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Introduction

Semiconductor nanocrystals doped with transition metal ions have been an emerging class of functional materials with great application potential in many fields, such as biological imaging, photovoltaics, light-emitting-diodes, and so on.^{1–5} Their superior performances could be associated with the unique changes of the optical, magnetic and electronic properties caused by the dopants, even in a small amount. For example, as far as the optical properties are concerned, the doped nanocrystals could exhibit a minimum self-absorption,⁶ a long excited-state lifetime,^{7–9} a large Stokes shift and a good thermal stability.^{10,11} All the features make them an excellent alternative to the conventional semiconductor nanocrystals for optical devices.

Compared with Mn-doped ZnSe nanocrystals, Cu-doped nanocrystals are studied to a lesser extent, because the huge difference between Cu_xSe and ZnSe crystal structures impedes the doping of Cu ions into ZnSe nanocrystals. However, their unique emission in the visible spectrum makes them important in some applications.^{7,8} The synthesis of Cu-doped ZnSe nanocrystals could be achieved by a similar approach to that of CdSe nanocrystals in tri-n-octylphosphine

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Successful doping of anisotropic semiconductor nanocrystals with impurities offers an effective pathway to manipulate their physical properties and enhance the application performances. However, such doping into anisotropic nanocrystals is seldom reported because it needs simultaneous controls in the crystal growth for a specific shape and composition engineering for transition-metal doping. Here, ultrathin Cu-doped ZnSe nanorods are synthesized by a growth-doping process. The doped nanorods are characterized by XRD and TEM techniques to reveal their crystal structure. Their optical properties are described in terms of UV-Vis absorption spectra and PL spectra. The tunable emission from 480 to 520 nm evidences the successful doping of Cu into ZnSe nanorods. The

Facile synthesis and optical properties of ultrathin

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Cu-doped ZnSe nanorods

spectra. The tunable emission from 480 to 520 nm evidences the successful doping of Cu into ZnSe nanorods. The effects of the reaction time, the reaction temperature and the surface ligand on the optical properties are discussed in detail. After purification, the doped nanorods with a Cu/Zn ratio of 1% give a quantum yield of 7%. This emission could be retained for weeks in air, which is important for its future applications in many fields.

(TOP)/tri-n-octylphosphine oxide (TOPO)¹² but the usage of organometallics like diethylzinc makes the synthesis toxic and expensive. Then, Peng and Pradhan developed a growth-doping strategy for Cu-doped ZnSe nanocrystals with "green" and safe reactants, like carboxylates or oxides.^{13,14} In order to further improve the quantum yield and the stability of the emission, surface coating of another semiconductor with a wide band gap has been demonstrated to be a necessary step.^{15,16}

Since the optical properties of semiconductor nanocrystals are highly dependent on their size, shape and structure,¹⁷⁻¹⁹ the doping of transition metal ions into anisotropic nanocrystals attracts our attention.²⁰ However, it is difficult to achieve the component modulation by dopants and simultaneously keep the anisotropic shape. As for one-dimensional Cu-doped ZnSe nano-crystals, there are only two reports to date.^{21,22} One of them presented the synthesis of Cu-doped ZnSe nanorods by the thermal annealing of a precursor obtained by a solvothermal method.²¹ The other reported a gold-catalyzed vapor transport method for the Cu-doped ZnSe nanowires.²² All these one-dimensional nanostructures have diameters in the range of 50-200 nm and lengths up to several micrometers. These sizes are too large to exhibit the obvious quantum size effect that is an important characteristic of semiconductor nanocrystals. Furthermore, the optical properties of these nanorods/nanowires have not been studied.

In this paper, ultrathin Cu-doped ZnSe nanorods with diameters of only a few nanometers have been synthesized under mild experiment conditions. The ultrathin nanorods are characterized by XRD patterns, TEM and HRTEM images, and UV-Vis absorption spectra. The successful doping of Cu

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Paper

ions into the ZnSe nanorods has been evidenced by PL spectra and ICP-AES analysis. The effects of the reaction temperature and reaction time on the product are also discussed in terms of their optical properties. To the best of our knowledge, it is the first report of the optical properties of Cu-doped ZnSe quantum nanorods.

Experimental

Materials

Zinc acetate dihydrate (ZnAc₂·2H₂O, 99%), methanol (99.5%), hexane (99.5%) and acetone (99.5%) were ordered from Sinopharm Chemical Reagent Co. Ltd. Selenium powders (Se, 99.5%); oleylamine (OAm, 80–90%) and quinine sulfate (99%) were purchased from ACROS organics. Stearic acid (SA) and CuAc₂ (99%) came from Shanghai Chemical Reagent Factory. Tetramethylammonium hydroxide (TMAH, 97%) was bought from Aldrich. 1-Octadecene (ODE, 90%) and tributyl phosphine (TBP, 95%) were obtained from Aladdin Chemical Reagent Co. Ltd. All these reagents were used without any further purification.

Synthesis of copper stearate

10 mmol of SA was dissolved in 20 mL of methanol and then the solution was heated to 50 °C to get a clear solution. After that, 10 mmol of TMAH in methanol was added to this solution. 20 min later, 5 mmol of $CuAc_2$ in methanol was introduced into the solution dropwise. As a result, a blue precipitate appeared in the solution immediately. The precipitate was collected by centrifugation and was dried in vacuum for the later use.

Synthesis of Cu-doped ZnSe nanorods

ZnSe nanorods were prepared based on a modified report.²³ Then, the obtained ZnSe nanorods, 5% of $CuSt_2$ to ZnSe in molar ratio, and 5 mL of ODE were added into a clean three-necked round-bottomed flask. The flask was connected to a Schlenk line and flushed with nitrogen three times to remove oxygen and moisture. After that, the solution was gradually heated to 100 °C at a rate of 2 °C min⁻¹. After reacting at 100 °C for 100 min, the solution was further heated to 180 °C immediately. Appropriate amounts of Se powder in TBP and ZnAc₂ in a mixture of OAm/ODE were injected into the solution for the shell growth. After 30 min, the solution was cooled to room temperature and was mixed with acetone. The product was collected by centrifugation and re-dispersed in hexane for characterization. The actual atomic ratio of Cu/Zn in these ZnSe nanorods is around 1.1%.

Characterization

X-ray diffraction (XRD) patterns were obtained from an X-ray powder diffractometer (Bruker D8 Advance, German) with monochromatic Cu K α as a radiation source. The working voltage of the diffractometer and the according current were kept at 40 kV and 40 mA, respectively. Transmission electron microscope (TEM) images were achieved by a transmission electron microscope of JEM-1011 at an accelerating voltage of 100 kV. High-resolution TEM (HRTEM) images and selected area electron diffraction (SAED) patterns were recorded on a JEOL 2010 microscope. Ultraviolet-visible (UV-Vis) absorption spectra were acquired in the range of 300–700 nm at room temperature by a Shimadzu UV-2450 spectrophotometer. Photoluminescence (PL) spectra were obtained from a Thermo fluorometer (Lumina 222-263000) at room temperature. The quantum yield (QY) of the doped nano-crystals was determined with quinine sulfate in 0.1 M H_2SO_4 solution as a reference. The Cu/Zn ratio in the doped nanocrystals was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo IRIS Intrepid IIXSP).

Results and discussion

Fig. 1 shows the XRD pattern of the product, which could be indexed as the zinc-blended phase of ZnSe (JCPDS card no. 37-1463). No diffraction peaks related to Cu impurities are observed in the figure. The results are the same as the undoped ZnSe nanorods,²³ indicating that the introduction of a small amount of Cu into the ZnSe nanorods (~1.1%) would not affect their crystal structure. This conclusion is also supported by the lattice constant calculation. The calculated lattice constant of the product is a = 5.668 Å, very close to that of ZnSe in the zinc-blended phase (a = 5.669 Å). Similar results are also reported for many doped semiconductor nanocrysals.^{5,24,25}

The shape and size of the product are investigated by TEM microscopy. Fig. 2a shows a typical TEM image of the ultrathin ZnSe nanorods prepared by a reported method.²³ The shape and size of the ultrathin nanorods are in good agreement with this report. Fig. 2b presents a TEM image of the product after the Cu-doping process. Both the one-dimensional structural feature and the ultrathin diameter of the ZnSe nanorods are maintained in the product. The nanorods exhibit diameters of ~3 nm and lengths of up to tens of nanometers, which would result in an obvious quantum-size effect in the optical properties. The clear lattice fringes in the HRTEM images confirm the crystal nature of the nanorods, as illustrated in Fig. 2c and d. The lattice



Fig. 1 XRD pattern of the Cu-doped ZnSe nanorods at 1.1%. The lines at the bottom present the standard XRD diffraction peaks of bulk ZnSe in a cubic phase (JCPDS card no. 37-1463).



Fig. 2 (a) TEM images of ZnSe nanorods, and (b) TEM images, (c, d) HRTEM images and (e) electron diffraction pattern of the Cu-doped ZnSe nanorods at 1.1%.

distances between neighboring fringes further suggest the growth direction of the nanorods along the [111] axis of the zinc blended phase. The crystal nature of the nanorods is also verified by the SAED pattern, as shown in Fig. 2e. The diffuse diffraction rings are in line with the zinc-blended phase of ZnSe, which is again consistent with the result from the XRD pattern.

The UV-Vis absorption spectra and PL spectra of the ZnSe nanorods before and after the Cu-doping process are shown in Fig. 3. It is noted that the absorption onset of the ZnSe nanorods is redshifted by about 10 nm after the doping process. This could be attributed to the size increase of the nanorods during the reaction. Compared with the UV-Vis



Fig. 3 UV-Vis absorption spectra (solid line) and PL spectra (dashed line) of the ZnSe nanorods (red) and the Cu-doped ZnSe nanorods at 1.1% (blue). The inset shows the digital images of the doped nanocrystals obtained without or with the irradiation of a hand-held lamp.

absorption spectra, there is a remarkable change in the PL spectra. The emission band of the ZnSe nanorods moves from 430 to 520 nm after the doping process. The emission band at 520 nm is the characteristic feature of Cu-doped ZnSe,13,14,24 which is assigned to the recombination of excited electrons from the conduction band of the host material (ZnSe) and holes from the d-orbital of copper ions.^{24,26-28} This result directly confirms the successful doping of Cu into ZnSe. The quantum yield of the emission is approximately 19%, lower than those of the Cu-doped ZnSe nanocrystals with excess S atoms on the surface²⁹ or with a ZnS shell.¹⁵ This could be attributed to the structure defects in/on the nanorods, which is also documented for the emission of the ultrathin ZnSe nanorods.23 After several more rounds of washing and centrifugation, the quantum yield goes down to 3-7%, comparable to that of the Cu-doped spherical nanocrystals.^{7,8,25} This result could be explained by the removal of the surface ligands on the nanorods during the repeated washing.

The formation process of the Cu-doped nanorods follows a typical growth-doping strategy well-demonstrated in the cases of the spherical nanocrystals.^{13,14,24} In brief, the host nanorods are synthesized by the reaction of Zn carboxylates and Se powders in oleylamine. Then, these nanorods react with copper stearate at 100 °C to cause Cu^{2+} ions to adsorb onto the surface or diffuse into the lattices of the host nanocrystals. In order to ensure the Cu^{2+} ions are wellencapsulated, another thin layer of ZnSe is grown on the doped nanorods (Scheme 1). The growth-doping strategy (Scheme 1) maintains the shape of nanocrystals and realizes the doping simultaneously.

Fig. 4 shows the temporal evolution of the UV-Vis absorption spectra and the PL spectra of the solution at 180 °C, which offers a possible pathway to tune the optical properties



Scheme 1 Schematic illustration of the formation of the ultrathin doped nanorods.



Fig. 4 Temporal evolutions of (a) UV-Vis absorption spectra and (b) PL spectra of the reaction solution at 180 $^\circ$ C for different reaction times.

of the doped nanorods. When the reaction temperature reaches 180 °C, the Cu-related emission centred at 483 nm could be easily observed in the PL spectra. This result indicates the doping of Cu into ZnSe could be achieved at a low temperature. As the reaction at 180 °C proceeds, the absorption onset of the nanorods is slowly redshifted (~11 nm), indicative of the size growth (Fig. 4a). Meanwhile, the emission shifts from 483 to 520 nm and increases in its intensity (Fig. 4b). The former could be attributed to the band-gap narrowing of ZnSe due to the particle growth. The latter might be caused by the better coverage of the shell growth of ZnSe on the doped nanorods, which is supposed to passivate the surface and avoid the dissipation of Cu ions into the solution again.

The effect of OAm used for the shell growth on the optical properties of the doped nanorods has been illustrated in Fig. 5a. As the molar ratio of ZnAc₂: OAm increases to 1:2, an emission at 430 nm is observed in the PL spectra, indicating the heterogeneous nucleation of ZnSe in the solution. This result indicates less Zn and Se for shell growth on the doped nanorods, resulting in the low intensity and the blue-shift of the Cu-doped emission. Both of them are confirmed in the comparison with the PL spectra of the nanorods obtained with a molar ratio of ZnAc₂: OAm at 1:1.2. Fig. 5b shows the effect of the reaction temperature for the shell growth on the optical properties of the doped nanorods. As this temperature reaches 240 °C, the doped nanorods display obvious redshifts both in the absorption spectra and in the PL spectra, which could be attributed to the band-gap narrowing caused by the particle growth. Meanwhile, the intensity of the dopantrelated emission decreases but that of the band-gap emission increases. The results could be attributed to the heterogeneous nucleation of ZnSe at a high temperature and the release of Cu²⁺ ions into the solution due to the selfpurification effect.^{6,13} The latter is supported by the formation of Cu_{2-x} Se (JCPDS card no. 06-0680) in the solution.

Fig. 6 shows the dependence of the actual molar ratio of Cu/Zn and the quantum yield on the nominal ratio of Cu/Zn in the reaction. It is noticed that the actual ratio of Cu/Zn in the doped nanorods increases with the nominal content of Cu ions in the solution. But the actual Cu/Zn ratios are



Fig. 5 UV-Vis absorption spectra (solid line) and PL spectra (dash line) of the Cu-doped ZnSe nanorods prepared by (a) different molar ratios of $ZnAc_2/OAm$ or (b) different annealing temperatures.



Fig. 6 The dependences of (a) the actual molar ratio of Cu/Zn and (b) the quantum yield (QY) on the nominal ratio of Cu/Zn.

always far below the nominal ones over the tested range, indicating that only a small amount of Cu ions are incorporated into the host nanorods. Different from this result, there is not a monotonic relationship between the quantum yield and the nominal Cu/Zn ratio. The quantum yield of the doped nanorods reaches the maximum at the nominal ratio of Cu/Zn at 1.0%. Too many Cu ions might induce the formation of Cu_{2-x}Se, as indicated from the color of the product. The emission of the doped nanorods could be retained for weeks even in air, which paves the way for its potential applications.

Conclusions

In conclusion, ultrathin Cu-doped ZnSe nanorods are synthesized by the adsorption of Cu ions on the surface of ultrathin ZnSe nanorods, followed by shell growth. The XRD pattern and the TEM images indicate that this doping does not affect the crystal structure and unique morphology of ZnSe. The good encapsulation of Cu inside the ultrathin ZnSe nanorods has been confirmed by its characteristic emission over 480 to 520 nm. The as-obtained doped nanorods in the solution could show a quantum yield as high as 19%. But it drops to 7% after purification, which could be attributed to the removal of the surface ligands during the purification process. The emission could be retained for weeks in air, which opens a door for its applications in biological imaging, sensitive detection and optoelectronic devices.

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References

1 N. Pradhan, D. M. Battaglia, Y. C. Liu and X. G. Peng, *Nano Lett.*, 2007, 7, 312-317.

- 2 R. Thakar, Y. C. Chen and P. T. Snee, *Nano Lett.*, 2007, 7, 3429–3432.
- 3 V. Wood, J. E. Halpert, M. J. Panzer, M. G. Bawendi and V. Bulovic, *Nano Lett.*, 2009, 9, 2367–2371.
- 4 D. R. Gamelin, R. Beaulac, L. Schneider, P. I. Archer and G. Bacher, *Science*, 2009, 325, 973–976.
- 5 S. K. Panda, S. G. Hickey, H. V. Demir and A. Eychmuller, *Angew. Chem., Int. Ed.*, 2011, **50**, 4432–4436.
- 6 D. J. Norris, A. L. Efros and S. C. Erwin, *Science*, 2008, 319, 1776–1779.
- 7 R. Viswanatha, S. Brovelli, A. Pandey, S. A. Crooker and V. I. Klimov, *Nano Lett.*, 2011, 11, 4753–4758.
- 8 S. Gul, J. K. Cooper, C. Corrado, B. Vollbrecht, F. Bridges, J. H. Guo and J. Z. Zhang, *J. Phys. Chem. C*, 2011, 115, 20864–20875.
- 9 H. Y. Chen, T. Y. Chen and D. H. Son, J. Phys. Chem. C, 2010, 114, 4418-4423.
- 10 B. B. Srivastava, S. Jana and N. Pradhan, J. Am. Chem. Soc., 2011, 133, 1007–1015.
- 11 N. Pradhan and X. G. Peng, J. Am. Chem. Soc., 2007, 129, 3339-3347.
- 12 C. B. Murray, D. J. Norris and M. G. Bawendi, J. Am. Chem. Soc., 1993, 115, 8706–8715.
- 13 D. A. Chen, R. Viswanatha, G. L. Ong, R. G. Xie, M. Balasubramaninan and X. G. Peng, *J. Am. Chem. Soc.*, 2009, 131, 9333–9339.
- 14 N. S. Karan, D. D. Sarma, R. M. Kadam and N. Pradhan, J. Phys. Chem. Lett., 2010, 1, 2863–2866.
- H. B. Shen, H. Z. Wang, X. M. Li, J. Z. Niu, H. Wang, X. Chen and L. S. Li, *Dalton Trans.*, 2009, 10534–10540.

- 16 G. C. Xing, W. Ji, Y. G. Zheng and J. Y. Ying, Opt. Express, 2008, 16, 5710–5715.
- 17 L. S. Li, N. Pradhan, Y. J. Wang and X. G. Peng, *Nano Lett.*, 2004, 4, 2261–2264.
- 18 P. D. Cozzoli, L. Manna, M. L. Curri, S. Kudera, C. Giannini, M. Striccoli and A. Agostiano, *Chem. Mater.*, 2005, 17, 1296–1306.
- 19 M. D. Regulacio and M. Y. Han, Acc. Chem. Res., 2010, 43, 621–630.
- 20 T. T. Yao, S. F. Kou, Y. H. Sun, Q. Zhao and J. Yang, *CrystEngComm*, 2012, 14, 8440–8445.
- 21 B. J. Xi, D. C. Xu, S. L. Xiong, C. M. Wang, X. M. Feng, H. Y. Zhou and Y. T. Qian, *J. Phys. Chem. C*, 2008, 112, 5333–5338.
- 22 J. W. L. Yim, D. Chen, G. F. Brown and J. Q. Wu, Nano Res., 2010, 2, 931–937.
- 23 T. T. Yao, Q. Zhao, Z. P. Qiao, F. Peng, H. J. Wang, H. Yu,
 C. Chi and J. Yang, *Chem.-Eur. J.*, 2011, 17, 8663-8670.
- 24 N. Pradhan, D. Goorskey, J. Thessing and X. G. Peng, *J. Am. Chem. Soc.*, 2005, **127**, 17586–17587.
- 25 J. S. Han, H. Zhang, Y. Tang, Y. Liu, X. Yao and B. Yang, J. Phys. Chem. C, 2009, 113, 7503–7510.
- 26 G. B. Stringfellow and R. H. Bube, *Phys. Rev.*, 1968, 171, 903–915.
- 27 J. F. Suyver, T. van der Beek, S. F. Wuister, J. J. Kelly and A. Meijerink, *Appl. Phys. Lett.*, 2001, 79, 4222–4224.
- 28 R. G. Xie and X. G. Peng, J. Am. Chem. Soc., 2009, 131, 10645-10651.
- 29 S. Jana, B. B. Srivastava, S. Acharya, P. K. Santra, N. R. Jana, D. D. Sarma and N. Pradhan, *Chem. Commun.*, 2010, 46, 2853–2855.

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