

Fast Doping of Cu into ZnSe NCs by Hydrazine Promoted Cation Exchange in Aqueous Solution at Room Temperature

Haibao Shao · Chunlei Wang · Shuhong Xu ·
Zhuyuan Wang · Haihong Yin · Yiping Cui

Received: 23 October 2014 / Accepted: 2 January 2015 / Published online: 22 January 2015
© Springer Science+Business Media New York 2015

Abstract Controllable doping is an effective way of tuning the properties of semiconductor nanocrystals (NCs). In this work, a simple strategy of fast doping Cu ions into ZnSe NCs under ambient conditions was proposed. The principle of doping is based on hydrazine (N₂H₄) promoted cation exchange reaction. By direct addition of Cu ion stock solution into the preformed ZnSe NCs, Cu doped ZnSe NCs can be obtained. Furthermore, the emission of doped NCs can be tuned by changing the amount of impurity ion addition. The cation exchange reaction is facilitated by three factors: 1) N₂H₄ addition, 2) fast impurity ions, and 3) partial stabilizer removal. The proposed cation exchange reaction in aqueous solution could be an alternate route for NC doping as well as synthesis of ionic NCs.

Keywords Doped · Cation exchange · Aqueous solution · Cu:ZnSe NCs

Introduction

Colloidal semiconductor nanocrystals (NCs) have been widely studied for their size-dependent optical and electronic

Electronic supplementary material The online version of this article (doi:10.1007/s10895-015-1509-1) contains supplementary material, which is available to authorized users.

H. Shao · C. Wang (✉) · S. Xu · Z. Wang · Y. Cui (✉)
Advanced Photonics Center, School of Electronic Science and Engineering, Southeast University, Nanjing 210096, People's Republic of China
e-mail: wangchl@seu.edu.cn
e-mail: cyp@seu.edu.cn

H. Shao · H. Yin
School of Electronics and Information, Nantong University,
Nantong, People's Republic of China

properties and applications such as light-emitting diodes, biomedical labels, and solar cells etc. [1–3]. Aside from changing the NC size, doping of semiconductor NCs provides another attractive way of producing functional materials with new properties [4–7]. For instance, doped semiconductor NCs usually possess large Stokes shift thus can avoid self-quenching problems of intrinsic NCs [8, 9]. In addition, wide-band-gap zinc chalcogenides doped with transition metal ions are less toxic than conventional cadmium chalcogenides, which is of great importance for biomedical diagnosis [8]. Furthermore, with different dopant types and concentration, the bandgap and Fermi level of the NCs can be controlled [10].

One challenge of the synthesis of doped semiconductor NCs is the so-called “self-purification” process in which the host matrix tends to expel the dopant ions to the NC surface [11]. Early doping approaches were generally based on the pre-mixing of dopant ions and competitive host ions followed by high-temperature growth [12–15]. Afterwards, Peng and coworkers proposed a new strategy called “nucleation-doping” which could achieve doping of almost all NCs in a given sample [8, 16]. Another challenge in the synthesis of doped semiconductor NCs is to develop greener method that is simpler, less time-consuming, and less toxic than that reported previously [17–20]. Synthesis in aqueous media is an alternative since it's more environmental friendly, safe, and easy for biological application, in comparison to high-temperature organometallic ways [21]. The nucleation-growth doping strategy can also apply to the synthesis of doped NCs in aqueous solution, such as Mn:ZnSe [22, 23]. However, aqueous synthesis of doped semiconductor NCs are time-consuming and the NC solution should be taken to reflux at relatively high temperature.

In recent years, chemical transformation has been emerged as a new route to nano-material synthesis by using well-developed NCs (such as CdSe NCs) as starting templates [24, 25]. It has been reported by Alivisatos and coworkers that

for ionic semiconductor NCs, cation exchange reaction could be greatly promoted by simply adding methanol in organic solution at room temperature [26, 27]. Very recently, Banin and coworkers developed a simple room-temperature method for synthesizing heavily doped semiconductor NCs with metal impurities by introducing of a dodecylamine [10]. These synthetic methods are amazing for their easy control of chemical composition and fast reaction speed at room temperature, except that they are all conducted in the organic media.

Herein we report a simple method for doping Cu ions into ZnSe NCs based on hydrazine (N_2H_4) promoted cation exchange reaction in aqueous solution at room temperature. The doping of Cu into the ZnSe NCs can be achieved by simply adding Cu ion precursor into preformed ZnSe NC solution. By varying the amount of Cu precursor addition, the emission of doped ZnSe NCs is tunable. Moreover, the ZnSe NCs can be completely transformed into $\text{Cu}_{1.8}\text{Se}$ NCs by excess amount of Cu precursor addition. The proposed cation exchange reaction in aqueous solution could be a versatile route for expanding the range of nanoscale materials.

Experimental Section

Chemicals

Selenium powder (Se, 99.99 %), 3-Mercaptoacetic acid (MPA, 99 %), Sodium borohydride (NaBH_4 , 95 %), Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99 %), Copper chloride (CuCl_2 , 99 %), hydrazine hydrate (N_2H_4 , 85 %), Sodium hydroxide (NaOH , 97 %), All chemicals used in this work were of analytical grade.

Synthesis of ZnSe NCs

NaHSe solution was prepared by using Se and NaBH_4 according to the reference methods [28, 29]. Aqueous ZnSe NCs were synthesized according to the reference method [30, 31]. Namely, the mixture of $\text{Zn}(\text{NO}_3)_2$ and MPA was adjusted to pH 11.4 by drop wise addition of 5.0 mol/L NaOH solution. After being bubbled with N_2 for 30 min, freshly prepared NaHSe solution was injected into the aforementioned mixture. The total concentration of Zn in the mixture was 0.01 mol/L, and the feeding ratio of Zn/MPA/Se was 1.0/2.0/0.20. The solution was then refluxed at 100 °C for 2 h. The as-prepared ZnSe NCs were purified by centrifugation after being precipitated by methanol and re-dispersed in water.

Synthesis of Cu doped ZnSe NCs

Cu doped ZnSe NCs were obtained by partial cation exchange of Cu with Zn ions. First, the ion exchange stock solution was prepared by mixing 4 μL MPA with 5 mL of 2×10^{-3} mol/L

CuCl_2 aqueous solution. In a typical doping process, the above Cu stock solution was added drop-wise into the solution of ZnSe NCs (concentration of NCs was 1×10^{-3} mol/L according to Zn) in the presence of 0.2 mol/L N_2H_4 under vigorous stirring. By adding different amount of Cu stock solution into the ZnSe NC solution in the presence of 0.2 mol/L N_2H_4 , different levels of Cu doped ZnSe NCs were obtained. The samples were taken for absorption and emission measurements immediately.

Complete Cation Exchange Reactions

ZnSe NCs could be converted into $\text{Cu}_{1.8}\text{Se}$ NCs by addition of excess amount of Cu ion exchange stock solution in the presence of 2 mol/L N_2H_4 . The added amount of Cu stock solution was 4 times the initial Zn content. After the addition of Cu stock solution, the solution color changed immediately (in a few seconds) from colorless to dark brown and the emission of the NCs was completely quenched, indicating the formation of $\text{Cu}_{1.8}\text{Se}$ NCs.

The converted $\text{Cu}_{1.8}\text{Se}$ NCs were recovered into ZnSe NCs through a reverse cation exchange reaction by addition of Zn ion stock solution. In the reverse reaction, certain amount of MPA was mixed with 0.5 mol/L $\text{Zn}(\text{NO}_3)_2$ aqueous solution ($\text{MPA}/\text{Zn}^{2+} \geq 2$). An excess amount (200 times the initial Zn content) of Zn stock solution was added into $\text{Cu}_{1.8}\text{Se}$ solution in the presence of 2 mol/L N_2H_4 . There was a slower change of the solution from brown back to colorless. The recovered NCs show green fluorescence due to remaining Cu ions inside NCs. The restored NCs were purified by centrifugation after being precipitated by methanol and re-dispersed in water. In order to remove the Cu ions as many as possible, the above reverse reaction was repeated for 4~5 times until the intrinsic fluorescence of ZnSe NCs showed up. All experiments were carried out under ambient atmosphere at room temperature.

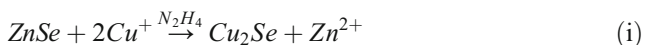
Characterization

UV–vis absorption spectra (UV) were recorded with a Shimadzu 3600 UV–vis near-infrared spectrophotometer. Fluorescence experiments were performed with an Edinburg FLS 920 spectrofluorimeter. The excitation wavelength in PL spectra was 350 nm. All optical measurements were performed at room temperature under ambient conditions. X-ray powder diffraction (XRD) investigation was carried out by using the D/max-2500/PC diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) was investigated by using a PHI550 spectrometer with a $\text{Mg K}\alpha$ excitation (1253.6 eV). Binding energy calibration was based on C 1 s at 284.6 eV. Before XRD and XPS measurement, the as-prepared Au decorated NC were purified. Namely, equal volume of methanol was added into aqueous

NC solution, and the obtained precipitates were used for XPS measurement.

Results and Discussion

Doping of Cu impurities into ZnSe NCs was facilitated by N₂H₄ promoted cation exchange reaction in aqueous solution. The reaction can be given by the following equation:

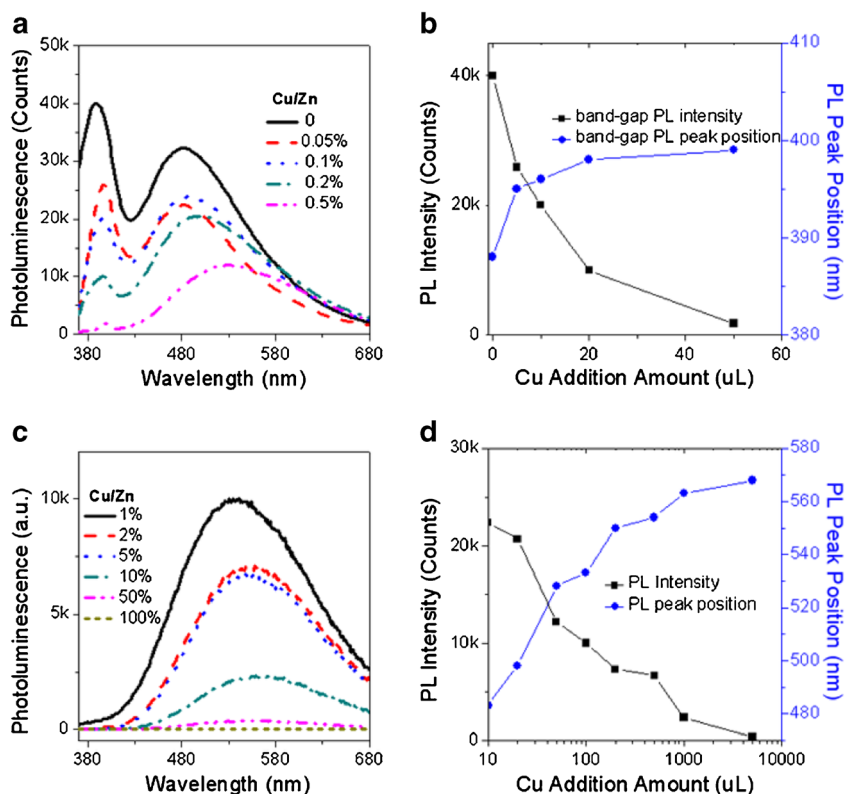


Basically, one Zn²⁺ ion in ZnSe NCs was replaced by two Cu⁺ ions for charge balance. As a result, the degree of cation exchange in these ZnSe NCs could be controlled by the amount of added Cu stock solution. Although the used Cu stock solution was a mixture of Cu²⁺ and MPA, it was found that the Cu ions were in the form of Cu⁺ rather than Cu²⁺ as discussed later in this paper.

Cu doped ZnSe NCs were synthesized by directly adding Cu stock solution into purified ZnSe NC solution in the presence of excess amount of N₂H₄ (N₂H₄/Zn = 200). In our experiments, very small amount of Cu addition would cause enormous change in the emission of ZnSe NCs immediately (Fig. 1). For pure ZnSe NCs, there are two emission peaks of the PL spectra. The emission peak at around 400 nm is

attributed to band-gap emission of ZnSe NCs: namely the irradiation recombination of electrons from ZnSe conduction band to ZnSe valence band (Scheme 1S). Whereas the emission peak at around 480 nm is related to surface defect emission: namely the irradiation recombination of electrons from defect energy levels to ZnSe valence band (Scheme 1S). The band-gap emission and surface defect emission can also be distinguished by the Stokes shift (Figure 1S). For pure ZnSe NCs, the excitonic absorption peak was at around 370 nm, a 30 nm Stokes shift implied the PL peak around 400 nm was bandgap emission. For PL peak around 480 nm, the Stokes shift is as large as 100 nm, which indicated surface defect related emission. This PL characteristic of water soluble ZnSe NCs and ZnSe:Cu was reported by earlier publications [28, 31]. Once addition of Cu stock solution into ZnSe solution, the emission of ZnSe NCs changed immediately, indicating the extremely fast cation exchange reaction. With increased Cu addition amount up to Cu/Zn ratio of 0.2 %, ZnSe band-gap emission nearby 400 nm became much weaker. Simultaneously, the longer-wave emission also shifted from 480 to 500 nm. Obviously, the emission change was caused by the rapid replacement of Zn cations by Cu ones in the NCs. When Cu addition amount increased to Cu/Zn ratio of 1 %, ZnSe bandgap emission around 400 nm disappeared, leaving only emission band at around 530 nm. By adding more Cu stock solution, there was a continuous red-shift of this emission band until the photoluminescence (PL) peak position of

Fig. 1 Evolution of photoluminescence of Cu doped ZnSe NCs. **a** Cu/Zn ratio between 0 and 0.5 %, **b** band-gap PL intensity and peak position with different Cu addition amount, **c** Cu/Zn ratio between 0.1 and 100 %, **d** PL intensity and peak position at longer-wavelength with different Cu addition amount



570 nm. It is still unknown the reason for the emission redshift with increased Cu amount since the Cu dopant energy level will not be affected by Cu dopant amount in NCs with unchanged size. To investigate the possible reason, the emission of as-prepared NCs were analyzed by deconvolution in Figure 2S. The fitted results were shown in Table 1S. As can be seen, the addition of Cu into ZnSe NCs led to a new emission band around 580 nm: namely Cu dopant emission. Due to the serious overlapping for ZnSe defect emission band and Cu dopant emission band, the observed emission at the longer-wave emission was actually an integration emission for aforementioned two bands. With increased Cu addition amount, ZnSe defect emission became weaker and weaker, leading to changed integration emission from ZnSe defect emission-dominant (480 nm) to Cu dopant emission-dominant (570 nm). This should be the reason for the emission redshift with increased Cu amount.

High-resolution transmission electron microscope (HRTEM) images showed that the size and shape of NCs were preserved over the doping process (Fig. 2). HRTEM images (insets) with well-resolved lattice planes indicated good crystalline structures of the NCs. The measured lattice spacing of the starting ZnSe and Cu doped ZnSe are both 0.325 nm, corresponding to (111) lattice plane of cubic ZnSe. It is noted here that NCs in aqueous solution were easily aggregated upon deposition and solvent evaporation because the TEM grids used for this analysis were hydrophobic carbon coated

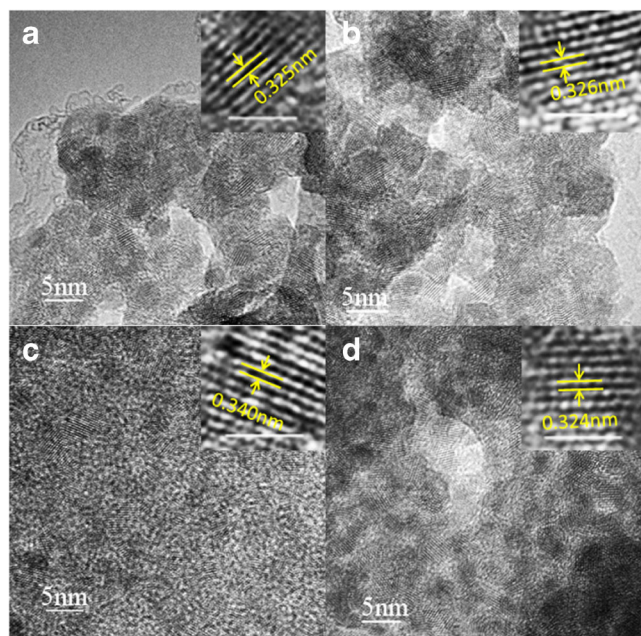


Fig. 2 High resolution transmission electron microscope (HRTEM) images of **a** initial ZnSe NCs, **b** Cu doped ZnSe NCs, **c** $\text{Cu}_{1.8}\text{Se}$ NCs and **d** recovered ZnSe NCs. Scale bars are 5 nm. Insets show the magnified HRTEM images of individual NCs with well resolved lattice planes. Scale bars are 2 nm

grids [32]. In our work, NCs all have good mono-dispersity in aqueous solution.

X-ray diffraction (XRD) patterns were further used to characterize the structure of Cu doped ZnSe NCs (Fig. 3). The starting ZnSe NCs and Cu doped ZnSe NCs showed almost identical diffraction characteristics, the major diffraction peaks at 27.5° , 45.6° and 54.1° are attributed to (111), (220) and (311) planes of cubic ZnSe respectively. The identical cubic structure of NCs is in consistent with HRTEM results.

To further understand the doping process, Cu doped ZnSe NCs were taken for XPS measurements (Fig. 4). Signals at 932.7 and 952.4 eV originated from Cu, which confirmed the presence of Cu ions in the doped ZnSe NCs. However, it is difficult to discriminate the valance state of Cu^+ or Cu^{2+} in ZnSe NCs by XPS because the binding energies of Cu^+ and Cu^{2+} are so close. Moreover, signals at 399.4 and 406.5 eV which were attributed to N were observed. According to the experiments, signals from N came obviously from the N_2H_4 addition. This result indicates the presence of N_2H_4 on the NC surface.

In the above doping process, Cu ions were easily incorporated into the host ZnSe NCs with surprisingly fast speed. In addition, the host ZnSe NCs seemed can take in as many Cu ions as possible. These properties implied that the doping process may probably be based on fast cation exchange reactions. As is known, ionic semiconductor NCs could be chemically transformed into new ones by adding new ions in organic solution [33, 34]. In order to figure this problem out, a complete cation exchange reaction was performed by mixing a solution of purified ZnSe NCs with over amount of Cu stock solution the presence of 2 mol/L N_2H_4 ($\text{N}_2\text{H}_4/\text{Zn} = 2000$). The

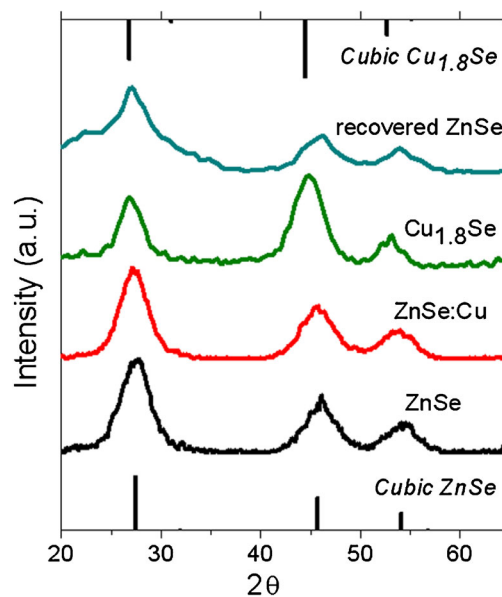


Fig. 3 XRD patterns of initial ZnSe NCs, Cu doped ZnSe NCs, $\text{Cu}_{1.8}\text{Se}$ NCs and recovered ZnSe NCs. For comparison, the reference peaks of bulk cubic ZnSe and $\text{Cu}_{1.8}\text{Se}$ are displayed

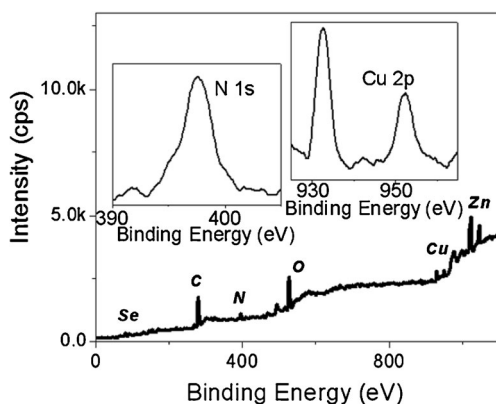


Fig. 4 X-ray photoelectron spectroscopy (XPS) of partially exchanged Cu doped ZnSe. Insets are the spectra of Cu 2p and N 1 s, respectively

color of the solution changed rapidly (in a few seconds) from colorless to brown and the fluorescence is completely quenched (Figure 1S).

X-ray diffraction patterns revealed that the reaction product was $\text{Cu}_{1.8}\text{Se}$ (Fig. 3). For small amount of Cu doping, the XRD patterns barely changed. By addition of more Cu impurities, the peaks of XRD gradually shifted to smaller 2θ values. After a complete cation exchange the XRD patterns of final product was in consistent with cubic $\text{Cu}_{1.8}\text{Se}$ and there was a obvious shift of the XRD peaks to the smaller 2θ values. This shifting of peaks can be explained by the contraction or expansion of the lattice. It has been reported that lattice contraction/expansion will cause the peaks shift to the larger/smaller 2θ values [35, 36]. In our experiments, lattice expansion was accompanied by the transition from ZnSe NCs to $\text{Cu}_{1.8}\text{Se}$ ones as observed from the lattice spacing in HRTEM results of Fig. 2. As a result, the diffractive peaks will shift to much smaller 2θ values. The diffraction peaks of the NCs at 26.9° , 44.7° , and 53.1° were attributed to (111), (220) and (311) planes of cubic $\text{Cu}_{1.8}\text{Se}$, respectively. It is noted that the major peak positions of ZnSe and $\text{Cu}_{1.8}\text{Se}$ are rather close due to the overlapping of the peaks. However, the conversion from ZnSe to $\text{Cu}_{1.8}\text{Se}$ could also be judged from the evolution of the relative intensity of the peaks at the positions of ZnSe compared with $\text{Cu}_{1.8}\text{Se}$.

Since Cu stock solution was prepared by mixing CuCl_2 with MPA, Cu^{2+} ions were probably reduced to Cu^+ by MPA in aqueous solution [31]. Interestingly, the product of complete cation exchange reaction was not Cu_2Se . $\text{Cu}_{1.8}\text{Se}$ which is lack of Cu^+ ions was more favorably formed. Anyway, it means the Cu ions in the NCs were in the form of Cu^+ rather than Cu^{2+} . From HRTEM image, the measured lattice spacing of the converted $\text{Cu}_{1.8}\text{Se}$ was 0.34 nm, corresponding to (111) lattice plane cubic $\text{Cu}_{1.8}\text{Se}$ (Fig. 2).

The converted $\text{Cu}_{1.8}\text{Se}$ NCs could be recovered back into ZnSe NCs through a reverse cation exchange reaction by addition of excess amount of Zn stock solution in the presence of

2 mol/L N_2H_4 . The recovered ZnSe NCs showed almost the same absorption and emission features as the initial ZnSe NCs (Figure 1S). Since the absorption and emission peak positions are strongly dependent by the NC size, the recovered ZnSe NCs should have almost identical size with the initial ones.

XRD patterns showed that ZnSe NCs changed back from $\text{Cu}_{1.8}\text{Se}$ had the same cubic structure as initial ZnSe NCs too (Fig. 3). XRD patterns of reversed ZnSe NCs also showed broadening features compared with initial ones. According to Scherrer's formula, the broadening of the XRD peaks was strongly dependent on the NC size. But in our experiment this broadening feature may probably caused by the degrading of lattice ordering during cation exchange rather than by NC size change since TEM images showed almost identical NC size between the reversed ZnSe NCs and the initial ZnSe NCs. From the above XRD results, the initial ZnSe NCs, Cu doped ZnSe NCs, $\text{Cu}_{1.8}\text{Se}$ NCs and recovered ZnSe NCs all had the same cubic zinc blend structure. In fact, it has been revealed that during cation exchange, the anion framework of the crystal was preserved [37]. The above XRD results are in consistent with the previous report. The measured lattice spacing from HRTEM image was 0.325 nm, corresponding to (111) lattice plane cubic ZnSe, confirming the recovering of ZnSe NCs (Fig. 2).

In our work, there are some key factors for the cation exchange reactions to take place so quickly at room temperature. First, there is no doubt that N_2H_4 addition is very important since it promotes the cation exchange reaction. As is known, hydrazine is a Lewis base which can bind to metal ions. In the above reactions, the coordinative interaction between N_2H_4 and cations (Zn^{2+} and Cu^+) may greatly increase the diffusion speed of cations thus creates the driving force to convert the ZnSe NCs into $\text{Cu}_{1.8}\text{Se}$. In fact, previous reports had revealed that N_2H_4 could promote the growth or transformation of NCs in aqueous solution by binding to the metal ions [38–40]. In addition, an extremely excessive amount of N_2H_4 in aqueous solution can also serve as an alkaline buffer to neutralize the acidic Cu or Zn stock solution. It should be noted that experiments without the presence of N_2H_4 showed barely any cation exchange. Second, the Cu ions are considered fast diffusers so that diffusion of the cations is allowed [41]. Previous report of doping Cu into ZnSe have demonstrated that Cu ions could be incorporated into ZnSe NCs under relatively mild conditions [42]. However, for traditional synthetic ways, no doping of Cu ions into ZnSe NCs could occur in such a fast speed or at room temperature before. Third, purification of the starting ZnSe NCs is also a very important step in our experiment, addition of Cu stock solution into ZnSe NCs without purification in the presence of N_2H_4 showed barely any change of emission color of ZnSe NCs. As thiol stabilizer was in a excess amount during the synthesis of ZnSe NCs, there was a close packed thiol stabilizer coating on the surface of the NCs. Purification of the NCs resulted in the partial

removal of the stabilizer thus facilitated the following doping process [43, 44].

Based on the proposed cation exchange reaction above, other two cations (Ag and Pb) were employed to verify that the reaction is broadly applicable. Over amount of Ag or Pb stock solution was added into purified ZnSe NCs in the presence of N_2H_4 and the solution was left to stir for 5 min. After that the NCs were purified by centrifugation after being precipitated by methanol and dried in vacuum. The samples were taken to X-ray diffraction test. It turned out that the initial ZnSe NCs were transformed into Ag_2Se and $PbSe$ respectively after cation exchange (Figure 3S). This result indicates that the proposed N_2H_4 promoted cation exchange may also be an alternative way for synthesizing ionic NCs.

Conclusion

In conclusion, we proposed a fast, simple doping method through cation exchange reaction in aqueous solution at room temperature. The proposed cation exchange reaction was promoted by N_2H_4 which can bind to cations and increasing the diffusion speed. By partial removal of NC stabilizer and employing fast ions (such as Cu, Ag, and Pb), the cation exchange reaction could be further facilitated. Cu doped ZnSe NCs with tunable emission was demonstrated through simply addition of different amount of Cu stock solution into preformed ZnSe NCs. This simple way of doping with flexible controllability offers an alternation for traditional high-temperature ways. The proposed cation exchange reaction in aqueous solution can also be an alternate route for NC doping as well as synthesis of ionic NCs.

Acknowledgments This work is supported by the National Key Basic Research Program of China (Grant No. 2015CB352002), National Natural Science Foundation of China (Grant Nos. 61475034, 21403034, 61177033), the Fundamental Research Funds for the Central Universities (No. 2242014R30006), the NSF of China (Grant No.61204018), the NSF of Jiangsu Province (Grant No. BK 20141239 and BK 20140635).

References

- Colvin VL, Schlamp MC, Alivisatos AP (1994) *Nature* 370:354
- Bruchez M, Moronne M, Gin P, Weiss S, Alivisatos AP (1998) *Science* 281:2013
- Chan WCW, Nie SM (1998) *Science* 281:2016
- Bhargava RN, Gallagher D, Hong X, Nurmikko A (1994) *Phys Rev Lett* 72:416
- Norris DJ, Efros AL, Erwin SC (2008) *Science* 319:1776
- Shim M, Guyot-Sionnest P (2000) *Nature* 407:981
- Mikulec FV, Kuno M, Bennati M, Hall DA, Griffin RG, Bawendi MG (2000) *J Am Chem Soc* 122:2532
- Pradhan N, Goorskey D, Thessing J, Peng XG (2005) *J Am Chem Soc* 127:17586
- Pradhan N, Battaglia DM, Liu Y, Peng X (2007) *Nano Lett* 7:312
- Mocatta D, Cohen G, Schattner J, Millo O, Rabani E, Banin U (2011) *Science* 332:77
- Dalpian GM, Chelikowsky JR (2006) *Phys Rev Lett* 96
- Norris DJ, Yao N, Charnock FT, Kennedy TA (2001) *Nano Lett* 1:3
- Norberg NS, Parks GL, Salley GM, Gamelin DR (2006) *J Am Chem Soc* 128:13195
- Erwin SC, Zu LJ, Haftel MI, Efros AL, Kennedy TA, Norris DJ (2005) *Nature* 436:91
- Suyver JF, Wuister SF, Kelly JJ, Meijerink A (2000) *Phys Chem Chem Phys* 2:5445
- Pradhan N, Peng X (2007) *J Am Chem Soc* 129:3339
- Dahl JA, Maddux BLS, Hutchison JE (2007) *Chem Rev (Wash DC US)* 107:2228
- Yu WW, Peng XG (2002) *Angew Chem Int Ed* 41:2368
- Peng ZA, Peng XG (2001) *J Am Chem Soc* 123:183
- Dai Q, Xiao N, Ning J, Li C, Li D, Zou B, Yu WW, Kan S, Chen H, Liu B, Zou G (2008) *J Phys Chem C* 112:7567
- Gaponik N, Talapin DV, Rogach AL, Hoppe K, Shevchenko EV, Kornowski A, Eychmuller A, Weller H (2002) *J Phys Chem B* 106:7177
- Shao P, Zhang Q, Li Y, Wang H (2011) *J Mater Chem* 21:151
- Wang C, Gao X, Ma Q, Su X (2009) *J Mater Chem* 19:7016
- Smith AM, Nie S (2011) *J Am Chem Soc* 133:24
- Mayers B, Jiang XC, Sunderland D, Cattle B, Xia YN (2003) *J Am Chem Soc* 125:13364
- Alivisatos AP, Son DH, Hughes SM, Yin YD (2004) *Science* 306:1009
- Robinson RD, Sadtler B, Demchenko DO, Erdonmez CK, Wang LW, Alivisatos AP (2007) *Science* 317:355
- Xu SH, Wang CL, Wang ZY, Zhang HS, Yang J, Xu QY, Shao HB, Li RQ, Lei W, Cui YP (2011) *Nanotechnology* 22
- Hao E, Zhang H, Yang B, Ren H, Shen J (2001) *J Colloid Interface Sci* 238:285
- Srivastava BB, Jana S, Pradhan N (2011) *J Am Chem Soc* 133:1007
- Han J, Zhang H, Tang Y, Liu Y, Yao X, Yang B (2009) *J Phys Chem C* 113:7503
- Gaponik N, Talapin DV, Rogach AL, Eychmuller A, Weller H (2002) *Nano Lett* 2:803
- Moon GD, Ko S, Xia YN, Jeong U (2010) *ACS Nano* 4:2307
- Moon GD, Ko S, Min Y, Zeng J, Xia YN, Jeong U (2011) *Nano Today* 6:186
- Jiaming Z, Xuke Z, Zhang JY (2009) *J Phys Chem C* 114:3904
- Sung Jun L, Bonghwan C, Taiha J, Shin SK (2008) *J Phys Chem C* 112:1744
- Jain PK, Amirav L, Aloni S, Alivisatos AP (2010) *J Am Chem Soc* 132:9997
- Han JS, Luo XT, Zhou D, Sun HZ, Zhang H, Yang B (2010) *J Phys Chem C* 114:6418
- Nair PV, Thomas KG (2010) *J Phys Chem Lett* 1:2094
- Shao H, Wang C, Wang Z, Li R, Xu Q, Xu S, Jiang Y, Sun Q, Bo F, Cui Y (2012) *J Colloid Interface Sci* 383:43
- Seeger A, Chik KP (1968) *Phys Status Solidi B* 29:455
- Chen D, Viswanatha R, Ong GL, Xie R, Balasubramanian M, Peng X (2009) *J Am Chem Soc* 131:9333
- Tang ZY, Kotov NA, Giersig M (2002) *Science* 297:237
- Tang ZY, Wang Y, Sun K, Kotov NA (2005) *Adv Mater* 17:358