Band gap tunable Sn-doped PbSe nanocrystals: solvothermal synthesis and first-principles calculations

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Received 7th June 2012, Accepted 14th August 2012
DOI: 10.1039/c2ce25905b

We have reported that the Sn-doped PbSe nanocrystals could be synthesized via a facile solution-based method. Structural and optical characterizations were employed to investigate the properties of the nanocrystals. The x value could be altered across the entire range from 0.58 to 1 by modulating the ratio of cation precursor contents. The band gap energy of the Sn-doped PbSe nanocrystals could be tuned and changed in a nearly linearly way with respect to the x value. Furthermore, using oleylamine as the solvent promoted the nanocrystals to self-assemble as nano-flowers. The theoretical analysis based on first-principles calculations and density of states (DOS) in the VASP code demonstrates the validity of the experimentally obtained band gap variation and values. The band gap energy values at the edge of the solar spectrum render them as competitive candidates for solar applications.

Introduction

Different from their bulk counterparts, the nanocrystals (NCs) always exhibit fantastic size-modulated optical and electronic properties due to the quantization of energy levels.1,2 As we know, the control of the composition, structure, and size plays a crucial role among all other physical parameters of the nanocrystals for the fabrication of optoelectronic or biomedical devices.3 Continuous physical properties, especially successive band gap energy (Eg), tuned by the sizes and compositions, are important for the nanocrystals’ further applications.4 For example, CdSe nanocrystals could be tuned by size to emit fluorescent light throughout the visible spectrum, showing versatile applicability in both biological imaging and optoelectronic devices.5 Thus, the choice of suitable materials and control of all the above factors in the manufacturing process became the two most significant issues that we should pay attention to. Comprised of the most promising materials active in the near-infrared and infrared fields, the group IV–VI NCs have received durable attention to date.6–9 Their ease of synthesis, relatively narrow band gap, as well as efficient multiple exciton generation (MEG), cause them to be considered as the most suitable alternatives for the absorption layers of the photovoltaics.10,11 The group IV–VI compounds usually have a large exciton Bohr radius (r0), such as SnS (14.8 nm), PbSe (46 nm), and PbTe (50 nm), which makes the device fabrication more convenient and increases the possibilities of large-scale production.

Many research groups have done a myriad of intensive investigations on the synthesis approaches of binary group IV–VI NCs, such as SnSe,14,15 SnTe,16 and PbSe.17 However, only a small fraction of the research focused on the ternary or quaternary group IV–VI composition-alloyed NCs. Although the recent advances and demands for solar cell applications have led to the exploration of the formation of anion-alloyed group IV–VI NCs, such as PbS,Se1−x−y,18,19 and PbS,Te1−x−y,19 the study on the cation-alloyed group IV–VI NCs still remains in its infancy. Some researchers20 pointed out the unique band structure behavior and anomalous trend in Eg of Pb,Sn1−x,Te NCs with a minimum Eg value of 0.28 eV (x = 0.67), which is far below the optimum region of high-conversion rates in the Shockley–Queisser limit.21 It has been considered recently that a comprehensive investigation on both the optical properties and Eg urgently needs to be conducted. Also, a suitable group IV–VI NCs with the Eg of 1.3–1.5 eV, which is the best range for single junction solar cells absorption layers,22,23 should be studied to meet the demands for solar energy applications.

In this paper, we report the cation-alloyed ternary Sn-doped PbSe NCs with rock-salt structure (Fm-3m), with alterable composition, nearly uniform sizes and multiple shapes were firstly synthesized via a simple solution-based, hot-injection routine. The elemental characterization shows that the x value can be tuned from 0.58 to 1 by controlling the Pb : Sn precursor ratios. Optical measurements were also introduced to investigate the NCs. According to the absorption spectra, the Eg ranging from 1.12 eV to 2.53 eV, at the edge of solar spectrum, renders them applicable for optoelectronic engineering uses. In addition, we found that the solvent employed as the reaction environment

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also influenced the final shape of the products. When oleylamine is used as the solvent it promotes the NCs to assemble into nanoflowers, while the products using oleic acid as the reagent environment are only monodisperse Sn-doped PbSe NCs.

Furthermore, use of computational methods to verify the experiments plays also an important role in modern research. To date, several theoretical investigations have focused on the stimulation of the electronic structures of cation-alloyed compounds. However, this area of research still retains several problems. The toughest one is that the calculations can only predict the band gap variation trend, but with imprecise \( E_g \) values that have huge differences compared with the experimental ones. An effective calculation method should be introduced to obtain both the valid varying trends and accurate \( E_g \) values. In this study, we use a first-principles calculation method in VASP codes to systematically investigate the electronic structures of cation-alloyed NCs. This models the experiments with strong evidence of valid band gap varying trends and accurate values. In all, the relative ease of cation alloying, \( E_g \) modulation, and the size control would accelerate the development of cation-alloyed group IV–VI NCs in photovoltaic fields.

**Experimental**

**Synthesis of Sn-doped PbSe NCs**

Although the preparation method of Sn-doped PbSe NCs still remains underdeveloped compared to the relatively widely studied other cation-alloyed chalcogenides, we employed a solution-phase synthesis approach to obtain monodisperse, high-quality Sn-doped PbSe NCs. Stannous oxide (SnO, >90%) and selenium powder (Se, 99.95%) were bought from Sinopharm Chemical Reagent Co. Ltd. and lead oxide (PbO, 93%), oleic acid (OA, technical grade, 90%), 1-octadecene (ODE, 90%), oleylamine (OLA, 90%) and tri-ctylo-phosphine (TOP, >90%) were bought from Aladdin Chemistry Co. Ltd. All the reagents above were purchased without further purification. NCs synthesis should be performed under nitrogen atmosphere using standard air-free Schlenk line techniques. The synthetic strategy is listed as follows: A solution consisting of 233 mg of PbO (1 mmol), 135 mg of SnO (1 mmol), 15 mL of OA, and 15 mL of ODE was degassed and heated to 250 °C in a 100 mL three-neck flask for about 1 h. The PbO: SnO precursor ratio was tuned to specific values, but the total amount was kept at 2 mmol. A mixture of about 1 M Se/TOP solution was heated to 60 °C for half an hour and then injected to the hot solution in the previous three-neck flask, rapidly. The nanocrystals were grown at 280 °C for 250 s, and the reaction was quickly quenched by placing the flask in a room-temperature water bath and injecting 30 mL of anhydrous ethanol after the quenching process. The nanocrystals were purified by precipitation twice in standard polar/nonpolar solvents and stored in a nitrogen environment.

**Characterization methods**

UV-vis absorption spectra were recorded using a Lambda 950 UV-vis spectrometer. For energy-dispersive X-ray spectrometer (EDS) measurements, purified NCs were deposited onto silicon substrates and loaded into a Zeiss Ultra 55 field-emission scanning electron microscopy (FESEM) equipped with an INCA EDS detector. High-resolution (HR) transmission electron microscopy (TEM) measurements were carried out using a JEOL 2100F at 200 kV accelerating voltage. Specimens were prepared by depositing several drops of a NCs chloroform solution onto a carbon-coated copper grid and then drying in air. X-ray powder diffraction (XRD) characterizations were conducted on a D/Max-2200/PC X-ray diffractometer using a Cu-K\( \alpha \) radiation source (\( \lambda = 1.54 \) Å).

**Theoretical calculations details**

Theoretical calculations with the density functional theory (DFT) were carried out on the basis of Perdew–Burke–Ernzerh of generalized gradient approximation (GGA) and the projected augmented wave method as implemented in the VASP code. The energy cut-off for the plane-wave expansion was 280 eV. The lattice parameters of Sn-doped PbSe were optimized by fitting the calculated total energies and volumes with the Murnaghan equation of state.

**Results and discussion**

The EDS results of the element compositions of seven samples, namely PbSe and the Sn-doped samples I, II, III, IV, V and VI, were listed in Table 1. The average stoichiometries of the six Sn-doped PbSe samples calculated from EDS are Pb\(_{0.92}\)Sn\(_{0.08}\)Se, Pb\(_{0.85}\)Sn\(_{0.15}\)Se, Pb\(_{0.73}\)Sn\(_{0.27}\)Se, Pb\(_{0.67}\)Sn\(_{0.33}\)Se, Pb\(_{0.58}\)Sn\(_{0.42}\)Se and Pb\(_{0.47}\)Sn\(_{0.53}\)Se, respectively. EDS shows that all the samples display Se rich composition, regardless of whether Se was in excess during the synthesis or not. To better evaluate the reactivity of the precursors, we also introduced a graph of the Pb ratio (Pb/(Pb + Sn)) of the precursors with a range varied from 0.1 to 1 versus the products. The curve shows a clear nonlinearity in the percent incorporation of anions in the NCs compared to ratios present in the initial precursors. Take the sample III, for instance; only 41% Pb in the precursor is needed to make the NCs with 73% Pb composition (inset of Fig. 1). Alivisatos and co-workers explained this nonlinear trend in alloyed NCs as the different reactivity of the precursors. Thus, the bowing of the curve in Fig. 1 is due to the higher reactivity of the lead precursor to that of the tin precursor. However, we found that extending the reaction time reduced the influence of the precursor reactivity and increases the mean size of NCs. To make all the experiments consistent, we fixed the reaction time as 250 s.

**Table 1** Chemical stoichiometries of the Sn-doped PbSe nanocrystals, determined from EDS analysis. The data collected by EDS should be considered as having \( \pm 2\% \) uncertainty in the elemental composition.

<table>
<thead>
<tr>
<th>Name</th>
<th>Pb/(Pb+Sn)</th>
<th>Se/(Pb+Sn)</th>
<th>Atomic (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbSe</td>
<td>1</td>
<td>1.16</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>0.92</td>
<td>1.05</td>
<td>46.3</td>
</tr>
<tr>
<td>II</td>
<td>0.85</td>
<td>1.35</td>
<td>44.8</td>
</tr>
<tr>
<td>III</td>
<td>0.73</td>
<td>1.11</td>
<td>36.2</td>
</tr>
<tr>
<td>IV</td>
<td>0.67</td>
<td>1.01</td>
<td>33.4</td>
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<tr>
<td>V</td>
<td>0.58</td>
<td>1.14</td>
<td>27.1</td>
</tr>
<tr>
<td>VI</td>
<td>0.47</td>
<td>1.12</td>
<td>22.2</td>
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</table>

<table>
<thead>
<tr>
<th>Name</th>
<th>Pb (%)</th>
<th>Sn (%)</th>
<th>Se (%)</th>
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<tr>
<td>PbSe</td>
<td>53.7</td>
<td>0</td>
<td>46.3</td>
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<tr>
<td>I</td>
<td>51.3</td>
<td>3.9</td>
<td>44.8</td>
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<tr>
<td>II</td>
<td>57.4</td>
<td>6.4</td>
<td>36.2</td>
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<tr>
<td>III</td>
<td>52.6</td>
<td>12.8</td>
<td>34.6</td>
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<tr>
<td>IV</td>
<td>50.2</td>
<td>16.4</td>
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<td>V</td>
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<tr>
<td>VI</td>
<td>52.8</td>
<td>25.0</td>
<td>22.2</td>
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Fig. 2 displays the XRD data of the seven samples with a standard powder diffraction files (PDF) card of Pb 0.6Sn 0.4Se (JCPDS no. 65-8303). Six of the samples agree well with the card, while the sample VI has several distinctive peaks at about 30°, 32° and 38°, which are likely to be caused by the secondary phase (orthodox SnSe phase, pnm a, JCPDS No. 48-1224). These three additional diffraction peaks appearing in sample VI correspond to the (111), (400), and (311) planes of SnSe. The other six samples all have three strong peaks at 29°, 42°, and 25°, which can be indexed to the (200), (220), and (111) planes of the rock-salt structure.

The doped secondary SnSe phase in the Sn-doped PbSe NCs would resist the synthesis of Sn-doped PbSe NCs having an x value below 0.58. The stronger reactivity of the Pb precursor would promote its priority to react with the anion precursor (Se) first. The Sn precursor would be reacting with Se to form the orthodox structure, which is more stable in normal temperature than the cubic one, when the relative ratios of Sn precursor have been raised to a certain value (0.53). Thus, this colloidal synthetic approach would not be an effective or suitable way to prepare the Sn-doped PbSe NCs with low x values. The positions of the strongest peak (200) varied with the change of the x value from 28.91° (x = 1) to 29.30° (x = 0.58). This shift of the (200) peak position indicates that the interplanar spacing of the (200) plane is decreasing with the introduction of Sn atoms into the PbSe crystal lattice. According to the data from the XRD, we can calculate the d-spacing of the (200) plane, the results of which fit well with the trends we found from the shift of the (200) peak position. The mean size (r 1) of the Sn-doped PbSe NCs, estimated from the full width at half maximum (FWHM) of the strongest (200) peaks of the seven samples by the Debye-Scherrer Formula, is about 22 nm.

The certain average element stoichiometries of Sn-doped PbSe NCs provides us with a way to calculate their crystal parameter (P), which could be used as a reference to the lattice constant counted from the XRD data (P XRD) by the Bragg equation. Vegard’s law 35 can be used to estimate the lattice constant as an empirical relationship between the parameter and the composition:

\[ P_{\text{SnSe}} (x) = xP_{\text{PbSe}} + (1-x)P_{\text{SnSe}} \]

where \( P_{\text{SnSe}} \) and \( P_{\text{PbSe}} \) represent the crystal parameters of SnSe and PbSe, respectively. Mariano and co-workers 36 reported that SnSe (Fm-3m) could be obtained under high pressure with a \( P_{\text{SnSe}} \) of 5.990 Å, while the \( P_{\text{PbSe}} \) is 6.134 Å according to the PDF card of PbSe (JCPDS no. 65-2941). The results of \( P_{\text{EDS}} \) and \( P_{\text{XRD}} \) are all listed in Table 2. Despite small differences that exist between the theoretical value (\( P_{\text{EDS}} \)) and experimental value (\( P_{\text{XRD}} \)) of both of them, they shared the same trends of variation of the crystal parameters, which corroborated the homogenous nature of the NCs.

Table 2 The relative Pb amounts in the cation precursor (Pb ratio), the position of the (200) peak ((200) Peak), the d-spacing of the (200) plane (d-spacing), the crystal parameter calculated by EDS results (\( P_{\text{EDS}} \)), and by XRD results (\( P_{\text{XRD}} \)) of the seven samples (Name)

<table>
<thead>
<tr>
<th>Name</th>
<th>Pb Ratio</th>
<th>(200) Peak</th>
<th>d-spacing</th>
<th>( P_{\text{EDS}} ) Å</th>
<th>( P_{\text{XRD}} ) Å</th>
</tr>
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<tbody>
<tr>
<td>PbSe</td>
<td>1</td>
<td>28.91</td>
<td>0.30698</td>
<td>6.134</td>
<td>6.140</td>
</tr>
<tr>
<td>I</td>
<td>0.92</td>
<td>29.04</td>
<td>0.30605</td>
<td>6.123</td>
<td>6.121</td>
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<tr>
<td>II</td>
<td>0.85</td>
<td>29.10</td>
<td>0.30564</td>
<td>6.112</td>
<td>6.113</td>
</tr>
<tr>
<td>III</td>
<td>0.73</td>
<td>29.18</td>
<td>0.30414</td>
<td>6.095</td>
<td>6.083</td>
</tr>
<tr>
<td>IV</td>
<td>0.67</td>
<td>29.25</td>
<td>0.30317</td>
<td>6.087</td>
<td>6.063</td>
</tr>
<tr>
<td>V</td>
<td>0.58</td>
<td>29.30</td>
<td>0.30302</td>
<td>6.073</td>
<td>6.060</td>
</tr>
<tr>
<td>VI</td>
<td>0.47</td>
<td>29.38</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Fig. 1 EDS is used to measure the relative composition (amount of product versus precursor) of the Sn-doped PbSe NCs. (Inset: the EDS spectrum of sample III.)

Fig. 2 The XRD patterns of the seven samples with an associated PDF (JCPDS No. 65-8303).
Fig. 3 shows TEM images without any size selective processing, HRTEM images and diameter distribution graphs of the four representative Sn-doped PbSe NCs samples dispersed in chloroform (samples I, II, III, and V). The statistically average size ($r_2$) of all the NCs in the four samples was around 23–24 nm, listed in Table 3, which is a little larger than the results calculated from XRD.

This discrepancy between the average sizes is due to an amorphous shell around the NCs, which can be seen clearly in Fig. 3h and k. The NCs took on various shapes, such as tetragon and hexagon, which could also be observed in the Pb$_x$Sn$_{1-x}$Te NCs as reported by Arachchige and co-workers. They explained this phenomenon of irregular, pseudospherical shape as a function of the surfactant. In our synthetic approach, the Pb and Sn precursors have a different reactivity/bind affinity with the oleic acid. However, an exploration of the elaborate growth mechanism of the Sn-doped PbSe NCs is still needed.

The Sn-doped PbSe displays excellent monodispersive properties in organic solvent (chloroform), which boost the possibility of Sn-doped PbSe nanoink preparation and the ease of synthesis and storage. The HRTEM images present well-resolved lattice fringes of the (200) plane with the correspondent interplanar spacing of each sample. The results fitted pretty well with the trend of the $d$-spacing value calculated from XRD data.

For better understanding and engineering of the band structure and optical properties of the cation-alloyed semiconductor NCs, we show the UV-vis-NIR absorption spectra of a series of Sn-doped PbSe NCs samples in Fig. 4. The red-shift trend of the band-edge absorption of the NCs could be observed in a gradual way, which should be attributed to the narrower band gap of PbSe ($Fm\text{-}3m$, bulk: 0.26 eV) compared with SnSe ($Pnma$, bulk: 0.90 eV).

The optical absorption experiments demonstrated in Fig. 4a were carried out to determine the $E_g$ of the six Sn-doped PbSe samples. All the samples are of the same size (average diameter, $d = 24$ nm), but different compositions. The measured wavelength region range of the optical absorbance spectra is from 250 nm to 1600 nm. The optical data were estimated at the near-absorption edge using the formula in eqn (1):

$$z = K \left( \frac{(h\nu - E_g)^n}{h\nu} \right)^{1/2}$$

where $h\nu$ is the photon energy, and $K$ and $n$ are parameters. The $n$ of an indirect band gap is equal to 1 while it is 4 for a direct band gap. The $E_g$ of the Sn-doped PbSe samples could be obtained from a plot of $(ah\nu)^2$ versus the photon energy ($h\nu$) (Fig. 4b). The estimated $E_g$ for the six Sn-doped PbSe samples were found to be $E_g = 1.48$ eV, 1.12 eV, 1.64 eV, 1.91 eV, 2.26 eV, and 2.53 eV, as plotted in Fig. 4c. The $E_g$ is seen to increase from $x = 0.58$ to 0.92 as the concentration of Pb increases in the Sn-doped PbSe.

The dependence of the $E_g$ on $x$ was indicated to fit a nearly linear variation and is described by the following equation (eqn (2)):

$$E_g = E_{g0} + Cx$$

where $E_{g0}$ is the band gap of pure PbSe, $C$ is the sensitivity constant, and $x$ is the mole fraction of Pb in the Sn-Pb-Se system.

Table 3 Statistically average size ($r_2$) and the standard deviation ($\sigma$) of the four Sn-doped PbSe NCs samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_2$</td>
<td>23.973 nm</td>
<td>23.594 nm</td>
<td>23.820 nm</td>
<td>23.311 nm</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>7.52%</td>
<td>9.49%</td>
<td>6.45%</td>
<td>8.38%</td>
</tr>
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</table>

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CrystEngComm, 2012, 14, 7408–7414 | 7411

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The sample VI shows a higher $E_g$ value (1.48 eV) than the predicted value from the above equation. This is due to the doped SnSe phase, which has a larger $E_g$ value. The experimental values of the other Sn-doped PbSe NCs $E_g$ fell in the optimum value region for photovoltaic conversion, which means that these NCs may be promising for applications in solar energy and for a wide range of optical devices operating in the NIR range. Further work to study and analyze their structures, optical properties, band structures, and technological uses is still underway.

In order to investigate the influence of solvent employed in the synthetic approach, we substituted the oleylamine for the oleic acid as the solvent. An interesting aspect was that a dozen of the Sn-doped PbSe NCs self-assemble to form nano-flowers (Fig. 5a). Both the HRTEM and TEM images show that the average diameter of the nano-flowers is 40–60 nm. The (200) interplanary spacing of 0.3020 nm of the nano-flowers, falling in the range of 0.3018 to 0.3075 nm, proves they consist of Sn-doped PbSe NCs. The XRD pattern agreeing with the Sn-doped PbSe (JCPDS No. 65-8303), with three main characteristic peaks, is shown in Fig. 5d. From the UV-vis-NIR absorption spectra (Fig. 5e), it is clear that there were several absorption peaks. Among those peaks, the most obvious one (around 1400 nm) revealed that the band gap energy of the flower-like nanocrystals was around 0.86 eV, which could be estimated from inset of Fig. 5e. The $E_g$ value was smaller than the other six samples’ values, because the average size of the nano-flowers was larger than that of the monodispersed nanocrystals. A series of smaller peaks (around 1150 nm, 850 nm etc.) appearing in the figure might be attributed to the variation of size or the irregularity of the flower-like shapes, since the electronic band gap was dependent on size and shape of nanocrystals.

Based on the different chemical properties of oleylamine and oleic acid, we put forward a possible formation mechanism of the Sn-doped PbSe nano-flowers. From some previous research, the SnSe phase,$^{45,46}$...
we found that oleic acid is a stronger coordinating ligand than oleylamine. In a common experiment, oleic acid could provide capping ligands and therefore prevent crystal dots from concentration.\textsuperscript{47,48} However, when oleylamine served as a surfactant instead of oleic acid, the more weakly coordinating capping ligands promoted the concentration of crystals at the growth stage, making an elongation with several preferred orientations possible. As a result, the nanocrystals finally exhibited a flower-like shape. Further studies on the growth mechanism of the nano-flowers are still needed to be deeply explored.

In further theoretical study, first-principles calculations were utilized to obtain the band gap values and the curves of DOS \textit{versus} the ratio of Pb/(Pb+Sn), and then analyze the electronic structures of the Sn-doped PbSe and their potential affecting factors. Table 4 shows the theoretically determined lattice parameters \(a\), \(b\) and \(c\) of the six chosen samples of Sn-doped PbSe. The GGA results are from 6.121 Å to 6.167 Å \textit{versus} Pb/(Pb+Sn) ratios of 0.625 to 0.9375, which lies within the typical error bar for the experimental result of PbSe, 6.124 Å.\textsuperscript{49}

Fig. 6 shows the theoretical band structure of Sn-doped PbSe (Pb/(Pb+Sn) = 0.875) calculated with a GGA functional. The band gap values of the Sn-doped PbSe NCs calculated through GGA functional method are shown in Fig. 7. We selected six typical samples of Sn-doped PbSe, of which the Pb/(Pb+Sn) ratios were 0.625, 0.6875, 0.75, 0.8125, 0.875, and 0.9375. The values of \(E_g\) showed an upward linear trend with the increase of Pb/(Pb+Sn) ratio, which was illustrated in Fig. 7. As regards the variation trend of \(E_g\), the results of the theoretical calculations are consistent with the experimental investigations. The \(E_g\) is 0.862 eV when the ratio of Pb/(Pb+Sn) is 0.625, while the value is 1.092 eV when it comes to 0.9375. An appropriate explanation of the variation of \(E_g\) obtained from the computational results might be that the replacement between Pb and Sn influences the distribution of the electronic structure in the whole crystal.

To further investigate the reasons, the DOS of Sn-doped PbSe NCs with different Pb/(Pb+Sn) ratios was also calculated, as shown in Fig. 8, and the energy zero is taken at the Fermi energy level (EF). A comparison was made among three DOS curves including Pb\textsubscript{0.625}Sn\textsubscript{0.375}Se, Pb\textsubscript{0.875}Sn\textsubscript{0.125}Se, and Pb\textsubscript{0.9375}Sn\textsubscript{0.0625}Se. In general, the three DOS curves share similar shapes except for several minute differences. Observing certain parts, it can be noted that the shapes of the DOS curves actually took on different tendencies in the regions near the valence band and conduction band.

The states near the valence band maximum (VBM) are mainly derived from Se-p, Pb-s, and Sn-s orbitals, and the conduction band minimum (CBM) is composed of Se-s and Pb-p, and Sn-p orbitals. Near the VBM, there is a significant Pb-s, Sn-s contribution, and near the CBM, there is also a noticeable Se-s contribution. Compared with the CBM, the influence of Pb and Sn is more obvious in the valence band. It is the different constitutions and the orbitals that provide a significant contribution in the VBM and CBM that cause the dissimilarities between them. From the curves, the it can be noted that the variation with the increase of Pb/(Pb+Sn) ratio in regions near the VBM are more obvious than those near the CBM. With the increase of the Pb constituent, the shape of the VBM is tending to be obvious, narrow and deep.

### Table 4

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pb/(Pb+Sn)</th>
<th>(a)/Å</th>
<th>(b)/Å</th>
<th>(c)/Å</th>
</tr>
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<tbody>
<tr>
<td>I</td>
<td>0.625</td>
<td>6.121</td>
<td>6.148</td>
<td>6.148</td>
</tr>
<tr>
<td>II</td>
<td>0.6875</td>
<td>6.131</td>
<td>6.159</td>
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</tr>
<tr>
<td>III</td>
<td>0.75</td>
<td>6.141</td>
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<tr>
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<td>0.8125</td>
<td>6.150</td>
<td>6.176</td>
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<tr>
<td>V</td>
<td>0.875</td>
<td>6.158</td>
<td>6.184</td>
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<tr>
<td>VI</td>
<td>0.9375</td>
<td>6.167</td>
<td>6.192</td>
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</tbody>
</table>

Fig. 6 Band structure of Pb\textsubscript{0.875}Sn\textsubscript{0.125}Se.

Fig. 7 The curve of calculated band gap energy \textit{versus} Pb/(Pb+Sn) ratio.

Fig. 8 The total density of states of Sn-doped PbSe system \textit{versus} Pb/(Pb+Sn) ratio of 0.625, 0.875, and 0.9375.
Conclusions
Novel, high-quality, cation-alloyed ternary semiconductor NCs of Sn-doped PbSe with compositions tunable across the entire x = 0.58–1 range have been synthesized. The crystal parameter (P) of the NCs increased with respect to x, consistent with Vegard’s law. The $E_g$ of the Sn-doped PbSe NCs could be tuned from 1.12 eV to 2.53 eV by decreasing the Pb content, which is also evidenced by our further theoretical calculations in the VASP code. These high-quality NCs could be dispersed in organic solvents and, thus, could be readily used in the form of nano-inks for the preparation of a Sn-doped PbSe absorber. The influence of the solvent environment in the reaction was also indicated. The oleylamine employed as solvent would facilitate the self-assembly of Sn-doped PbSe NCs to the shape of nano-flowers. The advantageous structural and optical properties demonstrated the potential for providing large quantities of stoichiometry-tunable cation-alloyed group IV–VI compounds NCs in applications for low-cost, relatively high-efficiency solar cells.

Acknowledgements
This work was supported by National Natural Science Foundation of China no. 61006002 and National High Technology Research and Development Program of China (863 Program) no. 2011AA050504.

References