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A Novel Approach to Synthesize Ultrasmall Cu Doped Zn-In-Se Nanocrystal Emitters in a Colloidal System

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A facile phosphine-free approach is presented to prepare Cu doped ternary Zn-In-Se nanocrystals with high performance photoluminescence. By doping during nucleation stage, Cu dopant serving as dominative emission centre was introduced into weak fluorescence ternary system to modify emission path. As a result of varying the ratios of zinc to indium, emission of the products is tunable ranging from 620 to 545 nm and photoluminescence quantum yield being up to 20%. Meanwhile, a large Stokes shift of 467 meV is achieved.

Introduction

Colloidal semiconductor nanocrystals (NCs) with radii smaller than that of the Bohr exciton of the material have received considerable attention because of their preferred optical properties such as excitation in the visible window, large Stokes shift and high quantum efficiency, for fundamental studies and technical applications in biomedical labelling, light emitting diodes, lasers, and sensors.¹⁻⁴ Semiconducting ternary NCs, being a good choice due to its narrow band-gap and low toxic elements, have been extensively investigated and reported over the past decades. Ternary semiconductor NCs such as CuInS₂, AgInS₂ and quaternary NCs such as Cu₂ZnSnSe₄, CuIn_xGa_(1-x)S₂, have been synthesized with a direct band gap of bulk materials.⁵⁻¹⁰ These semiconducting NCs are often utilized to prepare thin films via spin or spray techniques in linear and nonlinear optical devices and photovoltaic solar cells.^{11,12} Furthermore, optical and electronic properties of these materials could be accurately tuned by varying their elemental compositions.¹³⁻¹⁸ Yang's group and Chen's group reported the facile synthesis of different composition ratio (CuIn)_xZn_{2(1-x)}S₂ NCs with different photoluminescence wavelengths.^{19,20} In order to synthesize NCs with high quantum yield, several strategies have been extensively studied. It was reported that passivation of the surface of NCs with a wider band gap semiconducting material could enhance

the photoluminescence quantum yield by confining the excitons within the core of NCs and reducing the surface defects.²¹⁻²⁶

In ternary semiconductor NCs systems, strong photoluminescence stems from irradiative recombination of excited electrons in Cu or In vacancies, which is easy to change by means of varying the excitation wavelength.²⁷⁻³⁰ To the best of our knowledge, however, synthesis of ternary NCs with the desirable properties of large Stokes shift, excitation-independent and bright emission are rarely reported in the previous papers. Alternatively, the use of intentional impurities or dopants can also strongly influence the optical behaviour of host NCs. Metal doping strategies have been recently developed to adjust the energy transfer and the irradiative process.³¹⁻³⁵ Specifically, Cu dopant could be chosen as a primary emission centre and introduced to modify the optical properties of ternary NCs, which can not only dominate the whole fluorescent emission of ternary alloyed NCs, but also yield favourable large Stokes shift. Herein, a facile doping route for preparing Cu doped Zn-In-Se NCs without using highly toxic reagents, such as pyrophoric reagents, is present. By varying the ratios of zinc to indium, the emission of the obtained NCs is tunable from 620 to 545 nm. Meanwhile, a large Stokes shift of 467 meV is successfully achieved for the Cu doped Zn-In-Se NCs.

Experimental section

Materials

Technical grade 1-octadecene (ODE, 90%), indium chloride (InCl₃), copper chloride (CuCl₂), zinc stearate (ZnSt₂), 1-dodecanethiol (99%), oleic acid (OA, 90%), oleylamine (OAm, 98%) were purchased from Aldrich. Selenium powder (Se) and mercaptopropionic acid (MPA) were purchased from Acros Organics. All other reagents were of analytical grade and used as received.

Preparation of stock solutions

Cu stock solution was prepared by adding 0.1 mmol of CuCl₂ into 5 mL of OAm. And then to obtain a clear solution, the mixture was sonicated for 20 min. 30 mL of ODE and 10 mmol Se powder were mixed and then degassed to remove air and water at 120 °C for 30 min and purged for 30 min using a nitrogen gas inlet. A clear yellow solution was gained as Se-ODE stock. Zn

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[†] Electronic supplementary information (ESI) available.

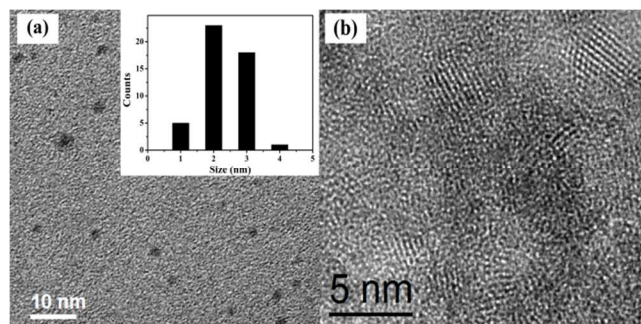


Fig. 1 TEM (a) and HRTEM images (b) of the as-obtained samples. The inset: the size distribution of the NCs.

stock solution was prepared by adding 1.0 mmol of ZnSt₂ into the mixture solution containing 2 mL of ODE and 2 mL of OAm and then heated to 150 °C under nitrogen gas for further use.

Synthesis of Cu doped ZnIn₂Se₄/ZnSe NCs

In a typical synthesis of Cu doped ZnIn₂Se₄/ZnSe NCs, indium chloride (0.1 mmol, 0.0293g), ZnSt₂ (0.05 mmol, 0.0316g), 1-dodecanethiol (2 mL, DDT), ODE (4 mL), OA (1 mL), and 0.05 mL Cu stock solution (0.001 mmol CuCl₂) were loaded into 50 mL three-necked round-bottom flask. The reaction mixture was degassed for 5 min before heated to 120 °C and then purged for 30 min with nitrogen gas. Afterwards, 3 mL of Se-ODE stock solution with 2.0 mmol OAm was injected when the temperature was raised to 220 °C. The reaction mixture was kept at the same temperature and monitored through UV/Vis and photoluminescence spectra.

Then, 0.5 mL of Zn stock solution was injected dropwise into the above colloidal solution using a syringe while the temperature of the system was maintained at the same value. The second or third addition of Zn stock solution has been injected in interval of 15 min. The reaction was quenched by the removal of heating and cooled to room temperature. The product of NCs was isolated by precipitating by the addition of acetone, centrifuging, and decanting the supernatant. The NCs could be re-dispersed in organic solvents such as chloroform. The precipitation/dispersion cycle was repeated at least three times in order to eliminate byproducts and unreacted precursors.

Characterizations

TEM and HRTEM images were taken on a FEI Tecnai G2 F20 with an acceleration voltage of 200 kV and 300kV. Chloroform solutions containing these nanocrystal samples were dropped on Carbon-coated copper grids. XRD patterns were obtained using a Rigaku D/max-2500 X-ray diffractometer with graphite monochromated Cu K α radiation ($\lambda=1.5418$ Å). The UV-vis absorption spectra were obtained on a Shanghai Tianmei Tech Ltd. The room temperature photoluminescence spectra of the NCs samples were measured using a Hitachi F-4500 fluorescence spectrometer. The PL quantum yield (QY) for these samples were calculated by referencing to a standard (Rhodamine 6G in ethanol, QY=95 %) at the excitation wavelength and similar fluorescence wavelength using the following equation.⁶

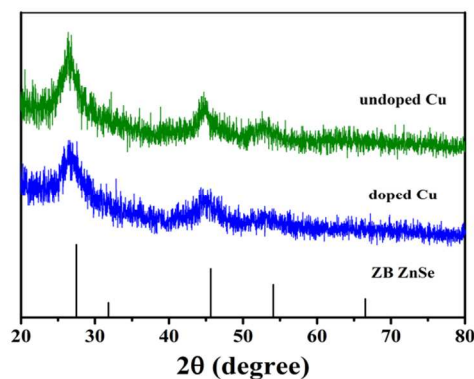


Fig. 2 XRD patterns of the obtained samples with (blue) and without (green) Cu dopants. The bottom lines are the standard XRD pattern (JCPDS 80-0021) of zinc blende ZnSe.

$$\phi = \phi' \times \left(\frac{I}{I'}\right) \times \left(\frac{A'}{A}\right) \times \left(\frac{n}{n'}\right)^2$$

where ϕ and ϕ' are the PL QY for these samples and organic dye, respectively; I (sample) and I' (dye) are the integrated emission peak areas at a given wavelength; A (sample) and A' (dye) are the absorption intensities at the same wavelength used for PL excitation; n (sample) and n' (dye) are the refractive indices of the solvents.

The purified samples were digested with aqua regia. The obtained clear solutions were diluted with distilled water and the content of In, Cu, and Zn ions were determined by an inductively coupled plasma atomic emission spectrometer, (PerkinElmer, Optima 2000DV). These Electron paramagnetic resonance (ESR) spectra were taken on a Bruker ECS106 X-Band spectrometer. Typical experimental conditions were as follows: frequency = 9.865 GHz, temperature = 298 K, modulation amplitude = 1.00G, microwave power = 20 mW, conversion time = 5.12 ms, time constant = 1.28 ms, resolution = 5000 pts, number of scans for an average = 10.³⁶ The recorded samples were picked out from the raw solutions at different temperatures, injected into chloroform and measured at room temperatures with the mentioned ESR instrument. Raman spectra of the samples were recorded by using 758 nm laser light source on Thermo Scientific DXR Raman microscope at room temperature.

Results and discussion

Synthesis and Characterizations of Cu doped ZnIn₂Se₄/ZnSe NCs

Fig.1 shows typical TEM and HRTEM images of Cu doped ZnIn₂Se₄/ZnSe NCs. The as-obtained NCs appear to be nearly spherical in shape and fairly monodisperse. The average size of these samples is about 2.5 nm, as determined from TEM images and size distribution (Fig. 1a and Fig. S1[†]), which does not show apparent contrast due to the ultrasmall size. The lattice fringes are observed clearly (Fig. 1b), which indicate the formation of the NCs with to some degree crystallinity. In the meantime, three broad and obvious peaks observed in XRD patterns (Fig.2) suggest the nature of ultrasmall-sized samples and demonstrate

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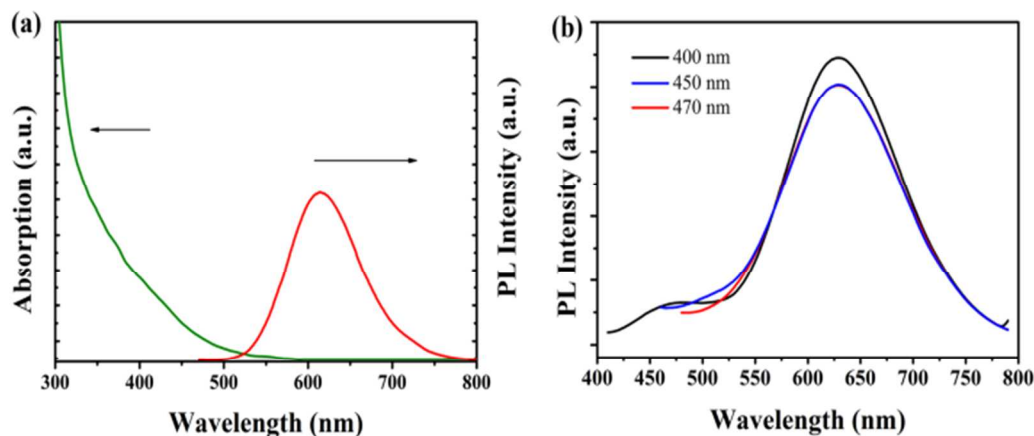
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Fig. 3 (a) Absorption and photoluminescence spectra of Cu doped NCs sample; (b) photoluminescence spectra of the Cu doped NCs samples under different excitations.

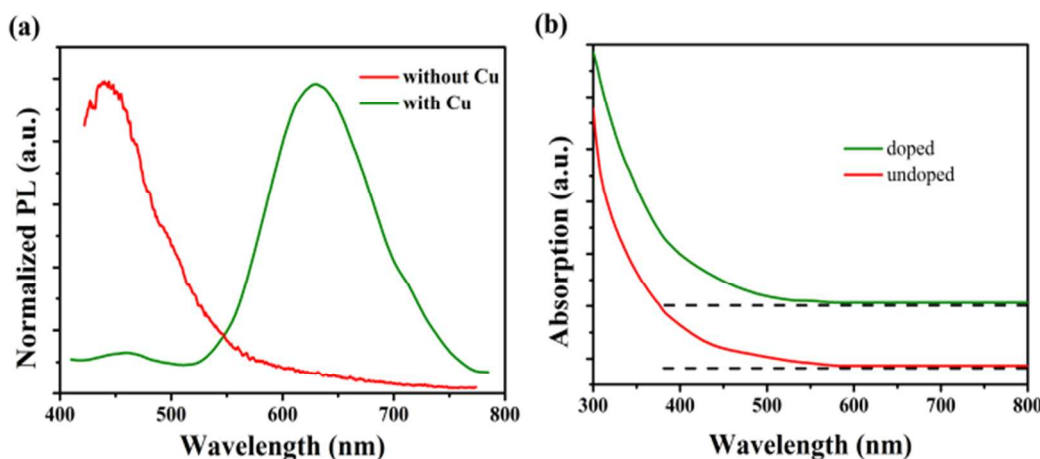


Fig. 4 Photoluminescence (a) and absorption(b) spectra of the samples with (green) and without (red) Cu dopant under 400 nm light excitation.

that the as-synthesized NCs have the characteristics of zinc blende (ZB) ZnSe (JCPDS 80-0021). Furthermore, XRD patterns of the samples in the absence and presence of Cu species have no apparent differences, which demonstrate that Cu species as dopant have insignificant influence on the crystal structure, similar to Mn doped binary QDs reported in previous papers.^{37,38} The element compositions of the samples were recorded using ICP-AES. The ratio of Cu to (Zn+In) is 0.3 %, which is lower than the initial ratio, 0.6 %, in initial precursor. The absorption and photoluminescence spectra of a typical Cu doped ZnIn₂Se₄/ZnSe NCs sample were shown in Fig. 3a. The sharp absorption peak of Cu doped ZnIn₂Se₄/ZnSe NCs was not observed for any sample around 500 nm, in contrast to the good resolution of absorption spectra in pure binary NCs. Photoluminescence (PL) spectrum of as-synthesized NCs shows a strong and broad emission peak at 616 nm. The big gap between

absorption spectrum and photoluminescence peak demonstrates that emission does not derive from intrinsic band gap emitting. Meanwhile, the photoluminescent emission of the NCs also has been measured under different the wavelengths of the excitation (Fig. 3b). It shows that the primary emission of the NCs does not vary with the changes of excitation wavelengths. In contrast, in pure ternary NCs, the emission derives from the recombination of excitons in copper or indium vacancies, which results in the excitation-dependent emission.²⁷ When copper ions as a dopant were introduced into ZnIn₂Se₄ NCs system, it act as the primary emitting center and dominate the whole emission of the as-obtained NCs.

35 Effects of Cu species on optical properties of NCs

In order to demonstrate the role of Cu species in optical properties of NCs, the corresponding NCs have been synthesized

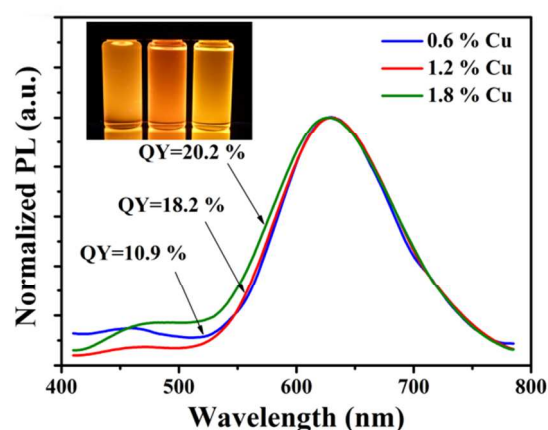


Fig. 5 Photoluminescence spectra of these NCs with different Cu initial concentrations. The inset: Photos of these NCs under UV light illumination.

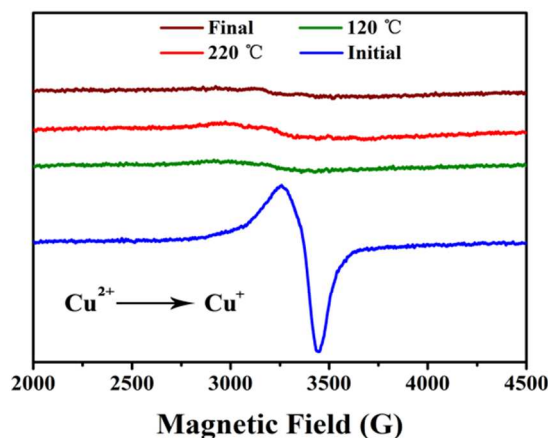


Fig. 6 ESR spectra of the raw samples when the synthesis reaction was at different stages.

without Cu species under the same condition. We observed that the NCs do not have the characteristic PL spectra caused by Cu dopant with strong emission but the weak PL related to the band gap (Fig.4a). Although apparent difference in emission spectra has been observed, the absence of Cu species did not alter the absorption spectra (Fig.4b), which is coincident with the results of XRD. More important, apparent change of the emission peak was not observed with increasing the concentration of Cu dopant, which demonstrates that the amount of Cu dopant has low correlation with peak wavelength of photoluminescence (Fig. 5). However, the initial amount of Cu precursor could to some extent enhance fluorescence intensity and increase quantum yield of the samples. Such result is similar to Mn doped binary NCs, that is, the PL QYs of doped NCs could be raised by increasing the dopant concentration without the formation of new crystalline phase.^{37,39,40} The emission is attributed to the dopant and originates from the Cu center, which is consistent with the apparent Stokes shift shown in Fig. 3. To obtain the valence of Cu ion in a single nanocrystal, ESR spectrum under room temperature was recorded (Fig. 6). We observed that the characteristic Cu^{II} signal of ESR spectrum disappeared after the

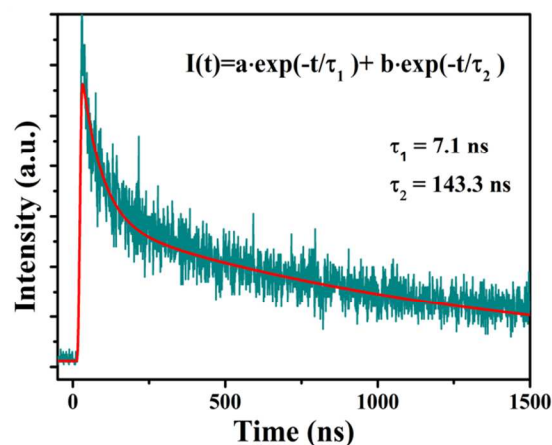


Fig. 7 Lifetime spectrum of the NCs at 616 nm and the fitted lifetime decay curve (red). The inset: biexponential function of lifetime.

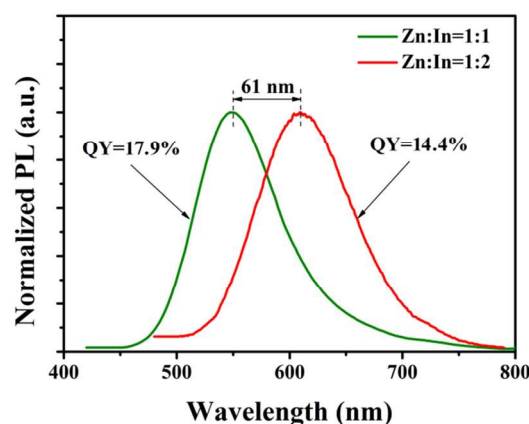


Fig. 8 PL spectra of the NCs samples with different ratios of Zn to In.

reaction, despite Cu^{II} salts were utilized in the initial reaction mixture. In previous studies, copper element was introduced into ternary NCs through Cu^I salts or organometallic precursors.^{21,41} The ESR spectra of those NCs are expected not to show the feature peak of Cu^{II} ions. These results suggest that Cu ion in the obtained NCs is in the oxidation state of +1. The reduction of Cu^{II} may take place in the presence of fatty amines when reaction temperature was raised. The time-resolved PL spectra of the sample measured at emission peak wavelength are shown in Fig. 7. The decay curve was fitted by a biexponential function (the inset in Fig. 7). The lifetimes are found to be 7.1 ± 0.1 ns (τ_1) and 143.3 ± 3 ns (τ_2) with $a = 0.2$ and $b = 0.8$, respectively.

Effects of the initial ratio of Zn to In on emission of NCs

Interestingly, apart from the variation of Cu dopant, the wavelength of emission peak altered when the initial ratio of Zn to In changed in the initial precursor. From Fig. 8, it can be observed that the wavelength of emission peak shifted to higher energy by 61 nm when the ratio of Zn to In increased from 0.5 to 1.0. When the molar ratio of zinc to indium reached 2.0, the characteristic emission almost disappeared, due to the failure of ZnIn₂Se₄ nanocrystals formation.²⁰ Therefore, the emission wavelength could be expected to be tuned through the variation

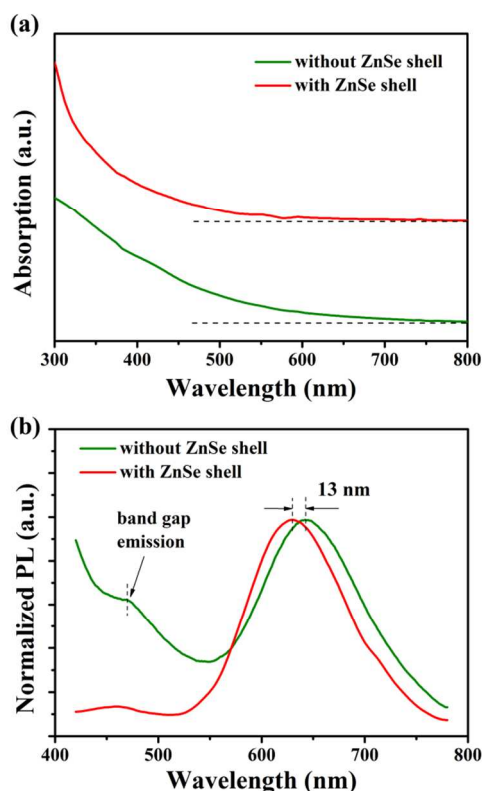


Fig. 9 Absorption (a) and photoluminescence spectra (b) of the sample with the 1:2 ratio of Zn to In with and without ZnSe shell under light excitation of 400 nm.

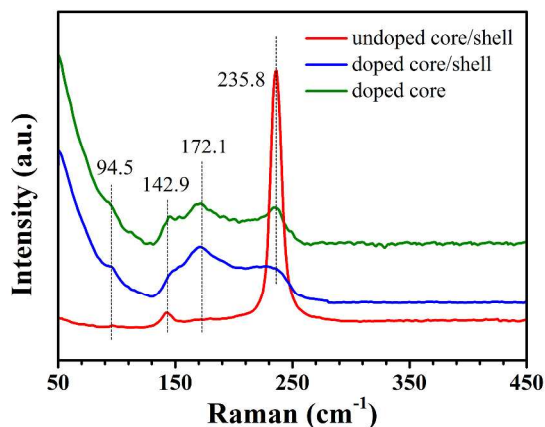


Fig. 10 Room-temperature Raman spectra of the samples with different compositions and structures. $\lambda_{\text{exc}} = 758$ nm.

of NCs composition.

The epitaxial shell is a necessary structure to enhance quantum yield of NCs, which has been investigated extensively in the past years.^{21,42} ZnSe was selected as the useful shell in the present study to passivate the as-obtained NCs so as to improve the quantum yield. The replacement of In^{3+} ions with Zn^{2+} ions happened at the initial stage of the addition of Zn stock solution, as shown in Fig. 9. The ion diameter of Zn^{2+} ($r = 0.74$ Å) is smaller than that of In^{3+} ($r = 0.94$ Å), which makes the

replacement of In^{3+} ions with Zn^{2+} easily at high temperature. As shown in Fig. 9a, the band gap of the as-obtained NCs samples was enlarged with the increase in reaction time because the replacement of Cu or In ions with Zn ions resulted in the decrease of core diameter and thus the increase of energy band gap due to quantum confinement effect.³⁹ The blue shift of PL emission peak indicated that ion exchange reaction had taken place with forming of ZnSe shell as displayed in Fig. 9b. The core of Zn-In-Se NCs shrank gradually as the zinc ions replaced the indium ions in the core, which resulted in the blue shift of emission. The blue-shifted phenomenon of PL emission peak has also been observed by other ternary semiconductor NCs, such as CuInS_2 , when zinc sulfide shell was deposited on the surface of core NCs.³⁹ Such blue-shifted PL emission peak caused by the formation of zinc chalcogenide shell is distinguished from the red-shifted PL emission peak in the binary QDs.⁴² Because of the different reactivity of the metallic-element precursors, types of existing defects are different. In the pure copper doped ZnIn_2Se_4 NCs, zinc ion as a critical acid easily binds to 1-dodecanethiol (DDT, soft base) compared with indium ion as a hard acid, that is, indium ion easily reacted with selenium precursor.⁴³ Therefore, zinc vacancy could be the major surface and deep defects, which is in agreement with those related conclusions.^{27,44-46} When shell grew at the outmost of core by the replacement of indium with zinc, zinc vacancy was gradually reduced, resulting in the formation of ZnSe shell. Finally, copper dopant as an emission center dominated the whole emission of core/shell NCs. The band-gap emission was suppressed simultaneously, as shown in Fig. 9.

To further identify the potential binary (ZnSe , In_2Se_3) impurities because of similar XRD patterns to ZnIn_2Se_4 , additional characterization with Raman was performed to confirm the absence of these impurities. Fig. 10 clearly shows that there is no presence of ZnSe and In_2Se_3 which would have strong Raman peaks at 351 cm^{-1} and 196 cm^{-1} , respectively.^{24,47} Three peaks at 94.5 cm^{-1} , 142.9 cm^{-1} and 235.8 cm^{-1} are ascribed to Zn-In-Se NCs. Another apparent characteristic peak at 172.1 cm^{-1} has been observed in the presence of Cu dopant, while it disappears in the absence of Cu dopant. Therefore, the Raman peak could be attributed to quaternary alloy Cu-Zn-In-Se NCs.⁴⁸ Meanwhile, by comparing the Raman spectra of doped with undoped NCs, we found the relative intensity of the peak at 235.8 cm^{-1} decreased, while the peak at 94.5 cm^{-1} enhanced. The spectral change might be due to the introduction of copper as well as the ion replacement of indium with zinc, resulting in the slight change from single crystal phase to alloy crystal phase.^{18,24}

The corresponding Zn:In ratios of the samples measured by ICP-AES indicate that the ratio of Zn to In reduced from the initial 1:1.94 to the final 1:1.76. As a result of the formation of ZnSe shell, quantum yield of the as-prepared samples was found to be slightly over 20 %, one order of magnitude higher than that of core NCs, 2.02 %. It is implied that the growth of shell reduces surface and deep defects deriving from Cu and In vacancies and suppresses the leak of excitons and non-irradiative probability, which to a large extent determines the PL QYs and photostability of semiconducting NCs.⁴⁹⁻⁵¹ A high quantum yield makes these NCs a good candidate for many applications, such as sensing,

imaging, LED.

Conclusions

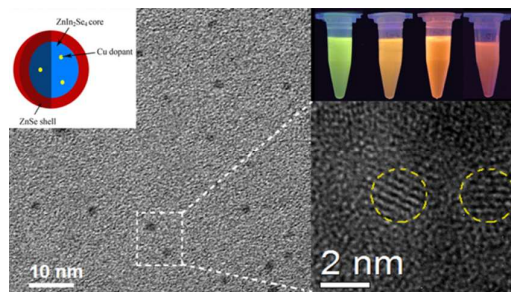
In conclusion, a facile synthesis of stable, cadmium-free, Cu doped Zn-In-Se NCs in ultrasmall size has been presented through doping technique with low toxic precursors in a colloidal solution. Emission of the as-obtained NCs has been successfully modified and dominated by low amount Cu dopant, which could easily be reproduced and controlled. Furthermore, the emission of these NCs ranging from 620 nm to 545 nm could also be tuned by varying the initial molar ratio of indium to zinc in the precursor. A large Stokes shift of 467 meV is successfully achieved for the Cu doped Zn-In-Se NCs. In addition, those as-obtained NCs possess high quantum yield slightly over 20 %, which could meet the demands of biomedical, LED, and sensing applications.

Acknowledgements

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References and notes

- 1 D. V. Talapin, J. S. Lee, M. V. Kovalenko and E. V. Shevchenko, *Chem Rev*, 2010, **110**, 389-458.
- 2 I. L. Medintz, H. T. Uyeda, E. R. Goldman and H. Mattoussi, *Nat Mater*, 2005, **4**, 435-446.
- 3 X. Michalet, F. F. Pinaud, L. A. Bentolila, J. M. Tsay, S. Doose, J. J. Li, G. Sundaresan, A. M. Wu, S. S. Gambhir and S. Weiss, *Science*, 2005, **307**, 538-544.
- 4 S. Kim, Y. T. Lim, E. G. Soltesz, A. M. De Grand, J. Lee, A. Nakayama, J. A. Parker, T. Mihaljevic, R. G. Laurence, D. M. Dor, L. H. Cohn, M. G. Bawendi and J. V. Frangioni, *Nat Biotechnol*, 2004, **22**, 93-97.
- 5 S. C. Riha, B. A. Parkinson and A. L. Prieto, *J Am Chem Soc*, 2011, **133**, 15272-15275.
- 6 T. Torimoto, T. Adachi, K. Okazaki, M. Sakuraoaka, T. Shibayama, B. Ohtani, A. Kudo and S. Kuwabata, *J Am Chem Soc*, 2007, **129**, 12388-12389.
- 7 Y. H. A. Wang, X. Y. Zhang, N. Z. Bao, B. P. Lin and A. Gupta, *J Am Chem Soc*, 2011, **133**, 11072-11075.
- 8 P. M. Allen and M. G. Bawendi, *J Am Chem Soc*, 2008, **130**, 9240-9241.
- 9 M. Ibáñez, R. Zamani, A. LaLonde, D. Cadavid, W. H. Li, A. Shavel, J. Arbiol, J. R. Morante, S. Gorsse, G. J. Snyder and A. Cabot, *J Am Chem Soc*, 2012, **134**, 4060-4063.
- 10 A. Singh, C. Coughlan, F. Laffir and K. M. Ryan, *ACS Nano*, 2012, **6**, 6977-6983.
- 11 W. U. Huynh, J. J. Dittmer and A. P. Alivisatos, *Science*, 2002, **295**, 2425-2427.
- 12 I. Gur, N. A. Fromer, M. L. Geier and A. P. Alivisatos, *Science*, 2005, **310**, 462-465.
- 13 C. Y. Jiang, J. S. Lee and D. V. Talapin, *J Am Chem Soc*, 2012, **134**, 5010-5013.
- 14 M. E. Norako, M. J. Greaney and R. L. Brutchey, *J Am Chem Soc*, 2012, **134**, 23-26.
- 15 S. E. Wark, C. H. Hsia, Z. P. Luo and D. H. Son, *J Mater Chem*, 2011, **21**, 11618-11625.
- 16 L. De Trizio, M. Prato, A. Genovese, A. Casu, M. Povia, R. Simonutti, M. J. P. Alcocer, C. D'Andrea, F. Tassone and L. Manna, *Chem Mater*, 2012, **24**, 2400-2406.
- 17 X. S. Tang, W. Cheng, E. S. G. Choo and J. M. Xue, *Chem Commun*, 2011, **47**, 5217-5219.
- 18 M. Ibáñez, D. Cadavid, R. Zamani, N. García-Castelló, V. Izquierdo-Roca, W. H. Li, A. Fairbrother, J. D. Prades, A. Shavel, J. Arbiol, A. Pérez-Rodríguez, J. R. Morante and A. Cabot, *Chem Mater*, 2012, **24**, 562-570.
- 19 J. Feng, M. Sun, F. Yang and X. R. Yang, *Chem Commun*, 2011, **47**, 6422-6424.
- 20 B. K. Chen, H. Z. Zhong, W. Q. Zhang, Z. A. Tan, Y. F. Li, C. R. Yu, T. Y. Zhai, Y. S. Bando, S. Y. Yang and B. S. Zou, *Adv Funct Mater*, 2012, **22**, 2081-2088.
- 21 R. G. Xie, M. Rutherford and X. G. Peng, *J Am Chem Soc*, 2009, **131**, 5691-5697.
- 22 L. Li, T. J. Daou, I. Texier, T. K. C. Tran, Q. L. Nguyen and P. Reiss, *Chem Mater*, 2009, **21**, 2422-2429.
- 23 E. Cassette, T. Pons, C. Bouet, M. Helle, L. Bezdetnaya, F. Marchal and B. Dubertret, *Chem Mater*, 2010, **22**, 6117-6124.
- 24 A. Singh, S. Singh, S. Levchenko, T. Unold, F. Laffir and K. M. Ryan, *Angew Chem Int Ed*, 2013, **52**, 9120-9124.
- 25 C. Coughlan, A. Singhand K. M. Ryan, *Chem Mater*, 2013, **25**, 653-661.
- 26 Q. Li, L. L. Zhai, C. Zou, X. S. Huang, L. J. Zhang, Y. Yang, X. A. Chen and S. M. Huang, *Nanoscale*, 2013, **5**, 1638-1648.
- 27 L. E. Oikkonen, M. G. Ganchenkova, A. P. Seitsonen and R. M. Nieminen, *J Phys-Condens Mater*, 2011, **23**, 422202.
- 28 K. Nose, T. Omata and S. Otsuka-Yao-Matsuo, *J Phys Chem C*, 2009, **113**, 3455-3460.
- 29 H. C. Ye, H. S. Park, V. A. Akhavan, B. W. Goodfellow, M. G. Panthani, B. A. Korgel and A. J. Bard, *J Phys Chem C*, 2011, **115**, 234-240.
- 30 J. Park, C. Dvoracek, K. H. Lee, J. F. Galloway, H. E. C. Bhang, M. G. Pomper and P. C. Searson, *Small*, 2011, **7**, 3148-3152.
- 31 D. J. Norris, A. L. Efros and S. C. Erwin, *Science*, 2008, **319**, 1776-1779.
- 32 R. Viswanatha, S. Brovelli, A. Pandey, S. A. Crooker and V. I. Klimov, *Nano Lett*, 2011, **11**, 4753-4758.
- 33 W. W. Zheng, P. Kumar, A. Washington, Z. X. Wang, N. S. Dalal, G. F. Strouse and K. Singh, *J Am Chem Soc*, 2012, **134**, 2172-2179.
- 34 D. J. Norris, N. Yao, F. T. Charnock and T. A. Kennedy, *Nano Lett*, 2001, **1**, 3-7.
- 35 G. Manna, S. Jana, R. Bose and N. Pradhan, *J Phys Chem Lett*, 2012, **3**, 2528-2534.
- 36 X. Y. Li, P. L. Yue, C. Kotal, *New J Chem*, 2003, **27**, 1264-1269.
- 37 A. Nag, S. Chakraborty and D. D. Sarma, *J Am Chem Soc*, 2008, **130**, 10605-10611.
- 38 N. Pradhan and X. G. Peng, *J Am Chem Soc*, 2007, **129**, 3339-3347.
- 39 J. Park and S. W. Kim, *J Mater Chem*, 2011, **21**, 3745-3750.
- 40 S. Wang, B. R. Jarrett, S. M. Kauzlarich and A. Y. Louie, *J Am Chem Soc*, 2007, **129**, 3848-3856.
- 41 S. J. Li, Z. C. Zhao, Q. H. Liu, L. J. Huang, G. Wang, D. C. Pan, H. J. Zhang and X. Q. He, *Inorg Chem*, 2011, **50**, 11958-11964.
- 42 J. Ke, X. Y. Li, Y. Shi, Q. D. Zhao and X. C. Jiang, *Nanoscale*, 2012, **4**, 4996-5001.
- 43 R. G. Pearson, *J Am Chem Soc*, 1963, **85**, 3533-3539.
- 44 H. Z. Zhong, S. S. Lo, T. Mirkovic, Y. C. Li, Y. Q. Ding, Y. F. Li and G. D. Scholes, *ACS Nano*, 2010, **4**, 5253-5262.
- 45 J. Hofhuis, J. Schoonman and A. Goossens, *J Phys Chem C*, 2008, **112**, 15052-15059.
- 46 K. Nose, T. Omata and S. Otsuka-Yao-Matsuo, *J Phys Chem C*, 2009, **113**, 3455-3460.
- 47 C. H. Chung, B. Lei, B. Bob, S. H. Li, W. W. Hou, H. S. Duan and Y. Yang, *Chem Mater*, 2011, **23**, 4941-4946.
- 48 C. C. Wu, C. Y. Shiau, D. W. Ayele, W. N. Su, M. Y. Cheng, C. Y. Chiu and B. J. Hwang, *Chem Mater*, 2010, **22**, 4185-4190.
- 49 C. Kirchner, T. Liedl, S. Kudera, T. Pellegrino, A. M. Javier, H. E. Gaub, S. Stolzle, N. Fertig and W. J. Parak, *Nano Lett*, 2005, **5**, 331-338.
- 50 Z. Fang, Y. Li, H. Zhang, X. H. Zhong and L. Y. Zhu, *J Phys Chem C*, 2009, **113**, 14145-14150.
- 51 J. Ziegler, S. Xu, E. Kucur, F. Meister, M. Batentschuk, F. Gindele and T. Nann, *Adv Mater*, 2008, **20**, 4068-4073.



Highlight: Ultrasmall doped ternary nanocrystal emitters have been successfully synthesized by means of a novel and green route.