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Cadmium and Zinc Alloyed Cu-In-S Nanocrystals and Their Optical Properties

Liming Huang^{a,b,c}, Xiaoshan Zhu^{a,b,*}, Nelson G. Publicover^{a,b,c}, Kenneth W. Hunter Jr.^{b,c}, Mojtaba Ahmadiantehrani^d, Ana de Bettencourt-Dias^e, and Thomas W. Bell^e

^aDepartment of Electrical and Biomedical Engineering, University of Nevada, Reno, NV, USA

^bBiomedical Engineering Program, University of Nevada, Reno, NV, USA

^cDepartment of Microbiology, University of Nevada, Reno, NV, USA

^dDepartment of Chemical and Materials Engineering, University of Nevada, Reno, NV, USA

^eDepartment of Chemistry, University of Nevada, Reno, NV, USA

Abstract

Cadmium (Cd) and zinc (Zn) alloyed copper-indium-sulfide (Cu-In-S or CIS) nanocrystals (NCs) in several nanometers were prepared using thermal decomposition methods, and the effects of Cd and Zn on optical properties, including the tuning of NC photoluminescence (PL) wavelength and quantum yield (QY), were investigated. It was found that incorporation of Cd into CIS enhances the peak QY of NCs whereas zinc alloying diminishes the peak. In contrast with Zn alloying, Cd alloying does not result in a pronounced luminescence blue shift. The further PL decay study suggests that Cd alloying reduces surface or intrinsic defects whereas alloying with Zn increases the overall number of defects.

INTRODUCTION

Alloyed semiconductor nanocrystals (NCs) are of great interest because introducing additional elements within NCs can significantly affect NC properties including the ability to tune band gaps, enhance absorbance coefficients, minimize intrinsic or surface defects, make crystals structure more stable, and/or control NC size/structure (Xie et al. 2005; Bae et al. 2009; Gaponik et al. 2010). Improved properties of alloyed NCs can bring about more efficient applications in electronic lighting and displays (Sarkar et al. 2011), photovoltaic devices (McDaniel et al. 2013), biosensing/imaging (Liang et al. 2009), etc. Moreover, synthetic approaches of alloyed NCs that are amenable to large scale production are needed in many applications such as the manufacture of light-emitting diodes (LED) and solar cells (Kim et al. 2012).

Recently, chalcopyrite semiconductor copper-indium-sulfide (Cu-In-S or CIS) NCs have gained considerable attention. CIS has a direct ~1.5 eV band gap corresponding to a >800 nm emission wavelength (Jaffe et al. 1984). Although CIS is a good material for near-infrared quantum dots (QDs) and photovoltaic devices, applications of CIS NCs have likely been hindered by their limited quality. A number of ongoing research efforts are focused on improving CIS NC quality (Bao et al. 2011; Chung et al. 2012; Deng et al. 2012; Feng et al. 2011; Li et al. 2011; Li et al. 2009; Wang et al. 2010; Wang et al. 2012; Xie et al. 2009; Zhong et al. 2008; Zhang et al. 2011a; Zhang et al. 2011b).

*To whom correspondence should be addressed. xzhu@unr.edu. Phone: 1-775-682-6298. Fax: 1-775-784-6627.

Alloying CIS NCs with other metals is one such approach. Specifically, zinc (Zn) and cadmium (Cd) alloyed CIS NCs have received considerable attention. Several laboratories have reported Zn-CIS NCs with tunable band gaps covering the whole visible spectrum. Green-to-red visible and near infrared QDs based on Zn-CIS have been developed (Zhang et al. 2011a; Chung et al. 2012; Feng et al. 2011; Zhang et al. 2011b). Cd alloyed CIS NCs, as an important class of materials for solar cells and photocatalysis, also demonstrate a capacity for band gap/size/structure tuning (Wang et al. 2010).

In spite of the progress on alloyed CIS NCs, several challenges remain. Few studies have reported how Zn within CIS NCs affects luminescence quantum yields (QYs) while tuning band gaps. Moreover, most reported synthetic approaches for Zn-CIS NCs also adopt hot injection processes which are challenging for large scale production. The reported Cd-CIS NCs were synthesized using a solvothermal process and no luminescence properties have been described, which may indicate excess intrinsic or surface defects causing quenching of luminescence. Excessive defects as trap states in Cd-CIS NCs could limit their applications in photovoltaic devices by means of carrier recombination. It is of interest to develop high quality Cd-CIS NCs with luminescence (or fewer defects) and further examine the role of Cd in NC luminescence wavelength tuning and QY.

In this work, luminescent Cd-CIS and Zn-CIS NC alloys were prepared using a simple, thermal decomposition method which allows scale-up for mass production. The effects of Zn and Cd on NC luminescence wavelength tuning and QY were further investigated and compared by analyzing optical spectra of NCs.

EXPERIMENTAL METHODS

Chemicals and Apparatus

Copper (I) acetate (97%), cadmium (II) acetate (99.995%), zinc acetate (99%), oleic acid (90%), oleylamine (70%), and 1-octadecene (ODE, 90%) were purchased from Sigma-Aldrich. Indium (III) acetate (99.99%) and 1-dodecanethiol (DDT, 98%), were purchased from Alfa Aesar. All other chemicals were analytical or HPLC grade and commercially available. Chemicals were used as received without further purification.

UV-Vis spectra of NCs were obtained with a dual-beam spectrophotometer (Perkin Elmer Lambda 950). Fluorescence spectra of NCs were acquired using a spectrofluorimeter (Jobin-Yvon Horiba Fluorolog 3-222 spectrophotometer). Fluorescence decay measurements of NCs were conducted using the Jobin-Yvon Horiba Fluorolog3 spectrofluorometer equipped with a 370 nm Nanoled and using the DataStation6 software package.

For transmission electron microscope (TEM) imaging, a small drop of dispersed NCs in chloroform was placed on a gold TEM grid and covered with a thin carbon film. 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 EDX energy dispersive X-ray spectrometer.

QYs were calculated according to the following equation, using standard references including perylene monoxide (emission peak at 560 nm, QY = 50% in methanol), Oxazine 170 (emission peak at 640 nm, QY = 20% in methanol), or Cy5.5 (emission peak at 707 nm, QY = 20% in DMSO)

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

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

Synthesis of Cd and Zn Alloyed CIS NCs Using Thermal Decomposition

Alloyed nanocrystals were synthesized by the addition of Cd or Zn precursor to a CIS synthetic reaction system as reported previously (Li et al. 2009; Deng et al. 2012). For the preparation of Cd alloyed CIS NCs, indium acetate (0.1 mmol), copper (I) acetate (0.1 mmol), DDT (2.0 mL), oleic acid (0.4 mL), and 6 mL of octadecene (ODE) were added into a 50 mL three-necked, round-bottom flask. The reaction solution was degassed under vacuum for 10 minutes at room temperature until no bubbles were observed and solutions were then heated to 140° C at a rate of 20° C/min under vacuum using a heating mantle. An argon atmosphere was next introduced into the flask and CdO (0 ~ 0.5 mL of 0.1 M in ODE/oleylamine/oleic acid (2:1:1)) was injected at 140° C. The temperature of the resulting solution was quickly raised to 260° C at a rate of 10° C/min.

As the temperature was increased, the color of the reaction solution changed gradually from yellow to red, dark red, and black, indicating the nucleation and growth of Cd-CIS NCs. Small amounts of the reaction solution (0.1 to 0.2 mL) were collected using a syringe at different time intervals and injected into hexane in clean vials to terminate growth of NCs. All solutions collected from the experiment were diluted in a glass cuvette with hexane for UV-Vis absorbance and photoluminescence (PL) measurements. Purification of Cd-CIS NCs was performed using hexane and ethanol.

For the synthesis of Zn alloyed CIS NCs, indium acetate (0.1 mmol), copper (I) acetate (0.1 mmol), zinc acetate (0 to 0.5 mmol), DDT (2.0 mL), oleic acid (0.4 mL), and 6 mL of ODE were added into a 50 mL three-necked, round-bottom flask. The reaction solution was degassed under vacuum for 10 minutes at room temperature until no bubbles observed and then the solution was heated to 140° C at a rate of 20° C/min under vacuum using a heating mantle. An argon atmosphere was introduced into the flask. The temperature of the solution was quickly raised to 230° C to 260° C at a rate of 10° C/min. All other steps were same as in the preparation of Cd-CIS NCs.

For the CIS NC preparation, no zinc acetate or CdO in ODE/oleylamine/oleic acid were added to the reaction. All other steps were the same as the preparation of Cd-CIS or Zn-CIS NCs.

Growth of ZnS Shell on CIS, Cd-CIS and Zn-CIS NCs

Zn-precursor solution (0.4 M zinc acetate in ODE/oleylamine (4:1)) was injected to the core growth solution after the temperature of the reaction mixture was lowered to 230° C. To minimize the formation of individual ZnS particles, 4.5 mL of Zn-precursor solution (0.4 M of zinc acetate in ODE-oleylamine (4:1)) was injected into the NC suspension solution, drop by drop with a syringe over two hours. About 0.1 to 0.2 mL of reaction mixture was collected before each aliquot of Zn-precursors and injected to hexane in clean glass vials to terminate growth of NCs.

All solutions collected from the experiment were diluted in glass cuvettes with hexane for UV-Vis absorbance and PL measurements. After reactions were complete, mixtures were cooled down to room temperature in air by removing the heating mantle. NCs were purified using hexane and ethanol.

RESULTS AND DISCUSSION

Without addition of Cd and Zn precursors, CIS NCs were produced in the thermal decomposition-based synthetic system. The system for producing CIS NCs was adjusted to determine optimum reaction parameters (e.g. temperature) for Cd-CIS and Zn-CIS alloys. These characteristics were also used as references to compare the effects of Cd and Zn.

Figure 1 (a) shows the QY and peak PL wavelength of manufactured CIS NCs at different temperatures during the time course of NC growth. At a reaction temperature of 230° C, the growth of CIS NCs is slow and PL wavelength peak shifts gradually from 665 nm to 720 nm. A maximum QY was reached after 70 minutes likely due to a minimum in total defects from both core and surface components. NC precipitation was observed after 150 minutes.

As temperature was increased, a similar trend of QY (and PL peak wavelength) was observed but reactions occur more quickly, due to a more rapid thermal decomposition of DDT. Clearly the reaction at 260° C produces CIS NCs of higher quality (i.e. relatively high QYs) within a short and controllable time frame. The relative high QYs of CIS NCs was used as a reference to explore how Cd and Zn in CIS NCs affect NC QYs. In addition, no significant PL spectral shift was observed at 260° C (where the shift is only ~10 nm, Figure 1(b)). At 260° C, DDTs may tend to be in a free or unbound status, and thus less able to coordinate copper or indium atoms on the NC surface to stabilize NCs. As a result, NCs precipitate quickly, before further growth. A stable PL helps examination of the effects of Cd and Zn in CIS NCs on wavelength tuning. Since a reaction temperature of 260° C is sufficient to promote the alloying of Cd and Zn into CIS NCs, this temperature was chosen for the preparation of Cd-CIS and Zn-CIS NCs.

At 260° C, 0.2 and 0.5 equivalents of Cd (with respect to the amount of In or Cu as starting materials) were alloyed into CIS NCs. As shown in Figure 2(a), peak QYs are increased to ~14% which are about double those compared to CIS NCs (~7%). The enhancement of the peak QY suggests that Cd minimizes NC intrinsic or surface defects. It also can be seen that without Cd, the system reacts for 15 minutes before product precipitation. However, with Cd the system reaction time is prolonged. During elongated reaction times, NC peak wavelengths shift toward infrared wavelengths, indicating further size growth of NCs. Higher concentrations of Cd in the reaction cause greater red-shift along with a longer reaction time. It is believed that Cd has stronger coordination properties with DDT. If more Cd atoms are exposed at Cd-CIS NC surfaces, they may facilitate colloidal stability and further NC growth. Additionally, Figure 2(a) shows minimal gaps among curves of peak PL wavelengths. This suggests that Cd composition percentage does not significantly change the NC bandgap but does impact NC size growth for the further bandgap tuning.

The role of Zn on CIS NCs is different from Cd with respect to wavelength tuning and QY. The PL peak wavelength and the QY versus time with 0.2 and 0.5 equivalents of Zn are shown in Figure 2(b). It can also be seen that during the first 15 minutes of reactions, Zn causes an observable blue shift of the PL peak wavelength. It is believed that incorporating Zn into CIS NCs increases the NC bandgap and also creates more defects to quench PL. Similar to Cd, Zn also extends the reaction time and causes NC growth and the wavelength red-shift during an extended reaction time. However, wavelengths do not shift beyond ~690 nm (the maximum peak wavelength of CIS NCs at 260° C).

The alloying of Cd or Zn does not result in an obvious change in the shape of PL or absorbance spectra. As an additional proof, Figure S1 shows PL spectra of the alloyed CIS NCs during the time course of NC growth. The full width at half maximum (FWHM) of Cd-CIS, Zn-CIS and CIS NCs are all around 110 nm. Compared to Figure 1(b), Figure S1 shows that Cd and Zn help to tune the PL peak wavelength during the time course of NC growth and increases synthesis flexibility. Further, TEM and HRTEM images (Figure 3 and Figure S3–S7) reveal that all NCs (the growth condition and the growth time listed in Table 1) are ~3 nm. The HRTEM images also show all NCs are of similar lattice-plane-spacing parameters, which are consistent with what have been reported previously (Zhong et al. 2008; Deng et al. 2012; Trizio et al. 2012). Energy-dispersive X-ray (EDX) spectra confirm that alloyed CIS NCs are composed of Cu, In, Zn or Cd, and S (Figure S2). More specifically, Table 1 shows the elemental atomic ratio of NCs illustrated in Figure 3. For all NC samples, the EDX analysis shows that the atomic ratio between In and Cu is about 1.5, indicating all NCs using the thermal decomposition method are In-rich particles. For alloyed NCs, the atomic ratio of Cd or Zn to Cu is close to 0.2 or 0.5, the original molar ratio of precursors before reaction. By comparing the input mole percentage of each cation precursor before reaction with the final atomic percentage of each cation within the resultant NCs, it can be seen that the reactivity of Cu is lower than that of In but similar to that of Cd or Zn. Considering In and Cu ions are dominant on concentrations in the reaction, the impact of Cd (or Zn) on NC size is minor. This is consistent with TEM images revealing resultant NC sizes. Overall, based on the experimental observation, the small percent of Cd or Zn in CIS NCs does not significantly change the NC size and the shape of the PL or absorbance spectra, but does play an important role in tuning PL peak wavelength and QY.

It is known that CIS NC surface passivation with a shell of ZnS can dramatically improve NC QY due to the minimization of surface defects (Bao et al. 2011; Deng et al. 2012; Li et al. 2011; Li et al. 2009; Wang et al. 2012; Xie et al. 2009; Zhong et al. 2008). The prepared Cd-CIS and Zn-CIS NCs were also grown with a ZnS shell and the QYs of these core-shell structures were further compared. The QYs of cores or core/shell structures are shown in Table 2. It can be seen that the QYs of core-shell structures are higher than those of cores only. However, it is also clear that the QYs of Zn-CIS/ZnS (~32% and ~27%) are much lower than that of CIS/ZnS (~72%). Cd-CIS have higher QYs (12% to 14%) than CIS (~7%), but their core-shell structures still have relatively lower QYs (~47% and ~53%) compared to CIS/ZnS.

PL QY can be affected by surface defects, intrinsic defects, donor-acceptor transition, etc. (Wang et al. 2002; Wang et al. 2003; Jones et al. 2003; Morello et al. 2007; Zhong et al. 2008; Zhong et al. 2010; Li et al. 2011; Zhang et al. 2011; Mao et al. 2011). To understand the role of Cd and Zn in increasing or decreasing NC QYs, the PL decays of these NCs and their core-shell structures were investigated using time-correlated single photon counting (TCSPC) techniques. Figures 4(a) and (b) show decay curves for all core NCs and corresponding core-shell NCs, respectively. Previous PL decay studies on CdSe NCs have revealed that CdSe NCs have a biexponential time distribution (Wang et al. 2002; Wang et al. 2003). Typically, the short lifetime extracted from decay curves is attributed to donor-acceptor transition or band-edge recombination, and long lifetime is ascribed to surface trap states. The biexponential model is usually adopted by researchers to explain the PL decay characteristics of NCs (Li et al. 2011). However, there are also studies adopting triexponential function for the decay curve fitting of various NCs (Morello et al. 2007; Mao et al. 2011; Jones et al. 2003; Zhong et al. 2008; Zhong et al. 2010). Moreover, the three different lifetime parameters can be to associate with three different electron-hole recombination pathways or mechanisms. Specifically, some studies on PL decay of CIS NCs report that CIS NCs have a tri-exponential decay curve with a short lifetime (several nanoseconds), medium lifetime (tens of nanoseconds) and a long lifetime (hundreds of

nanoseconds) (Zhong et al. 2008; Zhang et al. 2011). The long lifetime is attributed to electron (or hole) transition from donor states to acceptor states, which results in the broad emission peaks (wide FWHM) of CIS NCs. Donor states are due to sulfur vacancy, indium interstitial and indium atoms occupying the copper vacancy; and the acceptor states are due to the copper vacancies (Ueng et al. 1989). It has also been suggested that the short and medium lifetimes may be related to intrinsic and surface defects. Such suggestions are creditable because CIS NCs have more complicated lattice imperfections than a binary lattice due to the tetragonal lattice distortion (Ueng et al. 1989) and intrinsic defects should be as important as surface defects in acting as trap states for new recombination pathways.

In our study of CIS based NCs, a triexponential function ($I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3}$) mathematically converges and better describes (versus a biexponential function) decay curves (i.e. achieves a χ^2 goodness of fit closer to 1). Lifetime parameters are represented by τ_1 , τ_2 and τ_3 . A_1 , A_2 and A_3 represent the amplitudes of the decay components at $t = 0$. For all core NCs, three PL lifetimes τ_1 (5–12 ns), τ_2 (40–90 ns), and τ_3 (204–362 ns) were observed (Figure 4(a) and Table 3). Considering τ_3 is in the range of hundreds of nanoseconds and all PL emission spectra have broad peaks, we also attribute τ_3 to the donor-acceptor transition. In addition, upon comparing A_1 and A_2 parameters for each pair of a core and its corresponding core-shell (Table 3), both parameters are decreased after ZnS shell growth. The ZnS shell growth minimizes surface defects and may be involved in core etching (or core size reduction) due to exchange of copper or indium in the core with zinc ions from zinc precursor (Park et al. 2011; Trizio et al. 2012). It is reasonable to associate the decrease of A_1 and A_2 with the minimization of surface defects and intrinsic defects. In other words, τ_1 and τ_2 indicating two energy states between the conduction band and the valence band of NCs for electron-hole recombination, could be related to intrinsic and surface defects. However, it may not be appropriate to correlate which lifetime parameter to which type of defects, because both intrinsic and surface defects could contribute to both energy states.

On the basis of such analyses, A_1 and A_2 parameters were further compared among CIS, Cd-CIS and Zn-CIS NCs. As shown in Table 3, A_1 and A_2 parameters are decreased for both 0.2 Cd-CIS and 0.5 Cd-CIS compared to those of CIS. This indicates that Cd alloying may reduce surface or intrinsic defects of NCs. This observation could explain why the QYs of Cd-CIS increase to 12–14% compared to those of CIS (~ 7%). For 0.2 Zn-CIS and 0.5 Zn-CIS, A_1 parameters increase to 6% and 11% and A_2 parameters increase to 28% and 33%, respectively. This suggests that the Zn alloying increases surface or intrinsic defects, resulting in the low QYs of Zn-CIS. Moreover, more Zn alloyed in CIS causes more defects and thus a lower QY. An increased number of defects in Zn-CIS cores may largely remain even after ZnS shell growth. This could be the reason why the QYs of Zn-CIS/ZnS are much lower than those of CIS/ZnS and Cd-CIS/ZnS. However, based on PL decay, it is hard to explain why the QYs of Cd-CIS/ZnS are relatively lower than those of CIS/ZnS. Probably other factors (e.g., lattice mismatch introduced by Cd between Cd-CIS and ZnS for the formation of trap states in ZnS shell) need to be considered. In spite of the relatively lowered QYs, both Cd-CIS/ZnS and Zn-CIS/ZnS outweigh CIS/ZnS in PL wavelength tuning.

It is also worthy of discussing the impacts of Cd and Zn on τ_1 , τ_2 and τ_3 parameters of NCs. From Table 3, for all core NCs, it can be seen that τ_1 (or τ_2 or τ_3) of Cd-CIS NCs are comparable to those of CIS NCs, but the difference of τ_1 (or τ_2 or τ_3) between Zn-CIS NCs and CIS NCs is significant. This suggests that Cd alloying does not significantly influence the energy levels of all states (surface trap states, intrinsic trap states, donor states and acceptor states) but Zn alloying does. This may explain why Cd alloying does not cause a pronounced luminescence wavelength shift whereas Zn alloying does.

In addition, it should be noted that the ZnS shell growth on CIS, Cd-CIS and Zn-CIS causes a blue shift and QY enhancement. Both blue shift and QY enhancement caused by the ZnS shell growth on CIS cores have been observed by others (Park et al. 2011; Trizio et al. 2012). In their reports, both Park and Trizio agree that cation exchange between Zn ions (from Zn precursor) with Cu or In in NCs causes blue shift and QY enhancement; however, they have different explanations. Park et al. suggest that during ZnS shell growth, Zn ions etch cores, reducing core size, causing a PL blue shift and resulting in the formation of a thin ZnS shell around cores to enhance QY. Trizio et al. claim that no shell is formed in the core etching process by Zn ions but only Zn-CIS, and the blue shift is due to the nature of Zn-CIS (the more Zn in NC, the more blue shift). Moreover, Zn atoms fill vacancies in CIS NCs to enhance QY. Due to the limited availability of scientific tools in profiling composites in small NCs of several nanometers, both Park and Trizio did not investigate Zn distribution in NCs after core etching.

We observed that Zn alloyed in CIS causes a blue shift but it also quenches the NC PL. Moreover, ZnS shell growth on Zn-CIS cores (or Zn-CIS core etching by Zn ions) enhances NC QY and causes a further blue shift. In the shell growth or core etching process, according to Park and Trizio, Zn atoms enter into NCs by exchanging with Cu or In in cores (Cu or In are dominant in alloyed NCs as shown in Table 1). Both Park's and Trizio's theories can be applied to explain the blue shift – the reduction of NC core size or the Zn increment in Zn-CIS. On the other hand, as shown in Table 2, Zn in CIS quenches NC PL, but Zn entering into CIS or Zn-CIS in the ZnS shell growth causes NC QY enhancement. We suggest that a Zn increment in NCs through cation exchange introduces extra defects but also minimizes defects near NC surfaces where the latter process is dominant and thus the overall effect is to enhance NC QY.

The blue shift and the QY enhancement caused by the ZnS shell growth on Cd-CIS can be explained similarly, as discussed above for Zn-CIS. A scientific tool to profile composites in small domains, within several nanometers, will be useful in probing Zn distribution in NCs and further exploring whether the blue shift and QY enhancement are associated with Zn distribution.

CONCLUSION

In summary, luminescent Cd and Zn alloyed CIS NCs were prepared using a thermal decomposition method, and the effects of Cd and Zn on NC PL wavelength and QY were investigated and compared. It was found that the incorporation of Cd into CIS enhances the peak QY of NCs and, in contrast, Zn alloying with CIS diminishes the peak QY of NCs. Also distinct from Zn alloying, Cd alloying does not result in a pronounced luminescence blue shift. The further PL decay study suggested that Cd alloying reduces surface or intrinsic defects but Zn alloying causes more defects. As core-only particles, Cd-CIS NCs are more promising than Zn-CIS or CIS NCs for photovoltaics applications due to fewer defects. On the other hand, considering the fact that ZnS shell growth on the alloyed NCs results in further QY improvement, Cd-CIS/ZnS and Zn-CIS/ZnS core-shell NCs might find applications in displays, solid-state lighting, and biosensing/imaging due to their unique properties in PL wavelength tuning. Future work will focus on applications of the prepared NCs, establishing a dedicated model to explain PL decay spectra of these prepared NCs on the basis of precisely probing NC recombination states, and investigating Zn or Cd distribution in NCs and all related physical phenomena.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. (a) Quantum yield (bottom curves) and PL peak wavelength (upper curves) of CIS NCs versus growth time at different temperatures; (b) Evolution of CIS NCs' PL and absorbance spectra (inset) versus growth time at 260 °C.

Figure 2.

(a) Quantum yield (bottom curves) and peak PL wavelength (upper curves) of Cd alloyed CIS NCs during the time course of NC growth; and (b) Quantum yield (bottom curves) and peak PL wavelength (upper curves) of Zn alloyed CIS NCs during the time course of NC growth. The reaction temperature for both alloyed NCs is 260° C.

Figure 3. TEM images of CIS NCs (a), 0.2 equivalent of Cd alloyed CIS NCs (b), 0.5 equivalent of Cd alloyed CIS NCs (c), 0.2 equivalent of Zn alloyed CIS NCs (d), and 0.5 equivalent of Zn alloyed CIS NCs (e).

Figure 4.

PL decay curves of core NCs (a) and core-shell NCs (b). All samples were excited at 370 nm and the decay for each NC sample was measured at the corresponding PL peak wavelength of the sample.

Table 1

Elemental atomic ratios in CIS, Cd-CIS and Zn-CIS NCs resulting from EDX analysis.

Synthesis Conditions	Growth Time (min)	Measured Atomic Ratio by EDX			
		Zn or Cd	Cu	In	S
CIS (Cu:In=1:1)	10	-	18.1	28.8	53.1
Zn-CIS (Zn:Cu:In=0.2:1:1)	12	3.4	17.3	25.5	53.9
Zn-CIS (Zn:Cu:In=0.5:1:1)	12	8.1	15.3	24.6	52.0
Cd-CIS (Cd:Cu:In=0.2:1:1)	10	3.3	17.3	25.0	54.4
Cd-CIS (Cd:Cu:In=0.5:1:1)	10	8.2	15.3	23.6	52.9

Table 2Summary of QYs and PL peak wavelengths of cores and core-shell structures (sample $n = 3$)

Synthesis Conditions	Core QY (%)	Core- Shell QY (%)	Core PL Peak (nm)	Core-Shell PL Peak (nm)
CIS (Cu:In=1:1)	7.2±0.7	72.1±1.6	685	605
Zn-CIS (Zn:Cu:In=0.2:1:1)	5.1±0.7	32.7±2.7	620	570
Zn-CIS (Zn:Cu:In=0.5:1:1)	1.3±0.5	27.5±2.5	605	550
Cd-CIS (Cd:Cu:In=0.2:1:1)	14.5±0.3	47.3±3.9	675	620
Cd-CIS (Cd-Cu:In=0.5:1:1)	11.7±0.8	53.1±3.1	670	610

Table 3

PL decay parameters of cores and core-shell structures

NCs	τ_1/ns	A ₁	τ_2/ns	A ₂	τ_3/ns	A ₃	χ^2
CIS	11	4%	82	15%	356	81%	0.98
0.2Cd-CIS	12	2%	88	14%	362	84%	1.12
0.5Cd-CIS	10	2%	90	14%	355	84%	1.03
0.2Zn-CIS	8	6%	57	28%	237	66%	0.98
0.5Zn-CIS	5	11%	40	33%	204	56%	1.00
CIS/ZnS	NA	0%	98	12%	328	88%	1.11
0.2Cd-CIS/ZnS	NA	0%	90	11%	322	89%	1.03
0.5Cd-CIS/ZnS	NA	0%	85	9%	340	91%	0.99
0.2Zn-CIS/ZnS	6	1%	88	13%	324	86%	1.07
0.5Zn-CIS/ZnS	5	2%	93	15%	364	83%	1.07