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Hydrazine-promoted sequential cation exchange: a novel synthesis method for doped ternary semiconductor nanocrystals with tunable emission

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Abstract
Using ZnSe nanocrystals (NCs) as starting material, Ag-doped or Cu-doped ZnCdSe ternary NCs were prepared by hydrazine-promoted sequential cation exchange in aqueous media. The composition of the NCs can be flexibly controlled by varying the amount of intermediate Ag or Cu cation addition, thus changing the emission of the ternary NCs while preserving the NC size. According to Vegard’s law, the as-prepared ternary NCs possess an alloyed structure. In addition, the ternary NCs obtained have a high quantum yield, strong stability and a broad optical tuning range.

Keywords: ZnCdSe, ternary NCs, cation exchange

Online supplementary data available from stacks.iop.org/Nano/25/025603/mmedia
(Some figures may appear in colour only in the online journal)

1. Introduction
For binary nanocrystals (NCs) such as CdSe and CdTe, various emissions can be achieved over almost the entire visible range by band gap engineering through controlling the NC size [1–4]. Aside from changing the size of the NCs, the band gaps of NCs can also be tuned by changing their compositions [5–8]. For instance, ternary-alloyed ZnCdSe and CdSeTe NCs with different emission colors which are controlled by the constituents have been reported [7, 9]. Compared with binary NCs, alloyed NCs are more stable and flexible for tuning the band gap by introducing some band gap sensitive elements for light-emitting diodes and solar energy application [10, 11].

Synthesis of ternary-alloyed NCs is mainly based on the high-temperature growth strategies derived from the conventional protocol for the synthesis of CdSe NCs in organic solution. Recently, Smith et al reported that cation exchange could be an alternative way of obtaining ternary HgCdTe NCs with tunable near-infrared emission by using CdTe NCs as starting material [12]. Cation exchange reaction in semiconductor NCs, which was first proposed by Alivisatos group, can independently change the compositions of the starting NCs by introducing a different metal ion into the NC lattice while preserving the NC size and shape [13]. These properties make cation exchange a very convenient and useful way of obtaining multicomponent nanomaterials.

Herein, we propose a new strategy to obtain doped CdSe and ternary-alloyed ZnCdSe NCs which is based on hydrazine (N$_2$H$_4$)-promoted sequential cation exchange reaction in aqueous solution at room temperature. The band gap of the doped ZnCdSe NCs could be engineered by tuning the composition of the NCs, which was easily achieved by varying the amount of cation precursor addition. The doped ternary NCs obtained have high photoluminescence quantum yield (PLQY) and strong stability. By using Ag and Cu ions as intermediate cations, the emissions of the as-prepared...
ternary-alloyed ZnCdSe NCs are continuously tunable from green (510 nm) to near infrared (790 nm).

2. Experimental details

2.1. Chemicals

The selenium powder (Se, 99.99%), 3-mercaptoacetic acid (MPA, 99%), sodium borohydride (NaBH₄, 95%), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 99%), silver nitrate (AgNO₃, 99%), copper chloride (CuCl₂, 99%), cadmium chloride (CdCl₂, 99%), hydrazine hydrate (N₂H₄, 85%), and sodium hydroxide (NaOH, 97%) used in this work were of analytical grade.

2.2. Synthesis of ZnSe NCs

Aqueous ZnSe NCs were synthesized according to the reference method [14]. Namely, a mixture of Zn(NO₃)₂ and MPA was adjusted to pH 11.4 by drop-wise addition of 5.0 mol l⁻¹ NaOH solution. After being bubbled with N₂ 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⁻¹, 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.

2.3. Synthesis of ZnCdSe alloyed nanocrystals via cation exchange reactions

A two-step cation exchange reaction was employed to achieve ZnCdSe alloyed ternary NCs in the open air at room temperature. First, ZnSe was converted into ZnAgSe through partial exchange with Ag. The ion exchange stock solution was prepared by mixing MPA with 0.01 mol l⁻¹ AgNO₃ aqueous solution (MPA/Ag ≥ 1). The Ag–MPA solution turned turbid immediately and was kept under vigorous stirring. Note here that the silver in the turbid Ag stock solution is cationic when hydrazine is present (figure S1, Note S1 available at stacks.iop.org/Nano/25/025603/mmedia). The Ag stock solution (namely the mixture of Ag and MPA) turned turbid because of the formation of insoluble Ag–S–CH₂–CH₂–COO–Ag compound. At pH above 7.0, however, this insoluble compound will convert to soluble Ag–S–CH₂–CH₂–COO⁻ (figure S2 available at stacks.iop.org/Nano/25/025603/mmedia). Then the above Ag ion stock solution was added drop-wise into the preformed ZnSe NCs (concentration of NCs was 1 × 10⁻³ mol l⁻¹ according to Zn) in the presence of 2 mol l⁻¹ N₂H₄ under vigorous stirring. Hydrazine also serves as an alkaline solution with a pH value around 10.0. Thus, the turbid Ag stock solution was immediately clarified once addition into the mixture of ZnSe NCs and hydrazine (figure S2 available at stacks.iop.org/Nano/25/025603/mmedia). The feeding ratios of Ag/Zn varied from 0.02 to 1. There is an immediate change of color of the NC solution on the addition of Ag stock solution, depending on the feed ratio of Ag/Zn. At low feeding ratios the solution turned light brown, while at higher feeding ratios the solution color became darker. In the second step, the ZnAgSe NCs were converted into Ag-doped ZnCdSe alloyed nanocrystals by adding excess Cd stock solution. The Cd stock solution was prepared by dissolving 0.05 mol l⁻¹ CdCl₂ in 5 ml water in the presence of MPA (MPA/Cd ≥ 2). The Cd stock solution was then added into ZnAgSe solution in the presence of 2 mol l⁻¹ N₂H₄. A slower change of solution color was observed (from light yellow at low Ag/Zn feeding ratios to red at high Ag/Zn feeding ratios). The solution was kept stirring for 5 min to complete the cation exchange. Note here that the added Cd cations were in an excess amount (50 times the initial Zn content). By varying the amount of Ag ions added in the first step, the proportion of Cd in the final product of ZnCdSe can be tuned. After the synthesis, the Ag-doped ZnCdSe alloyed ternary NCs were purified by centrifugation after being precipitated by methanol and re-dispersed in water.

2.4. Complete conversion through cation exchange

A complete conversion of ZnSe NCs to Ag₂Se then to CdSe was achieved by sequential addition of Ag and Cd ion exchange stock solution. First, an over amount of Ag stock solution was added drop-wise into preformed ZnSe NCs in the presence of 2 mol l⁻¹ N₂H₄ under vigorous stirring. The Ag/Zn ratio was slightly larger than 2 as two Ag⁺ ions replace one Zn²⁺ ion for charge balance.) The color of the solution changed rapidly (in a few seconds) from colorless to dark brown and the fluorescence was completely quenched, indicating the formation of Ag₂Se NCs. Second, an excess amount of Cd (50 times the initial Zn content) stock solution was added into the Ag₂Se NC solution and the solution was kept stirring for 5 min to complete the cation exchange. After that, NCs mainly composed of CdSe (with some Ag remaining) were obtained.

2.5. Characterization

UV–visible (UV–vis) absorption spectra were recorded with a Shimadzu 3600 UV–vis near-infrared spectrophotometer. Fluorescence experiments were performed with an Edinburgh FLS 920 spectrophotometer. The excitation wavelength in the photoluminescence (PL) spectra was 350 nm. All optical measurements were performed at room temperature under ambient conditions. An x-ray powder diffraction (XRD) investigation was carried out by using a D/max-2500/PC diffractometer with Cu Kα radiation (λ = 1.5418 Å). X-ray photoelectron spectroscopy (XPS) was investigated by using a PHI550 spectrometer with Mg Kα excitation (1253.6 eV). Binding energy calibration was based on C 1s at 284.6 eV. Before the XRD and XPS measurement, the as-prepared Ag doped NCs were purified. Namely, an equal volume of methanol was added into aqueous NC solution, and the precipitates obtained were used for XPS measurement.
3. Results and discussion

Color-tunable Ag-doped ternary ZnCdSe NCs (Ag:ZnCdSe) were synthesized through N$_2$H$_4$-promoted sequential cation exchange reaction with preformed ZnSe NCs as starting material (scheme 1). The sequential cation exchange reaction included two steps: (i) formation of ternary ZnAgSe NCs through partial exchange of ZnSe NCs with Ag ions, (ii) formation of Ag:ZnCdSe NCs through expelling of Ag ions outside NCs by a biased amount of Cd addition (50 times the initial Zn content). The aforementioned cation exchange reactions were confirmed by a complete conversion from ZnSe to Ag$_2$Se and finally to CdSe (supporting information, Note 2, figures S3 and S4 available at stacks.iop.org/Nano/25/025603/mmedia).

The PL and absorption spectra were used to characterize the optical properties of as-prepared Ag:ZnCdSe NCs (figures 1(a), (b)). In the PL spectra, the NC emission wavelengths shifted continuously from green to red with increasing Ag/Zn feeding ratios in the first step. With Ag/Zn feeding ratios increasing from 0.1 to 0.8, the NC emission shifted from 515 to 660 nm, covering a range of 145 nm. The as-synthesized NCs showed very strong emissions and the PLQY could be as high as 28%. However, with Ag/Zn feeding ratios larger than 0.8, the as-prepared NCs showed poor emission. In the absorption spectra, with increasing Ag/Zn feeding ratios, the excitonic absorption peak of ZnSe NCs (about 380 nm) was gradually washed out and a new excitonic absorption peak (about 570 nm at Ag/Zn ratio of 0.8) gradually emerged. This new absorption peak was obviously caused by the incorporation of Cd inside the NCs. As-prepared ternary NCs show very large Stokes shift ($\geq$90 nm) (figure S3 available at stacks.iop.org/Nano/25/025603/mmedia), indicating that the emission probably originated from residual Ag impurities inside the NCs. It appears that Ag ions are hard to remove completely during cation exchange, according to reference reports, and
Figure 2. (a) XRD patterns of initial ZnSe NCs, Ag:ZnCdSe with different Cd/Zn ratios, and completely converted CdSe NCs. For comparison, the reference peaks of bulk cubic ZnSe and CdSe are displayed. (b) A linear relationship of the lattice parameter $b$ of Ag:ZnCdSe NCs as a function of Cd mole fraction, which is measured from XRD patterns (square data points) and calculated from Vegard’s law (solid line).

Figure 3 shows the temporal evolution of absorption spectra of purified ZnSe and Ag:ZnCdSe NCs. For purified Ag:ZnCdSe NCs, no precipitates appeared in 16 h, which is much longer than the time for the initial ZnSe NCs (1.5 h). This result implies strong stability of Ag:ZnCdSe NCs.

thus they behave as a doped impurity inside the NCs [15]. In our experiments, Ag impurities were observed to play a very important role in the emission of ternary NCs. However, the optical properties of these doped ternary NCs can be complicated. The large Stokes shift may also come from deep-trap emissions, which can also shift when the composition of the ZnCdSe is changed. Furthermore, the Stokes shift decreased with increasing Cd content in the ternary ZnCdSe NCs, indicating trap-level-related emission (figure S5 available at stacks.iop.org/Nano/25/025603/mmedia). Therefore, the emissions of as-prepared ternary NCs may come from either deep-trap emission or a combination of both deep-trap and impurity emissions (note S3 available at stacks.iop.org/Nano/25/025603/mmedia).

High-resolution transmission electron microscope (HRTEM) images showed monodispersed NCs with average size of 3.30 nm, which is the same as the initial ZnSe NCs (figure 1(c), S2 available at stacks.iop.org/Nano/25/025603/mmedia). HRTEM images (insets) with well-resolved lattice planes indicated good crystalline structures of the NCs. The measured lattice spacings of Ag-doped ternary ZnCdSe NCs (with the Ag/Zn feeding ratio of 0.2) was 0.330 nm, which is between the spacings of the (111) lattice plane of cubic ZnSe and cubic CdSe.

Inductively coupled plasma (ICP) mass spectrometry was used to study the chemical compositions of as-prepared Ag-doped ZnCdSe ternary NCs. When different Ag/Zn feed ratios were used during the first cation exchange reaction, the as-prepared ternary NCs showed different chemical compositions. For example, as-prepared ternary NCs show Zn/Cd ratios of 0.64 and 0.73 at Ag/Zn feed ratios of 0.6 and 0.8. Obviously, the changed chemical compositions of as-prepared ternary NCs should be the reason for the varied emissions at different Ag/Zn feed ratios. At lower Ag/Zn feed ratios (Ag/Zn $\leq 0.4$), the Ag concentration is much lower and may be below the detection limit. However, some Ag could be detected in the case of high Ag/Zn feed ratios. For example, Ag accounted for about 1% and 3% of the total atoms at Ag/Zn feed ratios of 0.8 and 2.0. This result confirms the presence of Ag impurities in the ternary NCs.

The XRD patterns were further used to characterize the structure of as-prepared Ag-doped ZnCdSe ternary NCs. No separate diffraction peaks of CdSe and ZnSe were observed. This indicated that the NCs obtained were ternary NCs rather than a mixture of CdSe and ZnSe NCs. To further investigate the structure of the ternary NCs, the relation between the chemical compositions and the lattice parameters of the ternary NCs was studied. The real chemical compositions of the NCs were measured by ICP mass spectrometry. As can be seen from figure 2(b), a systematic shift of diffraction peaks to lower angles was observed with increased Cd mole fractions from 0.51 to 0.77. The calculated lattice parameters from the XRD patterns of the ternary NCs showed an almost linear increase with increasing Cd content. This result indicates the alloyed structure of the ternary NCs obtained, in accordance with Vegard’s law [16].

The as-synthesized Ag-doped ternary NCs were kept under a 24 W UV lamp to study their chemical stability. According to the absorption spectra, when precipitates appear in the NC solution, the strong light scattering of macroscopic precipitates will lead to the elevated spectral baseline [17]. Figure 3 shows the temporal evolution of absorption spectra of purified ZnSe and Ag:ZnCdSe NCs. For purified Ag:ZnCdSe NCs, no precipitates appeared in 16 h, which is much longer than the time for the initial ZnSe NCs (1.5 h). This result implies strong stability of Ag:ZnCdSe NCs.
There are some key points in preparing Ag-doped ZnCdSe ternary NCs. First, an N\textsubscript{2}H\textsubscript{4} environment was necessary for the sequential cation exchange reaction to proceed. If no N\textsubscript{2}H\textsubscript{4} is present, no obvious cation exchange reaction is observed. Second, purification of the starting NCs was also important. Purification can partially remove the stabilizer on the NC surface, and thus facilitate the cation exchange reaction [18]. In our experiment, no cation exchange was observed on Ag ion addition into unpurified ZnSe NCs even under the N\textsubscript{2}H\textsubscript{4} environment. Third, selection of proper intermediate cations was required. In a contrasting experiment (supporting information, figure S6 available at stacks.iop.org/Nano/25/025603/mmedia), Cd stock solution was directly added into the ZnSe NC solution in the presence of N\textsubscript{2}H\textsubscript{4}. It turned out that Cd ions could indeed be incorporated into the ZnSe NCs, but to a very limited extent. And the diffusion of Cd into the ZnSe lattice took a very long time, on the order of days. Therefore, the introduction of intermediate Ag ions greatly accelerated the cation exchange reaction. Besides Ag, Cu ions can also be used as intermediate cations. As shown in figure S5 (supporting information available at stacks.iop.org/Nano/25/025603/mmedia), Cu-doped ZnCdSe ternary NCs showed a much broader tunable spectrum range, covering emission from 550 to 790 nm. The difference of the emission wavelength between Ag-doped and Cu-doped ternary NCs should originate from the different impurity levels.

4. Conclusion

In conclusion, we have proposed a fast, facile ‘green’ method for preparing doped ternary-alloyed ZnCdSe NCs through sequential cation exchange reaction in aqueous media promoted by N\textsubscript{2}H\textsubscript{4} at room temperature under ambient conditions. The introduction of intermediate Ag and Cu ions facilitates the sequential reaction and inherently brings impurities into the NC lattice. The as-prepared doped ternary-alloyed ZnCdSe NCs have high quantum yield, and the emission wavelength can be tuned in a broad range. The proposed sequential cation exchange reaction in aqueous solution could be expanded to synthesizing other multicomponent ionic NCs in aqueous solution.

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