

## A Novel Mild Route to Nanocrystalline Selenides at Room Temperature

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Selenides have been widely used as thermoelectric cooling materials,<sup>1</sup> optical filter,<sup>2</sup> optical recording materials,<sup>3–5</sup> solar cells,<sup>6,7</sup> superionic materials,<sup>8</sup> and sensor and laser materials.<sup>9</sup> Recently, low-dimensional selenides, such as nanorods<sup>10</sup> and quantum dots,<sup>11,12</sup> have become the focus due to their brilliant prospects.

Traditionally, selenides have been synthesized by solid-state reactions,<sup>13</sup> solid-state metathesis,<sup>14</sup> and self-propagating high-temperature synthesis.<sup>15</sup> All of the above reactions require high temperature (> 500 °C) for initiating the reactions. When gaseous H<sub>2</sub>Se has been used to prepare selenides, the process has been relatively dangerous and highly toxic.<sup>16</sup> High-energy ball milling<sup>17</sup> of metals and Se at room temperature has also been used to prepare selenides. However, the product quality was difficult to control. Parkin et al. reported a low-temperature route to selenide in liquid ammonia.<sup>18,19</sup> During their experiments, several manipulations had to be carefully carried out at –77 °C in thick-walled glass vessels, and all operations had to be conducted with care and behind a safety screen.

Organometallic precursors<sup>20–22</sup> have also been used to obtain selenides. Using Se(TMS)<sub>2</sub> and Cd(ClO<sub>4</sub>)<sub>2</sub> in the presence of LiHB(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, Steigerwald<sup>20</sup> prepared CdSe at room temperature. Bawendi<sup>22</sup> used Me<sub>2</sub>Cd and [TOPSe] to prepare CdSe. However, all the manipulations involving organometallic precursors had to be performed with standard airless techniques, and only amorphous CdSe was obtained. In these two reports, a following

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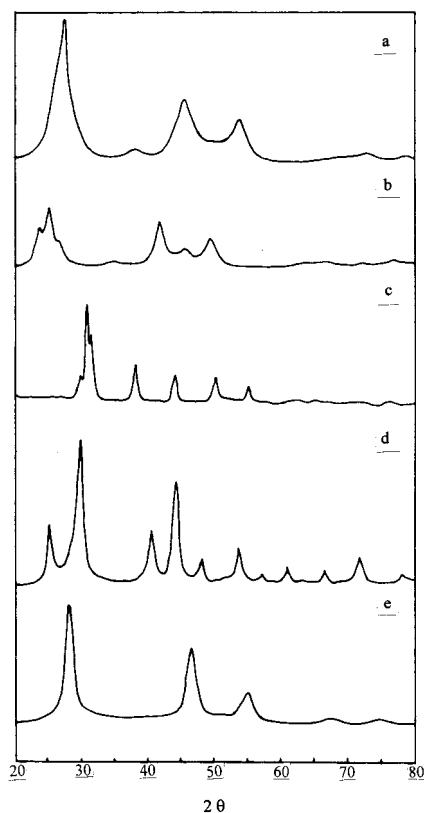
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**Figure 1.** XRD patterns of as prepared nanocrystalline selenides (a) ZnSe, (b) CdSe, (c) Bi<sub>2</sub>Se<sub>3</sub>, (d) SnSe, and (e) Cu<sub>2-x</sub>Se.

posttreatment at relatively high temperature (250–500 °C) was necessary when crystalline products were needed. Wang and co-workers obtained only PbS<sup>23</sup> and CdS<sup>24</sup> crystals at room temperature using organometallic precursors.

In this communication, we report a room-temperature route to nanocrystalline selenides with different morphologies. Se, KBH<sub>4</sub>, and MCl<sub>n</sub> (M = Zn, Cd, Cu, Sn, Bi) are reacted in ethylenediamine in sealed flasks at room temperature under ambient pressure. Compared with the above methods, this technique is relatively mild and no complicated equipment or organometallic precursors are needed.

Appropriate amounts of analytically pure metal chlorides MCl<sub>n</sub> (ZnCl<sub>2</sub>, CdCl<sub>2</sub>, CuCl<sub>2</sub>, BiCl<sub>3</sub>, SnCl<sub>2</sub>), KBH<sub>4</sub>, and Se powder were mixed in the flasks. Then the flasks were filled with ethylenediamine, sealed, and kept at room temperature (about 20 °C) for 4 h. The precipitates were filtered, washed with distilled water, then dried in a vacuum at room temperature for 10 h.

The X-ray powder diffraction (XRD) patterns of as prepared samples are shown in Figure 1. The phases and cell constants of as prepared samples are listed in Table 1. No impurity phase was detected. On the basis of the Scherrer equation,<sup>26</sup> the broadening of the peaks is in accordance with their small grain sizes.

Figure 2 shows the Transmission electron microscopy (TEM) microphotographs of as prepared nanocrystalline samples. It is apparent that ZnSe, CdSe grains are spherical, SnSe, Bi<sub>2</sub>Se<sub>3</sub> grains are rodlike, and Cu<sub>2-x</sub>Se is platelike. The average grain sizes from the TEM images are listed in the table. The results are consistent

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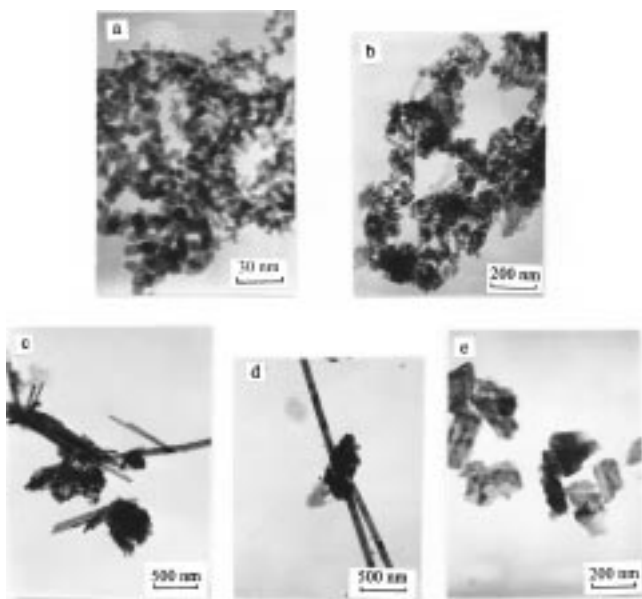
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**Table 1.** Characterization of As Prepared Products

products	morphology	av size	phase	cell constants	
				obsd	reptrd <sup>25</sup>
ZnSe	spherical	6 nm	cubic	$a = 0.58$	$a = 0.5669$
CdSe	spherical	8 nm	hexagonal	$a = 0.43,$ $c = 0.71$	$a = 0.4299,$ $c = 0.7010$
Bi <sub>2</sub> Se <sub>3</sub>	nanorod	60 nm × 1.0 μm	rhombohedral	$a = 0.40,$ $c = 2.85$	$a = 0.4140,$ $c = 2.8636$
SnSe	nanorod	30 nm × 1.5 μm	orthorhombic	$a = 1.14,$ $b = 0.42,$ $c = 0.46$	$a = 1.142,$ $b = 0.419,$ $c = 0.446$
Cu <sub>2-x</sub> Se	plate-like	0.1 μm × 0.2 μm	cubic	$a = 0.58$	$a = 0.5739$

**Figure 2.** TEM images of typical samples of nanocrystalline selenides (a) ZnSe, (b) CdSe, (c) Bi<sub>2</sub>Se<sub>3</sub>, (d) SnSe, and (e) Cu<sub>2-x</sub>Se.

with that calculated from XRD patterns by the Scherrer equation. The reason that the various selenides have different morphologies may be related to the different behavior of ethylenediamine chelates with various  $M^{n+}$  ions, which possibly affects the growing direction of the selenides grains.

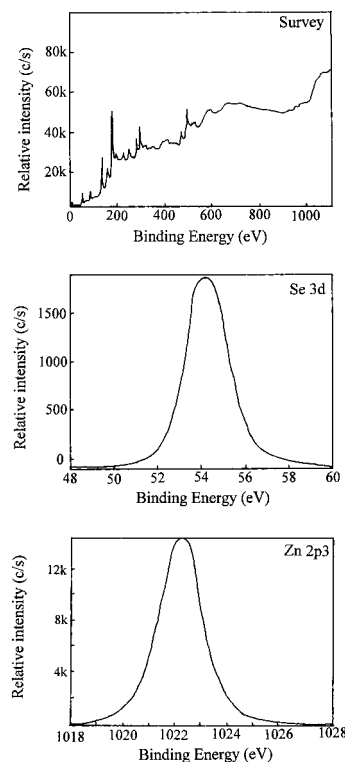
X-ray photoelectron spectra (XPS) analysis of ZnSe nanocrystals is shown in Figure 3. The two strong peaks at 1022.4 and 54.4 eV correspond to Zn 2p<sup>3</sup> and Se 3d binding energy for ZnSe, respectively. This result is close to that of bulk ZnSe.<sup>27</sup> No impurity peaks such as Zn 2p (1021.75 eV) from ZnO and Se 3d (59.8 eV) from SeO<sub>2</sub> are detected. The quantification of the peaks gives the ratio of 1:0.93 for Zn to Se.

There is a blue shift in the photoluminescence (PL) spectrum of as prepared CdSe nanocrystals: a strong emission peak is observed at 578 nm, in comparison with that of bulk CdSe at 731 nm. The excitation wavelength was 454 nm. This effect may be related to its small grain size based on the Brus equation.<sup>28</sup>

Ethylenediamine is a strongly coordinating Lewis base and has N-chelation. When Se, MCl<sub>n</sub>, and KBH<sub>4</sub> were mixed with ethylenediamine in the flask, the mixture slowly dissolved and the solution color changed. Then the reactions between MCl<sub>n</sub> and Se at room temperature were initiated. The possible role of KBH<sub>4</sub> is that it reduces Se to Se<sup>2-</sup> first, then Se<sup>2-</sup> reacts with M<sup>n+</sup> to

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**Figure 3.** XPS analysis of as prepared nanocrystalline ZnSe.

form MSe at room temperature. This mechanism is supported by the fact that no trace of metallic M was observed when only MCl<sub>n</sub> and KBH<sub>4</sub> were added to ethylenediamine and kept for 1 week at room temperature. It may relate to the chelation of ethylenediamine with M<sup>n+</sup>, which prevents it from being reduced by KBH<sub>4</sub>.

Another important factor was that KBH<sub>4</sub> was difficult to replace with other reductants. When it was replaced by other reductants such as zinc powder or sodium, no obvious reactions happened under the similar conditions. The possible reason is that there is active hydride in KBH<sub>4</sub>, which activates the reactions between Se and MCl<sub>n</sub> and makes them happen easily at room temperature.

The chelation of ethylenediamine played an important role in the formation of MSe nanocrystals at room temperature. When the weak monodentate ligand pyridine was used, the yields were very low and the crystallinities were poor. When benzene or THF, having no chelation and basicity, were utilized as the solvent, no reaction happened. Moreover, the reactions were not initiated even at higher temperature (200 °C) for longer time (24 h) in the stainless steel tank.

For comparison, the preparation of MSe nanocrystals was also carried out at relatively higher temperature, the other conditions remaining the same. This led to larger grain sizes of as prepared MSe. For instance, when the temperature increased from room temperature to 80 °C, the grain sizes of ZnSe increased from 6 to 30 nm.

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(29) XRD were carried out on a Japan Rigaku D/max γA rotation anode X-ray diffractometer with Ni-filtered Cu Kα radiation. TEM images were taken with a Hitachi H-800 transmission electron microscope. XPS were recorded on ESCALAB MKII with M Kα as the exciting source. PL spectra were obtained on a Hitachi 850 fluorescence spectrophotometer with a Xe lamp at room temperature.