

# A novel two-step radiation route to PbSe crystalline nanorods

Meng Chen, Yi Xie,\* Jiechao Lu, Yinjie Zhu and Yitai Qian

Structure Research Lab and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui, 230023, P. R. China

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Ultrasonic radiation and  $\gamma$ -irradiation techniques have been combined to prepare one-dimensional PbSe nanorods. X-Ray powder diffraction (XRD) patterns, electron diffraction (ED) patterns and transmission electron microscopy (TEM) images showed that the PbSe nanorods were well crystallized with diameters of *ca.* 60 nm and lengths up to 700 nm. The effects of different solvents, the anions of the lead salts and the other metal salts were investigated, and the formation process of the PbSe nanorods has been discussed.

## Introduction

Since the earlier studies, starting in the mid-1990s, various synthetic routes have been exploited to fabricate nanosized II–VI (Zn and Cd chalcogenides) and IV–VI (Pb chalcogenides) semiconductors in one dimension, then form nanowires or nanorods. These nanoparticles with 1D structure are expected to have the fundamental electronic and optical properties and potential applications in both mesoscopic research and development of nanodevices. Roughly speaking, metal chalcogenides with one-dimensional nanostructure can be fabricated by a variety of synthetic techniques, including electrochemical deposition of semiconductors into porous anodic aluminium oxide templates,<sup>1</sup> a solvothermal route using ethylenediamine as solvent,<sup>2</sup>  $\gamma$ -irradiation of the starting solution including organic monomers with a polar group such as maleic anhydride<sup>3</sup> or vinyl acetate.<sup>4</sup> In our opinion, these methods can be considered as template-mediated techniques. Ethylenediamine probably serves as a template for directing the growth of metal chalcogenides in a solvothermal process, and oligomeric chains formed upon  $\gamma$ -irradiation may guide the construction of ordered arrays of the incorporated particles.

Recently, PbSe nanowires have been obtained at room temperature by the reaction of PbCl<sub>2</sub> with Se in ethylenediamine using KBH<sub>4</sub> as the reducing agent.<sup>5</sup> Yang and Wang<sup>6</sup> have prepared rod-shaped PbS nanocrystals dispersed in a polymer film using a functionalized lead(II) salt of the surfactant anion AOT<sup>-</sup>, Pb(AOT)<sub>2</sub>, as the precursor [AOT = || sodium bis(2-ethylhexyl)sulfosuccinate]. The polymer matrix acted as both a stabilizer and a robust template for the nanocrystal growth. To our knowledge, there are few reports on the preparation of 1D structural lead chalcogenides with a large aspect ratio.

In most cases, therefore, much attention has concentrated on II–VI semiconductors especially the CdE (E = S, Se, Te) system, while fewer reports exist on the synthesis of 1D nanostructural chalcogenides of group IV. Compared to II–VI compounds, nanosized IV–VI semiconductors have larger Bohr exciton (BE) radii (*e.g.* 18 nm for PbS), which result in a strong confinement of the electron–hole pair<sup>7</sup> and larger optical nonlinearity.<sup>8</sup> For example, lead chalcogenides could be widely used for sensor and laser materials,<sup>9</sup> solar cells, infrared detectors,<sup>10</sup> thermoelectric cooling materials,<sup>11</sup> and so on. Our research group have also prepared spherical PbSe nanoparticles by sonolysis of a mixture of Pb(NO<sub>3</sub>)<sub>2</sub> or PbCl<sub>2</sub> with selenium in ethylenediamine,<sup>12</sup> and by  $\gamma$ -irradiation of an ethylenediamine solution containing lead acetate and elemental Se under ambient conditions.<sup>13</sup> Prompted by these studies and

the generation of PbSe nanowires using KBH<sub>4</sub> as the reducing agent,<sup>5</sup> we developed ultrasonic and  $\gamma$ -irradiation techniques to prepare well crystallized PbSe nanorods in an ethylenediamine solution at room temperature.

## Experimental

All reagents were of analytical grade or better and used without further purification. Ethylenediamine has a trace of water and was used without being dried. In a standard experimental run, an appropriate amount of selenium powder was added to 100 mL ethylenediamine in a vessel at room temperature. Then the tank was sealed and partly submerged in 1 dm<sup>3</sup> water in a commercial ultrasonic cleaner (WuXi, H-66025, 220 V, 100 W). The mixed liquid slurry was sonicated at 18 kHz under ambient conditions for more than an hour. The reaction temperature was maintained at 15–25 °C by cooling the water bath with iced water. Following this step, a stoichiometric amount of lead acetate was added to the sonicated slurry, which was then irradiated in the field of a  $2.59 \times 10^{15}$  Bq <sup>60</sup>Co  $\gamma$ -ray source. The irradiation dose was  $6.0 \times 10^4$  Gy. The irradiated suspension colloids were kept for several hours or longer to precipitate powders, which were then filtered off and washed with distilled water and absolute ethanol in sequence to remove the by-products. The obtained product was then dried in a vacuum at 50 °C for 8 h.

The as-prepared samples were characterized by X-ray powder diffraction (XRD) using a MAC Science Co. Ltd MXP18AHF  $\gamma$ A rotation anode X-ray diffractometer with graphite monochromatized Cu-K $\alpha$  radiation ( $\lambda = 1.54056$  Å). Transmission electron microscopy (TEM) investigation was made on a Hitachi H-800 transmission electron microscope with an accelerating voltage of 200 kV.

X-Ray photoelectron spectroscopy (XPS) was performed on a VGESCALAB MKII X-ray photoelectron spectrometer, using nonmonochromatized Mg-K $\alpha$  X-rays as the excitation source. The binding energies obtained in the XPS analysis were corrected by referencing the C 1s peak to 284.60 eV. Elemental analyses were performed by atomic absorption spectroscopy using a Perkin-Elmer 1100B Atomic Absorption Spectrophotometer.

## Results and discussion

Fig. 1 shows the XRD pattern of PbSe crystalline nanorods prepared in ethylenediamine. All the diffraction peaks have a one-to-one correspondence to those of the cubic rock-salt

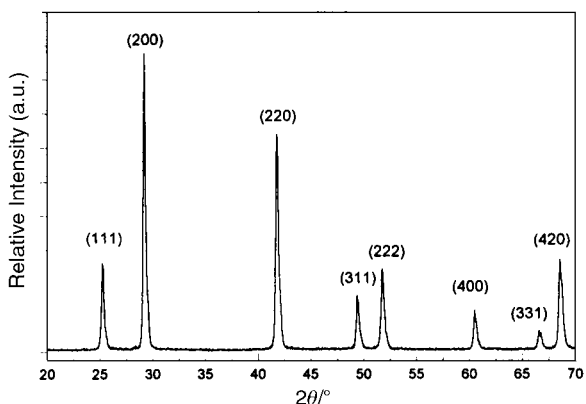


Fig. 1 XRD pattern of the as-obtained PbSe nanorods.

structure of bulk PbSe (JCPDS card no. 6-0354). No characteristic peaks for impurities, such as selenium and lead oxides, were detected. Calculated on the basis of the Scherrer equation<sup>14</sup> with a geometric factor of 0.9 applied, the average diameter of the PbSe nanorods was *ca.* 60 nm, in close agreement with that observed from the TEM image.

A typical TEM image of the as-prepared sample is given in Fig. 2a. It clearly shows that the PbSe nanocrystals are rod-like with diameters of *ca.* 60 nm, lengths ranging from 100 to 700 nm and aspect ratios in the range of 1.5–11. Apart from the rod-shaped particles, there is some aggregation of PbSe nanoparticles with irregular morphologies, whose volume makes up 40% or so of the as-prepared sample as estimated by TEM. Fig. 2b shows a selected image in another area, where the morphology of as-obtained PbSe nanorods with a size of 60 × 380 nm is more clearly revealed. The electron diffraction pattern (Fig. 2c) from a selected area of the PbS nanorod

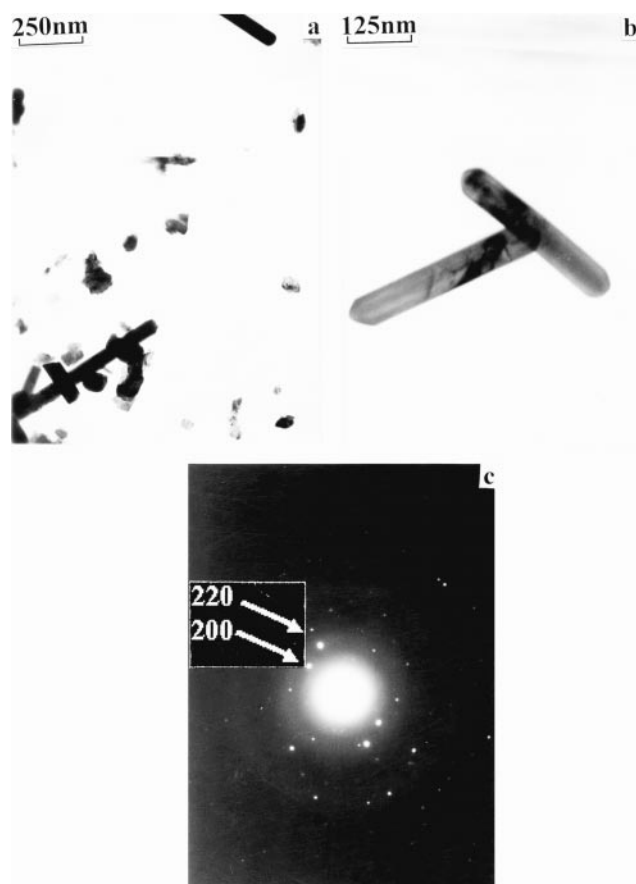


Fig. 2 TEM images (a, b) and the ED pattern (c) of the as-prepared PbSe nanorods.

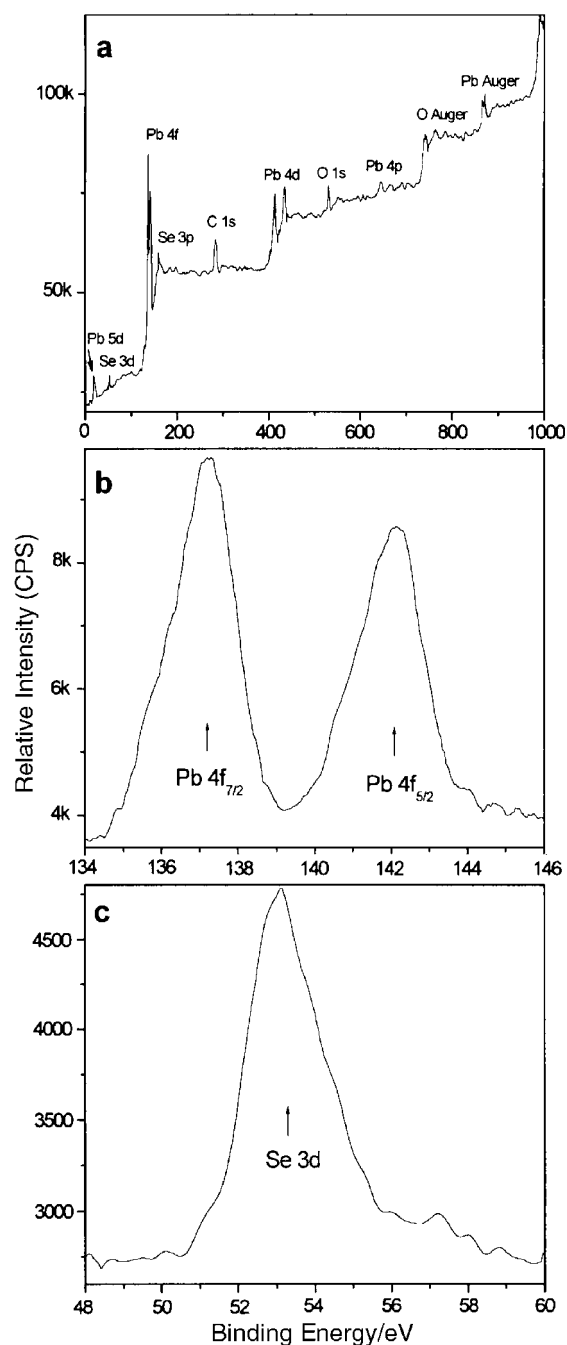


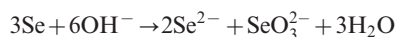
Fig. 3 XPS spectra for PbSe nanorods: (a) a typical XPS survey spectrum for PbSe nanorods; (b) high-resolution XPS scans for Pb 4f core; (c) high-resolution XPS scans for Se 3d core.

(shown in Fig. 2b) clearly shows the diffraction dots of PbSe, which revealed that the PbSe nanorod was well crystallized.

X-Ray photoelectron spectroscopy (XPS) has been used to investigate the elemental composition of the PbSe nanorods and examine the oxidation of the nanocrystalline surface. Fig. 3a is the typical survey spectrum of the PbSe nanorods, which indicates the presence of Pb, Se from the nanorods and their surface as well as C from reference and O from absorbed gaseous molecules. Higher resolution spectra were also taken of the Pb 4f region (Fig. 3b) and S 2p region (Fig. 3c). The Pb core is spin-orbit split to the 4f<sub>7/2</sub> peak at 137.2 eV and 4f<sub>5/2</sub> peak at 142.15 eV. The peak at 53.15 eV corresponds to Se 3d of PbSe. These results are close to the reported values of bulk PbSe.<sup>15</sup> No impurity peaks were observed, such as Pb 4f of PbO (138.85 eV) or Se 3d of SeO<sub>2</sub> (59.8 eV). The peak areas of these high-resolution scans were measured and used to calculate the Pb-to-Se ratio for the nanorods. The quantification of the

peaks gives an average composition of  $\text{Pb}_{1.05}\text{Se}$ , which is consistent with a Pb-to-Se ratio of 1.08 obtained by elemental analysis.

PbSe nanoparticles with homogeneously spherical morphologies have been prepared in a similar reaction system under ultrasonic radiation<sup>12</sup> or  $\gamma$ -irradiation,<sup>13</sup> while PbSe nanorods formed in the present study by a two-step irradiation process. Parkin *et al.* also reported the preparation of agglomerated PbSe nanoparticles by the reaction of elemental lead with selenium in liquid ammonia.<sup>16</sup> No rod-shaped PbSe particles, however, were found. Therefore, it can be concluded that the two-step irradiation route plays an important role in the formation of PbSe crystalline nanorods. Under the sonolysis, Se powder tends to disproportionate in liquid ethylenediamine with basic, N-chelation properties, and form divalent selenium, hydroxyl ( $\text{OH}^-$ ) ion may exist in ethylenediamine with traces of water.



In addition, the divalent selenium can further interact with N atoms in organic amines to form a pseudo-high-valent selenium,<sup>17</sup> although there is no report about the direct reaction between Se powder and amines. Therefore, one hour sonication can favor the formation of  $\text{Se}^{2-}$  and the non-valence interaction between  $\text{Se}^{2-}$  and ethylenediamine. One hour was sufficient for the favorable actions: no obvious effect was observed on the morphology of the product through prolonging the sonication time.

Our research group<sup>5</sup> has reported the preparation of PbSe nanowires in ethylenediamine using  $\text{KBH}_4$  as the reductant, and proposed that the formation of PbSe nanowires may be attributed to the existence of active  $\text{H}^-$  in  $\text{KBH}_4$ , and the special structure and N-chelation properties of ethylenediamine. In the present study, the second step of  $\gamma$ -irradiation plays the same role as  $\text{KBH}_4$ . Upon  $\gamma$ -irradiation, solvated electrons ( $e_s^-$ ) with strong reductive properties can be formed in ethylenediamine,<sup>18</sup> hydrogen radicals ( $\text{H}\cdot$ ) and hydrated electrons can also be generated due to the presence of traces of water.<sup>19</sup> These reductive species can activate the reaction and favor the formation of nanorods in ethylenediamine.

To investigate the influence of different solvents, the experimental results obtained in different solvents reveal that ethylenediamine may be more suitable for the formation of PbSe nanorods than other solvents. Other solvents such as water and ethanol produced impure PbSe nanoparticles, while pyridine gave PbSe particles with morphologies never far from spherical particles. In addition, other lead salts, such as  $\text{PbCl}_2$ ,  $\text{Pb}(\text{NO}_3)_2$ , were used to substitute  $\text{Pb}(\text{Ac})_2$  with all other reaction conditions kept constant. In these experiments not only PbSe spherical particles but also Se powder can be detected by XRD and TEM. The solubility of lead salts in ethylenediamine may be responsible for the fact that  $\text{Pb}(\text{Ac})_2$  readily dissolves in ethylenediamine, whereas other lead salts seem to be only sparingly soluble in ethylenediamine, which leads to the existence of Se residue and decreases the controlled effect of ethylenediamine with lead ions. Metal salts such as  $\text{Cd}(\text{Ac})_2$  and  $\text{Zn}(\text{Ac})_2$  have also been applied in similar experiments. To our surprise, neither selenides with a 1D nanostructure, nor metal selenides were obtained. Many diffraction peaks, especially in the region under  $20^\circ$  ( $2\theta$ ), appeared in the XRD pattern of the as-obtained powder, and no characteristic peaks of metals, selenium or metal selenides were seen. Thus it may be assumed that the obtained powders

are the stable coordination phase consisting of metal ions, selenium and ethylenediamine. Similar results for the reaction between elemental zinc, selenium powder and ethylenediamine have also been reported elsewhere.<sup>20</sup>

## Conclusion

In summary, we have developed a novel synthetic route for growing one-dimensional PbSe nanorods using a combination of ultrasonic and  $\gamma$ -irradiation techniques. These nanorods were well crystallized with diameters of *ca.* 60 nm and lengths up to 700 nm. The effects of different solvents, the anions of the lead salts and the other metal salts were investigated. This may provide some clues for understanding the mechanism of PbSe nanorod growth in ethylenediamine.

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