

Hierarchical, Star-Shaped PbS Crystals Formed by a Simple Solution Route

Yurong Ma, Limin Qi,* Jiming Ma, and Humin Cheng

State Key Laboratory for Structural Chemistry of Stable and Unstable Species,
College of Chemistry, Peking University, Beijing 100871, China

Received September 22, 2003; Revised Manuscript Received October 29, 2003

ABSTRACT: Hierarchical eight-arm, star-shaped PbS single crystals have been successfully synthesized by the controlled release of sulfide ions from thioacetamide (TAA) at 80 °C in aqueous solutions of lead acetate and acetic acid. The unique star-shaped PbS crystals have eight symmetric arms along the $\langle 111 \rangle$ directions, each of which shows a trident-like, dendritic structure and consists of parallel PbS nanoleaflets. It has been revealed that the presence of acetate ions as well as appropriate pH and temperature are crucial for the formation of the unusual star-shaped PbS crystals. Moreover, other morphologies of PbS nanocrystals, such as nanorods, nanostrips, and nanosheets, have been obtained facilely at 40 °C by using similar synthetic procedures.

Introduction

The architectural control of nano- and microcrystals with well-defined shapes is an important goal of modern materials chemistry because of the importance of the shape and texture of materials in determining their widely varying properties.^{1–3} Specifically, many recent efforts have been devoted to the morphological control and spatial patterning of semiconductor nanocrystals of metal sulfides. Multi-armed CdS nanorod architectures were synthesized by surfactant-assisted routes,⁴ whereas CdS nanohelices were fabricated by templating supramolecular ribbons.⁵ ZnS nanosheets were synthesized from a layered molecular precursor,⁶ whereas ZnS nanobelts, nanocombs, and nanowindmills were produced using a thermal evaporation technique.⁷ Moreover, a unique pattern of radially aligned Ag₂S nanorods⁸ and a variety of assemblies of Cu₂S nanoparticles⁹ have been created directly by solution routes. However, the development of facile, mild, and effective methods for creating novel architectures or hierarchical structures based on semiconductor nanocrystals remains a key scientific challenge.

PbS is an attractive sulfide semiconductor with a narrow band gap energy of 0.41 eV and potential applications including near-IR communication and switches. The synthesis of PbS particles with a variety of morphologies has been achieved so far. For example, cubic-shaped PbS microcrystals and nanocrystals have been produced by decomposition of thioacetamide¹⁰ and a single source precursor,¹¹ respectively. Spherical PbS nanocrystals¹² have been obtained in random copolymer ionomers, whereas rodlike PbS nanocrystals¹³ have been produced using a combination of surfactant and polymer matrix as the template. PbS nanowires as well as nanosheets have been prepared by a polymer-assisted solvothermal method.^{14,15} Notably, unique star-shaped PbS nanocrystals with six symmetric horns along the $\langle 100 \rangle$ direction were recently synthesized from the thermal decomposition of a molecular precursor.¹⁶ Recently, novel PbS dendrites consisting of nanorods have

also been synthesized via hydrothermal or solvothermal process.¹⁷ Herein, we report a simple synthesis of well-defined, star-shaped PbS microcrystals with eight symmetric arms along the $\langle 111 \rangle$ directions, each of which shows a trident-like, dendritic structure and consists of parallel PbS nanoleaflets. To the best of our knowledge, the obtained hierarchical single-crystalline PbS crystals are unprecedented. Furthermore, other morphologies of PbS nanocrystals, such as nanorods, nanostrips, and nanosheets, were easily obtained under modified conditions by using similar synthetic procedures.

Experimental Section

The synthesis of PbS products was carried out by the thermal decomposition of thioacetamide (TAA) in aqueous solutions of lead acetate and acetic acid at suitable temperatures. In a typical synthesis of star-shaped PbS crystals, 0.2 mL of 0.5 M Pb(Ac)₂ was mixed with 4 mL of 0.1 M HAc at first. Then, 0.2 mL of 0.5 M TAA was added to the solution, followed by 5 min of ultrasonic stirring. The concentrations for HAc, Pb(Ac)₂, and TAA in the mixture are 0.091, 0.027, and 0.027 M, respectively. The mixture was kept at 80 °C for 5 h under static conditions, resulting in the precipitation of a black solid, which was recovered by centrifugation, washed with water, and dried in air. In the experiment, the reaction temperature as well as the concentrations for HAc, Pb(Ac)₂, and TAA were varied. Scanning electron microscopy (SEM) measurements were performed with an Amray 1910FE microscope. Transmission electron microscopy (TEM) investigations were conducted on a JEM-200CX microscope. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Dmax-2000 diffractometer with Cu K α radiation.

Results and Discussion

Well-defined, starlike PbS crystals (Figure 1a) were synthesized by a controlled release of sulfide ions from TAA at 80 °C in aqueous solutions of lead acetate and acetic acid. The XRD pattern of the starlike crystals (Figure 2a) shows sharp peaks corresponding to cubic PbS with an fcc rock-salt structure (JCPDS 5-592), suggesting that the “stars” are well-crystallized PbS crystals. The star-shaped crystals were viewed from different angles to show their hierarchical character

* To whom correspondence should be addressed. E-mail: liminqi@chem.pku.edu.cn.

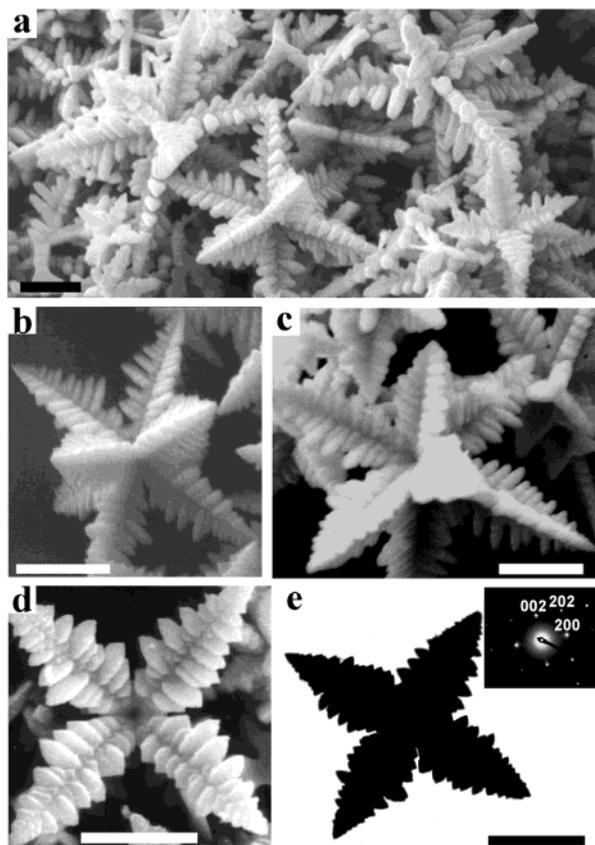


Figure 1. SEM (a–d) and TEM (e) images of star-shaped PbS crystals obtained at 80 °C in 0.1 M HAc solution. $[\text{Pb}(\text{Ac})_2] = [\text{TAA}] = 0.027 \text{ M}$. Inset shows electron diffraction pattern corresponding to the upper right corner. Scale bars = 1 μm .

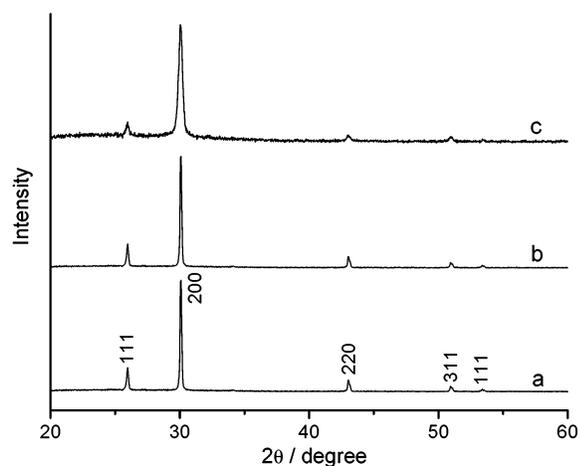


Figure 2. XRD patterns of PbS products obtained under different conditions: (a) 80 °C, $[\text{HAc}] = 0.1 \text{ M}$, $[\text{Pb}(\text{Ac})_2] = [\text{TAA}] = 0.027 \text{ M}$; (b) 40 °C, $[\text{HAc}] = 0.025 \text{ M}$, $[\text{Pb}(\text{Ac})_2] = 0.027 \text{ M}$, $[\text{TAA}] = 0.054 \text{ M}$; (c) 40 °C, $[\text{HAc}] = 0.025 \text{ M}$, $[\text{Pb}(\text{Ac})_2] = 0.054 \text{ M}$, $[\text{TAA}] = 0.027 \text{ M}$.

(Figure 1b–d). It can be seen that the stars have eight symmetric arms extending radially from the center with a distance between two neighboring corners of about 2 μm . An arm shows a trident-like, dendritic structure and consists of three groups of parallel PbS leaflets, each group of which is perpendicular to one of the three symmetric ridges constituting the trident-like arm. The thickness of the leaflets is about 80–100 nm, and their length (up to $\sim 400 \text{ nm}$) and width (up to $\sim 200 \text{ nm}$) vary

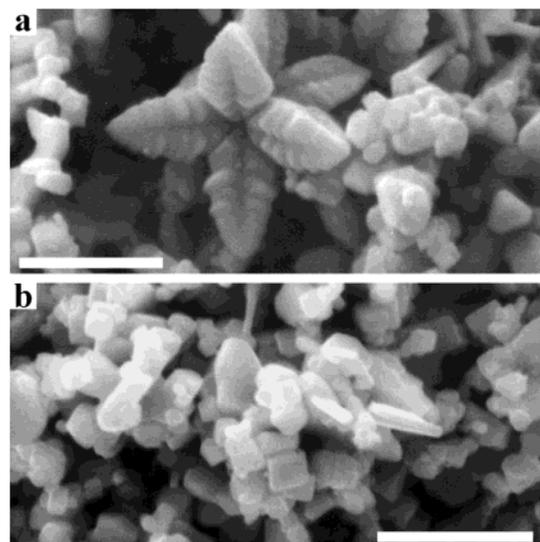


Figure 3. SEM images of PbS products obtained at 80 °C in 0.01 M HAc solution (a) and in the absence of HAc (b). $[\text{Pb}(\text{Ac})_2] = [\text{TAA}] = 0.027 \text{ M}$. Scale bars = 1 μm .

with changing position on the arm. Figure 1e presents a typical TEM image of a star-shaped PbS crystal with its four arms standing on the copper grid. The electron diffraction pattern corresponding to the upper right corner shows clearly the $[100]$ zone of cubic PbS. Moreover, the electron diffraction patterns corresponding to the other three corners as well as the central part are observed to be exactly the same, suggesting that the whole star is a PbS single crystal with its eight symmetric arms extending along the eight $\langle 111 \rangle$ directions of cubic PbS. It indicates that the three ridges constituting the trident-like arm along a $[111]$ direction are parallel to the $(1\bar{1}0)$, $(01\bar{1})$, and $(10\bar{1})$ planes, respectively, whereas the three groups of nanoleaflets are parallel to the $\{111\}$ planes, respectively. This hierarchical eight-arm, star-shaped morphology of PbS crystals is obviously different from the novel six-arm, star-shaped morphology of PbS crystals obtained from the thermal decomposition of a molecular precursor.¹⁶

The acetic ions played a key role in the formation of the unusual star-shaped PbS crystals. Cubic-shaped PbS crystals showing well-defined $\{100\}$ faces were the predominant product when there were no acetic ions present in the solution, i.e., $\text{Pb}(\text{NO}_3)_2$ was used instead of $\text{Pb}(\text{Ac})_2$ as the lead source and HNO_3 was used instead of HAc, which is consistent with the result obtained previously in the preparation of uniform cubic-shaped PbS crystals.¹⁰ The concentration of HAc also influences the morphology of the PbS crystals significantly. It was found that well-defined, star-shaped PbS crystals were obtained at HAc concentrations between 0.05–0.1 M, and irregular stars were produced at higher HAc concentration. When the HAc concentration was decreased to 0.01 M, the product was a mixture of irregular crystals and eight-arm, star-shaped crystals, which did not show well-separated leaflets (Figure 3a). It is noteworthy that the present star-shaped PbS crystals were somewhat similar to the eight-arm, star-shaped calcite crystals obtained in agarose gels where ion transport was controlled by the gel media,¹⁸ indicating that the controlled release of reactant ions (both S^{2-} and Pb^{2+} ions) could largely contribute to the formation

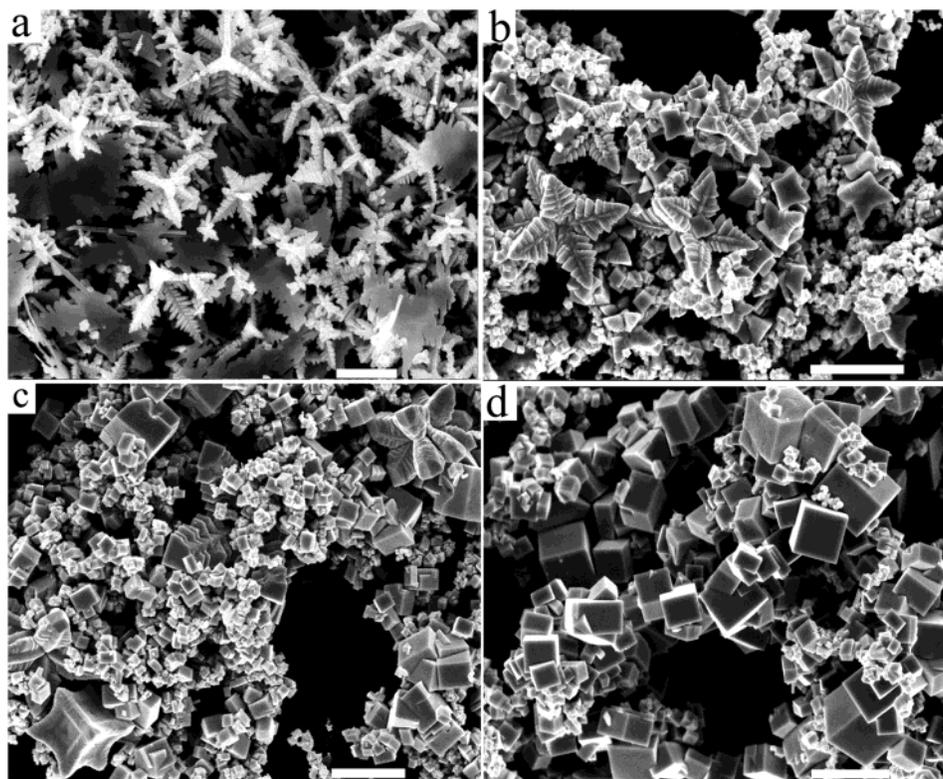


Figure 4. SEM images of PbS crystals obtained at 80 °C in 0.1 M HAc solution at adjusted pH values: (a) pH = 4.5, (b) pH = 2.4, (c) pH = 1.9, and (d) pH = 1.7. Scale bars: (a) 2 μm , (b–d) 5 μm .

of the highly symmetric star-shaped PbS crystals. Only irregular PbS crystals about 100–200 nm were produced in the absence of HAc (Figure 3b). Hence, an appropriate HAc or Ac^- ions concentration is crucial for the formation of the hierarchical star-shaped PbS crystals. It is known that lead acetate is a rather weak electrolyte with a low degree of dissociation and the Ac^- ions can coordinate with the Pb^{2+} ions to form various complexes such as PbAc^+ , PbAc_2 , and PbAc_3^- in aqueous solution. The formation of the complexes between the Ac^- ions and the Pb^{2+} ions may lead to controlled release of the Pb^{2+} ions as well as controlled crystallization of PbS at the elevated temperature (80 °C). Therefore, it is supposed that the Ac^- ions acted as a shape-controlling ligand in the formation of the unusual star-shaped PbS crystals.

The pH values of the reaction solution also showed a significant effect on the crystallization of PbS crystals in the presence of acetate ions. Figure 4 shows the SEM images of PbS obtained at different pH values adjusted by using 2 M NaOH or HNO_3 . While well-defined star-shaped PbS crystals as shown in Figure 1 were obtained in the 0.1 M HAc solution without pH-adjusting (pH \sim 3.8), lots of sheetlike crystals were produced in addition to the star-shaped crystals when the pH was adjusted up to 4.5 (Figure 4a). In contrast, many cubic crystals as well as some large star-shaped crystals (about 5–8 μm) showing coalescent leaflets were produced when the pH of the solution was decreased to 2.4 (Figure 4b). If the pH was decreased to 1.9, cubic crystals were the predominant product, but imperfect stars with eight outspread arms were observed occasionally (Figure 4c). Only cubic PbS crystals were obtained when the pH of the reaction solution was further decreased to 1.7 (Figure 4d). It is noted that the

pH of the reaction solution exhibits considerable effects on both acetate equilibria and sulfide equilibria, thereby controlling both concentrations of Pb^{2+} ions and S^{2-} ions in the solution. Therefore, the pH exerted a delicate control on the crystallization process of PbS in the solution of acetic acid and TAA at the elevated temperature; however, the inherent mechanism is still unclear due to the presence of the complex equilibria.

The reaction temperature is another important factor that influences the PbS morphology. PbS crystals with morphologies other than eight-arm stars appeared if the temperature was lowered from 80 °C, and the proportion of the star-shaped crystals in the product was decreased with decreasing temperature generally. The product obtained at 60 °C exhibited a mixture of irregular crystals and star-shaped crystals containing nanoleaflets. When the temperature was decreased to 40 °C, the PbS stars disappeared completely and PbS nanostrips with a length about several micrometers and a breadth 60–150 nm were obtained. A lower temperature would result in a slower release of the S^{2-} ions from TAA; furthermore, the temperature would also affect the complexation between the Ac^- ions and the Pb^{2+} ions, which may show an effect on the release of the Pb^{2+} ions and the crystallization of PbS.

At 40 °C but a lower HAc concentration (0.025 M), PbS nanorods as well as nanosheets can be easily produced at suitable reactant concentrations. As shown in Figure 5a, PbS nanorods about 60 nm in diameter and several micrometers in length were obtained at a $[\text{Pb}(\text{Ac})_2]/[\text{TAA}]$ ratio of 1:2. The corresponding XRD pattern (Figure 2b) shows that the products are well-crystallized PbS with a cubic rock-salt structure. If the $[\text{Pb}(\text{Ac})_2]/[\text{TAA}]$ ratio was increased to 2:1, micrometer-sized PbS nanosheets were produced (Figure 5b). The

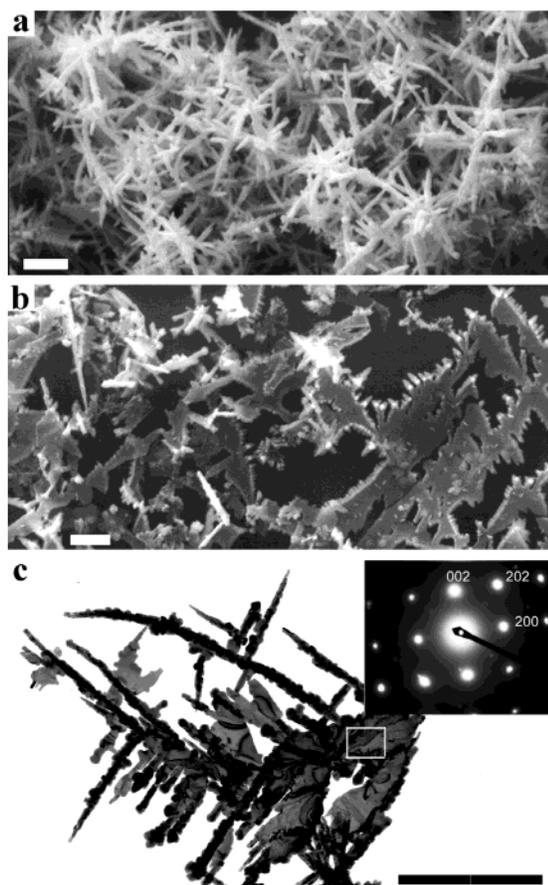


Figure 5. SEM (a,b) and TEM (c) images of PbS products obtained at 40 °C in 0.025 M HAc solution at different reactant concentrations: (a) $[\text{Pb}(\text{Ac})_2] = 0.027 \text{ M}$, $[\text{TAA}] = 0.054 \text{ M}$; (b,c) $[\text{Pb}(\text{Ac})_2] = 0.054 \text{ M}$, $[\text{TAA}] = 0.027 \text{ M}$. Inset shows electron diffraction pattern corresponding to the framed area. Scale bars = 1 μm .

typical TEM image shown in Figure 5c clearly shows its thin film structure. The selected area electron diffraction pattern indicates that the nanosheets are parallel to the (100) plane, which is similar to the case of PbS single-crystal films obtained by a polymer-assisted solvothermal method.¹⁵ The corresponding XRD pattern (Figure 2c) suggests that the intensity ratio between (200) and (111) peaks is much larger than the standard value, confirming that the {100} planes are preferentially lying on the substrate surface. It also shows that the (200) peak is considerably broadened, indicating a nanometer-sized thickness of the sheetlike crystals. The thickness of the nanosheets was estimated to be about 34 nm according to the line width analysis of the (200) peak based on the Scherrer formula.

In summary, hierarchical eight-arm, star-shaped PbS single crystals have been successfully synthesized by a simple and mild solution method. The unique star-shaped PbS crystals have eight symmetric arms along the $\langle 111 \rangle$ directions, each of which shows a trident-like, dendritic structure and consists of parallel PbS nanoleaflets. It has been revealed that the presence of acetic ions as well as appropriate pH and temperature are crucial for the formation of the unusual star-shaped PbS crystals. Full mechanistic studies for the shape-controlled formation of the star-shaped PbS crystals are in progress. It is possible that this approach can be extended as an effective synthetic method for hierarchical, single-crystalline nanostructures of other inorganic semiconductors.

Acknowledgment. This work was supported by NSFC (20003001, 20325312, 20233010), the Special Fund of MOE, China (200020), and the Doctoral Program Foundation of MOE, China.

References

- (1) Mann, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 3392.
- (2) (a) Qi, L.; Cölfen, H.; Antonietti, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 604. (b) Yu, S.-H.; Antonietti, M.; Cölfen, H.; Jürgen, H. *Nano Lett.* **2003**, *3*, 379.
- (3) (a) Shi, H.; Qi, L.; Ma, J.; Cheng, H. *J. Am. Chem. Soc.* **2003**, *125*, 3450. (b) Lao, J. Y.; Wen, J. G.; Ren, Z. F. *Nano Lett.* **2002**, *2*, 1287.
- (4) (a) Jun, Y.-W.; Lee, S.-M.; Kang, N.-J.; Cheon, J. *J. Am. Chem. Soc.* **2001**, *123*, 5150. (b) Gao, F.; Lu, Q.; Xie, S.; Zhao, D. *Adv. Mater.* **2002**, *14*, 1537.
- (5) Sone, E. D.; Zubarev, E. R.; Stupp, S. I. *Angew. Chem., Int. Ed.* **2002**, *41*, 1706.
- (6) Yu, S.-H.; Yoshimura, M. *Adv. Mater.* **2002**, *14*, 296.
- (7) Ma, C.; Moore, D.; Li, J.; Wang, Z. L. *Adv. Mater.* **2003**, *15*, 228.
- (8) Lu, Q.; Gao, F.; Zhao, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 1932.
- (9) Lu, Q.; Gao, F.; Zhao, D. *Nano Lett.* **2002**, *2*, 725.
- (10) Wilhelmy, D. M.; Matijević, E. *Colloids Surf.* **1985**, *16*, 1.
- (11) Trindade, T.; O'Brien, P.; Zhang, X. M.; Motevalli, M. *J. Mater. Chem.* **1997**, *7*, 101.
- (12) Zeng, Z.; Wang, S.; Yang, S.; *Chem. Mater.* **1999**, *11*, 3365.
- (13) Wang, S.; Yang, S. *Langmuir* **2000**, *16*, 389.
- (14) Yu, D.; Wang, D.; Meng, Z.; Lu, J.; Qian, Y. *J. Mater. Chem.* **2002**, *12*, 403.
- (15) Yu, D.; Wang, D.; Zhang, S.; Liu, X.; Qian, Y. *J. Cryst. Growth* **2003**, *249*, 195.
- (16) Lee, S.-M.; Jun, Y.-W.; Cho, S.-N.; Cheon, J. *J. Am. Chem. Soc.* **2002**, *124*, 11244.
- (17) (a) Kuang, D.; Xu, A.; Fang, Y.; Liu, H.; Frommen, C.; Fenske, D. *Adv. Mater.* **2003**, *15*, 1747. (b) Wang, D.; Yu, D.; Shao, M.; Liu, X.; Yu, W.; Qian, Y. *J. Cryst. Growth* **2003**, *257*, 384.
- (18) Yang, D.; Qi, L.; Ma, J. *Chem. Commun.* **2003**, 1180.

CG034174E