Published in final edited form as:

J Alloys Compd. 2016 April 25; 665: 137–143. doi:10.1016/j.jallcom.2016.01.035.

Heat-up Synthesis of Ag-In-S and Ag-In-S/ZnS Nanocrystals: Effect of Indium Precursors on Their Optical Properties

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Abstract

Cadmium-free I-III-VI nanocrystals (NCs) have recently attracted much research interests due to their excellent optical properties and low toxicity. In this work, with a simple heat-up synthetic system to prepare high quality Ag-In-S (AIS) NCs and their core/shell structures (AIS/ZnS NCs), we investigated the effect of different indium precursors (indium acetate and indium chloride) on NC optical properties. The measurements on photoluminescence spectra of AIS NCs show that the photoluminescence peak-wavelength of AIS NCs using indium acetate is in the range from 596 to 604 nm, and that of AIS NCs using indium chloride is from 641 to 660 nm. AIS and AIS/ZnS NCs using indium acetate present around 15% and 40% QYs, and both AIS and AIS/ZnS NCs using indium chloride present around 31% QYs. The photoluminescence decay study indicates that the lifetime parameters of AIS and AIS/ZnS using indium chloride are 2 ~ 4 times larger than those of AIS and AIS/ZnS NCs using indium acetate. Moreover, AIS NCs using indium chloride have a slower photobleaching dynamics than AIS NCs using indium acetate, and ZnS shell coating on both types of AIS NCs significantly enhances their photostability against UV exposure. We believe that the unique optical properties of AIS and AIS/ZnS NCs will open an avenue for these materials to be employed in broad electronic or biomedical applications.

Abstract

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INTRODUCTION

I-III-VI nanocrystals (NCs) such as Cu–In–S (CIS) and Ag–In–S (AIS) as well as their core-shell structures (CIS/ZnS and AIS/ZnS NCs) have excellent optical properties and low toxicity, and they are promising materials to replace the cadmium-based NCs in electronics industry and biomedical research [1–2]. Compared to CIS NCs, AIS NCs can be easily prepared in a milder synthesis temperature (120 ~ 180 °C) [2]. The low-temperature synthesis is very attractive because it is an energy-saving process. Up to date, significant efforts have been made to develop high quality AIS NCs with tunable photoluminescence properties and high quantum yields (QYs). Since low synthesis temperatures are relatively hard to promote the NC growth in a wide size range, controlling nonstoichiometry (adjusting Ag:In molar ratio in reactions), zinc doping, or a combination of them are major strategies for the tuning of AIS photoluminescence properties [3–18]. Regarding high QYs, they usually can be achieved through ZnS shell growth on NC cores [11, 15–17]. In spite of the progress on the development of high quality AIS NCs, most of the reported synthesis approaches are hot-injection based ones, which have intrinsic limits for NC scalable production.¹⁹ Moreover, controlling nonstoichiometry and zinc doping are complex procedures in precursor preparation/injection [3, 5, 8–9, 16]. Unwanted by-products can be produced after the injection of sulfur precursors due to the excess of metal precursors (not involved in AIS formation or not doped into AIS) [13]. Even though some heat-up approaches were reported, the preparation of metal precursors involved multiple steps using highly toxic materials [5, 8, 16].

In this work, we adopted an easy heat-up approach involving silver nitrate, indium precursor (indium acetate or indium chloride), and oleic acid in dodecanethiol at 175 °C to prepare AIS NCs, which are followed by ZnS shell growth to form AIS/ZnS NCs. We found that in the AIS growth, the photoluminescence peak-wavelength of AIS NCs using indium acetate is in the range from 596 to 604 nm, and that of AIS NCs using indium chloride is from 641 to 660 nm. AIS and AIS/ZnS NCs using indium acetate have around 15% and 40% QYs, and both AIS and AIS/ZnS NCs using indium chloride possess around 31% QYs. The further photoluminescence decay study indicates the lifetime parameters of AIS and AIS/ZnS using indium chloride are much larger than those of AIS and AIS/ZnS NCs using indium acetate. Moreover, AIS NCs using indium chloride have a slow photobleaching

dynamics than AIS NCs using indium acetate, and ZnS shell coating on both types of AIS NCs significantly enhances their photostability against UV exposure. In other words, the optical properties of AIS and AIS/ZnS NCs including their photoluminescence peak-wavelength ranges, QYs, lifetimes and photostability can be tuned or impacted by using different indium precursors. In this study, material characteristics and the photoluminescence mechanisms were explored to explain the unique optical properties of all these NCs. To the best of our knowledge, it is the first time to report the effect of indium precursors on the optical properties of AIS and AIS/ZnS NCs prepared in a heat-up system.

EXPERIMENTAL METHODS

Materials and Apparatus

Silver nitrate (AgNO_3 , 99.9%), indium (III) acetate ($\text{In}(\text{Ac})_3$, 99.99%), and zinc stearate (ZnO : 12.5–14%) were purchased from Alfa Aesar. Indium (III) chloride (InCl_3 , 99.999%), 1-dodecanethiol (DDT, 98%), 1-octadecene (ODE, 90%), oleic acid (99%), acetone (>99%) and methanol (99.93%) were purchased from Sigma Aldrich. Ethanol (>99%), chloroform (>99.9%), and hexane (95%) were purchased from Pharmco-AAPER.

The ultraviolet and visible (UV-Vis) spectra of materials were obtained with a UV-Vis spectrometer (UV-2450 from Shimadzu). Photoluminescence spectra of NCs were acquired using a spectrophotometer (RF-5301PC from Shimadzu). Transmission electron microscope (TEM) images and Energy-dispersive X-ray (EDX) spectra were acquired using a JEOL analytical transmission electron microscope (model JEM 2100F operated with a 200 kV acceleration voltage) equipped with an Oxford Energy-Dispersive X-ray (EDX) spectrometer. Time-resolved photoluminescence lifetimes were measured by a Horiba Jobin Yvon Fluorolog-3 with a QY accessory and a time-correlated single-photon counting (TCSPC) spectrometer. The continuous excitation source was a 150 W ozone-free xenon arc-lamp. A pulsed xenon lamp or NanoLED (N-405L or N-300) was utilized as the excitation source for the photoluminescence decay measurement.

AIS/ZnS NC Synthesis

For a typical synthetic reaction, silver nitrate (0.1 mmol), $\text{In}(\text{Ac})_3$ or InCl_3 (0.2 mmol), 1-DDT (8 mL) and oleic acid (250 μL) were added in a three-necked round bottom flask equipped with a condenser and magnetic stir bar. This mixture was degassed under vacuum for 30 min at 135 °C until the solution became clear. The solution temperature was then increased to 175 °C under a flow of Argon. Small amounts of the reaction solution (around 0.1 mL) were collected using a syringe at different time intervals and injected into hexane in clean vials to terminate the growth of NCs. All solutions collected from the experiment were diluted in a quartz cuvette with hexane for UV-Vis absorbance and photoluminescence measurements. The solution was cooled to room temperature after the reaction was completed. The NCs solution was purified repeatedly with the solvent combinations of hexane/ethanol and chloroform/acetone by centrifugation and then dried under vacuum.

For ZnS shell growth, the Zn precursor was prepared by mixing zinc stearate (0.32 mmol) and ODE (4 mL) in a round-bottom flask. The mixture was gradually heated to ~100 °C

with stirring under vacuum until no vigorous bubbling was observed. The temperature of the solution was then increased to 160 °C under argon until a clear solution was generated. The growth of the ZnS shell on AIS NCs was conducted *in situ* without purification of the core solution. 4 mL of ODE was added to the crude AIS NC solution once the growth of cores was completed. This core solution was heated up to 210 °C under argon. Then the zinc precursor was injected in sequence 5 times to the core growth solution at 210 °C in 0.5 mL portions at 15 min intervals. After reactions were finished, mixtures were cooled down to room temperature and AIS/ZnS NCs were purified using hexane/ethanol and chloroform/acetone, and dried under vacuum. In our experiments, by using In(Ac)₃ precursor, we can collect around 40 mg AIS NCs and around 100 mg AIS/ZnS NCs per reaction; by using InCl₃ precursor, we can collect around 20 mg AIS NCs and around 45 mg AIS/ZnS NCs per reaction.

QYs of NCs were calculated according to the following equation, using standard references including Rhodamine 6G (emission peak at 556 nm, QY = 95% in ethanol) and Oxazine 170 (emission peak at 640 nm, QY = 63% in methanol),

$$QY_S = QY_R \times (I_S/I_R) \times (A_R/A_S) \times (n_S/n_R)^2$$

where QY_S and QY_R are the quantum yields of sample and a standard reference, respectively; I_S and I_R are the integrations of fluorescence emissions of sample and a standard reference, respectively; A_S and A_R are the corresponding absorbance of sample and a standard reference, respectively; and n_S and n_R are the refractive indices of the corresponding solvents.

During QY measurements, the absorbance of each sample or each standard reference should be less than 0.1. For each sample, the standard reference with the most similar absorption and/or luminescence characteristics was chosen for QY measurements.

RESULTS AND DISCUSSION

Figure 1 (a) and (b) show the evolution of photoluminescence spectra of AIS NCs prepared using In(Ac)₃ and InCl₃ as precursors at 175 °C, respectively. The QY of AIS NCs using In(Ac)₃ was gradually improved from 5% to 15% during the growth within 60 min, and their photoluminescence spectra present slight red shift (from 596 to 604 nm). Meanwhile, the AIS NCs using InCl₃ achieve a QY as high as 38% at the first 5 min after the reaction temperature reached 175 °C, and then the QY gradually decreased to 31% during the 20 min reaction. The photoluminescence spectra of the AIS NCs using InCl₃ show a continuous red shift from 641 to 660 nm. Through further comparing the photoluminescence spectra of these two types of AIS NCs, it can be seen that their shapes are different. The shape difference implicates that the two types of AIS NCs may have different photoluminescence mechanisms. It should be noted that as shown in Figure S1, the absorption spectra of the AIS NCs using InCl₃ present much distinct excitonic absorption peaks compared to those of AIS NCs using In(Ac)₃. According to the literature [4], the excitonic absorption peak is associated with a relatively narrow size-distribution or minimal surface defects for AIS NCs using InCl₃.

It is well known that the surface coating of semiconductor NCs can lower surface defects of NCs, and thus increases the photoluminescence QY of NCs. For these two types of AIS NCs, the same ZnS coating procedure was applied to them. Figure 2(a) and (b) show the photoluminescence spectra of AIS/ZnS NCs using $\text{In}(\text{Ac})_3$ -based AIS cores and InCl_3 -based AIS cores, respectively. In Figure 2(a) and (b), as comparisons, the photoluminescence spectra of the original cores are also plotted. Moreover, all spectra are scaled by their QYs. From Figure 2(a), for $\text{In}(\text{Ac})_3$ -based AIS and AIS/ZnS NCs, it is clear that ZnS shell growth or zinc etching on the AIS cores causes the blue-shift of the photoluminescence spectra. The ZnS-coating or zinc etching caused blue-shift is a typical feature of I-III-VI NCs including Cu-In-S (CIS) and Ag-In-S (AIS) NCs. Generally, it is thought that cation exchange between Zn ions (from Zn precursor) with Cu, Ag, or In in NCs occurs during ZnS-coating or zinc etching [11, 16, 20–21]. The cation exchange could etch cores and result in size-reduced cores, which are corresponding to short emission wavelength. The cation exchange also could cause the zinc doping into the original NCs to form a hybrid materials of CIS-ZnS or AIS-ZnS. Considering the wider band gap of ZnS (~ 3.9 eV), the zinc doping into CIS or AIS NCs with narrow band gaps ($1.5 \sim 1.9$ eV) will increase the NC band gap and thus the blue-shift of NCs. It also can be seen in Figure 2(a) that the QY of AIS/ZnS NCs using $\text{In}(\text{Ac})_3$ -based cores is as high as $\sim 40\%$, and it is a significant enhancement compared to the $\sim 15\%$ QY of the original cores. The QY enhancement can be attributed to the minimization of surface defects during ZnS coating or zinc etching. For InCl_3 -based AIS and AIS/ZnS NCs, as shown in Figure 2(b), the blue-shift of the photoluminescence spectra is observed for ZnS coating or zinc etching on the cores. However, interestingly, the QY ($\sim 31\%$) of AIS/ZnS NCs using InCl_3 -based cores remains almost unchanged compared to the original cores. The blue-shift without QY enhancement indicates that zinc atoms are incorporated into AIS NCs but the surface defects of InCl_3 -based AIS could be very minimal. We believe that the minimal surface defects is true considering the AIS NCs using InCl_3 achieve a $\sim 38\%$ QY in the first 5 min of the synthesis. Otherwise, significant surface defects will cause a low QY as that for the $\text{In}(\text{Ac})_3$ -based AIS.

To understand the optical properties of AIS and AIS/ZnS synthesized using two different indium precursors, these NCs were first characterized using TEM and EDX. Figure 3 presents representative TEM and high resolution TEM images of two types of AIS NCs with different growth times and the related AIS/ZnS NCs. For all AIS cores, the lattice spacing parameters are measured to be around 0.24 nm, which are matching the reported lattice spacing of AIS NCs [8]. However, for all AIS/ZnS NCs, the lattice spacing parameters are around 0.34 nm, which is close to that of ZnS NCs [17]. Such a change on the lattice spacing is consistent with what other researchers reported [9], suggesting that ZnS lattice structure or its similar dominates on the surface of AIS/ZnS NCs. The sizes of all NCs were measured and their averages and the related standard deviations were calculated. As shown in Table 1, the average size of the AIS NCs using $\text{In}(\text{Ac})_3$ with 10 min growth is 3.06 nm with a standard deviation (SD) of 0.47 nm. With the 60 min reaction time, the average size is slightly increased to 3.36 nm (SD = 0.47 nm). Their core/shell AIS/ZnS NCs are mainly distributed at 3.79 nm (SD = 0.51 nm). For the AIS NCs using InCl_3 , the average particle size is 3.76 nm (SD = 0.39 nm) after a 5-min reaction at 175 °C. The average size quickly is increased to 6.14 nm (SD = 0.88 nm) within 20-min reaction. Their core/shell AIS/ZnS NCs

have an average size at 6.18 nm (SD = 0.66 nm). These results show that InCl_3 based AIS NCs grew much faster than $\text{In}(\text{Ac})_3$ based AIS NCs. The TEM data are consistent with the observation on the photoluminescence or UV-Vis spectra of AIS NCs during their growth (Figure 1 and Figure S1). The obvious and fast red-shift spectra of AIS NCs using InCl_3 (Figure 1(b)) indicate the NC size increase in the reaction. According to the hard, soft acid and base theory model [22–23], softer acids prefer binding to the hard bases. In^{3+} is a hard acid. Ac^- is a hard base, but Cl^- is softer than Ac^- . Therefore, the binding between In^{3+} and Ac^- is stronger than that between In^{3+} and Cl^- . It is reasonable to conclude that InCl_3 was experienced a fast decomposition for a quick NC growth while $\text{In}(\text{Ac})_3$ was decomposed slowly for a gradual NC growth.

Regarding the QY change during the AIS growth, the AIS NCs using $\text{In}(\text{Ac})_3$ present a low QY in the early stage of growth probably due to significant surface defects as well as inner defects. Since the sizes of AIS NCs using $\text{In}(\text{Ac})_3$ are relatively stable in the reaction, the long reaction time or heating process can reduce crystalline misalignment on surfaces or in cores and thus improve QYs in the time course of NC growth. The fast AIS growth using InCl_3 can involve more inner defects due to enlarged NC volumes and thus cause a drop-off of NC QY. However, much different from AIS NCs using $\text{In}(\text{Ac})_3$, AIS NCs using InCl_3 present high QYs at 30 ~ 40% in the very beginning of reaction. The reasons for such high QYs is not clear yet. In the recent literature [24–26], chloride surface passivation has been reported for some types of NCs such as PbS, PbSe and CdTe. It has been found that chloride can diffuse to the surfaces of these types of NCs and fill some trap states, and thus minimize surface defects and further affect the optical properties of QDs such as enhancing photoluminescence efficiency and enhancing surface stability. It is highly possible that the chloride surface passivation *in situ* occurs during AIS NC synthesis using InCl_3 . Currently, we are investigating this hypothesis. For both types of AIS NCs, the ZnS coating process does not cause significant size-increase of NCs. Considering AIS/ZnS NC surface possesses ZnS lattice structure or similar (on the basis TEM measurement on lattice spacing), zinc doping into AIS NCs through cation exchange or diffusion should be the major mechanism for the photoluminescence blue shift as shown in Figure 2.

In addition, as shown in Figure S2 and Figure S3, EDX spectra confirm that both two types of AIS NCs are composed of Ag, In, and S and all AIS/ZnS NCs are composed of Ag, In, Zn and S. More specifically, Table 2 shows the elemental atomic ratios of these AIS and AIS/ZnS NCs. For all AIS NCs, the atomic ratios between Ag and In are around 1:1 during the core growth. For AIS/ZnS NCs, the atomic percentages of Ag and In drop off but the Ag percentage is reduced to a greater extent, and the atomic percentages of Zn and S are increased. It is believed that the significant reduction of Ag atomic percentage in AIS/ZnS is due to Zn etching to replace Ag during the ZnS shell growth. Of note, although the chloride surface passivation could be a reason for high QYs of AIS NCs using InCl_3 , the EDX data (Figure S2 (c) and (d)) on AIS NCs using InCl_3 do not show the detection of chloride. In the next research stage, more sophisticated tools or skills will be adopted or developed in the investigation of the chloride surface passivation.

To further explain the photoluminescence spectrum shape difference between two types of AIS cores ($\text{In}(\text{Ac})_3$ -based or InCl_3 -based, Figure 1) and the QY changes before and after

ZnS coating on AIS cores (Figure 2), it is necessary to investigate the photoluminescence decays of all these NCs using time-correlated single photon counting techniques. The photoluminescence decay characteristics disclose the photoluminescence mechanism of NCs, which can be used to elucidate the NC optical properties. Figures 4(a) and (b) show the decay curves for all AIS cores and the corresponding core/shell structures, respectively. For each decay curve, a biexponential function ($I(t)=A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2}$) was used to fit the curve. τ_1 and τ_2 are the short and long lifetime parameters, respectively. A_1 and A_2 are the amplitudes of the decay components at $t = 0$. Table 3 lists the extracted characteristics parameters (τ_1 , τ_2 , A_1 , and A_2) for all prepared NCs. Although AIS photoluminescence mechanisms are not clear yet, recent studies have reported that the photoluminescence lifetime parameters of AIS NCs could be associated with different electron-hole recombination pathways or mechanisms [27–33]. After light excitation, electrons will jump up to conduction bands followed by the relaxation to surface trap states and donor states. Specifically, the short lifetime (40 ~ 100 ns) is attributed to electron transition from surface trap states (caused by surface defects) to valence bands. The long lifetime (200 ~ 400 ns) is attributed to electron transition from donor states to acceptor states, which results in the broad emission peaks of AIS NCs. Donor states are due to sulfur vacancy, indium interstitial and indium atoms occupying the silver vacancy, and the acceptor states are due to the silver vacancies.

From Table 3, it can be seen that the lifetime parameters (τ_1 and τ_2) of AIS NCs using $\text{In}(\text{Ac})_3$ fall into the ranges that have been reported in literature. Upon comparing A_1 parameters for AIS cores (60 min growth) and their corresponding core/shell AIS/ZnS NCs, A_1 parameter is decreased after ZnS shell growth. Considering the ZnS shell growth on $\text{In}(\text{Ac})_3$ -based AIS cores cause QY enhancement, it is reasonable to associate the decrease of A_1 with the minimization of surface defects. It also can be seen the drop of A_1 in the time course of the AIS growth (10 min and 60 min), indicating the decrease of surface defects for QY enhancement. However, the lifetime parameters ($\tau_1 = \sim 200$ ns and $\tau_2 = \sim 700$ ns) of AIS NCs using InCl_3 are much larger compared to those of AIS NCs using $\text{In}(\text{Ac})_3$. Considering AIS NCs using InCl_3 has a broad emission peak, we still attribute τ_2 to the donor-acceptor transition. The larger τ_1 at around 200 ns is hard to be explained. Here we propose that electron transition from surface trap states to valence bands is very minimal or neglectable, and τ_1 is mainly attributed to electron transition from near-surface trap states or deep trap states (caused by inner lattice stress or other defects) to valence bands. The near-surface trap states or deep trap states could be closer to the donor states in energy levels and thus have a relatively longer lifetime for electrons. Such an assumption is reasonable because it is consistent with what we observed on the QY drop during AIS growth and no QY enhancement after ZnS coating on AIS. Of note, the photoluminescence spectrum of AIS NCs is a synergistic effort of electron transition pathways. We believe that the shape difference between the photoluminescence spectra of these two types of AIS NCs results from some differences in electron transition pathways. The electron transition mechanisms for the larger τ_1 and τ_2 of AIS NCs using InCl_3 could be associated with the chloride surface passivation, if it *in situ* occurs. These points are currently under our further investigation.

The photostability of the AIS and AIS/ZnS NCs was also tested. All samples in degassed organic solvents were exposed to a 6W, 365 nm UV lamp for two hours. Their photoluminescence spectra were recorded every 15 min. For each sample, the experiment was repeated three times. The calculated average and its related standard deviation of the photoluminescence peak intensity for each sample in its time course of UV light exposure are presented in Figure 5. As shown in Figure 5, the photobleaching of both types of AIS NCs are observed. The photobleaching of AIS NCs could be caused by complex UV-induced chemical reactions at the interface between AIS NCs and organic solvents. For instance, electrons excited or photons emitted from AIS NCs could be transferred to or absorbed by organic solvents to form free radicals. The free radicals could further interact with AIS surface electron states or etch AIS surface atoms, and thus quench the AIS photoluminescence. As shown in Figure 5, the photobleaching of AIS NCs using $\text{In}(\text{Ac})_3$ is faster than that of AIS NCs using InCl_3 . On the basis of the photoluminescence decay study, AIS NCs using InCl_3 could have fewer surface defects compared to AIS NCs using $\text{In}(\text{Ac})_3$. Surface defects could provide potential reactive sites or surface electron states for UV-induced chemical reactions. Fewer surface defects may inhibit the photo-corrosion of AIS NCs and thus result in a slow photobleaching. On the other hand, all AIS/ZnS NCs almost remain their photostability, no matter they adopt InCl_3 -based AIS cores or $\text{In}(\text{Ac})_3$ -based AIS cores. The photostability of AIS/ZnS NCs suggests that UV-induced chemical reactions at the interface between AIS NCs and organic solvents could be a major mechanism for photobleaching, and physically separating AIS surfaces from organic solvents through a ZnS shell is an effective approach avoiding photobleaching. No doubts that both types of AIS/ZnS NCs are useful as stable labels for bioimaging.

CONCLUSION

In summary, with a simple heat-up synthesis approach, high quality AIS and AIS/ZnS NCs using different indium precursors ($\text{In}(\text{Ac})_3$ and InCl_3) were synthesized and characterized. Experimental results disclose that: (1) the photoluminescence peak-wavelength of AIS NCs can be tuned by using different indium precursors; (2) AIS and AIS/ZnS NCs using $\text{In}(\text{Ac})_3$ as precursor achieve around 15% and 40% quantum yields (QYs), and both AIS and AIS/ZnS NCs using InCl_3 have QYs at around 31%; (3) the lifetime parameters of AIS and AIS/ZnS using InCl_3 are much larger than those of AIS and AIS/ZnS NCs using $\text{In}(\text{Ac})_3$; and (4) AIS NCs using InCl_3 have a slow photobleaching dynamics than AIS NCs using $\text{In}(\text{Ac})_3$, and the ZnS shell coating on both types of AIS NCs significantly enhances photostability against UV exposure. We believe that these NCs can find wide applications in displays, solid-state lighting, and biosensing/imaging due to their unique optical properties. Specifically, it is worth mentioning that the surprisingly long photoluminescence lifetime of AIS/ZnS NCs prepared with InCl_3 precursor is attractive for these NCs to be used superior bioimaging probes. The long photoluminescence lifetimes can distinguish the probe signal from the fast decaying autofluorescence in biological systems [34], and thus these NCs can be used as a tool for ultrasensitive biomedical diagnostics. Future work will focus on applications of all prepared NCs as well as the effects of chloride surface passivation on optical properties of AIS NCs.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This research was supported by the National Institute of Health via grant #1P20GM103650.

REFERENCES

1. Zhong H, Bai Z, Zou B. J. Phys. Chem. Lett. 2012; 3:3167–3175. [PubMed: 26296024]
2. Torimoto T, Kameyama T, Kuwabata S. J. Phys. Chem. Lett. 2014; 5:336–347. [PubMed: 26270709]
3. Allen PM, Bawendi MG. J. Chem. Soc. 2008; 130:9240–9241.
4. Chang JY, Wang GQ, Cheng CY, Lin WX, Hsu JC. J. Mater. Chem. 2012; 22:10609–10618.
5. Dai M, Ogawa S, Kameyama T, Okazaki KI, Kudo A, Kuwabata S, Tsuboi Y, Torimoto T. J. Mater. Chem. 2012; 22:12851–12858.
6. Hong SP, Park HK, Oh JH, Yang H, Do YR. J. Mater. Chem. 2012; 22:18939–18949.
7. Xiang W, Xie C, Wang J, Zhong J, Liang X, Yang H, Luo L, Chen Z. J. Alloys Compd. 2014; 588:114–121.
8. Torimoto T, Adachi T, Okazaki KI, Sakuraoka M, Shibayama T, Ohtani B, Kudo A, Kuwabata S. J. Chem. Soc. 2007; 129:12388–12389.
9. Yang X, Tang Y, Tan ST, Bosman M, Dong Z, Leck KS, Ji Y, Demir HV, Sun XW. Small. 2013; 9:2689–2695. [PubMed: 23589511]
10. Tang X, Ho WBA, Xue JM. J. Phys. Chem. C. 2012; 116:9769–9773.
11. Mao B, Chuang CH, Lu F, Sang L, Zhu J, Burda C. J. Phys. Chem. C. 2012; 117:648–656.
12. Deng D, Cao J, Qu L, Achilefu S, Gu Y. Phys. Chem. Chem. Phys. 2013; 15:5078–5083. [PubMed: 23450151]
13. Gabka G, Bujak P, Giedyk K, Ostrowski A, Malinowska K, Herlich J, Golec B, Wielgus I, Pron A. Inorg. Chem. 2014; 53:5002–5012. [PubMed: 24786548]
14. Mao B, Chuang CH, McCleese C, Zhu J, Burda C. J. Phys. Chem. C. 2014; 118:13883–13889.
15. Shinchu H, Wakao M, Nagata N, Sakamoto M, Mochizuki E, Uematsu T, Kuwabata S, Suda Y. Bioconjugate Chem. 2014; 25:286–295.
16. Torimoto T, Ogawa S, Adachi T, Kameyama T, Okazaki KI, Shibayama T, Kudo A, Kuwabata S. Chem. Commun. 2010; 46:2082–2084.
17. Tang X, Yu K, Xu Q, Choo ESG, Goh GK, Xue J. J. Mater. Chem. 2011; 21:11239–11243.
18. Buonsanti R, Milliron DJ. Chem. Mater. 2013; 25:1305–1317.
19. van Embden J, Chesman ASR, Jasieniak JJ. Chem. Mater. 2015; 27:2246–2285.
20. Park J, Kim SW. J. Mater. Chem. 2011; 21:3745–3750.
21. Trizio LD, Prato M, Genovese A, Casu A, Povia M, Simonutti R, Alcocer MJP, D'Andrea C, Tassone F, Manna L. Chem. Mater. 2012; 24:2400–2406.
22. Pearson RG. J. Chem. Educ. 1968; 581–587.
23. Pearson RG. J. Chem. Soc. 1963; 85:3533–3539.
24. Bae WK, Joo J, Padilha LA, Won J, Lee DC, Lin Q, Koh W, Luo H, Klimov VI, Pietryga JM. J. Chem. Soc. 2012; 134:20160–20168.
25. Zhang J, Gao J, Miller EM, Luther JM, Beard MC. ACS Nano. 2014; 8:614–622. [PubMed: 24341705]
26. Page RC, Espinobarro-Velazquez D, Leontiadou MA, Smith C, Lewis EA, Haigh SJ, Li C, Radtke H, Pengpad A, Bondino F, Magnano E, Pis I, Flavell WR, O'Brien P, Binks DJ. Small. 2015; 11:1548–1554. [PubMed: 25348200]
27. Hamanaka Y, Ogawa T, Tsuzuki M, Ozawa K, Kuzuya T. J. Lumin. 2013; 133:121–124.

28. Mao B, Chuang CH, Wang J, Burda C. J. Phys. Chem. C. 2011; 115:8945–8954.
29. Torimoto T, Kameyama T, Kuwabata S. J. Phys. Chem. Lett. 2014; 5:336–347. [PubMed: 26270709]
30. Hamanaka Y, Ozawa K, Kuzuya T. J. Phys. Chem. C. 2014; 118:14562–14568.
31. Park YJ, Oh JH, Han NS, Yoon HC, Park SM, Do YR, Song JK. J. Phys. Chem. C. 2014; 118:25677–25683.
32. Ogawa T, Kuzuya T, Hamanaka Y, Sumiyama K. J. Mater. Chem. 2010; 20:2226–2231.
33. Hamanaka Y, Ogawa T, Tsuzuki M, Kuzuya T. J. Phys. Chem. C. 2011; 115:1786–1792.
34. Mandal G, Darragh M, Wang YA, Heyes CD. Chem. Commun. 2013; 49:624–626.

Highlights

- High quality of AIS and AIS/ZnS NCs were prepared by heat-up.
- Different indium precursors in AIS synthesis can impact AIS optical properties.
- The impacted optical properties include emission colors, brightness and life time.
- The reason why different indium precursors impact optical properties was explored.
- The prepared NCs may have broad electronic and biomedical applications.

Figure 1.

Evolution of photoluminescence spectra of AIS NCs prepared by using $\text{In}(\text{Ac})_3$ (a) and InCl_3 (b) as indium precursors in the time course of growth, respectively. In (a) and (b), all photoluminescence spectra of NCs are scaled by their quantum yields.

Figure 2.

(a) Photoluminescence spectra of AIS NCs and AIS/ZnS NCs with In(Ac)₃ precursor and 60 min core growth, and the inset is a photograph of these NCs in organic solvents; (b) Photoluminescence spectra of AIS NCs and AIS/ZnS NCs with InCl₃ precursor and 20 min core growth, and the inset is a photograph of these NCs in organic solvents. In (a) and (b), all spectra are scaled by their quantum yields.

Figure 3. TEM and high resolution TEM images of NCs: (a-c) AIS and AIS/ZnS NCs using $\text{In}(\text{Ac})_3$ precursor; (d-f) AIS and AIS/ZnS NCs using InCl_3 precursor.

Figure 4.

Photoluminescence decay curves of core NCs (a) and core-shell NCs (b). All samples were excited at 405 nm and the decay for each NC sample was measured at the corresponding photoluminescence peak wavelength of the sample.

Figure 5. Photostability of AIS and AIS/ZnS NCs in organic solvents under continuous exposure of 365 nm UV light for 120 minutes. NC photoluminescence was measured every 15 minutes.

Table 1

Average sizes of AIS and AIS/ZnS NCs prepared by different indium precursors

Precursor	AIS (10min)	AIS (60min)	AIS/ZnS
In(Ac) ₃	3.06 ± 0.47	3.36 ± 0.47	3.79 ± 0.51
Precursor	AIS (5min)	AIS (20min)	AIS/ZnS
InCl ₃	3.76 ± 0.39	6.14 ± 0.88	6.18 ± 0.66

Table 2

Element atomic ratio (EDX analysis) of AIS and AIS/ZnS NCs

Synthesis Conditions	Measured Atomic Ratio by EDX				QY (%)	
	Zn	Ag	In	S		
In(Ac) ₃	AIS (10min)	-	23.3	22.4	54.3	7.2
	AIS (60min)	-	21.0	24.3	54.7	14.8
	AIS/ZnS	15.2	11.9	16.6	56.4	40.4
InCl ₃	AIS (5min)	-	15.4	20.9	63.7	38.2
	AIS (20min)	-	25.0	23.6	51.4	30.9
	AIS/ZnS	12.4	15.1	17.5	55.0	31.8

Table 3

Photoluminescence decay parameters of cores and core-shell structures

Precursor	NCs	τ_1/ns	A_1	τ_2/ns	A_2
In(Ac) ₃	AIS (10 min)	47	57%	316	43%
	AIS (60 min)	86	48%	422	52%
	AIS/ZnS (60 min core)	54	40%	351	60%
InCl ₃	AIS (5 min)	177	53%	685	47%
	AIS (20 min)	205	55%	730	45%
	AIS/ZnS (20 min core)	223	57%	757	43%