was used as S source. After the formation of these nanocrystals, 0.3 mL reaction product of InAs, InAs-zinc stearate, InAs/ZnSe or InAs/ZnSe/ZnS nanocrystals was dissolved in 5 mL hexane to give clear solutions which were stored in gloom. The absorption and PL spectra of the nanocrystal solutions were recorded at different times to monitor the evolution of optical property.

Synthesis of InP and InP/ZnS nanocrystals: colloidal InP-zinc stearate nanocrystals were synthesized at 250 °C using the same method with that of InAs-zinc stearate nanocrystals while Ca_3P_2 is used as phosphorus source which was not divided into two parts. InP/ZnS nanocrystals were synthesized using the same method with that of InAs/ZnSe nanocrystals except the TOPSe was replaced by DDT. Analogously, after the formation of InP-zinc stearate or InP/ZnS nanocrystals, 0.5 mL of the reaction solution was removed and dissolved in 4 mL hexane. The absorption and photoluminescence spectra of the nanocrystal solutions were recorded at different times to monitor the evolution of optical property.

Characterization: Absorption and PL spectra were measured at room temperature on a Perkin-Elmer Lambda 35 UV-vis spectrometer and a Jasco FP-6500 fluorescent spectrometer respectively. QYs at 0 day were obtained by comparing the integrated emission spectra to standard dyes, and then the QYs at the following times were obtained relative to 0 day.

The powder X-ray diffraction (XRD) patterns, absorption and PL spectra of these core and core/shell nanocrystals can be found in the Supporting Information.

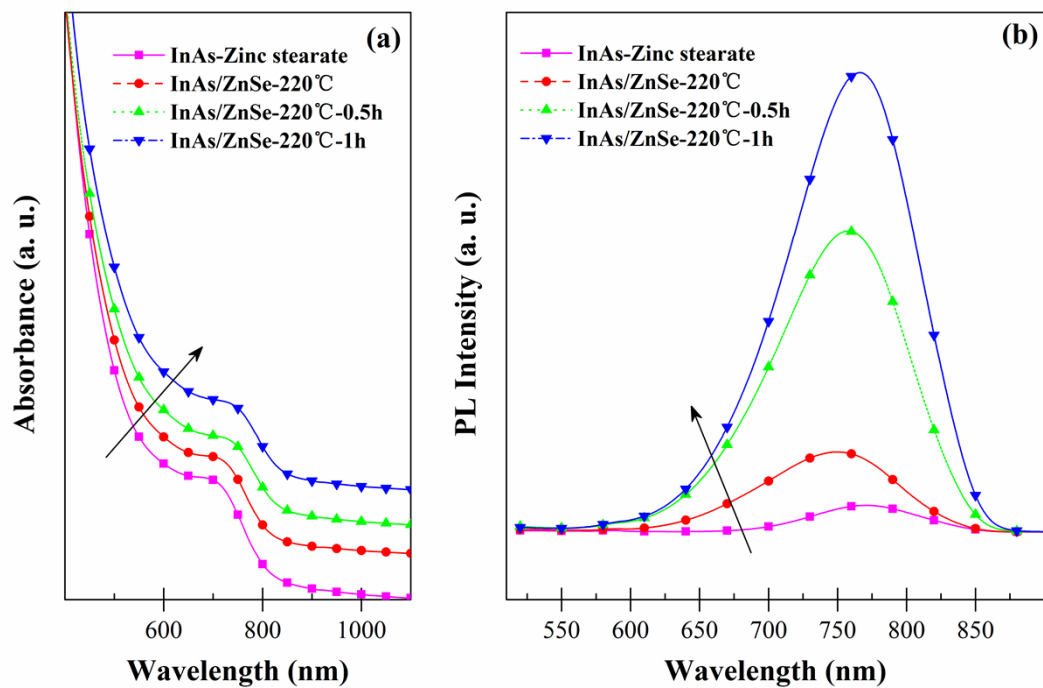


Figure S1. The evolution of absorption and PL spectra of the nanocrystals during the growth of ZnSe shell. The blue-shift of the optical peaks of InAs/ZnSe-220 °C nanocrystals compared to that of InAs-zinc stearate (InAs-ZnSt) nanocrystals is due to the dissolution of InAs nanocrystals during the slow rise of the reaction temperature.^[1]

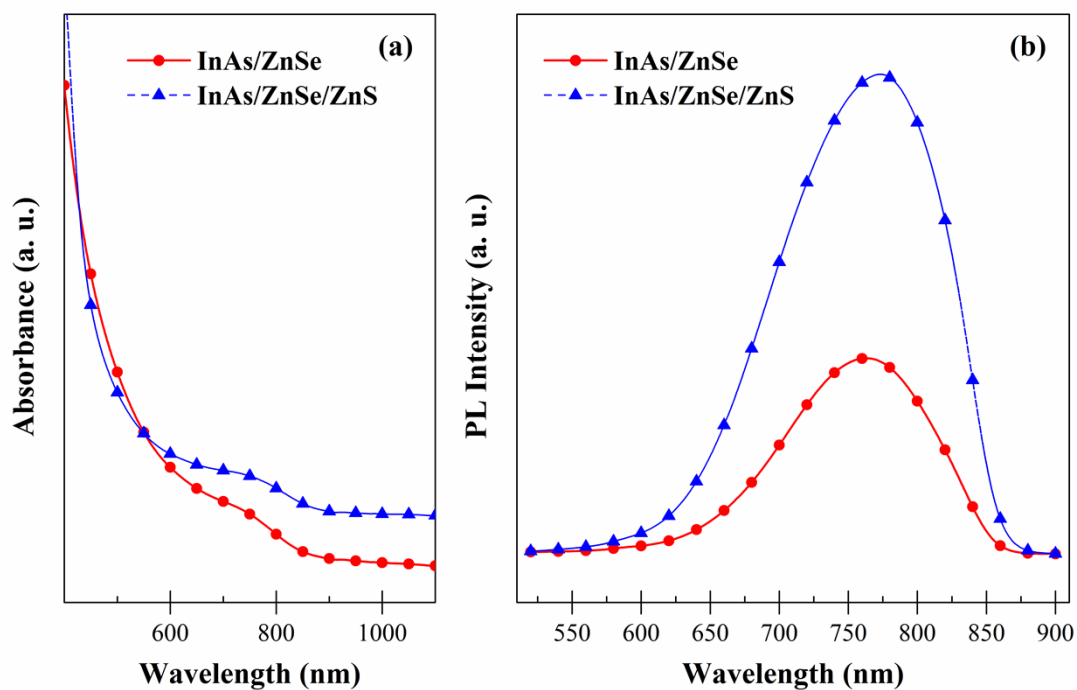


Figure S2. The absorption and PL spectra of InAs/ZnSe and InAs/ZnSe/ZnS nanocrystals in a synthesis of InAs/ZnSe/ZnS nanocrystals.

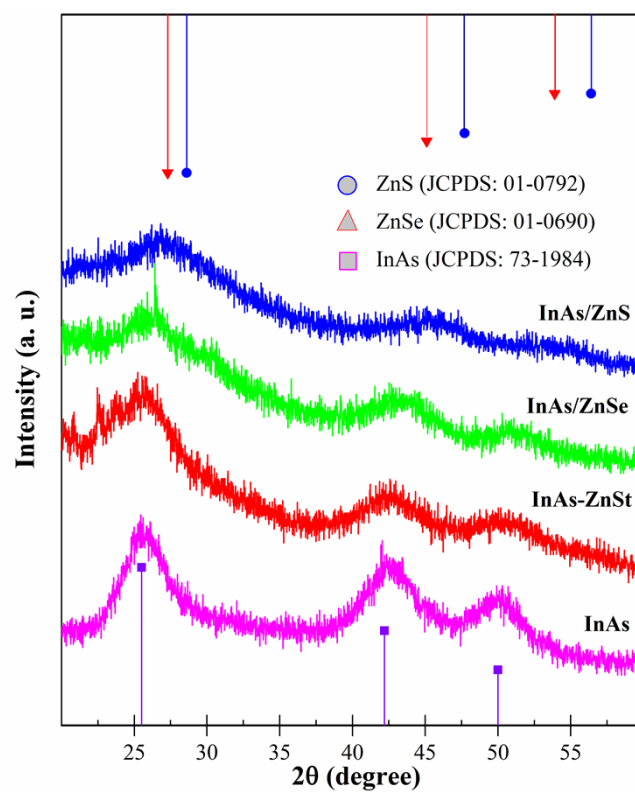


Figure S3. XRD diffraction patterns of InAs, InAs-ZnSt, InAs/ZnSe and InAs/ZnS nanocrystals.

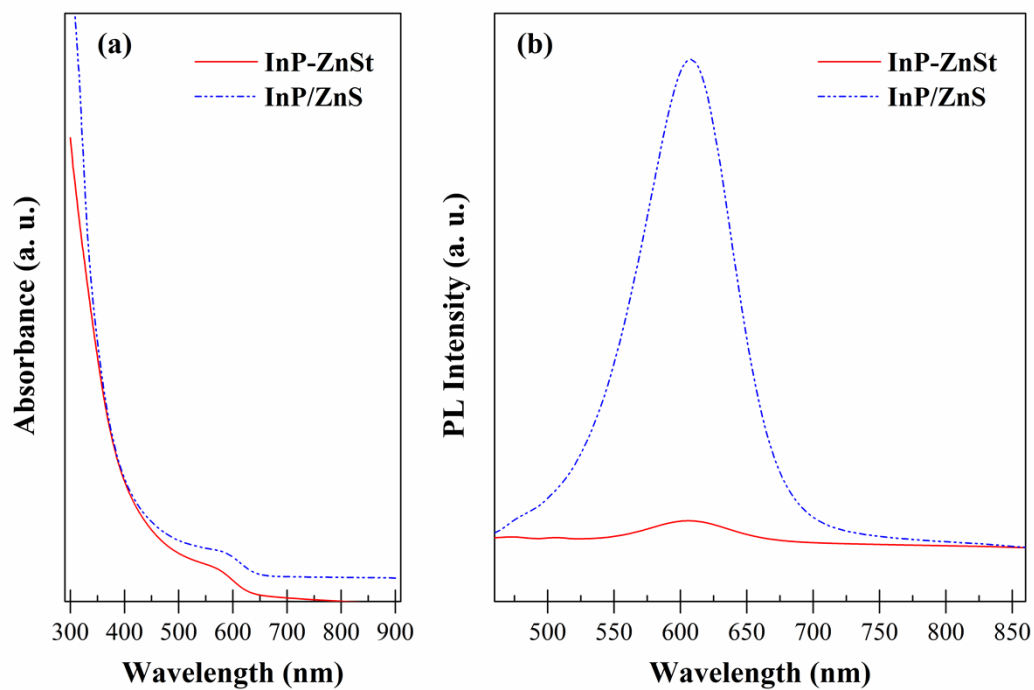


Figure S4. The absorption and PL spectra of InP-ZnSt and InP/ZnS nanocrystals in a synthesis of InP/ZnS nanocrystals.

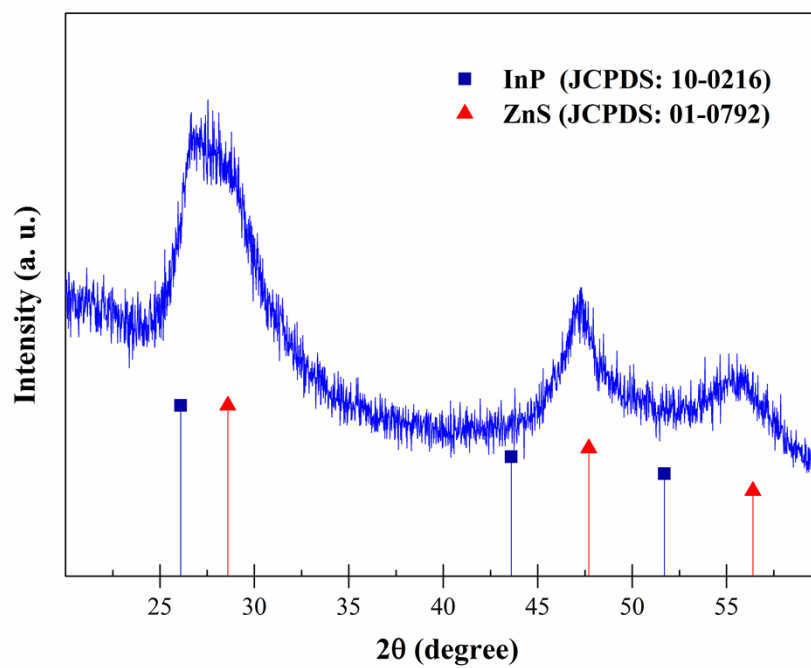


Figure S5. XRD diffraction pattern of InP/ZnS nanocrystals.

[1] J. B. Zhang, D. L. Zhang, *CrystEngComm*, **2010**, 12(2): 591

[2] J. B. Zhang, D. L. Zhang, *Chemistry of Materials*, **2010**, 22 (4): 1579