

A Single-Source Precursor Route to Unusual PbSe Nanostructures by a Solution–Liquid–Solid Method

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S Supporting Information

ABSTRACT: PbSe nanowires (NWs) have been synthesized by using a single-source precursor route. Carefully controlling the conditions of individual reactions leads to PbSe NWs with well-defined diameters (8–25 nm) and lengths (100 nm–1 μm). The as-grown PbSe NWs are highly crystalline, defect free, and readily dispersible in organic solvents. The NWs have been characterized by X-ray diffraction and high-resolution transmission electron microscopy.

One-dimensional nanowires (NWs) of semiconductors have received considerable attention due to their novel size and dimensional-dependent physical and electronic properties. They have two quantum confined directions, and the unconfined direction may allow electrical conduction. This unique feature makes them suitable candidates to be employed in technologically important applications where electrical conduction is required. In addition, they have remarkably increased surface area, a very high density of electronic states, enhanced exciton binding energy, and increased surface scattering for electrons and phonons.^{1–4}

PbSe is an important narrow band gap semiconductor and is used in LEDs, photovoltaic cells, sensing applications, and biological markers.^{5–8} NWs of PbSe have been grown by a number of methods: electrodeposition,^{5–7} vapor–liquid–solid methods,⁸ chemical vapor deposition (CVD),^{9,10} oriented attachment,¹¹ colloidal methods,¹² and solution methods.¹³ Among these, solution-based methods can give good yields of NWs at low temperatures (<400 °C) with a controlled aspect ratio.¹⁴ In addition, passivation of their surfaces by surfactants can minimize the potential for oxide formation. The as-prepared NWs are often dispersible in organic solvents, making them useful for practical applications.

Single-source precursors are often less noxious than conventional precursors with the potential for an intrinsic control of reactivity and stoichiometry.¹⁵ In many cases such precursors were originally developed for the deposition of thin films by metal–organic CVD.^{16,17} To date, a number of reports on PbSe NWs are available, but all involve the use of dual sources.^{4–14} Herein, we report the synthesis of PbSe NWs by a solution–liquid–solid (SLS) approach from bis-[*N,N*-diethyl-*N'*-naphthoyselenoureaato]lead(II) as a single-source precursor.

The lead complex was prepared by reaction between aqueous Pb(NO₃)₂ and an ethanolic solution of *N,N*-diethyl-*N'*-naphthoyselenourea at room temperature (see Supporting Information (SI)).

The single-crystal structure and selected bond lengths and bond angles of bis[*N,N*-diethyl-*N'*-naphthoyselenoureaato]lead(II) are given in Figure 1. The structure is monoclinic, with space group

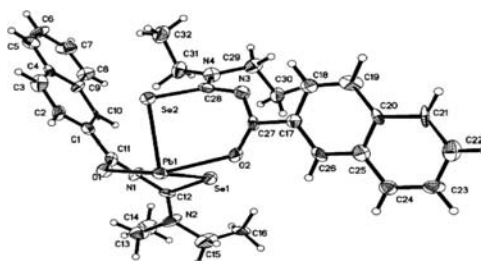


Figure 1. Single-crystal structure of bis[*N,N*-diethyl-*N'*-naphthoyselenourea]lead(II). Selected bond lengths (Å) and angles (deg): O(1)–Pb(1) 2.42(1), O(2)–Pb(1) 2.45(1), Pb(1)–Se(2) 2.79(0), Pb(1)–Se(1) 2.78(0), O(2)–Pb(1)–Se(1) 75.3(2), Se(2)–Pb(1)–Se(1) 101.73(5).

P2(1)/c. Each lead atom is monomeric and ligated by two selenium atoms and two oxygen atoms, from each of the two *cis-N,N*-diethylnaphthoyselenourea groups. The Pb–Se bond distances are significantly longer than those of Pb–O, i.e., Pb(1)–Se(1) 2.78 Å and Pb(1)–Se(2) 2.78 Å, while Pb(1)–O(1) 2.42 Å and Pb(1)–O(2) 2.45 Å.

A typical procedure involved heating 5.5 g of trioctylphosphine oxide (TOPO) under vacuum for 10 min at 130 °C and then up to 290–295 °C under nitrogen in a two-neck round-bottom flask. Next, 0.2 g of bis[*N,N*-diethyl-*N'*-naphthoyselenourea]lead(II) was dissolved in 40–120 μL of Au@Bi solution (Bi-coated Au nanocrystals (NCs); see SI) under nitrogen and stirred at room temperature. This stock solution was rapidly injected into the TOPO at 290–295 °C. A growth time of 1–60 min was used. The Au@Bi NCs (solid) melt upon injection into TOPO/TOP at 290–295 °C and form eutectic mixture droplets (liquid). These seeds then act as catalytic sites where PbSe, formed by decomposition of bis[*N,N*-diethyl-*N'*-naphthoyselenourea]lead(II), adsorbs and grows into 1D NW structures. The droplets can initiate growth in more than one direction, which explains the formation of T- and cross-shaped NWs as well. The whole process is shown in SI Figure S1. Figure 2 shows a schematic diagram for the SLS method. Figure 3 shows a powder X-ray diffraction pattern for as-grown PbSe NWs. All peaks can be indexed to the cubic phase. The as-prepared PbSe NWs were nearly defect-free with

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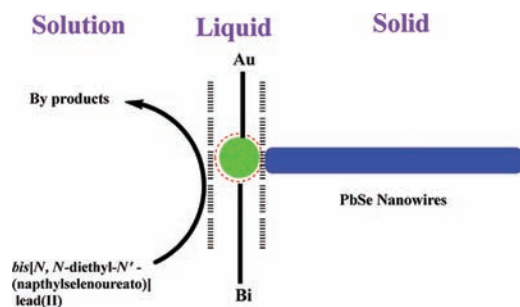


Figure 2. Schematic illustration for the formation of PbSe NWs by the SLS method.

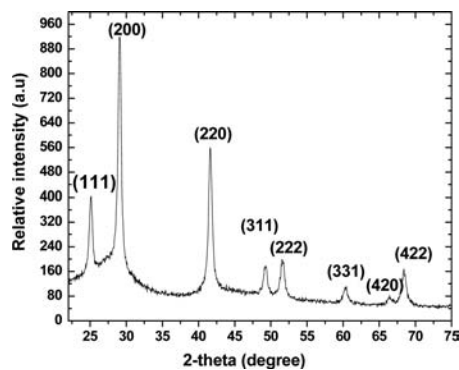


Figure 3. Typical powder XRD pattern of PbSe NWs synthesized from 0.2 g of precursor using 15 min growth time.

uniform diameter along the entire length. The wires' dimensions could be tuned from ~ 8 to ~ 25 nm in diameter, and lengths up to several micrometers were obtained by tailoring reaction conditions, such as concentration of the Au@Bi catalyst and the growth time (Table 1).

Table 1. Experiments, Reaction Times, Shapes, and Dimensions of PbSe NWs^a

amount of Au@Bi (μL)	time (min)	morphology	length (L) and width (W)
40	1, 5	NWs	$L = 100$ nm, $W = 8$ nm
40 (slow injection)	15	branched NWs	$L =$ several μm , $W = 15$ nm
120	5, 60	branched NWs	$L =$ several μm , $W = 18$ – 22 nm
Au NCs	5, 15, 30	nanotubules	
Au 120 μL	5, 15, 30	nanotubules	
without catalyst	1, 5	spherical particles	20 nm

^aIn each experiment, 0.2 g of precursor was used at 290–295 °C.

In order to observe the morphology of as-prepared PbSe NWs, transmission electron microscopy (TEM) analysis was carried out. TEM images of PbSe NWs prepared using a growth time of 1 min are shown in Figure 4. The estimated diameter of these PbSe NWs is about 8.8 nm, and lengths are up to 400 nm. In another experiment, the precursor and Au@Bi mixture was injected dropwise over a period of 5 min in TOPO at 290 °C to study the shape of PbSe NWs formed. A number of different shapes of PbSe NWs were seen, including ring-like structures, T-shapes, and branched shapes; these are shown in Figure 5. The inset in Figure 5b shows the selected electron area diffraction pattern of the PbSe NWs. The surface of all these NWs is passivated by the coordination surfactant/solvent

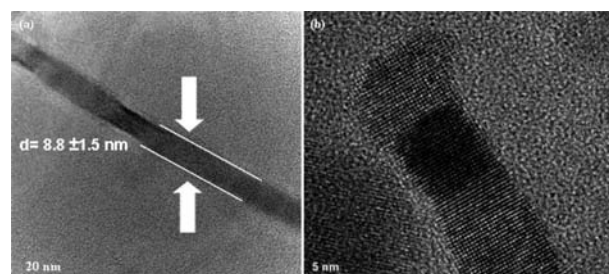


Figure 4. TEM images of PbSe NWs prepared with growth time of 1 min at 290 °C.

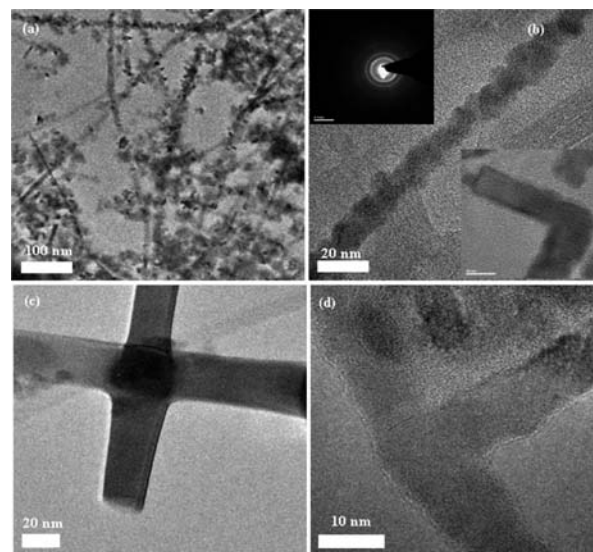


Figure 5. TEM images of PbSe NWs of various shapes prepared at 290 °C: (a,b) rings, (c) cross-shaped, and (d) T-shaped. The precursor and Au@Bi mixture was injected dropwise over 5 min and kept at 290 °C for 15 min. The inset in (b) shows the SAED pattern of the PbSe NWs.

(TOPO), which makes them stable in the colloidal form and appears to preserve them from oxidation.

Figure 6 shows TEM images of PbSe NWs obtained from 0.2 g of the precursor and 40 μL of Au@Bi with a growth time of 15 min. Figure 6a–c shows selected images of PbSe NWs. The average diameter estimated from these images was 23.5 ± 2.5 nm. Figure 6d–f shows high-resolution TEM (HRTEM) images of PbSe NWs. The d -spacing of 0.21 nm calculated from the HRTEM image in Figure 6d corresponds to the [220] plane. Table 1 summarizes the experimental details and morphologies of the as-prepared PbSe NWs.

Figure 7 shows TEM images of PbSe NWs prepared by using 120 μL of Au@Bi stock solution, keeping all reaction conditions constants. The as-prepared PbSe NWs are branched and have lengths up to several micrometers. The d -spacing of 0.35 nm calculated from TEM image shown in Figure 7f corresponds to the (111) plane.

In order to compare the catalytic activity of Au and Au@Bi NCs, PbSe NWs were prepared under similar conditions using Au NCs. TEM studies showed that instead of NWs, a random net is formed with dense spots like knots, as shown in Figure 8. Repeating the reaction without Au and Au@Bi NCs under similar conditions resulted in formation of globular NCs.

In summary, we have demonstrated here that high-quality PbSe nanowires with controlled diameter and lengths can be

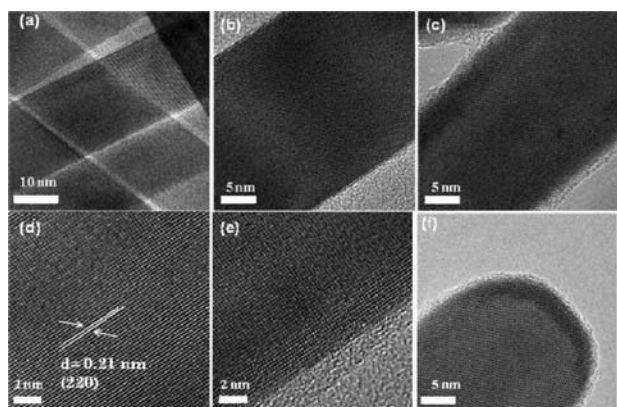


Figure 6. TEM images of PbSe NWs prepared using 0.2 g of precursor, reaction time 15 min, 40 μL of Au@Bi, and injection at 290 $^{\circ}\text{C}$.

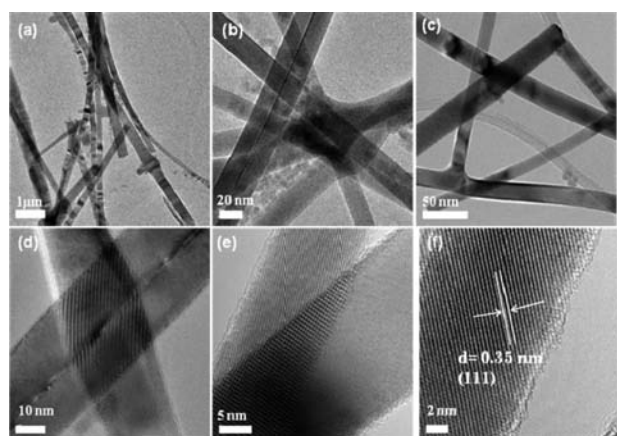


Figure 7. TEM images of PbSe NWs prepared using 0.2 g of precursor and 120 μL of Au@Bi catalyst at 290 $^{\circ}\text{C}$.

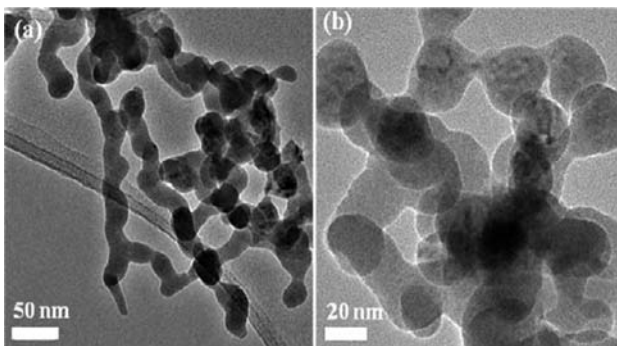


Figure 8. PbSe random net formed with dense spots like knots by using Au nanocrystals at 290 $^{\circ}\text{C}$.

prepared by using a single-source precursor route. These as-prepared PbSe NWs can be used as efficient sensitizers in photovoltaic devices.

■ ASSOCIATED CONTENT

● Supporting Information

Synthesis of ligand *N,N*-diethyl-*N'*-naphthoyleseleurea and its complex with Pb, synthesis of Au@Bi NCs, schematic of SLS method, and CIF file for bis[*N,N*-diethyl-

N'-naphthoyleseleurea]lead(II). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Wang, G.; Gou, X.; Horvat, J.; Park, J. *J. Phys. Chem. C* **2008**, *112*, 15220.
- (2) Chao, G.; Li, K.; Peng, H.; Chen, K.; Zhang, Z. *J. Phys. Chem. C* **2008**, *112*, 16452.
- (3) Wang, Z. L. *ACS Nano* **2008**, *2*, 1987.
- (4) Rupasov, V. I. *Phys. Rev. B* **2009**, *80*, 115306.
- (5) Peng, X. S.; Meng, G. W.; Zhang, J.; Wang, X. F.; Wang, C. Z.; Liu, X.; Zhang, L. D. *J. Mater. Res.* **2002**, *17*, 1283.
- (6) Wu, X. J.; Zhu, F.; Mu, C.; Liang, Y.; Xu, L.; Chen, Q.; Chen, R.; Xu, D. *Coord. Chem. Rev.* **2010**, *254*, 1135.
- (7) Hujdic, J. E.; Taggart, D. K.; Kung, S. C.; Menke, E. J. *J. Phys. Chem. Lett.* **2010**, *1*, 1055.
- (8) Zhu, J.; Peng, H.; Jarausch, C. K. K.; Zhang, X. F.; Cui, Y. *Nano Lett.* **2007**, *7*, 1095.
- (9) Matthew, J. B.; Lau, Y. K. A.; Kvit, A. V.; Schmitt, A. L.; Jin, S. *Science* **2008**, *230*, 1060.
- (10) Bierman, M. J.; Lau, Y. K. A.; Jin, S. *Nano Lett.* **2007**, *7*, 2907.
- (11) Cho, K. S.; Talapin, D. V.; Gaschler, W.; Murray, C. B. *J. Am. Chem. Soc.* **2005**, *127*, 7140. Lifshitz, E.; Bashouti, M.; Kloper, V.; Kigel, A.; Eisen, M. S.; Berger, S. *Nano Lett.* **2003**, *3*, 857.
- (12) Mokari, T.; Habas, S. E.; Zhang, M.; Yang, P. *Angew. Chem., Int. Ed.* **2008**, *47*, 5605.
- (13) Sun, J.; Buhro, W. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 3215.
- (14) Fan, D.; Afzaal, M.; Malik, M. A.; Nguyen, C. Q.; O'Brien, P.; Thomas, P. J. *Coord. Chem. Rev.* **2007**, *251*, 1878.
- (15) Malik, M. A.; Afzaal, M.; O'Brien, P. *Chem. Rev.* **2010**, *110*, 4417. Croach, D. J.; O'Brien, P.; Malik, M. A.; Skabara, P. J.; Wright, S. P. *J. Chem. Soc., Chem. Commun.* **2003**, 1454. O'Brien, P.; Walsh, J. R.; Watson, I. M.; Hart, L.; Silva, S. R. P. *J. Cryst. Growth* **1996**, *167*, 133.
- (16) Nguyen, C. Q.; Adeogun, A.; Afzaal, M.; Malik, M. A.; O'Brien, P. *Chem. Commun.* **2006**, 2182.
- (17) Grebinski, J. G.; Richter, K. L.; Zhang, J.; Kosel, T. H.; Kuno, M. *J. Phys. Chem. B* **2004**, *108*, 9745.