

Small Molecule-Controlled Spontaneous Growth of Rose-Like Se Crystals at Room Temperature

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The spontaneous growth of rose-like Se crystals in aqueous solutions at room temperature is reported. The formation of rose-like Se crystals is based on the oxidation of Na₂Se in the presence of thioglycerol solution at pH = 11 in a dark ambient atmosphere. In alkaline solutions, the growth evolution of rose-like Se crystals with aging time was followed by scanning electron microscopy (SEM), and an interesting formation process from initial Se monomers to amorphous Se (a-Se) spheres, and to the final rose-like complex structures of Se crystals was observed. Seven kinds of small molecules with different structures, including 1-thioglycerol (TG), mercaptamine (MA), L-cysteine (L-cys), 3-mercaptopropionic acid (MPA), thioglycolic acid (TGA), glycerol (GLY), and L-serine (L-ser), were used to manipulate the growth of Se crys-

tals. The experimental results show that the structures of the small molecules play a key role in the growth of the Se crystals. The presence of thiols in the structure of the small molecules is favorable for the formation of the aggregates of Se crystals, and other termini, such as -NH₂, -OH, or -COO⁻, will determine whether the aggregates of Se crystals are made up of Se slices or Se prisms. These observations suggest that the ligand molecules have a crucial effect on the nucleation, monomers, and growth of nanocrystals. The selection of ligands can be extended to other important materials for further preparation of nanocrystals with desired shapes.

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Introduction

The preparation of shape-controlled inorganic nanocrystals and their assembly into complex patterns have attracted considerable attention because the geometrical uniqueness of nanocrystals may translate into similarly unique properties.^[1] Among several growth techniques, the solution-phase chemical methods have distinct advantages in the cost, throughput, and potential for large-scale production. However, the difficulty of chemical reactions in isotropic solution is how to effectively control the rates of nucleation and growth of nanocrystals directed toward a controlled shape.^[2] The solution-phase chemical synthesis of shape-controlled nanocrystals can normally be accomplished through the design of special experimental conditions, such as using organic solvents at high temperature,^[3] using template molecules,^[4] and with ultrasonic, microwave, or heating^[5] in the aqueous phase. Under these conditions, the intrinsic anisotropic properties of nanocrystals generally play a key role in the growth of the desired shapes,^[6] for example nanocrystals with one-dimensional (1D) and branched

structures (e.g. bipods and tripods). The chemical nature and structure of the ligand molecules have been also considered as important factors for manipulating the growth of nanocrystals.^[7] To date, various shapes of semiconductor nanocrystals including wires,^[8] rods,^[9] and multipods^[10] have been obtained by controlling the rate of growth of different faces of crystals in solution. However, under ambient conditions of room temperature, can one obtain the desired shape of nanocrystals only by depending on spontaneous growth and control through small molecules?

Selenium has promising photoelectrical and semiconductor properties and it has been successfully used in electrical rectifiers, xerography, and solar cells.^[11] Nano- and micro-scale Se crystals with highly complex structures may be desired functional materials with new or improved photoconductivity, nonlinear optical response, thermoelectric or piezoelectric responses, and catalytic activity compared to bulk selenium. Recently, a great number of solution-based chemical synthetic strategies have been reported for the preparation of Se 1-D nanostructures, such as nanowires,^[12] nanorods,^[13] nanotubes,^[14] and nanobelts.^[15] The successful synthesis of these selenium nanomaterials was attributed to the unique helical conformation of the selenium crystal structure which provided a natural template to guide the growth of the one-dimensional shape.^[11] In the above cases, most of the previous strategies were carried out with the assistance of structure-directing reagents or externally added forces such as ultrasonic, microwave, and heat-

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ing.^[12–15] However, room-temperature spontaneous growth of Se crystals has been insufficiently studied and small molecule-controlled spontaneous growth of Se crystals into unusual shapes in aqueous solution at room temperature has not yet been reported.

Herein, we present the first example of Se crystals with rose- and orchid-like shapes synthesized in aqueous solutions at room temperature. Since trigonal Se (t-Se) has a strong tendency to grow into one-dimensional structures due to its unique natural template property which defines and guides growth along the *c*-axis of the hexagonal lattice,^[11] the formation of Se crystals with rose- and orchid-like shapes in aqueous solution is quite unexpected. The growth evolution of rose-like Se crystals with aging time was followed by scanning electron microscopy (SEM), and an interesting formation process for the rose-like Se crystals was observed. To explore the formation mechanism of Se roses, seven kinds of small molecules with different structures were used to manipulate the spontaneous growth of these Se crystals, including 1-thioglycerol (TG), mercaptamine (MA), L-cysteine (L-cys), 3-mercaptopropionic acid (MPA), thioglycolic acid (TGA), glycerol (GLY), and L-serine (L-ser). We discuss the role of these small molecules during the formation of Se crystals with unusual shapes.

Results and Discussion

The Spontaneous Growth of Rose-Like Se Crystals

In a typical synthesis of rose-like Se crystals, NaOH solution containing thioglycerol was used to absorb H₂Se gas (pH = 11). H₂Se gas was generated by the reaction of the ethanol solution of NaHSe with dilute H₂SO₄ added (see the Experimental Section). The concentrations of Se atoms and thioglycerol in solution are 2 mM and 6 mM, respectively. The obtained solution of Na₂Se was then stored in the dark at room temperature for ca. 10 h. During storage, the solution would change gradually from nearly colorless to brownish-red within ca. 1 h and at the same time the solution became gradually slightly turbid. Subsequently, the color of the solution became pale, and ca. 3 h later, the precipitates started to appear at the bottom of the bottle. After ca. 10 h storage, a large quantity of dark precipitates of Se was obtained. At this time, the upper solution turned colorless and clear. Then, the dark Se precipitates were directly transferred onto a Si substrate to assess their morphology and composition by means of SEM. The SEM images of the dark Se precipitate are shown in Figure 1. The SEM images (Figure 1, A–D) show mainly an interesting rose-like Se crystal morphology. The typical size of the final rose-like complex structures of Se crystals is ca. 10–15 μm in diameter, and the typical thickness of leaves is ca. 400 nm. The energy-dispersed X-ray spectrum (EDX) confirms that the products are highly pure Se (Figure 1, E). The XRD pattern in Figure 2 shows that the obtained products were well-crystallized hexagonal Se (JCPDS: 06-0362). All the diffraction peaks can be readily indexed to the hexagonal Se.

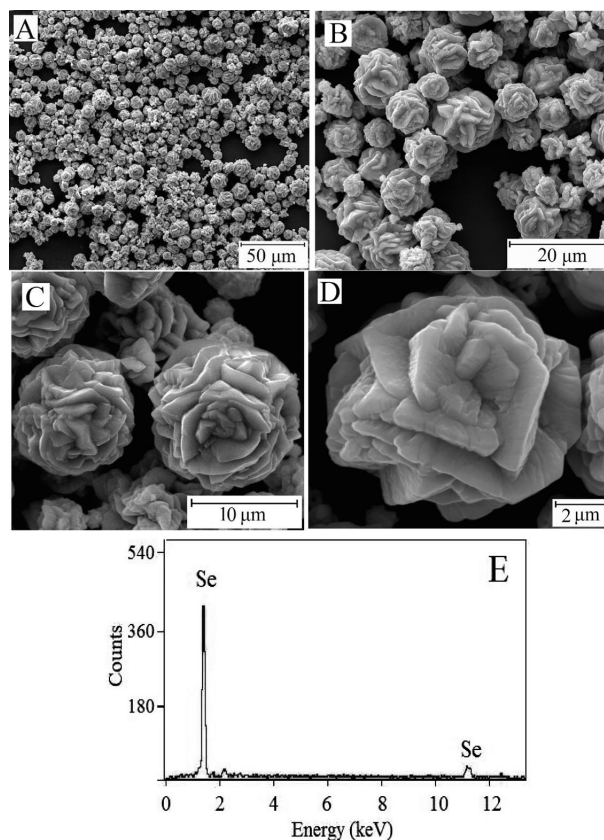


Figure 1. A–D: SEM images of rose-like microstructured Se crystals obtained in the presence of TG (6 mM) at room temperature. E: EDX spectrum of rose-like Se crystals.

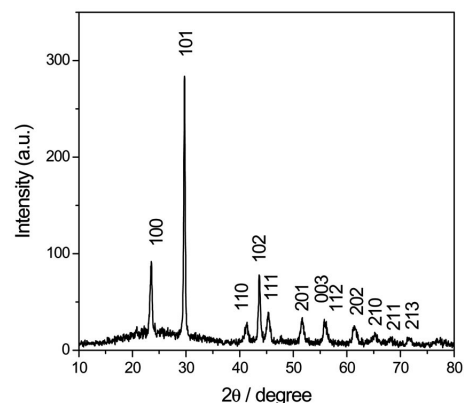


Figure 2. A typical X-ray diffraction pattern of an as-prepared rose-like complex structure.

The Evolution of Rose-Like Se Crystals with Aging Time

As noted above, the rose-like shape of the Se crystals obtained is very unique and unexpected. We used SEM to follow further the growth processes of the Se complex structure. Five samples were collected at different intermediate reaction stages. Their SEM images are shown in Figure 3, which presents the time-dependent shape evolution of the rose-like complex structures. In the early stages of aging (0–40 min), Se²⁻ anions are oxidized to Se monomers by

dissolved oxygen (the standard redox potentials for Se^{2-}/Se and O_2/OH^- pairs are -0.924 V and 0.401 V , respectively^[16]). As presented in the SEM images in parts A and B of Figure 3, a portion of the Se monomers aggregate together into amorphous Se (a-Se) spheres, whereas another portion might crystallize spontaneously into bunches of trigonal Se slices due to its 1-D anisotropic growth nature. At this time, the dispersion is a complicated mixture of amorphous spheres and bunches of Se slices. It was also observed that the initially nearly colorless solution turns brownish-red and becomes slightly turbid. When aging proceeded to 1 h, the formed bunches of Se slices start to twist spontaneously and form relatively incompact slice-twisting Se (Figure 3, C and D) with an average diameter of ca. $4\text{ }\mu\text{m}$. These twist structures gradually become more compact as the twisting proceeds. Subsequently (after about 3 h), as shown in Figure 3 (E and F), the newly formed slices are rice-leaf like (their typical size is ca. $2\text{--}3\text{ }\mu\text{m}$ in length, ca. 200 nm in width, and ca. 50 nm in thickness),

and will twist continuously around the surfaces of the as-formed twisted Se and form a bud-like shape. At this stage of growth, a small quantity of precipitates would appear gradually at the bottom of the bottle. Here, it should be mentioned that in the present synthetic system ($\text{pH} \geq 8.5$), amorphous selenium colloids could transform spontaneously into trigonal Se crystals because a-Se has a higher free energy ($5\text{--}10\text{ kJ/mol}$) relative to trigonal selenium.^[11] As observed in the SEM images in Figure 3 (A–F), the quantity of amorphous Se spheres decreases obviously with the growth of rose-like t-Se crystals. With the aging time increased to 5 h, the rose-like morphology of Se can be seen, and the surfaces of the rose-like Se have a large amount of Se silks (Figure 3, G and H) with the average diameter of the rose-like Se increasing to ca. $12\text{ }\mu\text{m}$. When aging time is close to 7 h, Se rose-like complex structures have formed by and large (Figure 3, I and J), and only a small amount of Se silks exists on the surfaces. The average diameter of the rose-like Se is now ca. $15\text{ }\mu\text{m}$. At this time, the quantity of precipitates that have formed at the bottom of the bottle increases greatly. As a result, the color of the upper solution turns pale obviously. Finally, after ca. 10 h storage, the upper solution becomes colorless and clear, and a large quantity of dark precipitates is obtained at the bottom of the bottle. As shown in the SEM images in Figure 1 (A–D), the dark precipitates obtained finally are uniform rose-like Se crystals, and their surfaces are relatively smooth. The size of the selenium microstructures has reached a plateau in growth due to the depletion of the Se component in solution.

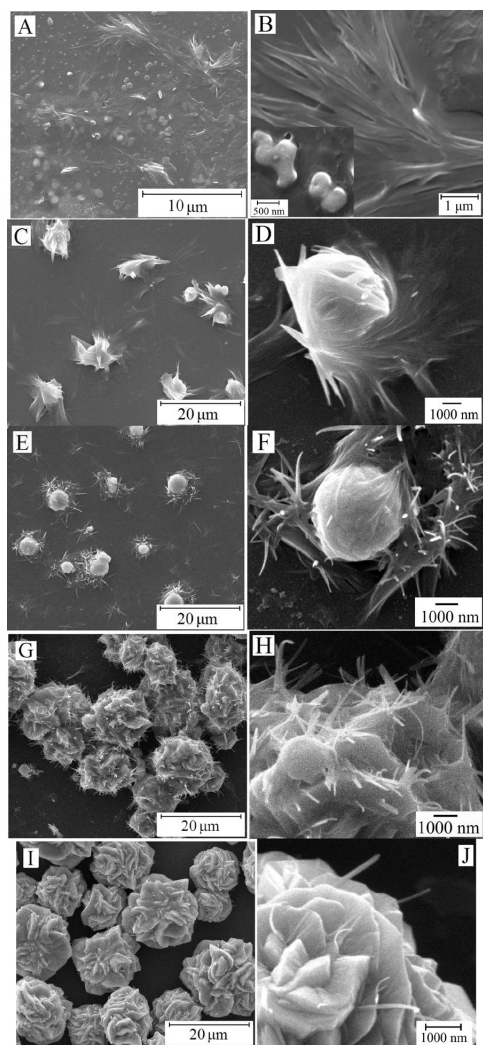


Figure 3. SEM images of the evolution of a rose-like Se crystal with aging time in the presence of TG (6 mM) at room temperature; A,B: 0.5 h , C,D: 1 h , E,F: 3 h , G,H: 5 h , I, J: 7 h . Inset of panel B: magnified SEM image of amorphous Se particles.

The Influence of Small Molecules on the Morphology of Se Crystals

The interesting rose-like shape of the Se crystals inspired us to consider factors that would effect the growth of the Se crystals. Therefore, we examined further the oxidation of Na_2Se in the absence of any small molecules in the alkaline solution at $\text{pH} = 11$. As shown in the SEM image in Figure 4 (A), when the NaOH solution containing no organic small molecules was used as the absorption solution for the H_2Se gas (see the Exp. Sect.), the obtained products were Se rods whose typical size was ca. $1\text{--}3\text{ }\mu\text{m}$ in length and ca. $1\text{ }\mu\text{m}$ in diameter. These Se products are very different in morphology from the rose-like Se crystals obtained in the

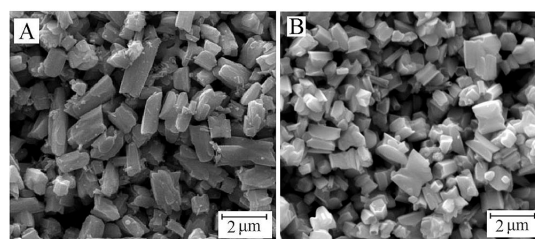


Figure 4. The typical SEM images of Se products obtained by the oxidation of Na_2Se in the absence of any organic small molecules (A) and in the presence of glycerol (6 mM) (B).

presence of thioglycerol. This observation suggests that TG plays an important role in controlling the spontaneous growth of the Se complex structures. In order to further understand the role of TG, another small molecule, glycerol was used as a substitute for TG because the molecular structure of glycerol is similar to that of TG except for the –SH terminus. We found that the morphologies (Figure 4, B) of the products obtained in the presence of GLY are very similar to those obtained by the oxidation of Na_2Se in the absence of any organic small molecules (Figure 4, A), and no rose-like Se crystals were observed. These experimental results indicate strongly that the –SH terminus in the TG molecule has an important role in the formation of rose-like Se complex structures.

The results mentioned above encouraged us to further investigate the role of small molecules in the growth of Se crystals. Four thiols (MA, $\text{HSCH}_2\text{CH}_2\text{NH}_2$; L-cys, $\text{HSCH}_2\text{CH}(\text{NH}_2)\text{COOH}$; MPA, $\text{HSCH}_2\text{CH}_2\text{COOH}$; and TGA, HSCH_2COOH) with various functional termini were used. Parts A and B of Figure 5 show that when the NaOH solution used for the absorption of the H_2Se gas contains MA, the major products are orchid-like Se crystals, besides a portion of rose-like Se crystals. The typical diameter of orchid-like Se crystals is ca. 7–10 μm and the typical thickness of their leaves is ca. 500 nm. However, when L-cysteine was used, the product was aggregates of Se prisms (Figure 5, C and D). The typical diameter of the aggregates of Se prisms is ca. 5–10 μm ; the typical size of the Se prisms is ca. 2–4 μm in length and ca. 2 μm in diameter. And if MPA and TGA were used, respectively, the products (Figure 5, E and F) are similar to those obtained in the presence of L-cysteine; only the diameter of the aggregates of Se prisms is relatively small (their typical diameter is ca. 3 μm). XRD patterns of Se products obtained in the presence of MA, L-cys, or MPA are shown in Figure 6, which indicates clearly that these as-prepared products are all pure single-crystalline trigonal Se. All the diffraction peaks in Figure 6 can be readily indexed to the hexagonal Se. Furthermore, when L-cysteine was substituted by L-serine—the molecular structures of which are similar except for a –SH terminus—the morphology of the products obtained was also Se rods (not shown), similar to that (Figure 4, A) obtained by the oxidation of Na_2Se in the absence of any organic small molecules, and no aggregates of Se prisms were observed, which confirms further the role of the –SH terminus.

These experimental results show that in the present synthetic system, the structural differences of small molecules have a vital effect on the growth of Se crystals. In the absence of any organic small molecules, the products obtained from the oxidation of Na_2Se are Se rods, which indicates that the growth process of Se crystals is spontaneously proceeding in aqueous solution at $\text{pH} = 11$. In the presence of small molecules, the spontaneous growth process of Se crystals was tuned selectively. Molecular structures containing the –SH terminus promote the aggregation of Se crystals; those including –SH and – NH_2 or –OH termini favor the formation of flower-type complex structures, that is to

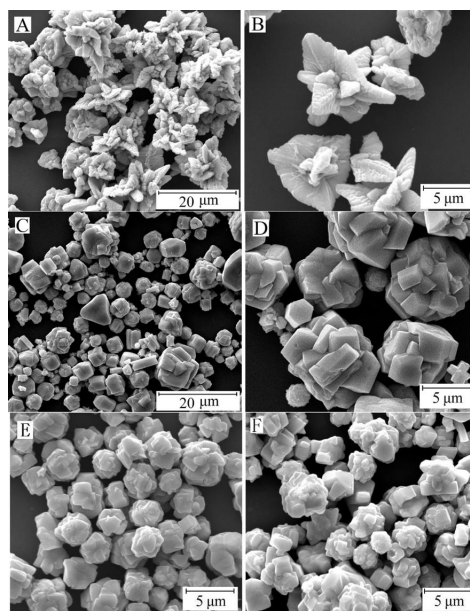


Figure 5. The typical SEM images of Se products obtained in the presence of different small molecules (6 mM); A,B: MA, C, D: L-cys, E: MPA, F: TGA.

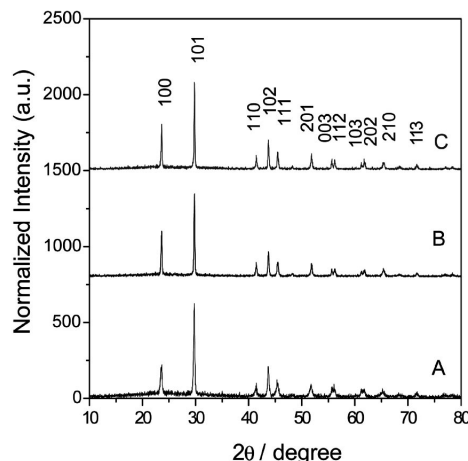


Figure 6. Normalized XRD patterns of Se products obtained by the oxidation of Na_2Se in the presence of various small molecules (6 mM); A: MA, B: L-cys, C: MPA, according to the intensity of the (110) peak.

say, the aggregates of Se crystals are made up of Se slices; whereas thiols containing the – COO^- terminus control the formation of aggregates of Se crystals made up of Se prisms.

Conclusions

In summary, Se crystals with complex structures such as rose- and orchid-like shapes, and prism aggregates have been successfully synthesized in aqueous solutions at $\text{pH} 11$ at room temperature. The interesting growth evolution of a rose-like t-Se crystal with aging times was observed. In addition, seven kinds of small molecules, including five

kinds of thiols, were used to explore the formation mechanism of Se rose-like complex structures. According to these experimental observations, several points should be addressed. (1) The growth process of Se crystals spontaneously proceeds under natural conditions of room temperature. (2) The small molecules might selectively manipulate the spontaneous nucleation and growth process of Se crystals at room temperature. It can be further concluded from the study that the role of small molecules of thiols in the growth of Se crystals is crucial in that: (i) the –SH terminus dominates the formation of the aggregates of Se crystals; (ii) other termini, such as –NH₂, –OH, or –COO[–], will determine whether the aggregates of Se crystals are made up of Se slices or Se prisms. The formation mechanism of these Se crystals may help us understand ligand effects on nucleation, monomers, and growth of nanocrystals. The selection of ligands can be extended to other important materials for further preparation of nanocrystals with desired shape.

Experimental Section

Chemicals: Selenium powder, sodium borohydride (99%), absolute ethanol, thioglycerol (90%), mercaptamine hydrochloride (98%), L-cysteine hydrochloride monohydrate (99%), mercaptopropionic acid (99%), thioglycolic acid (90+%), glycerol (99+%), L-serine (98+%), sodium hydroxide (96+%), sulfuric acid are commercially available products and were used as received. Redistilled water was used in all preparations.

Preparation of Se Crystals: The synthesis of Se crystals was carried out following similar procedures to those developed in our recent report.^[17] Firstly, under N₂, Se powder (8 mg) was reduced by excessive NaBH₄ (8 mg) in ethanol at 40 °C, to form a colorless solution of NaHSe. Subsequently, whilst stirring, H₂Se gas generated by the reaction of the ethanol solution of NaHSe with added dilute H₂SO₄ was passed to NaOH solution (pH 11) in the presence of various small molecules. Thus, the alkaline solution of Na₂Se containing the small molecules was prepared (the total volume of the solution was 50 mL). Finally, the obtained solution was stored further in the dark under ambient conditions at room temperature. After incubating for about 10 h, a large quantity of dark precipitates of Se would appear at the bottom of the beaker. The dark precipitates were collected by centrifugation, washed several times with distilled water to completely remove the adhered small organic molecules, and then allowed to dry in air at room temperature. In this study, the seven kinds of small molecules used include TG, MA, L-cys, MPA, TGA, GLY, and L-ser. The concentrations of Se atoms and organic small molecules in solution are 2 mM and 6 mM, respectively.

Characterization: The scanning electron microscope images and energy dispersive X-ray spectra were obtained with a Philips FEI Quanta 200 electron microscope. The specimens for SEM measurements were prepared by depositing a drop of the dilute aqueous suspension of the sample on a Si substrate, and drying in air at room temperature. Transmission electron microscopy (TEM) images were obtained with a Philips FEI Tecnai G² 20 S-TWIN or a JEOL JEM-200CX TEM operating at 200 kV. Powder XRD patterns of the products were recorded with a Philips X'Pert X-ray diffractometer (Cu-K_α radiation, λ = 0.15419 nm).

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- [1] a) Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H. Yan, *Adv. Mater.* **2003**, *15*, 353–389; b) A. P. Alivisatos, *Science* **1996**, *271*, 933–937; c) X. Duan, Y. Huang, Y. Cui, J. Wang, C. M. Lieber, *Nature* **2001**, *409*, 66–69; d) S. Frank, P. Poncharal, Z. L. Wang, W. A. de Heer, *Science* **1998**, *280*, 1744–1746.
- [2] a) Z. A. Peng, X. Peng, *J. Am. Chem. Soc.* **2001**, *123*, 1389–1395; b) C. J. Johnson, E. Dujardin, S. A. Davis, C. J. Murphy, S. Mann, *J. Mater. Chem.* **2002**, *12*, 1765–1770.
- [3] a) L. Manna, E. C. Scher, A. P. Alivisatos, *J. Am. Chem. Soc.* **2000**, *122*, 12700–12706; b) Y. Jun, J. Choi, J. Cheon, *Angew. Chem. Int. Ed.* **2006**, *45*, 3414–3439.
- [4] a) H. J. Niu, M. Y. Gao, *Angew. Chem. Int. Ed.* **2006**, *45*, 6462–6466; b) L. Zhang, N. Gaponik, J. Müller, U. Plate, H. Weller, G. Erker, H. Fuchs, A. L. Rogach, L. F. Chi, *Small* **2005**, *1*, 524–527.
- [5] a) V. V. Namboodiri, R. S. Varma, *Green Chem.* **2001**, *3*, 146–148; b) Y. Mastai, R. Polisky, Y. Koltypin, A. Gedanken, G. Hodes, *J. Am. Chem. Soc.* **1999**, *121*, 10047–10052; c) S. V. Ley, C. M. R. Low, *Ultrasound in Synthesis*, Springer-Verlag, New York, **1989**.
- [6] a) S. M. Lee, S. N. Cho, J. Cheon, *Adv. Mater.* **2003**, *15*, 441–444; b) X. G. Peng, *Adv. Mater.* **2003**, *15*, 459–463; c) S. Kumar, T. Nann, *Small* **2006**, *2*, 316–329.
- [7] a) W. W. Yu, Y. A. Wang, X. G. Peng, *Chem. Mater.* **2003**, *15*, 4300–4308; b) H. Zhang, D. Y. Wang, B. Yang, H. Möhwald, *J. Am. Chem. Soc.* **2006**, *128*, 10171–10180.
- [8] a) N. Pradhan, H. Xu, X. Peng, *Nano Lett.* **2006**, *6*, 720–724; b) F. Shieh, A. E. Saunders, B. A. Korgel, *J. Phys. Chem. B* **2005**, *109*, 8538–8542.
- [9] a) X. G. Peng, L. Manna, W. D. Yang, J. Wickham, E. Scher, A. Kadavanich, A. P. Alivisatos, *Nature* **2000**, *404*, 59–61; b) D. V. Talapin, R. Koeppel, S. Götzinger, A. Kornowski, J. M. Lupton, A. L. Rogach, O. Benson, J. Feldmann, H. Weller, *Nano Lett.* **2001**, *3*, 1677–1681; c) Z. A. Peng, X. Peng, *J. Am. Chem. Soc.* **2002**, *124*, 3343–3353.
- [10] a) L. Manna, D. Milliron, A. Meisel, E. C. Scher, A. P. Alivisatos, *Nat. Mater.* **2003**, *2*, 382–385; b) Y. W. Jun, S. M. Lee, N. J. Kang, J. Cheon, *J. Am. Chem. Soc.* **2001**, *123*, 5150–5151; c) L. Carbone, S. Kudera, E. Carlino, W. J. Parak, C. Giannini, R. Cingolani, L. Manna, *J. Am. Chem. Soc.* **2006**, *128*, 748–755; d) Y. Li, H. Zhong, R. Li, Y. Zhou, C. Yang, Y. Li, *Adv. Funct. Mater.* **2006**, *16*, 1705–1716.
- [11] R. A. Zingaro, W. C. Cooper (Eds.), *Selenium*, Van Nostrand Reinhold, New York, **1974**.
- [12] a) B. Gates, B. Mayers, B. Cattle, Y. Xia, *Adv. Funct. Mater.* **2002**, *12*, 219–227; b) B. Gates, B. Mayers, A. Grossman, Y. Xia, *Adv. Mater.* **2002**, *14*, 1749–1752; c) Z. Tang, Y. Wang, K. Sun, N. A. Kotov, *Adv. Mater.* **2005**, *17*, 358–363; d) Q. Li, V. W. W. Yam, *Chem. Commun.* **2006**, 1006–1008; e) C. H. An, K. B. Tang, X. M. Liu, Y. T. Qian, *Eur. J. Inorg. Chem.* **2003**, 3250–3255.
- [13] a) J. M. Song, J. H. Zhu, S. H. Yu, *J. Phys. Chem. B* **2006**, *110*, 23790–23795; b) B. Zhang, W. Dai, X. C. Ye, F. Zuo, Y. Xie, *Angew. Chem. Int. Ed.* **2006**, *45*, 2571–2574.
- [14] a) Y. R. Ma, L. M. Qi, J. M. Ma, H. M. Cheng, *Adv. Mater.* **2004**, *16*, 1023–1026; b) J. Lu, Y. Xie, F. Xu, L. Zhu, *J. Mater. Chem.* **2002**, *12*, 2755–2761; c) S. Y. Zhang, Y. Liu, X. Ma, H. Y. Chen, *J. Phys. Chem. B* **2006**, *110*, 9041–9047; d) B. Zhang, W. Hou, X. Zhu, X. Ye, L. Fei, X. Liu, J. Yang, Y. Xie, *Small* **2007**, *3*, 101–105.

- [15] a) Y. R. Ma, L. M. Qi, W. Shen, J. M. Ma, *Langmuir* **2005**, *21*, 6161–6164; b) Q. Y. Lu, F. Gao, S. Komarneni, *Chem. Mater.* **2006**, *18*, 159–163; c) J. M. Song, Y. J. Zhan, A. W. Xu, S. H. Yu, *Langmuir* **2007**, *23*, 7321–7327.
- [16] D. R. Lide, *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, **2003**.
- [17] D. W. Deng, J. S. Yu, Y. Pan, *J. Colloid Interface Sci.* **2006**, *299*, 225–232.

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