

# Photovoltaic Devices Employing Ternary $\text{PbS}_x\text{Se}_{1-x}$ Nanocrystals

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## ABSTRACT

We report solar cells based on highly confined nanocrystals of the ternary compound  $\text{PbS}_x\text{Se}_{1-x}$ . Crystalline, monodisperse alloyed nanocrystals are obtained using a one-pot, hot injection reaction. Rutherford back scattering and energy-filtered transmission electron microscopy suggest that the S and Se anions are uniformly distributed in the alloy nanoparticles. Photovoltaic devices made using ternary nanoparticles are more efficient than either pure PbS or pure PbSe based nanocrystal devices.

Colloidal semiconductor nanocrystals display a wealth of size-dependent physical and chemical properties, including quantum confinement effects, shape dependent electronic structure,<sup>1,2</sup> and control over assembly through modification of surface functionalization.<sup>3,4</sup> Photovoltaic devices are an easily recognized potential application for nanocrystals due, in part, to their high photoactivity, solution processability and low cost of production. Several schemes for using nanocrystals in solar cells are under active consideration, including nanocrystal-polymer composites,<sup>5</sup> nanoparticle array solar cells,<sup>6</sup> films of partially sintered nanoparticles,<sup>7</sup> and nanocrystal analogues to dye-sensitized solar cells.<sup>8</sup> A persistent challenge for any nanoparticle-based solar cell is to take advantage of quantum confinement effects to improve the optical absorption process without overly hindering the subsequent transport of charge to the electrodes. Various binary semiconductor nanoparticles, like CdSe, CdTe,  $\text{Cu}_2\text{S}$ , InP, and InAs, have been explored for photovoltaic devices but the reported efficiencies remain low, mostly limited by poor charge transport between the nanocrystals.<sup>5,7-12</sup> With so many parameters to adjust in terms of size and shape, little work has focused on ternary or quaternary compositions of nanoparticles for solar cells. Yet it is well known from thin film solar cell studies that such compositional tuning can sometimes yield significant improvements in performance.

The Pb chalcogenide family of nanocrystals is actively investigated for nanocrystal solar cell applications because they have such large exciton Bohr radii (PbS 18 nm, PbSe 47 nm, and PbTe 150 nm). In the limit where the nanocrystals are only a tenth or so of the bulk exciton diameter, electrons and holes can tunnel through a thin organic surface coating, and therefore strong electronic coupling between particles

facilitates transport of charge between nanocrystals. So far, Schottky solar cells based on binary compositions of PbSe and PbS nanocrystals have been investigated. PbSe nanocrystal solar cells generate larger short circuit photocurrents while PbS nanocrystal devices with similar bandgap have shown a larger  $V_{\text{OC}}$ .<sup>6</sup> This opens the possibility to better engineer particles, by creating ternary  $\text{PbS}_x\text{Se}_{1-x}$  to simultaneously optimize both carrier transport and voltage. Moreover, the properties of PbS and PbSe lead to an ideal substitutional alloy; the atomic anion radii are within 15% of each other, the lattice mismatch factor is only 2% between PbS and PbSe (see Supporting Information for the similarity of the XRD patterns), and of course the anions are isovalent.

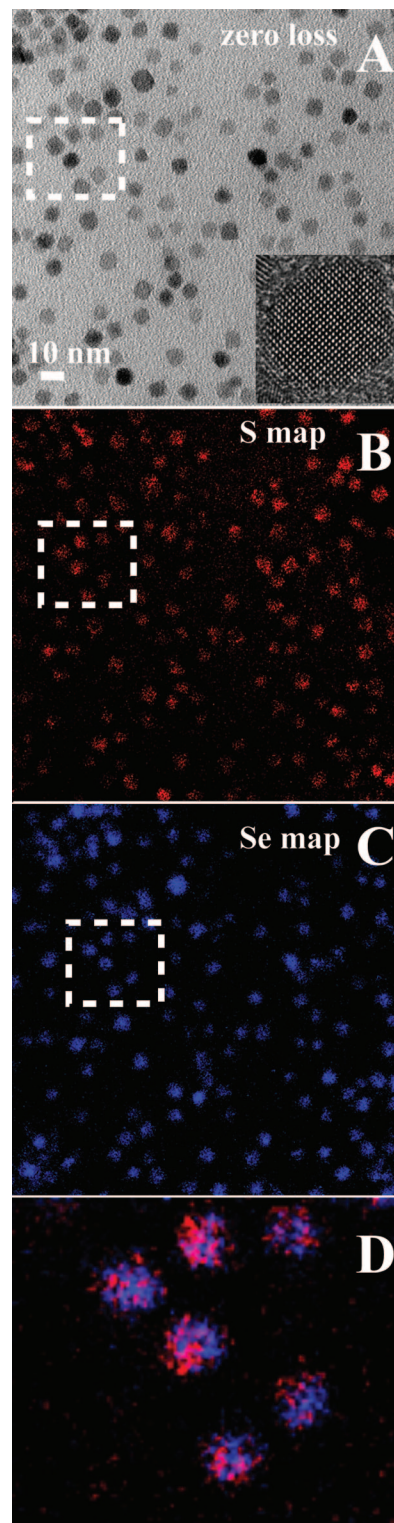
Although the synthesis of ternary  $\text{PbS}_x\text{Se}_{1-x}$  nanocrystals<sup>13,14</sup> remains underdeveloped compared to the widely studied cadmium chalcogenides alloys,<sup>15-17</sup> we successfully obtained monodisperse, highly crystalline nanocrystals using a one-pot, hot injection synthesis. Lead oxide (PbO, 99.999%), selenium (99.99%), oleic acid (OA, technical grade, 90%), diphenylphosphine (DPP, 98%), 1,3-benzenedithiol (BDT, >98%), bis(trimethylsilyl) sulfide ( $\text{TMS}_2\text{S}$ , purum), 1-octadecene (ODE, 90%), anhydrous solvents and aluminum shot (99.999%) were purchased from Aldrich and used as received. Trioctylphosphine (TOP, >97%) was acquired from Strem. Nanocrystal synthesis was performed under argon atmosphere using standard air-free Schlenk line techniques. The synthesis scheme is as follows: A solution of 446 mg PbO (2 mmol), 1.4 g oleic acid (5 mmol), and 10 g ODE was degassed and heated to 150 °C in a 50 mL three-neck flask for one hour. A mixture of the proper amount 1 M TOP/Se solution,  $\text{TMS}_2\text{S}$ , DPP (40 mg), and ODE was then rapidly injected into this hot solution. The Se and S precursor ratio was tuned to specific values, but the total amount was kept at 1 mmol. ODE was added to dilute the precursor

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solution to 2 mL total. The nanocrystals were grown at 150 °C for 90 s, and the reaction was rapidly quenched by placing the flask in a room-temperature water bath and injecting 5 mL of anhydrous hexane. The nanocrystals were purified by precipitation twice in hexane/ethanol and once in hexane/acetone and stored in a glovebox.

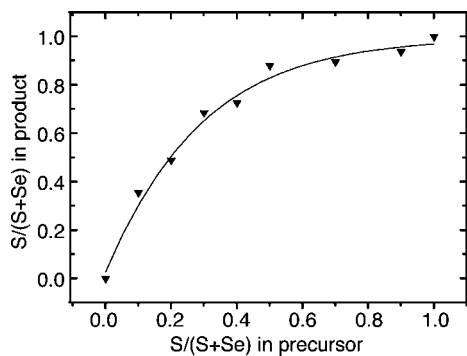
Achieving and characterizing a uniformly alloyed nanocrystal remains difficult.<sup>16</sup> Complications arise from the difference in precursor solubility and reactivity at a given temperature, and in the difference between nucleation and growth of nanocrystals. Since TMS<sub>2</sub>S is more reactive than TOP/Se, the stoichiometric ratio of S to Se in the resulting nanocrystal sample was greater than the injected precursor ratio. The composition of the resulting nanocrystals was characterized using energy-filtered transmission electron microscopy (EF-TEM)<sup>18</sup> to determine whether the nanocrystals resulted in separately nucleated PbS and PbSe, core-shell architectures, or alloyed composites. Figure 1A–C show zero loss and EF-TEM images of a sample of ~7 nm PbS<sub>0.7</sub>Se<sub>0.3</sub> taken at the same position on a TEM grid. To achieve strong elemental signals, for EF-TEM we found it necessary to use large nanocrystals and exchange the oleate ligands on the nanocrystal surface by adding a small amount of butylamine and washing the nanocrystals the following day such that the nanocrystals will not self-assemble into close packed arrays. All nanocrystals in Figure 1A (zero loss) appear in both the S mapping of Figure 1B and at a corresponding location in the Se mapping of Figure 1C. The selected areas in Figure 1A–C make the comparison easier and are shown in greater detail in Figure 1D with the S and Se maps overlaid. The TEM results indicate that to some extent both Se and S are distributed inside each nanocrystal without apparent phase separation. Note that S is more prevalent than Se in the sample (i.e., PbS<sub>0.7</sub>Se<sub>0.3</sub>). Figure 1A inset shows a high-resolution TEM image of a single nanocrystal. Uniform lattice structure with no obvious stack faults or core-shell structure is observed. See Supporting Information for additional TEM images of well-packed oleate-capped ternary PbSSe nanocrystals.

Rutherford backscattering spectroscopy (RBS) was then used to investigate the actual anion ratio. Figure 2 shows results from RBS data taken on a series of samples where the relative amount of S in the precursor ratio (S/(S+Se)) was systematically varied from 0 to 1. The graph shows a clear nonlinearity in the percent incorporation of anions in the nanocrystals compared to fraction present in the original precursor solution. For example, only 30% S in the precursor is needed to make nanocrystals with 70% S composition. Presumably, this nonlinearity results from the different reactivity of the chalcogen precursors. We also find that for longer reaction times, more Se is incorporated (see Figure S5 in Supporting Information) indicating a possible radial gradient in composition; however, to be consistent, all nanocrystals used in devices were only allowed to grow for 90 s, thus suppressing such a gradient. RBS data shows that all samples display Pb rich composition regardless of whether or not Pb was in excess during synthesis.



**Figure 1.** (A) Bright-field TEM image showing 7 nm PbS<sub>0.7</sub>Se<sub>0.3</sub> nanocrystals. Scale bar represents 10 nm. Inset shows the high degree of crystallinity of a single ternary nanocrystal without an obvious core-shell configuration. (B) Energy filtered TEM image at the same location as in panel A, showing in red regions containing sulfur. (C) EF-TEM showing selenium map in blue. (D) The outlined region in panels A–C is enlarged and overlaid to show sulfur and selenium in each nanocrystal.

For optical characterization, the alloyed nanocrystals were suspended in tetrachloroethylene. Absorbance spectra for nanocrystals with different compositions are displayed in



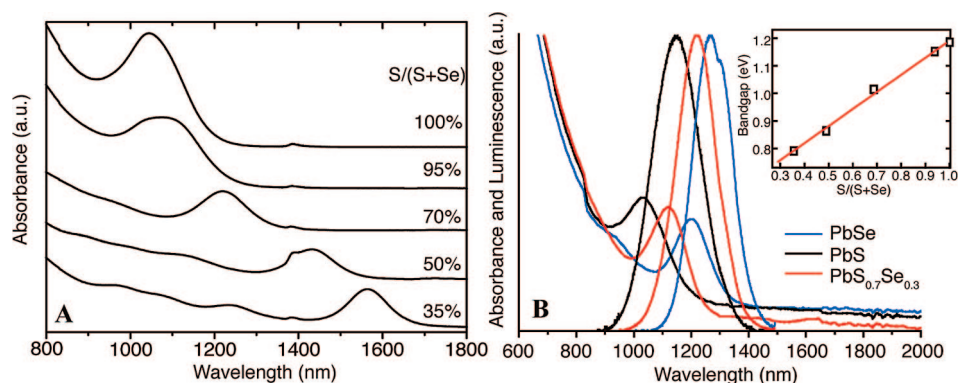
**Figure 2.** Rutherford back scattering is used to measure the relative amount of sulfur in the product versus the relative amount of sulfur in the precursor injection solution. The bowing is due to the higher reactivity of the sulfur precursor ( $\text{TMS}_2\text{S}$ ) to that of the selenium precursor ( $\text{TOP/Se}$ ).

Figure 3A. Arising from the smaller bandgap of PbSe relative to PbS for a given size,<sup>19</sup> we notice the red shift of the first excitation peak with reduced S composition. This trend can be observed more clearly in the inset of Figure 3B, which shows a linear relationship between the nanocrystal bandgap energy and the composition ratios. Vegard's Law predicts the structure and function of many alloyed materials:  $E_{\text{alloy}} = \chi E_A + (1 - \chi)E_B$ , where  $\chi$  is the mole fraction,  $E_A$ ,  $E_B$ , and  $E_{\text{alloy}}$  are the band gap energy (or other properties) of pure composition A, pure composition B, and the alloyed material, respectively. However, this linear relationship does not apply to several classes of semiconductor alloys. For example, both bulk and nanocrystal  $\text{CdSe}_x\text{Te}_{1-x}$  alloys display pronounced nonlinear "optical bowing" effects.<sup>16,17</sup> Zunger and co-workers explain this type of observation by identifying three structural and electronic factors leading to nonlinearity of ternary compounds: different atomic size, electronegativity values of ions, and different lattice constants of the binary structures.<sup>20,21</sup> A substantial lattice mismatch (11%) also exists between the binary semiconductors CdS and CdTe that leads to enhanced nonlinear effects there also. However, in the case of  $\text{PbS}_x\text{Se}_{1-x}$  there is only a 2% lattice mismatch between PbS and PbSe, so it is reasonable to observe less nonlinearity with composition in this alloy system, considering also that the difference in atomic size

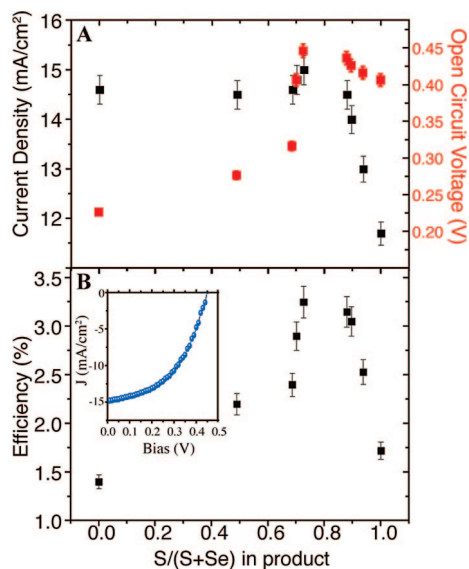
and electronegativity are the same as that for the cadmium chalcogenides. The absorbance and photoluminescence (PL) of PbS, PbSe, and  $\text{PbS}_{0.7}\text{Se}_{0.3}$  nanocrystals with similar diameter are shown in Figure 3B. The full width at half-maximum (fwhm) of PL is 188, 136, and 122 meV for PbS,  $\text{PbS}_{0.7}\text{Se}_{0.3}$ , and PbSe, respectively. The structured absorbance and relatively narrow PL peaks of alloyed nanocrystal indicate the sample is nearly monodisperse, which exclude the possibility of the coexistence of separate PbSe and PbS in the final synthesized nanocrystals. The uniformity of our alloyed nanocrystal structure can be further indicated by the 100 nm Stokes shift, which lies between 120 nm for PbS and 70 nm for PbSe. This result is also consistent with Vegard's Law for a true alloy.

We have fabricated back contact Schottky junction devices containing ternary Pb chalcogenide nanocrystals using methods reported by Nozik and co-workers for binary PbX nanocrystals.<sup>6,22</sup> Briefly, patterned ITO coated glass slides were acquired from Thin Film Devices Inc. ( $20 \pm 5$  ohms/sq, ITO thickness  $\sim 300$  nm). The substrates were cleaned by ultrasonication in various solvents and films of nanocrystals were deposited by sequentially dipping the substrate in a hexane solution containing the nanocrystals ( $\sim 25$  mg/ml) followed by dipping in a 0.01 M BDT solution in acetonitrile.<sup>23</sup> This process was repeated such that the resulting film thickness was near 100 nm as was shown to be the optimum for PbSe devices.<sup>24</sup> Aluminum back contacts were then evaporated on the nanocrystal film in a glove box, and all processing and measurements were air free. To verify reproducibility of the data, three devices were made for each batch of nanocrystal with eight working pixels on each device (active area of  $4 \text{ mm}^2$ ). AM1.5G illumination was obtained with a Spectra Physics Oriel 300 W Solar Simulator. The integrated intensity was set to  $100 \text{ mW/cm}^2$  using a thermopile radiant power meter (Spectra Physics Oriel, model 70260) with fused silica window and verified with a Hamamatsu S1787-04 diode.

Figure 4 shows the composition-dependent device performance. The  $x$ -axis represents composition change from pure PbSe, to pure PbS, versus various photovoltaic device parameters. Previous reports of PbS and PbSe nanocrystal



**Figure 3.** (A) Absorbance spectra of alloyed nanocrystals with gradually increased S concentration. All nanocrystals are  $\sim 4$  nm in diameter and are grown for 90 s. (B) Absorbance and photoluminescence of pure PbSe, pure PbS, and  $\text{PbS}_{0.7}\text{Se}_{0.3}$  with similar size. The PL shows no broadening over the pure binary nanocrystals. Inset shows the variation of nanocrystals bandgap energy with different S concentrations.



**Figure 4.** (A) Short circuit current density (black) and open circuit voltage (red) of solar cells made of nanocrystals with different varying S concentrations. (B) 1-sun efficiency of devices made of nanocrystals with different S concentrations.  $J$ - $V$  curve of best performing solar cell device based on  $\text{PbS}_{0.7}\text{Se}_{0.3}$  nanocrystals is shown in the inset of part (B). The error bars indicate the variance among 8 devices on each substrate.

devices have revealed higher  $V_{OC}$  for PbS devices but larger  $J_{SC}$  with PbSe.<sup>6,23,25</sup> Our binary PbS and PbSe results agree but interestingly, we find ternary  $\text{PbS}_x\text{Se}_{1-x}$  nanocrystals perform better. The  $J_{SC}$  is mostly unaffected between S concentrations of 0–65%. Beyond 65% the  $J_{SC}$  rises slightly and then begins dropping at 80%. The  $V_{OC}$  is as much as double that of PbSe when using  $\text{PbS}_{0.7}\text{Se}_{0.3}$ .

As a result of both improved  $J_{SC}$  and  $V_{OC}$ , ternary  $\text{PbS}_x\text{Se}_{1-x}$  nanocrystals achieve higher efficiency than pure binary nanocrystal PbSe and PbS, as shown in Figure 4B. In fact, all devices employing ternary nanocrystals regardless of the actual anion ratio performed better than each binary control device.  $\text{PbS}_{0.7}\text{Se}_{0.3}$  has the best 1-Sun power conversion efficiency of 3.3% with a  $J_{SC}$  of 14.8 mA/cm<sup>2</sup>, a  $V_{OC}$  of 0.45 V, and a fill factor of 50%. The  $J$ - $V$  curve is shown in the inset of Figure 4B. The efficiency of devices based on pure PbS and PbSe is 1.7 and 1.4%, respectively, which is consistent with previously reported results.<sup>6,25</sup> In our devices, there is a 2-fold improvement for optimized alloyed nanocrystals compared to binary nanocrystals.

It has been documented that PbS and PbSe arrays of this nature have charge-trapping states within the bandgap arising from ligand exchange and potentially damage during the metal deposition.<sup>22,26,27</sup> We hypothesize that the better performance of ternary nanocrystals is due to a combination of material properties as well as a redistribution of the trap states. The higher current produced by  $\text{PbS}_x\text{Se}_{1-x}$ , may arise from a significantly larger exciton Bohr radius than PbS (but smaller than PbSe) due to the incorporation of Se (46 nm for PbSe and 18 nm for PbS). The larger Bohr radius delocalizes the carriers, establishing greater electronic coupling between nanocrystals, which can diminish the effects of nanocrystal surface traps and therefore facilitate charge

transport. As indicated in Figure 4A, an incorporation of ~30% Se into PbS substantially improves the current density of the cell.

PbS cells have a larger  $V_{OC}$  compared to PbSe with the same bandgap. According to Schottky junction theory, the barrier height (proportional to  $V_{OC}$ ) of an ideal metal-semiconductor contact is determined by the relative position between metal work function and semiconductor Fermi energy.<sup>28</sup> In all devices reported here, aluminum (work function of 4.28 eV)<sup>29</sup> is used as the contact and the  $p$ -type nanocrystal films have a Fermi level deeper than aluminum. The size dependent conduction and valence band edge of PbS and PbSe nanocrystals have recently been measured and PbS is reported to have energy levels closer to vacuum energy than PbSe.<sup>19</sup> However, in practical Schottky junctions, one major limitation is that the  $V_{OC}$  cannot exceed half the bandgap. Otherwise, the minority carrier density would be larger than the majority carrier density at the junction, thus forming an inversion layer.<sup>30</sup> In the situation of these devices, therefore, the true limit of the  $V_{OC}$  is governed by the difference between the intrinsic level (at mid gap) and the Fermi level of the nanocrystal film, so long as the work function of the metal contact is closer in energy to vacuum than the intrinsic energy of the semiconductor. Since the Fermi level of nanocrystals is closely related to the trap states, the density of trap states within the bandgap is most likely the cause of the differing voltages of the materials. Because of different surface energies of the binary phases to the ternary, the position and density of traps states at least at the surface in PbS, PbSe, and  $\text{PbS}_x\text{Se}_{1-x}$  may vary. This difference could determine the relative position of the Fermi level to the valence band edge of the nanocrystal film and therefore may lead to different open circuit voltages.

The combination of better  $J_{SC}$  and  $V_{OC}$  are realized in PV devices containing  $\text{PbS}_x\text{Se}_{1-x}$  nanocrystals relative to pure phase PbS and PbSe nanocrystals. Se and S compositions are closely related to the photovoltaic parameters  $J_{SC}$  and  $V_{OC}$  respectively. Alloying is demonstrated to be a successful approach to tune the composition and achieve the ternary nanocrystal with optimum photovoltaic properties. Lead chalcogenides are the only materials thus far to make high efficiency nonsintered nanocrystal solar cells because of their large exciton Bohr radius. Therefore, alloying proves to be a very simple and effective method to obtain nanocrystals with desirable bandgap, transport, and surface passivation while maintaining the advantages of the binary compound counterparts. The novel photovoltaic properties introduced by alloying derive from quantum confinement effects, and rely upon the residual nanoscale size of the components in the film. Alloying, as a methodology, may soon become an effective approach for future nanocrystal solar material engineering.

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