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# Photoluminescence and Growth Kinetics of High-Quality Indium Arsenide and InAs-Based Core/Shell Colloidal Nanocrystals Synthesized Using Arsine ($AsH_3$) Generated via Zinc Arsenide as the Arsenic Source

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High quality indium arsenide (InAs) and InAs/ZnS, InAs/ZnSe core/shell nanocrystals were synthesized using arsine ($AsH_3$) generated via zinc arsenide ($Zn_3As_2$) as arsenic precursor. Injection of additional solvent was adopted to control the nucleation. The growth process and different reaction parameters were studied by monitoring the absorption or photoluminescence spectra. The growth of InAs nanocrystals should be controlled in 20−30 min, an extension of growth will lead to dissolution of the NCs due to the instability of the monomer formed from $AsH_3$. The $Zn_3As_2$ was divided into two parts to extend the duration of size distribution narrowing. Addition of zinc stearate along with indium source not only improved the photoluminescent property without leading to doping of InAs nanocrystals, but also facilitated the one-pot growth of InAs-based core/shell nanocrystals. The photoluminescence quantum yields of InAs/ZnS and InAs/ZnSe core/shell nanocrystals were 8% and 15%, respectively.

## Introduction

Colloidal semiconductor nanocrystals (NCs) are inorganic semiconductor nanoparticles of 1−100 nm in size, which are single crystals and capped with ligands. They are often referred to as colloidal quantum dots (QDs) for the reason that their fundamental electronic and optical properties are size dependent due to the effect of quantum confinement.[1] Semiconductor NCs with high degree of size control can be synthesized by convenient organometallic methods. They exhibit unique optical and electronic properties,[2] and are attracting more and more interest due to their remarkable quantum confinement effect.[1] Semiconductor NCs can be applied in biological imaging,[3−6] lasers,[7,8] light emitting diodes,[9−11] solar cells,[12−14] nanosensors,[15−17] electronic devices,[18] telecommunication,[19] etc. All of these applications demand high quality semiconductor NCs being prepared.

Colloidal semiconductor NCs (QDs) are typically grown in an organic solvent under air-free condition. Their synthetic chemistry has attracted substantial interest in recent years. However, there is less literature on the synthesis of III-V materials (indium phosphide being an exception) than that of II-VI and IV-VI analogues. Nevertheless, compared with Cd- and Pb-containing II-VI and IV-VI nanocryatals, III-V NCs are less toxic. Moreover, they have larger exciton diameters, so they exhibit more remarkable quantum confinement effect with the same size as the II-VI and IV-VI NCs. Therefore, it is essential to develop the low-cost synthesis of high

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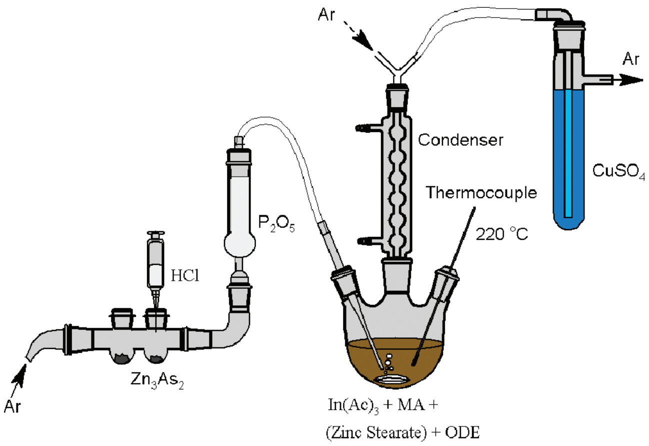
quality III-V NCs. Up to now, most of the studies on III-V NCs focused on indium phosphide (InP) NCs,[20-26] while indium arsenide (InAs) NCs are less developed. Nevertheless, the exciton diameter of InAs (~740 Å) is larger than that of InP (~200 Å), and InAs NCs emit in near-infrared (NIR) window, so they are more suitable for the applications in biological and telecommunication.

Recently, Peng and co-worker reported the synthesis of high quality InAs NCs based on self-focusing.[27] Like previous InAs NCs syntheses,[28-30] they used $As(SiMe_3)_3$ as the arsenic source. Nevertheless, $As(SiMe_3)_3$ can not be obtained commercially, and they were prepared according to ref 31 in all of the syntheses of InAs NCs. This made the synthesis of InAs NCs more complicated obviously. What is more, the quality of the prepared $As(SiMe_3)_3$ affected the quality of the synthesized InAs NCs substantially. Recently, Fang and co-worker demonstrated an economic and convenient synthesis of InP NCs using $PCl_3$ as the phosphorus source, and they also succeeded in the synthesis of InAs NCs using $AsCl_3$ as the arsenic source.[32] Although there were other arsenic sources,[33,34] the quality of the InAs NCs synthesized from them was poor. Herein, we tried to use $AsH_3$ generated via zinc arsenide as the arsenic source to synthesize InAs NCs as an alternative method. Although $AsH_3$ is a toxic gas, the whole experiment was carefully operated in a fume hood and the unreacted $AsH_3$ was treated with $CuSO_4$ aqueous solution. So it will be an alternative method, which is simple, economic, and of high repeatability. Additionally, the growth process was studied by monitoring the absorption spectra.

In order to optimize the synthesis of InAs NCs, we systematically explored the effects of different reaction parameters. For the purpose of improving the luminescent property, we epitaxially grew a semiconductor shell with broader band gap—ZnSe or ZnS—on InAs NCs to form InAs/ZnSe and InAs/ZnS core/shell NCs. Additionally, the stability of InAs and their core/shell NCs were studied as well.

**Scheme 1. Experimental Setup for the Synthesis of InAs NCs**



## Experimental Section

**Chemicals.** Indium acetate ($InAc_3$), zinc arsenide ($Zn_3As_2$), myristic acid (MA), 1-octadecene (ODE), trioctylphosphine (TOP), and zinc stearate were purchased from Alfa Aesar, dodecanethiol (DDT) and Se powder were purchased from Sinopharm Chemical Reagent Co., Ltd. All the chemicals were used as received. $AsH_3$ generated from the reaction between $Zn_3As_2$ and HCl was used as the arsenic source. The $AsH_3$ gas, which is very toxic and should be handled carefully, was dried prior to use.

**Synthesis of Indium Arsenide NCs.** In a typical process, $InAc_3$ (0.3 mmol) was mixed with 0.9 mmol MA and 8 mL 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 $Zn_3As_2$ powder was divided into two parts (0.05 and 0.1 mmol). First, the 0.05 mmol $Zn_3As_2$ reacted with HCl, about 10 min later, excess HCl was injected into the 0.1 mmol partition. Then the generated $AsH_3$ was bubbled into the hot indium precursor under Ar flow. The growth of InAs NCs was controlled in 20−30 min, an extension of growth would deprave the quality of the NCs. Zinc stearate could be added along with indium source to improve the luminescent property without leading to doping. The whole experiment was carefully operated in a fume hood and the unreacted $AsH_3$ was treated with $CuSO_4$ aqueous solution. The experimental setup is schematically shown in Scheme 1.

**Study of the Growth Process.** In order to study the growth process, we injected additional ODE into the reaction flask to stop nucleation and did not divide the $Zn_3As_2$ into two parts. In the synthesis, 2 mL ODE was injected into the hot reaction flask when the $AsH_3$ was bubbled for ~5 min. Then, at various time intervals, aliquots of the reaction mixture were removed and diluted in hexane to monitor optical spectra evolutions.

**Synthesis of InAs-Based Core/Shell NCs.** For the formation of ZnS shell, InAs NCs were synthesized at 240 °C in the presence of 0.3 mmol zinc stearate. After the formation of InAs NCs, the reaction temperature was dropped down to ~130 °C, and 0.3 mmol DDT dissolved in 1 mL ODE was injected into the hot mixture. Then the reaction mixture was heated to 240 °C very slowly and maintained at this temperature for 1 h. The growth of ZnSe shell was similar with that of ZnS, except the DDT was replaced by 0.3 mL 1.0 M TOPSe (Se powder dissolved in TOP) solution and the reaction temperature was 220 °C.

**Characterization of Indium Arsenide and their Core/Shell NCs.** Absorption and photoluminescence (PL) spectra were

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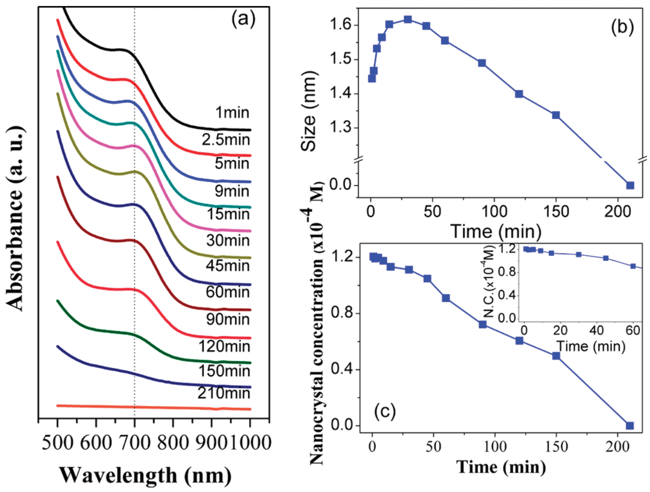

**Figure 1.** Temporal evolution of absorption spectra (a) of the InAs NCs prepared without the presence of zinc stearate. Temporal evolution of NC size (b) and concentration (c) extrapolated from the absorption spectra.

measured on a Perkin-Elmer Lambda 35 UV−vis spectrometer and a Jasco FP-6500 fluorescent spectrometer respectively. Powder X-ray diffraction (XRD) patterns were collected on a PANalytical X'Pert PRO. Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai G2 20 transmission electron microscope operating at an accelerating voltage of 200 kV.

## Results and Discussion

**Growth Kinetics of Indium Arsenide NCs.** Because most of the properties of nanocrystals depend on the size,[1] monodispersity is a basic request for high quality nanocrystals. Monodispersed nanocrystals demand temporal separation of nucleation and growth,[35] which can be partially satisfied by injection for liquid precursors, but it is difficult for gaseous precursors, especially for the gaseous precursors which are generated continuously. Reiss and co-workers used a stronger gas flow in the nucleation duration and a weaker gas flow in the growth duration to partially separate nucleation and growth.[25] In the present work, the $AsH_3$ was generated continuously and the production was strongest in the first 5 min then it weakened slowly until the $Zn_3As_2$ was exhausted (~20 min). In order to study the growth process, an injection of additional solvent was adopted to stop nucleation. The injection of more solvent will decrease the temperature of the mixture and concentration of the monomer, and both of them can inhibit nucleation.

Figure 1a shows the temporal evolution of the absorption spectra of InAs NCs after the injection of ODE. The absorption peak shows red-shift in the first 30 min and blue-shift in the following time, indicating the InAs NCs grew bigger first then became smaller. Accompanied with the decrease in size, the absorption peak becomes broadened and weakened slowly. Finally, there is no absorption in the spectrum and the reaction mixture became colorless while black deposition left at the bottom of the flask. These phenomena imply that InAs NCs dissolved slowly and disappeared at last. The dissolution of InAs NCs may be due to the instability of the monomer formed from $AsH_3$. As a result, the monomer decomposed to $AsH_3$, and the $AsH_3$ further decomposed to arsenic at high temperature. This was confirmed by the black deposition proved to be As (Supporting Information (SI) Figure S1).

Using the relationship between the first excitonic absorption peak and average size given by Peng and Xie,[27] we extrapolated the temporal evolution of the average size of the InAs NCs which is shown in Figure 1b. Based on the average sizes, molar extinction coefficients were obtained using the relationship between average size and molar extinction coefficient.[27] Then, applying the Lambert−Beer's law,[36] we calculated the temporal evolution of NC concentration which is shown in Figure 1c.

In the first 9 min, the monomer increased substantially and the NC size increased a little (Figure 1b), whereas the NC concentration decreased slightly rather than increased (Figure 1c inset), indicating the injection of ODE controlled the nucleation effectively. Meanwhile, the size distribution narrowed continuously (Figure 1a) which indicated the NCs grew in self-focusing regime.[27,37] In 9−30 min, because the production of $AsH_3$ became weaker, the addition and decomposition of the monomer was approximately equal, so the monomer concentration kept nearly constant. In consequence, the NCs grew in Ostwald ripening regime,[38] which was demonstrated by the relatively slow growth (Figure 1b) and the slight decrease of the NC concentration (Figure 1c inset). After 30 min, $Zn_3As_2$ was exhausted and the monomer began to decrease monotonously due to thermal decomposition, so InAs NCs began to release monomer (dissolution) to maintain the balance between the NC size and concentration with the monomer concentration, with the result that InAs NC size and concentration decreased monotonously (Figure 1 b and c) and the size distribution broadened slowly due to the decomposition rate depends on size. Therefore, the InAs NCs disappeared (~200 min) when the monomer decomposed completely.

Based on the previous analysis, the synthesis of InAs NCs should be controlled in 20−30 min. Excessive growth does not substantially improve the luminescent property (Figure 2) but results in broadening of the size distribution. The size distribution will narrow via size-focusing[39] or self-focusing growth when the monomer concentration is increased substantially. So in order to obtain InAs NCs with narrower size distribution, we divided the $Zn_3As_2$ into two parts. The first part was mainly used for nucleation and a second part was used for supplementation of monomer.

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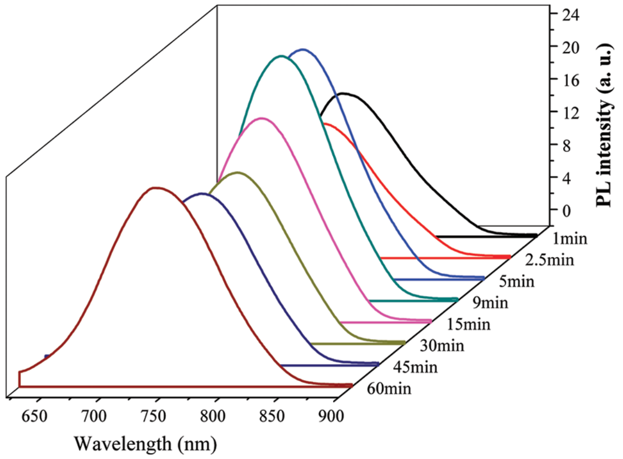

**Figure 2.** Temporal evolution of PL spectra for InAs NCs prepared without the presence of zinc stearate.

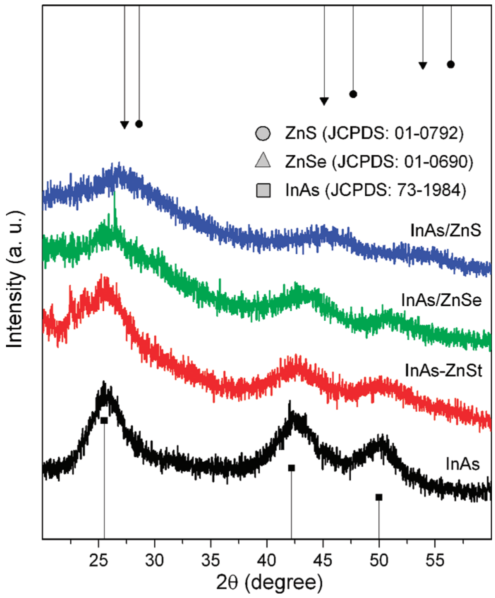

**Figure 3.** XRD diffraction patterns of InAs, InAs-zinc stearate, InAs/ZnSe, and InAs/ZnS NCs.

The addition of zinc stearate along with indium precursor was helpful for passivation of InAs NC surfaces, because zinc carboxylates can coordinate to arsenic sites on the surface to strengthen the luminescent property without result in lattice doping, which is analogous with that of InP.[25,26,40] The XRD pattern of InAs NCs prepared in the presence of zinc stearate (InAs-zinc stearate) matches well with the standard diffraction peaks of bulk InAs like that of InAs NCs prepared without the presence of zinc stearate (Figure 3). Additionally, the addition of zinc stearate in advance facilitated the formation of ZnS and ZnSe shell.

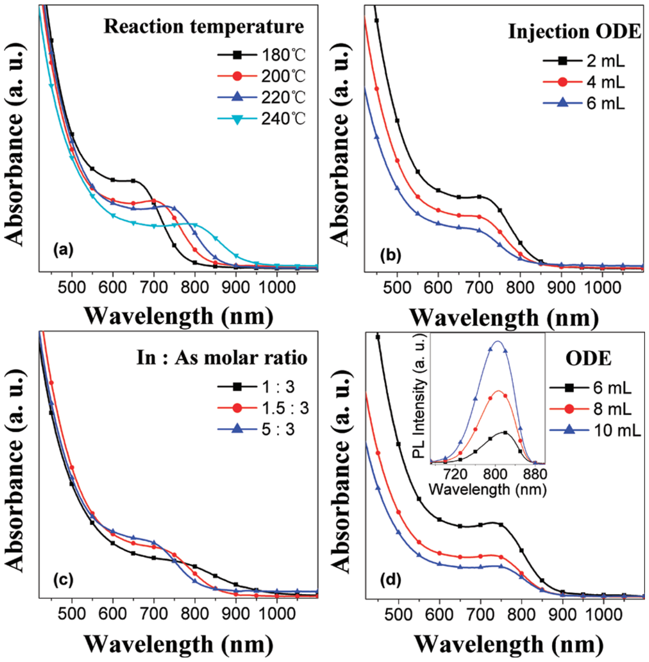

**Figure 4.** Absorption or PL spectra of InAs NCs synthesized at different reaction parameters. Standard reaction parameters (reaction temperature: 220 °C; $InAc_3$: 0.3 mmol; MA: 0.9 mmol; $Zn_3As_2$: 0.15 mmol; original ODE: 8 mL; injection ODE: 2 mL; reaction time: 30 min) were adopted while one of them varied in different experiments: (a) reaction temperature; (b) injection amount of ODE; (c) ratio of In: As while $Zn_3As_2$ is 0.15 mmol; (d) original amount of ODE, (inset) PL spectra of InAs NCs synthesized in different amount of original ODE.

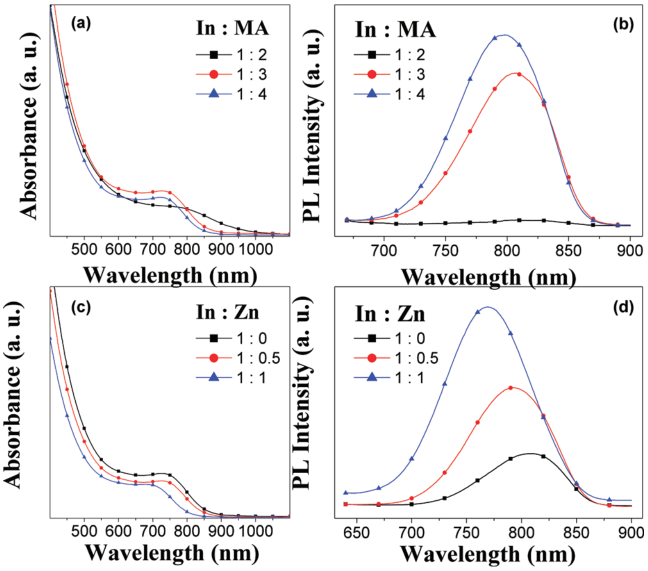

**Figure 5.** Absorption (a, c) and PL spectra (b, d) of InAs NCs with the presence of different amount of MA and zinc stearate while standard parameters were adopted: (a, b) ratio of In: MA while $InAc_3$ is 0.3 mmol; (c, d) ratio of In: Zn while $InAc_3$ is 0.3 mmol.

**Effects of Different Reaction Parameters.** Different reaction parameters were studied to explore their effects on the growth of InAs NCs, involving the reaction temperature, the ratio of indium to arsenic precursors, the amount of MA, zinc stearate, original ODE, and the injection amount of ODE. Figure 4a shows the absorption spectra of InAs NCs prepared at different reaction temperatures. As shown in this figure, higher reaction temperature results in the formation of larger InAs NCs with lower particle concentration.[25] When prepared at 200 and 220 °C, InAs NCs have better monodispersity. At relatively low reaction temperature, such as 130 °C, extremely small InAs NCs with broad size distribution

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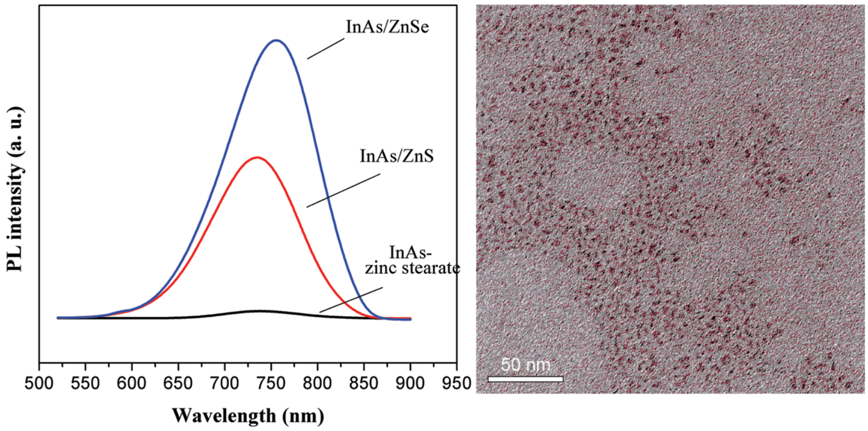

**Figure 6.** (left) PL spectra of InAs-zinc stearate, InAs/ZnS and InAs/ZnSe NCs. (right) TEM image of InAs NCs.

were formed (SI Figure S2). At even lower temperature, such as 70 °C, neither NCs nor nanoclusters[27] were formed (SI Figure S3), but if the same reaction solution was heated to 200−240 °C, InAs NCs could be formed. Higher reaction temperature ( > 240 °C) is not advisible because it will increase the decomposition rate of the monomers. The effect of the injection amount of ODE is shown in Figure 4b, which reveals that the more the injection amount of ODE was, the smaller InAs NCs became. Figure 4c shows the effect of the ratio of indium and arsenic precursors when the amount of $Zn_3As_2$ was kept invariable. More indium precursor resulted in higher monomer concentration, and higher monomer concentration leads to smaller nuclei with higher concentration.[41] At last, smaller NCs with higher particle concentration were obtained as the indium precursor increased. The three reaction parameters mentioned above did not affect the PL intensity substantially, but the amount of original ODE impacted the PL intensity remarkably but the NC size slightly. Less original ODE resulted in weaker PL intensity although it led to higher particle concentration (Figure 4d).

In contrast with the above reaction parameters, the amounts of MA and zinc stearate affect both the NC size and PL intensity substantially. The presence of MA will increase the reactivity of the indium precursor,[25] and the best reactivity can be obtained when the molar ratio of indium precursor to MA is about 1:3. If the ratio is larger than 1:3, the lower reactivity of indium precursor results in fewer nuclei and larger NCs at last (Figure 5a). If the ratio is smaller than 1:3, there will be some free MA except the part used to increase the reactivity of the indium precursor, the additional free MA serves as stabilizer,[42] which leads to smaller NCs and lower particle concentration (Figure 5a). Additionally, MA is key important for the PL property. When the molar ratio of In: MA is 1:2, the InAs NCs almost did not show PL due to inadequate surface capping (Figure 5b). When the ratio is 1:3, InAs NCs showed remarkable PL, and when the amount of MA increased again, the PL intensity increased slightly (Figure 5b). Figure 5c and d showed the effects of the amount of zinc stearate that served as stabilizer like the excess free MA. So as the increase of zinc stearate, InAs NCs became smaller and the PL intensity increased.

**Growth of InAs-Based Core/Shell NCs.** Although the addition of zinc stearate can improve the luminescent property, it is still not good enough for application. A general method is to overcoat a wide band gap semiconductor shell. DDT was adopted as sulfur source to grow ZnS shell[26,43] on InAs NCs here. In order to ensure DDT decomposed completely, we increased the reaction temperature for the synthesis of InAs NCs to 240 °C. The XRD pattern of InAs/ZnS NCs shown in Figure 3 reveals that three prominent peaks shift to resemble the XRD pattern of ZnS obviously, and no mixed peaks of InAs and ZnS are found. The weaker XRD peaks can be attributed to tiny amount of NCs in the XRD measurements. The PL quantum yield (QY) increased to 8% from below 1% after the formation of ZnS shell (Figure 6 left). Because the lattice mismatch between InAs core and ZnS shell is 10.7%,[29] we had grown a ZnSe shell on the InAs core at 220 °C, employing TOPSe as selenium source. The PL QY of InAs/ZnSe core/shell NCs is up to 15% due to fewer interface defects caused by smaller lattice mismatch (6.44%).

Figure 7 shows the evolution of absorption and PL spectra during the growth of ZnSe shell. As shown in this figure, when the reaction temperature was slowly increased to 220 °C again after the addition of TOPSe, PL intensity increased a little, indicating that a very thin ZnSe shell was formed, meanwhile, the PL peak shows slight blue-shift relative to that of InAs-zinc stearate NCs, which is attributed to the dissolution of InAs NCs during the slow rise of the reaction temperature. When the reaction temperature was maintained at 220 °C for 1 h, the absorption and PL peaks shift to long wavelength successively, accompanied by the increase of PL intensity, which indicates the formation of core/shell structure rather than alloy.[44] Additionally, as the ZnSe shell grew

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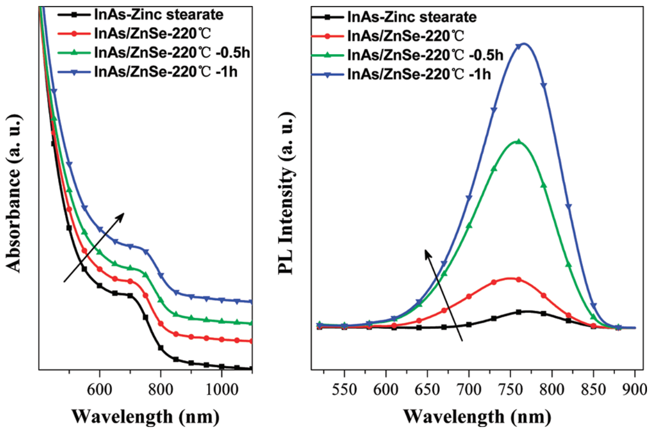

**Figure 7.** The evolution of absorption and PL spectra of the NCs during the growth of ZnSe shell.

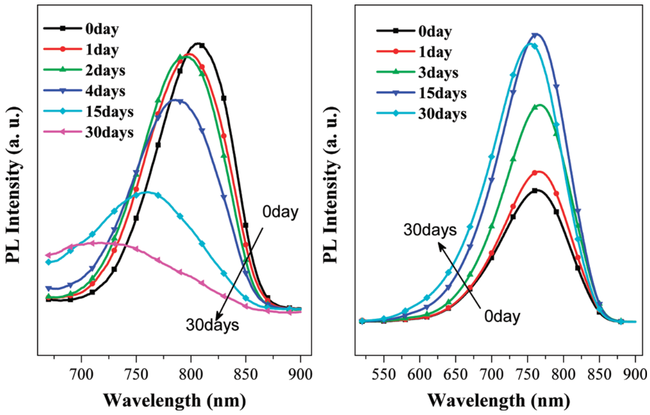

**Figure 8.** The evolution of PL spectra of InAs and InAs/ZnSe NCs stored in hexane.

thicker, the absorption spectra maintained their profiles, which implies the growth of shell maintained the original size distribution.

**Stability of InAs and Their Core/Shell NCs.** In consideration of the importance of the stability of NCs for their applications, we studied thoroughly the stability of InAs and InAs/ZnSe core/shell NCs stored in hexane. As shown in Figure 8, InAs NCs became smaller and lost PL property gradually because of surface oxidation. On the contrary, the InAs/ZnSe core/shell NCs showed increase of PL intensity which is also because of surface oxidation.[45,46] However, excessive oxidation would lead to decrease of PL intensity of the InAs/ZnSe NCs, such as when they were stored for 30 days. The diametrically opposed stability of InAs and InAs/ZnSe NCs is due to different chemical property between InAs and ZnSe.

## Conclusions

High quality InAs NCs were synthesized using $AsH_3$ generated via zinc arsenide as arsenic source. The growth kinetics and different reaction parameters were also studied by monitoring the absorption or PL spectra, which indicated that, the growth of InAs NCs should be controlled in 20−30 min, and excessive growth would lead to dissolution of the NCs due to the instability of the monomer formed from $AsH_3$. The investigation of the growth process reveals that the nucleation controlled efficiently by the injection of additional solvent. Highly luminescent InAs/ZnS and InAs/ZnSe core/shell NCs were formed using zinc stearate, DDT and TOPSe. This method is applicable for the synthesis of other III-V NCs.

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**Supporting Information Available:** X-ray fluorescence (XRF) spectrum of the black deposition in the ultimate transparent reaction solution in the synthesis of InAs NCs, absorption and PL spectra of InAs NCs synthesized at 130 °C, and absorption spectrum of the reaction mixture in the synthesis of InAs NCs at 70 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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