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## Ionic liquid-assisted synthesis of CdSe dendrites from nanospheres through oriented attachment†

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CdSe nanospheres and dendrites have been successfully synthesized *via* an ionic liquid-assisted hydrothermal synthetic method. The samples are characterized by X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). Our experimental results demonstrate that the CdSe dendrites are obtained by self-assembly from nanospheres under the driving force of oriented attachment process. Moreover, we found that the sizes and morphologies of the crystals depended on the concentration of the ionic liquid, and we obtained the CdSe nanospheres with low concentration of [BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)] and CdSe dendrites with high concentration of [BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)]. The effects of [BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)] on the formation of the CdSe have been investigated systematically. This method is expected to be a useful technique to prepare other metal selenides for controlling the diverse shapes and sizes.

## Introduction

The syntheses of inorganic semiconductor nanoparticles have motivated much interest due to their size-dependent optical and electronic properties, and potential applications in the fields of nonlinear optics, light-emitting devices, electronics, and so on.<sup>1–7</sup> As one of the most important II–IV group semiconductors, CdSe has a direct band gap of 1.74 eV at room temperature, and it is now widely used for photovoltaic devices, electroluminescence, and catalysts.<sup>8</sup> Over the past few years, great effort has been made to control the size and shape of CdSe nanomaterials, and many methods have been developed to prepare CdSe-based nanostructures, among which hydrothermal/solvothermal methods have been widely utilized to synthesize CdSe with various morphologies, such as nanorods,<sup>9</sup> nanoflowers,<sup>10</sup> nanowires,<sup>11</sup> and nanoclusters.<sup>12</sup> Among the many synthesis methods, the ionothermal synthesis and ionic liquid-assisted synthesis, as a “green” synthesis route, have obtained more and more attention.<sup>13</sup> In view of today’s environmental concerns, room temperature ionic liquids (RTILs) are considered as “green” solvents as a new class of compounds for replacement of conventional organic solvents due to their high fluidity, low melting temperature and extended temperature range in the liquid state, air and water stability, low toxicity, nonflammability, high ionic conductivity, ability to dissolve a variety of materials, and importantly no measurable

vapor pressure.<sup>14</sup> The low interface tension and the associated high nucleation rate as well as high thermal stability make ionic liquids an attractive reaction medium for the synthesis of nanostructures. More importantly, they are referred as “designer liquids” with tunable physico-chemical properties and desired functions by changing cations and anions; furthermore, the possible combination number of cations and anions is uncountable (high to  $\sim 10^{18}$ ).<sup>15</sup> Thereby, ILs with special cations and anions can be tailored, according to the composition, initial crystalline structure, and crystal growth habit of the material, to purposefully synthesize inorganic nanomaterials with novel morphology and improved property.

Although much effort has been made on the synthesis of metal oxides using ionic liquids, the synthesis of metal chalcogenides using ionic liquids has been rarely studied.<sup>16</sup> Our research group focuses on ionic liquids in the synthesis of inorganic nanomaterials. For instance, in the previous work, our group has reported the synthesis of pure rutile and rutile-anatase composite TiO<sub>2</sub> nanoparticles,<sup>17</sup>  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with various morphologies,<sup>18</sup> a series of shape-controllable ZnO nanocrystals,<sup>19</sup>  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanostructures<sup>20</sup> using different ionic liquids. Recently, we have found that an IL 1-n-butyl-3-methylimidazolium methylselenite ([BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>))] may represent a new Se precursor and have successfully employed it as a selenium source to obtain ZnSe hollow nanospheres.<sup>21</sup> Compared to the other previous Se precursors, such as Na<sub>2</sub>SeO<sub>3</sub> or SeO<sub>2</sub>, [BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)] has special structure to slow release of Se, and it is highly expected that such a powerful Se precursor could prepare metal selenides with special morphologies and novel properties.<sup>22</sup>

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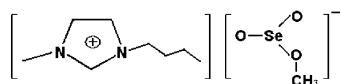
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In this study, we report the synthesis of CdSe dendrites from nanoparticles using ionic liquid precursor ([BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)]). Our experimental results demonstrate that the CdSe dendrites are obtained by self-assembly through oriented attachment, in which secondary mono-crystalline particles can be obtained through attachments of primary particles in an irreversible and highly oriented fashion.<sup>23</sup> Moreover, we found that the critical factor to form CdSe dendrites is the concentration of the ionic liquid. There are two significant features in this work: (i) The results may represent a new example of oriented attachment mechanism-based formation of inorganic dendrites, in which the adjacent nanoparticles are self-assembled by sharing a common crystallographic orientation and docking of these particles at a planar interface. The driving force for this mechanism is that the elimination of the pairs of high energy surfaces will lead to a substantial reduction in the surface free energy from the thermodynamic viewpoint. (ii) To our knowledge, the preparation of CdSe dendrites from nanoparticles using ionic liquids is rarely reported, and we expect that such a simple and mild route could also be extended to prepare other metal selenides.

## Experimental

### Materials

All the reagents were analytical grade and used without further purification. The IL [BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)] was prepared according to the literature procedures,<sup>24</sup> and its general structural feature is as follows:



### Synthesis of CdSe nanospheres

In a typical synthesis, 0.06 mmol of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and 0.06 mmol of [BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)] were dissolved into 19 mL of deionized water under vigorous magnetic stirring to form a clear solution, followed by adding 1.5 mL of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (80%). Then the mixture was transferred into a Teflon-lined stainless steel autoclave (30 mL) and maintained at 150 °C for 12 h. The resulting powders were centrifuged, washed with deionized water and anhydrous ethanol several times, and finally dried at 60 °C for 4 h under vacuum.

### Synthesis of CdSe dendrites

In a typical synthesis procedure of the CdSe dendrites, 0.30 mmol of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and 0.30 mmol of [BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)] were dissolved into 19 mL deionized water under vigorous magnetic stirring to form a clear solution, followed by adding 5 mL of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (80%). The rest synthesis and reaction steps are similar to those mentioned above.

### Instruments and characterizations

The crystallographic information of the obtained CdSe nanospheres and dendrites was established using X-ray diffraction (XRD) (Rigaku D/max 2500V/PC, Cu-Kα radiation, λ = 1.54056 Å). The morphology and nanostructure of the products were

observed by Scanning electron microscopy (JSM 6700F), transmission electron microscopy (Hitachi H-7650, 100 kV), and high-resolution TEM (Hitachi H-7650, 200 kV). The compositional analysis for the as-prepared sample was performed with energy-dispersive spectrometer, an accessory of SEM (JSM 6700F).

## Results and discussion

### Structural characterization

Typical X-ray diffraction patterns from the as-prepared CdSe nanocrystals are shown in Fig. 1. All of the diffraction peaks can be indexed to wurtzite CdSe with lattice parameters  $a = b = 5.670$  Å,  $c = 6.992$  Å, which is in good agreement with the value reported in the literature (JCPDS card No. 08-0459). No characteristic peaks corresponding to impurities are found, showing the high purity of the sample. Compared with CdSe nanospheres, the peak intensity ratio for (002) to (101) of CdSe dendrites, distinct variations for the ratios occurred for the different morphologies, which indicates the preferred growth along the <001> and <101> directions in the formation of dendrites. Such variations suggest anisotropic growth of these planes during the nanostructures' growing processes.

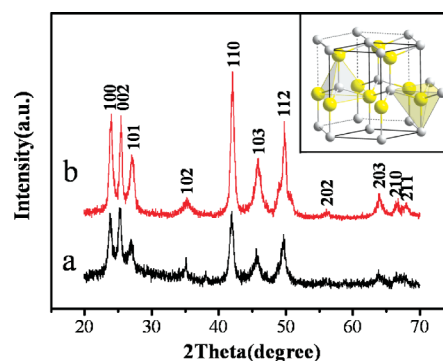
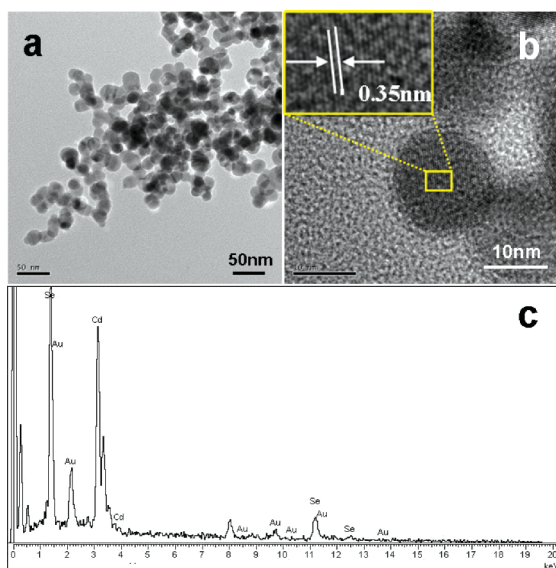


Fig. 1 XRD pattern of the as-prepared CdSe: (a) nanospheres; (b) dendrites.

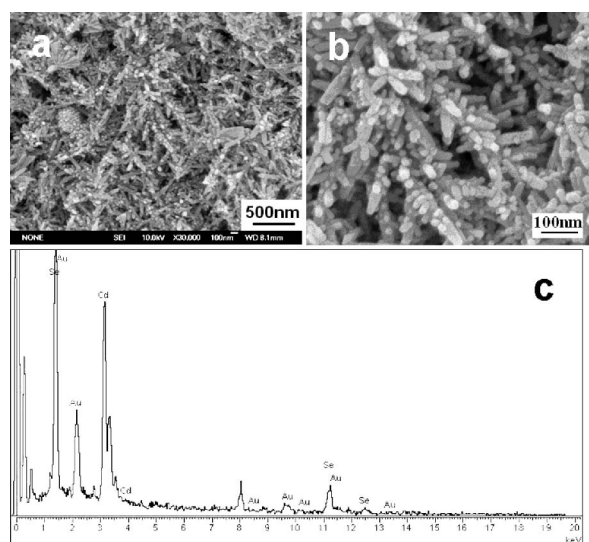
### Morphology of CdSe nanospheres and dendrites

The morphology of the obtained CdSe nanoparticles is investigated by TEM. Fig. 2a presents an overview TEM image of the sample. It can be seen that the products have relatively uniform spherical shape with diameter of about 15 nm. A high-resolution TEM (HRTEM) image of representative spheres is shown in Fig. 2b, the lattice fringes show that the nanospheres are single crystals, and the 0.35 nm spacing is consistent with the (002) lattice plane spacing of wurtzite CdSe. In order to further confirm the composition of the sample, EDS analysis are recorded for the nanospheres under N<sub>2</sub> atmosphere and the result is shown in Fig. 2c. In the spectrum, besides the Au signals from the Au film which coated on the sample for good electrical conductivity, only Cd and Se are observed. Based on the relative areas of the peaks of Cd and Se, the atomic ratio of Cd to Se is calculated to be about 47.02 : 44.84, which is close to 1 : 0.95.

The SEM images shown in Fig. 3 clearly reveal the dendritic structure of CdSe nanocrystals. The low magnification image (Fig. 3a) indicates the high yield of such dendrites. The higher magnification image (Fig. 3b) demonstrates typical dendrites in



**Fig. 2** (a) TEM image of the obtained CdSe nanospheres; (b) HRTEM image of representative nanospheres; (c) EDS spectrum of the CdSe nanospheres.



**Fig. 3** (a) SEM image of the large-scale CdSe dendrites; (b) the higher magnification image of CdSe dendrites; (c) EDS spectrum of the CdSe dendrites.

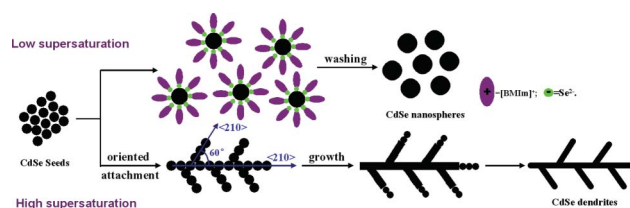
which the branches perpendicular to the stem are evenly spaced alternately on the major stem with a regular periodicity. In general, the length of the stem and the diameter of the branch range from 200 to 500 nm and 50 to 80 nm, respectively. EDS analysis (Fig. 3c) was employed to determine the composition of CdSe dendrites. The cadmium and selenium elements existed in the nanostructures with an atom ratio of 42.40:46.38, which is very close to the stoichiometric ratio of CdSe. Compared to the CdSe nanosphere, Se content of the dendrites increases, which may insinuate the nanospheres tend to form the dendrites in the presence of the superfluous Se.

### Effect of [BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)] on the CdSe nanocrystals

Up to now, only a few Se sources have been developed for fabricating metal selenides. Na<sub>2</sub>SeO<sub>3</sub> was widely used due to its high activity and good water-solubility. However, Na<sub>2</sub>SeO<sub>3</sub> could react with metal ions (M<sup>n+</sup>) to form precipitates in some systems.<sup>22</sup> To obtain uniform reaction conditions, M<sup>n+</sup> ions should be transformed into stable complexes, which would make the systems complicated, affect the thermodynamics and kinetics in the nanocrystal nucleation stage, and further influence the morphology of the products, sometimes even bring about an increase of impurity concentration in the final product. For comparison, we use the Na<sub>2</sub>SeO<sub>3</sub> as Se sources under the same experimental conditions of CdSe nanospheres preparation. The SEM and corresponding XRD pattern of the obtained sample are shown in Fig. S1 (see ESI†). It can be seen that the morphology and the size are not uniform and the particles reunite badly (see Fig. S1a). The XRD pattern indicates the sample is wurtzite CdSe.

In comparison, [BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)] with high reaction activity is selected in our synthesis to provide Se source. As to this IL, the reactivity of [SeO<sub>2</sub>(OCH<sub>3</sub>)]<sup>-</sup> is similar to SeO<sub>3</sub><sup>2-</sup> (see the general structural feature). More importantly, one oxygen among SeO<sub>3</sub><sup>2-</sup> is replaced by a methoxy; thereby, [SeO<sub>2</sub>(OCH<sub>3</sub>)]<sup>-</sup> has weaker polarizing capability and accordingly Mn<sup>+</sup> can exist as free ions. Motivated by these potentials, we consider that [BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)] could be used to synthesize metal selenides with special morphologies and novel properties. As is well known, the nucleation stage and growth process are involved in the synthesis of crystals.<sup>25</sup> When nucleation rate is faster than growth rate, the average crystal size can be decreased, and vice versa.<sup>26</sup> As mentioned above, CdSe nuclei can be quickly formed because of the employment of [BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)], which would cause the CdSe nanocrystals have smaller diameters. Actually, the diameters of the primary CdSe nanocrystals, ranging between 10–15 nm, is much smaller than that of CdSe nanocrystals synthesized in other hydrothermal systems. Moreover, it is found that the dispersibility of the CdSe nanocrystals is affected by [BMIm]<sup>+</sup>. The interactions between unprotected building units with nanoscale size are generally not able to form stable and uniform microstructures. As reported in some of the literature, some ILs have been chosen to serve as stabilizers based on the selective adsorption of ILs on the surfaces of the samples. Therefore, in the work reported here, the presence of the [BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)] was believed to play a strategic role on the formation of the monodisperse nanospheres. We and others have demonstrated the synthesis of nanostructures by ionic liquid-assisted route, and the electrostatic attractions mechanism is helpful to understand the influence of ionic liquids on the size control of nanostructures.<sup>27</sup> It is assumed that the stabilization in these cases is essentially due to electrostatic attraction, which is induced by the adsorption of IL onto the nanostructure surface, similar to the classic, DLVO (Derjaguin-Landau-Verwey-Overbeek) type coulombic repulsion model.<sup>28</sup> Along with the Se<sup>2-</sup>, [BMIm]<sup>+</sup> will also adsorb on the CdSe spheres surfaces possibly driven by the electrostatic attractions between [BMIm]<sup>+</sup> and Se<sup>2-</sup> (Scheme 1). As a result, [BMIm]<sup>+</sup> ions have large steric hindrance, which would hinder the agglomeration of the obtained CdSe nanospheres in the solution and accordingly the dispersibility of the CdSe nanospheres can be improved. It is also found that the IL can influence on the morphologies of the



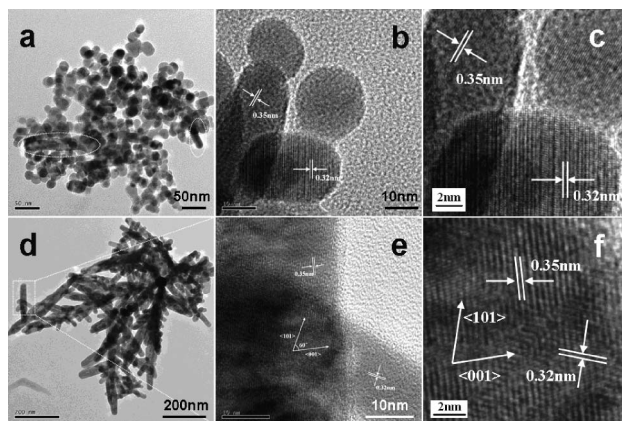


**Scheme 1** Schematic illustration of the formation process of CdSe dendrites from nanospheres.

products, detailed discussions would be conducted in the growth mechanism section.

### Formation mechanism of CdSe dendrites

To explore the formation mechanism of the CdSe dendrites, a series of concentration dependence experiments were further carried out. The synthesis was carried out in aqueous solution just containing [BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)], Cd(NO<sub>3</sub>)<sub>2</sub>, and N<sub>2</sub>H<sub>4</sub>. We found that the reactant concentration is the essential factor to influence the morphology. The evolution can be obtained by adjusting the reactant concentration gradually with other conditions remaining unchanged (keep the ratio between the reactants). TEM and HRTEM were employed to further investigate the obtained CdSe. Fig. 4 shows the typical TEM and corresponding HRTEM images of CdSe nanocrystals with 0.08 mmol and 0.30 mmol, respectively. When the concentration of [BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)] is 0.06 mmol, we obtain CdSe monodisperse nanospheres with diameter of about 15 nm (Fig. 2a). Increasing the [BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)] concentration to 0.08 mmol, the nanospheres are tended to assemble to nanorod, which could be found in the dashed area of Fig. 4a. The HRTEM image (Fig. 4b and c) is taken from the connecting region of the adjacent particles in Fig. 4a. The clear lattice fringes indicate that they are single crystals, the interplane distances are calculated as 0.35 and 0.32 nm, respectively, corresponding to (002) and (101) crystal planes of wurtzite CdSe. When the [BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)] concentration increase to 0.30 mmol, the main framework of the dendritic crystals has been built (see Fig. 4d). The HRTEM images (Fig. 4e and f) taken from the dashed region of Fig. 4d show that the angles between the (101) lattice fringes and the long axis is found to be about 60°, which is very

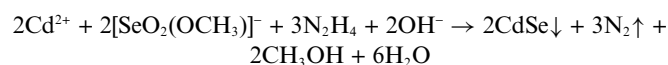


**Fig. 4** TEM and corresponding HRTEM images of CdSe nanocrystals with different reactant concentration: (a–c) 0.08 mmol [BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)]; (d–f) 0.30 mmol [BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)].

close to the angle (62°) between the (002) and (101) crystals planes in wurtzite CdSe. This angular relationship is consistent with the direction of (002) lattice fringes in Fig. 4, implying that the branches grow along the same direction. By combining the (002) and (101) fringe images in Fig. 4, it can be judged that these branches grow along the <210> direction.<sup>22d</sup> This means that the growth of the dendrites corresponds to the preferential stacking of (100) planes of hexagonal wurtzite CdSe.

Generally, the growth process of crystals can be separated into two steps, an initial nucleating stage and a subsequent crystal growth process. At the initial nucleating stage, the crystalline phase of the seeds is critical for directing the intrinsic shapes of the crystals due to its characteristic symmetry and structure. At the subsequent step, the crystal growth stage strongly governs the final architecture of the crystals through the delicate balance between the kinetic growth and thermodynamic growth regimes. In the present study, we speculate that the final CdSe nanostructures are mainly determined by the reactant concentration: the CdSe nanospheres are generated mainly under a thermodynamically preferential crystal growth regime at low supersaturation. Comparatively, the CdSe dendrites are formed through diffusion-controlled crystal growth controlled by the kinetic parameters under high supersaturation conditions.

In a typical synthesis, the formation of CdSe nanocrystals can be formulated as follows:



In the synthesis, when Cd(NO<sub>3</sub>)<sub>2</sub> and [BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)] are dissolved into the deionized water, a clear solution can be obtained. As we known, [SeO<sub>2</sub>(OCH<sub>3</sub>)]<sup>−</sup> ions can be firstly reduced by N<sub>2</sub>H<sub>4</sub> to Se atoms, which have high reactivity and are easy to be further disproportionated into Se<sup>2−</sup> ions. Then, Se<sup>2−</sup> ions can directly reacts with Cd<sup>2+</sup> ions and CdSe monomers can be quickly formed in the solution. With a lower reactant concentration, it results in lower CdSe monomers concentration at the initial stage. The lower CdSe monomers concentration does not favor anisotropic growth, it favors the formation of concave structure and forms thermodynamically favored morphology. It is known that isotropic unit cell structure generally results in isotropic growth of particles and accordingly leads to spherical morphology of the products, so we obtain the CdSe monodisperse nanospheres. With the reactant concentration increasing, the Se<sup>2−</sup> ions are seem to be supersaturated, and high supersaturation causes the three-dimensional growth of preformed nuclei and result in the formation of dendritic structure. Because at higher supersaturation, progressive nucleation would occur, and the diffusion of source materials to existing nuclei might be hindered.<sup>29</sup> Thus, the postgrowth of those existing nuclei would be restrained to allow their growth to larger particles through oriented attachment, and a larger size distribution could be envisioned. As above, the possible formation mechanism of the as-synthesized CdSe dendrites from nanospheres through oriented attachment is shown in Scheme 1.

### Conclusions

In this paper, we reported our recent efforts on the synthesis of CdSe with nanospheres and dendrites morphologies on a large scale using ionic liquid-assisted process. A Se-containing ionic

liquid [BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)] was used as a new Se precursor to purposely prepare CdSe nanocrystals. We found that the sizes and morphologies of the crystals depended on the concentration of the ionic liquid. The as-prepared CdSe nanospheres with good dispersity are relatively uniform with an average diameter of about 15 nm with low concentration of [BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)]. It is believed that the CdSe dendrites are obtained by self-assembly form nanospheres with high concentration of [BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)] under the driving force of oriented attachment. It would be expected that [BMIm][SeO<sub>2</sub>(OCH<sub>3</sub>)] could be used to prepare other nanoscale metal selenides with special morphologies and improved properties on a large scale.

## Acknowledgements

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## Notes and references

- 1 C. Burda, X. Chen, R. Narayanan and M. A. El-Sayed, *Chem. Rev.*, 2005, **105**, 1025.
- 2 X. Peng, L. Manna, W. Yang, J. Wickham, E. Scher, A. Kadavanich and A. P. Alivisatos, *Nature*, 2000, **404**, 59.
- 3 L. Manna, E. C. Scher and A. P. Alivisatos, *J. Am. Chem. Soc.*, 2000, **122**, 12700.
- 4 F. Shieh, A. E. Saunders and B. A. Korgel, *J. Phys. Chem. B*, 2005, **109**, 8538.
- 5 D. J. Norris, A. L. Efros and S. C. Erwin, *Science*, 2008, **319**, 1776.
- 6 X. Wang, X. Ren, K. Kahen, M. A. Hahn, M. Rajeswaran, S. Maccagnano-Zacher, J. Silcox, G. E. Cragg, A. L. Efros and T. D. Krauss, *Nature*, 2009, **459**, 686.
- 7 P. Naha'lkova, D. Sprinzl, P. Maly', P. Nemecek, V. N. Gladilin and J. T. Devreese, *Phys. Rev. B*, 2007, **75**, 113306.
- 8 (a) G. Riveros, J. Vasquez, H. Gomez, T. Makarova, D. Silva, R. E. Marotti and E. A. Dalchiele, *Appl. Phys. A: Mater. Sci. Process.*, 2008, **90**, 423; (b) L. K. Teh, V. Furin, A. Martucci, M. Guglielmi, C. C. Wong and F. Romanato, *Thin Solid Films*, 2007, **515**, 5787; (c) N. Shpaisman, U. Givan and F. Patolsky, *ACS Nano*, 2010, **4**, 1901.
- 9 J. D. Doll, G. Pilania, R. Ramprasad and F. Papadimitrakopoulos, *Nano Lett.*, 2010, **10**, 680.
- 10 W. T. Yao, S. H. Yu, S. J. Liu, J. P. Chen, X. M. Liu and F. Q. Li, *J. Phys. Chem. B*, 2006, **110**, 11704.
- 11 (a) Z. F. Feng, Q. B. Zhang, L. L. Lin, H. H. Guo, J. Z. Zhou and Z. H. Lin, *Chem. Mater.*, 2010, **22**, 2705; (b) N. Fu, Z. Li, A. Myalitsin, M. Scolari, R. T. Weitz, M. Burghard and A. Mews, *Small*, 2010, **6**, 376; (c) L. F. Xi and Y. M. Lam, *Chem. Mater.*, 2009, **21**, 3710.
- 12 (a) H. Zhang, X. Quan, S. Chen, H. T. Yu and N. Ma, *Chem. Mater.*, 2009, **21**, 3090; (b) E. E. Foos, J. Wilkinson, A. J. Mäkinen, N. J. Watkins, Z. H. Kafafi and J. P. Long, *Chem. Mater.*, 2006, **18**, 2886.
- 13 (a) J. Dupont, G. S. Fonseca, A. P. Umpierre, P. F. P. Fichtner and S. R. Teixeira, *J. Am. Chem. Soc.*, 2002, **124**, 4228; (b) F. Endres, M. Bukowski, R. Hempelmann and H. Natter, *Angew. Chem., Int. Ed.*, 2003, **42**, 3428; (c) D. P. Liu, G. D. Li, Y. Su and J. S. Chen, *Angew. Chem., Int. Ed.*, 2006, **45**, 7370; (d) E. R. Cooper, C. D. Andrews, P. S. Wheatley, P. B. Webb, P. Wormald and R. E. Morris, *Nature*, 2004, **430**, 1012; (e) L. Wang, Y. Xu, Y. Wei, J. Duan, A. Chen, B. Wang, H. Ma, Z. Tian and L. Lin, *J. Am. Chem. Soc.*, 2006, **128**, 7432; (f) B. G. Trewyn, C. M. Whitman and V. S. Y. Lin, *Nano Lett.*, 2004, **4**, 2139; (g) S. W. Cao and Y. J. Zhu, *Acta Mater.*, 2009, **57**, 2154.
- 14 (a) K. R. Seddon, *Nat. Mater.*, 2003, **2**, 363; (b) T. Welton, *Chem. Rev.*, 1999, **99**, 2071; (c) D. Adam, *Nature*, 2000, **407**, 938.
- 15 (a) M. Antonietti, D. Kuang, B. Smarsly and Y. Zhou, *Angew. Chem., Int. Ed.*, 2004, **43**, 4988; (b) K. Fukumoto, M. Yoshizawa and H. Ohno, *J. Am. Chem. Soc.*, 2005, **127**, 2398; (c) Y. Jiang, Y. J. Zhu and G. F. Cheng, *Cryst. Growth Des.*, 2006, **6**, 2174; (d) W. Dobbs, J. M. Suisse, L. Douce and R. Welter, *Angew. Chem.*, 2006, **118**, 4285; (e) Z. Li, A. Friedrich and A. Taubert, *J. Mater. Chem.*, 2008, **18**, 1008; (f) D. M. Djokic, W. B. Stern and A. Taubert, *Cryst. Growth Des.*, 2008, **8**, 330; (g) H. G. Zhu, J. F. Huang, Z. W. Pan and S. Dai, *Chem. Mater.*, 2006, **18**, 4473; (h) E. R. Parnham and R. E. Morris, *J. Am. Chem. Soc.*, 2006, **128**, 2204.
- 16 (a) Z. Ma, J. H. Yu and S. Dai, *Adv. Mater.*, 2009, **21**, 1; (b) M. Green, P. Rahmana and D. Smyth-Boyle, *Chem. Commun.*, 2007, 574; (c) A. Taubert and Z. Li, *Dalton Trans.*, 2007, 723.
- 17 W. J. Zheng, X. D. Liu, Z. Y. Yan and L. J. Zhu, *ACS Nano*, 2009, **3**, 115.
- 18 J. B. Lian, X. C. Duan, J. M. Ma, P. Peng, T. I. Kim and W. J. Zheng, *ACS Nano*, 2009, **3**, 3749.
- 19 L. Wang, L. X. Chang, B. Zhao, Z. Y. Yuan, G. S. Shao and W. J. Zheng, *Inorg. Chem.*, 2008, **47**, 1443.
- 20 T. I. Kim, J. B. Lian, J. M. Ma, X. C. Duan and W. J. Zheng, *Cryst. Growth Des.*, 2010, **10**, 2928.
- 21 X. D. Liu, J. M. Ma, P. Peng and W. J. Zheng, *Langmuir*, 2010, **26**, 9968.
- 22 (a) C. B. Murray, D. J. Norris and M. G. Bawendi, *J. Am. Chem. Soc.*, 1993, **115**, 8706; (b) Y. A. Yang, H. Wu, K. R. Williams and Y. C. Cao, *Angew. Chem., Int. Ed.*, 2005, **44**, 6712; (c) O. Chen, X. Chen, Y. Yang, J. Lynch, H. Wu, J. Zhuang and Y. C. Cao, *Angew. Chem.*, 2008, **120**, 8766; (d) Q. Peng, Y. Dong, Z. Deng and Y. Li, *Inorg. Chem.*, 2002, **41**, 5249; (e) M. Chen and L. Gao, *J. Am. Ceram. Soc.*, 2005, **88**, 1643; (f) Z. Zhuang, Q. Peng, J. Zhuang, X. Wang and Y. Li, *Chem.-Eur. J.*, 2006, **12**, 211; (g) S. Xiong, B. Xi, C. Wang, G. Xi, X. Liu and Y. Qian, *Chem.-Eur. J.*, 2007, **13**, 7926.
- 23 Q. Zhang, S. J. Liu and S. H. Yu, *J. Mater. Chem.*, 2009, **19**, 191.
- 24 (a) S. K. Kim, J. K. Kim, H. Lee, K. Y. Park, C. Lee and C. S. Chin, *Angew. Chem., Int. Ed.*, 2002, **41**, 4300; (b) S. K. Kim, J. K. Kim, H. Lee, K. Y. Park and C. S. Chin, *J. Catal.*, 1998, **176**, 264.
- 25 (a) N. F. Mott, *Nature*, 1950, **165**, 295; (b) B. L. Cushing, V. L. Kolesnichenko and C. J. O'Connor, *Chem. Rev.*, 2004, **104**, 3893.
- 26 (a) G. Ren, Z. Lin, B. Gilbert, J. Zhang, F. Huang and J. Liang, *Chem. Mater.*, 2008, **20**, 2438; (b) A. Taubert, G. Glasser and D. Palms, *Langmuir*, 2002, **18**, 4488.
- 27 (a) Y. Zhou, J. H. Schattka and M. Antonietti, *Nano Lett.*, 2004, **4**, 477; (b) Y. Zhou and M. Antonietti, *J. Am. Chem. Soc.*, 2003, **125**, 14960; (c) A. Taubert, *Angew. Chem., Int. Ed.*, 2004, **43**, 5380; (d) T. Nakashima and N. Kimizuka, *J. Am. Chem. Soc.*, 2003, **125**, 6386; (e) H. Kaper, F. Endres, I. Djerdj, M. Antonietti, B. M. Smarsly, J. Maier and Y. S. Hu, *Small*, 2007, **3**, 1753.
- 28 (a) P. Migowski and Dupont, *Chem.-Eur. J.*, 2007, **13**, 32; (b) Ozkar and R. G. Finke, *J. Am. Chem. Soc.*, 2002, **124**, 5796; (c) E. J. W. Verwey, and J. T. G. Overbeek, *Theory of the Stability of Lyophobic Colloids*, Dover Publications, New York, 1999.
- 29 (a) Z. P. Peng, Y. S. Jiang, Y. H. Song, C. Wang and H. J. Zhang, *Chem. Mater.*, 2008, **20**, 3153; (b) Z. A. Peng and X. G. Peng, *J. Am. Chem. Soc.*, 2001, **123**, 1389; (c) X. G. Peng, *Adv. Mater.*, 2003, **15**, 459; (d) Y. H. Zhang, L. Guo, P. G. Yin, R. Zhang, Q. Zhang and S. H. Yang, *Chem.-Eur. J.*, 2007, **13**, 2903.