Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Solid State Chemistry 177 (2004) 2205–2209
JOURNAL OF SOLID STATE CHEMISTRY
http://elsevier.com/locate/jssc

Rapid Communication

# Synthesis and characterization of $MgF_2$ and $KMgF_3$ nanorods

Minhua Cao,[a] Yonghui Wang,[a] Yanjuan Qi,[a] Caixin Guo,[a] and Changwen Hu[a,b,*]

[a] *Faculty of Chemistry, Institute of Polyoxometalate Chemistry, Northeast Normal University, Changchun 130024, PR China*
[b] *Department of Chemistry, Beijing Institute of Technology, Beijing 100081, PR China*

Received 20 October 2003; received in revised form 6 January 2004; accepted 14 January 2004

**Abstract**

$MgF_2$ nanorods with diameters of 60–100 nm were synthesized by a microemulsion method. Subsequent hydrothermal reaction of as-synthesized $MgF_2$ nanorods and KF at 240°C for 3 days or 140°C for 7 days resulted in $KMgF_3$ nanorods, which retained the rod-like morphology of the source material $MgF_2$ in the reaction process. The morphology of as-synthesized $MgF_2$ strongly depended on the molar ratio between water and the surfactant CTAB and the concentration of CTAB.


*Keywords:* One-dimensional nanostructures; $MgF_2$; $KMgF_3$; Microemulsion; Hydrothermal reactions

One-dimensional (1D) nanostructures (such as nanowires, nanorods, and nanotubes) have attracted considerable attention in recent years due to their potential applications in constructing nanoscale electronic, optoelectronic, and sensing devices [1]. 1D nanostructures with different compositions have been synthesized by using various methods including the vapor-phase transport process, chemical vapor deposition, arc discharge, laser ablation, solution, and a template-based method [2–11]. While a large part of this work has focused on materials, such as elemental carbon, carbon-based substances, metals, oxides, sulfides, nitrides, considerably fewer studies have been carried out on 1D nanostructures of fluorides and complex fluorides. It is thus necessary to study the fluoride system with interesting optical properties.

Fluorides and complex fluorides have been extensively studied due to their particular photoluminescence properties. Magnesium fluoride ($MgF_2$) has been identified as a positive uniaxial crystal, which possesses the highest birefringence and a wide range of transparency in the spectrum region [12]. These properties have led to the use of $MgF_2$ for infrared transparent windows [13]. Complex fluoride $KMgF_3$, with a typical cubic perovskite structure, is an ideal material for searching for a new solid-state laser because of its several advantages: good homogenous optics, high thermal stability, low melting point, anisotropy, and high optical transparency, etc. [14]. However, due to the corrosive nature of fluorides, conventional solid-state synthetic method of complex fluorides suffers from the requirements of high temperature, special synthetic apparatus, or rigid conditions, and has thus limited the study of complex fluoride chemistry [15]. Recently, Zhao et al. have developed a hydrothermal route to the synthesis of complex fluorides, which gives rise to the possibility of making complex fluorides under mild conditions [16]. Very recently, studies on fluorides nanoparticles have shown that nanoscale fluorides exhibit enhanced luminescence and photomagnetic properties [17]. However, to the best of our knowledge, studies on $MgF_2$ and $KMgF_3$ materials are still at bulk levels, and no work has dealt with their 1D nanostructures. Due to the promising applications of $MgF_2$ and $KMgF_3$ in optoelectronic devices, it is important to synthesize the two materials with 1D nanostructures. Here, we report a hydrothermal microemulsion method for the preparation of $MgF_2$ nanorods. Furthermore, using the as-synthesized $MgF_2$ nanorods as the magnesium source material, $KMgF_3$ nanorods were obtained under hydrothermal conditions at 240°C, whereas the preparation of $KMgF_3$ by solid-state reactions was typically carried out at about 1000°C [15]. Although the microemulsion method is well known as a mature method of synthesizing nanoparticles, it can also be used to fabricate some

*Corresponding author. Faculty of Chemistry, Institute of Polyoxometalate Chemistry, Northeast Normal University, Changchun 130024, PR China. Fax: +86-10-8257-1381.
*E-mail address:* huchw@nenu.edu.cn (C. Hu).

0022-4596/$ - see front matter © 2004 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2004.01.005

1D nanostructures under certain conditions. In fact, many 1D nanostructures, such as ZnO, $BaCO_3$, $BaSO_4$, CdS, $BaWO_4$, $K_3[PMo_{12}O_{40}]\cdot nH_2O$, $BaF_2$ and so forth [18–24], were all fabricated via similar microemulsion methods. In addition, the hydrothermal method has been widely utilized in synthesizing nanoscale materials because of its several advantages, resulting from its unique reaction environment. It has been shown that when the hydrothermal method is used to synthesize nanomaterials, it cannot only evidently decrease reaction temperature of systems, but also improve the crystallinity of the products.

First, $MgF_2$ nanorods were prepared via a quaternary microemulsion, cetyltrimethylammonium bromide (CTAB)/water/cyclohexane/*n*-pentanol, under hydrothermal conditions, in which the molar ratio of water to CTAB was $w=[H_2O]:[CTAB]=10$ and the concentration of CTAB was [CTAB] = 0.1 M. In this process, CTAB (4 g) was dissolved in 100 mL of cyclohexane and 5 mL of *n*-pentanol. Two such solutions were stirred for 30 min and became transparent. Then 2 mL of aqueous $MgCl_2$ solution (1 M) and 2 mL of 10% HF aqueous solution were added to the above solutions, respectively, both forming colorless suspensions of microemulsion droplets. Afterward, the two microemulsion solutions were mixed and stirred for another 10 min. The resulting microemulsion solution was then transferred into stainless Teflon-lined autoclaves and heated at 120°C for 12 h. Finally, a white precipitate ($MgF_2$ nanorods) was collected by centrifuging, washed several times with absolute ethanol and distilled water, and dried in a vacuum oven at 50°C for 5 h. $KMgF_3$ nanorods were synthesized under hydrothermal conditions, which is similar to the preparation of $KMgF_3$ particles developed by Zhao et al. [16]. The above-prepared $MgF_2$ (0.31 g) and KF (0.29 g) were added to 9 mL deionized water, to which 0.04 mL HF (40 mass%, A. R.) was added with stirring. Here HF was used as a mineralizer. The reaction mixture (pH ca. 6) was sealed in a Teflon-lined stainless-steel autoclave and heated at 240°C for 3 days or 140°C for 7 days. After the reaction was completed, the resulting white product ($KMgF_3$ nanorods) was collected, washed several times using deionized water, centrifuged, and dried under vacuum at room temperature.

The phase purity of the products was examined by X-ray diffraction (XRD) measurement performed on a Rigaku X-ray diffractometer with Cu*K*α radiation. All of the peaks of the XRD pattern in Fig. 1a can be perfectly indexed to a pure tetragonal phase (space group: $P4_2/mnm$ [136]) of $MgF_2$ with lattice constants $a=4.620$ Å and $b=3.050$ Å (JCPDS 72-2231). Since the XRD pattern of $KMgF_3$ nanorods obtained at 140°C for 7 days is very similar to that of samples obtained at 240°C for 3 days, here we only show the XRD pattern of the latter. Fig. 1b shows the XRD pattern of $KMgF_3$ nanorods obtained at 240°C for 3 days. All of the peaks can be indexed to a pure cubic phase (space group: $Pm3m$ [221]) of $KMgF_3$ with lattice constant $a=3.980$ Å (JCPDS 75-0307). These results are in good agreement with those of $MgF_2$ and $KMgF_3$ bulk crystals, respectively. Particularly for $KMgF_3$, the XRD pattern indicates that pure $KMgF_3$ phases can be obtained under mild hydrothermal conditions.

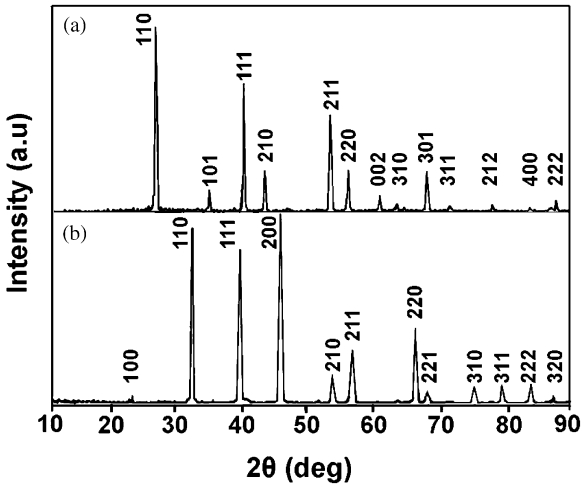


Fig. 1. XRD patterns of (a) $MgF_2$ and (b) $KMgF_3$.

Fig. 2a shows the transmission electron microscopy (TEM) image of the sample prepared in CTAB microemulsions at $w=10$. As shown in Fig. 2a, the samples display a rod-like morphology with diameters of 60–100 nm and lengths up to 2 μm. Fig. 2b shows the TEM image of two $MgF_2$ nanorods, indicating the uniformity in diameter along the nanorod and the straightness along the longitudinal axis of the nanorod. In addition, all nanorods have two cuspate-shaped ends. Fig. 2c shows a high-magnification TEM image of an individual $MgF_2$ nanorod, showing the cuspate-shaped morphology of the end of the nanorod. The inset selected area electron diffraction (SAED) pattern was taken from a single $MgF_2$ nanorod and reveals the single-crystalline nature of the sample. Moreover, SAED patterns taken from different parts of the nanorod show exactly an identical pattern without further tilting the nanorod, indicating the single crystallinity of the whole nanorod. A high-resolution TEM (HRTEM) shows that the nanorod is structurally uniform with an interplanar spacing of about 0.325 nm, which corresponds to the (110) plane of tetragonal $MgF_2$. $KMgF_3$ nanorods were obtained by the hydrothermal reaction of the as-synthesized $MgF_2$ nanorods and KF at 240°C for 3 days or 140°C for 7 days, as clearly shown in Figs. 3a and b, respectively. It can be seen that the morphology of the products obtained under different conditions is almost the same, and both $KMgF_3$ nanorods have an average diameter of

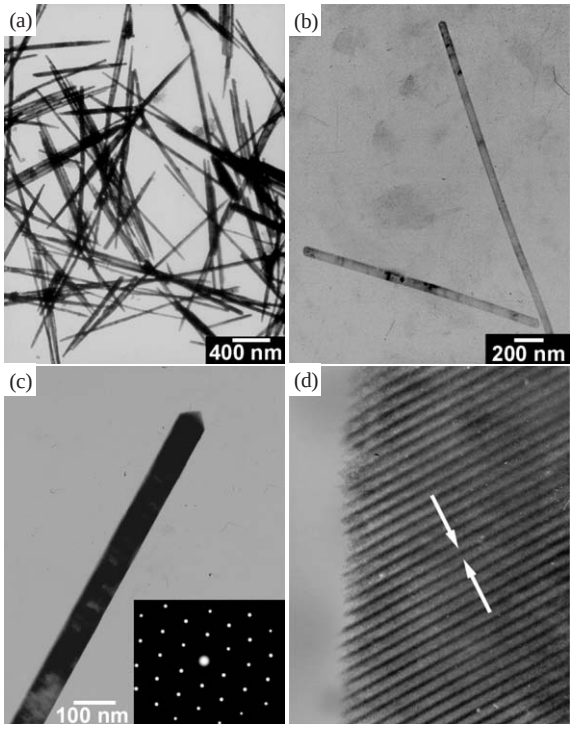


Fig. 2. (a) TEM image of $MgF_2$ nanorods. (b) TEM image of two nanorods, indicating the uniformity in diameter along the nanorods and the straightness along the longitudinal axis of the nanorods. (c) High-magnification TEM image of a single nanorod, showing the cuspate-shaped morphology of the end of the nanorod. The inset shows the corresponding SAED pattern. (d) HRTEM image of a single nanorod (spacing = 0.325 nm).

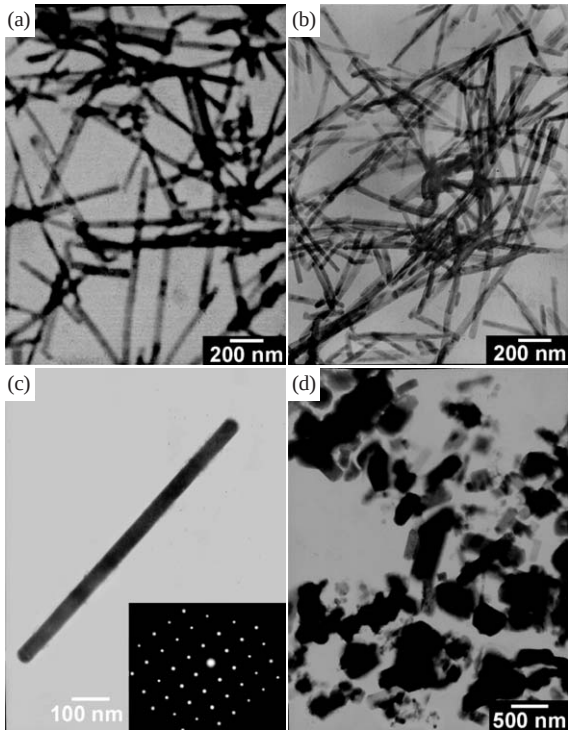


Fig. 3. (a) TEM image of $KMgF_3$ nanorods obtained at 140°C for 7 days. (b) TEM image of $KMgF_3$ nanorods obtained at 240°C for 3 days. (c) TEM image of a single $KMgF_3$ nanorod taken from (3b). The inset shows the corresponding SAED pattern. (d) TEM image of $KMgF_3$ obtained from a solid-state reaction at 1000°C.

about 80 nm and lengths up to 1 μm, clearly shorter than that of $MgF_2$ nanorods. The SAED (inset in Fig. 3c) pattern taken from a single nanorod (Fig. 3c) can be indexed as a cubic $KMgF_3$ single crystal. Previously, Zhao et al. reported the synthesis of $KMgF_3$ using a similar procedure but with bulk $MgF_2$ as magnesium source material, except that their synthesized $KMgF_3$ is in the form of particles. It can thus be concluded that in the formation of $KMgF_3$ it still retained the rod-like morphology of the source material $MgF_2$. For comparison, using the same as-synthesized $MgF_2$ nanorods as magnesium source material we have also repeated the synthesis but using solid-state reactions at a high temperature of 1000°C. Pure $KMgF_3$ were obtained as expected. But most of the samples were large irregular aggregates of roughly spherical particles instead of uniform nanorods, and only a few considerably shorter nanorods were observed, as shown in Fig. 3d. The reasons may be that $MgF_2$ nanorods partly sintered in the process of high-temperature reactions, resulting in the agglomeration of the product. Thus, it can be seen that the hydrothermal reaction of $MgF_2$ nanorods and KF cannot only remarkably decrease the temperature of reaction systems, but also yield uniform nanorod product, which the high-temperature solid-state reactions cannot obtain. In addition, it is particularly worth noting that this hydrothermal reaction also achieved the phase transition from tetragonal phase $MgF_2$ to cubic $KMgF_3$ under mild conditions, which was typically carried out under high-temperature conditions.

The morphology of as-synthesized $MgF_2$ strongly depended on the molar ratio between the water and surfactant CTAB, in which the concentration of CTAB was kept at a constant of 0.1 M. Fig. 4 shows the TEM images of as-synthesized products obtained under the same conditions but with $w = 5$ and 20, respectively. Only uniform particles were obtained in the product when the molar ratio of $w = 5$ was used. The TEM image (Fig. 4a) shows that the sample was composed of $MgF_2$ nanoparticles with an average diameter of 60 nm. When the molar ratio was increased to 20, relatively shorter nanorods, 50–80 nm wide and 80–200 nm long, were observed (Fig. 4b). Compared with the products synthesized at different molar ratios, we can conclude that the molar ratio of $w = 10$ is most favorable for the formation of $MgF_2$ nanorods. In addition, the concentration of surfactant CTAB also has significant effects on the shape of $MgF_2$. Neither lower nor higher concentrations of CTAB induce the formation of $MgF_2$ nanorods. At a low micellar concentration ([CTAB] = 0.04 M), particles with a mean diameter of 80 nm were observed

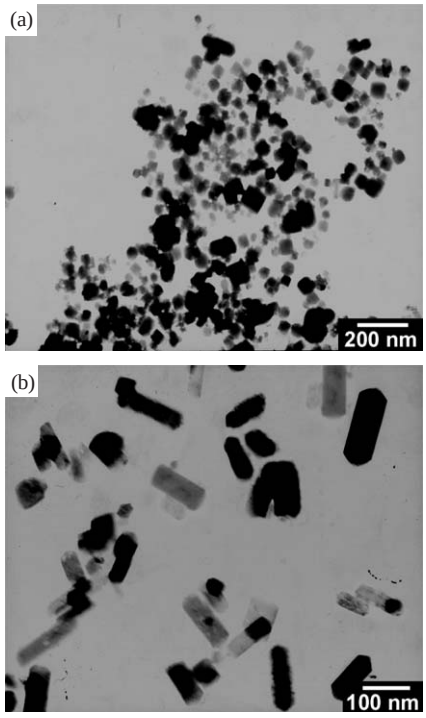


Fig. 4. (a) TEM image of the sample produced at a molar ratio of water to CTAB ($w$) of $w = 5$. (b) TEM image of the sample produced at the molar ratio of water to CTAB of $w = 20$.

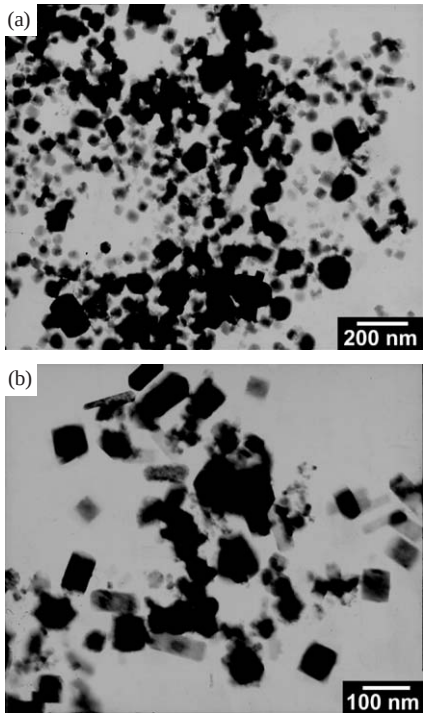


Fig. 5. (a) TEM image of the sample produced at a lower CTAB concentration ([CTAB] = 0.04 M) (b) TEM image of the sample produced at a higher CTAB concentration ([CTAB] = 1.5 M).

by the TEM image (Fig. 5a). XRD showed that the obtained particles were also a pure tetragonal $MgF_2$ phase. While at a higher surfactant concentration of 1.5 M, particles were also observed, most of the particles were square (Fig. 5b), which is different from the products formed in microemulsions at a lower surfactant concentration. These square-shaped particles have a mean edge length of 80 nm. The reason for producing square-shaped particles may be that excess surfactant CTAB may act as a capping agent to confine the growth of particles [25]. On the basis of these facts, it can be deduced that lower or higher surfactant concentrations may destroy the dynamic equilibrium of microemulsions, resulting in the loss of microemulsion function.

Very recently, we have reported the preparation of $PbO_2$, $Pb_3O_4$, Cu, $Cu_2O$, CuO, and $BaF_2$ 1D nanostructures, in which $BaF_2$ whiskers were obtained via this hydrothermal microemulsion method under mild hydrothermal conditions [24]. Although $MgF_2$ and $BaF_2$ both belong to group II fluorides and have structural similarity, by using the identical synthesis method, $MgF_2$ nanorods were obtained instead of whiskers. Previously, we have expounded that $BaF_2$ whiskers were formed via a directed aggregation growth process. In the case of $MgF_2$, based on our experimental results, we also prefer the directed aggregation mechanism in the nanorod formation process. Since $MgF_2$ nanorods with higher aspect ratios ($>50$) were obtained in the microemulsions, according to the micellar size and shape, it is not likely to lead to the formation of such a long water nanochannel in oils in such a low water content environment. However, different morphologies were obtained in the two cases. This may be accountable for different crystal habits of inorganic materials. As among the group II fluorides, $MgF_2$ and $BaF_2$ have the smallest and the largest size of the unit cell, respectively. Furthermore, they possess different crystal structures. All these facts may result in the formation of 1D $MgF_2$ and $BaF_2$ nanostructures with different aspect ratios.

In conclusion, $MgF_2$ nanorods with uniform diameters have been first synthesized by the hydrothermal microemulsion method. Furthermore, using the $MgF_2$ nanorods as magnesium source material, $KMgF_3$ nanorods have also been successfully fabricated under mild hydrothermal conditions at 240°C for 3 days or 140°C for 7 days. It has been confirmed that the as-synthesized $KMgF_3$ retained the rod-like morphology of $MgF_2$. We expect that this methodology will be a general method to synthesize other 1D fluorides and complex fluorides.

This work was supported by NSFC (No. 20071007 and 20271007) and SRFDP (No. 20030007014).

## References

[1] J. Hu, M. Ouyang, C.M. Lieber, Nature 399 (1999) 48.
[2] Y. Wu, P. Yang, Chem. Mater. 12 (2000) 605.

[3] C.C. Chen, C.C. Yeh, Adv. Mater. 12 (2000) 738.
[4] Z.G. Bai, D.P. Yu, H.Z. Zhang, Y. Ding, X.Z. Gai, Q.L. Hang, G.C. Xiong, S.Q. Feng, Chem. Phys. Lett. 303 (1999) 311.
[5] M. Yazawa, M. Koguchi, A. Muto, M. Ozawa, K. Hiruma, Appl. Phys. Lett. 61 (1992) 2051.
[6] Y.C. Choi, W.S. Kim, Y.S. Park, S.M. Lee, D.J. Bae, Y.H. Lee, G.S. Park, W.B. Choi, N.S. Lee, J.M. Kim, Adv. Mater. 12 (2000) 746.
[7] (a) X.F. Duan, C.M. Lieber, Adv. Mater. 279 (2000) 208.
(b) A.M. Morales, C.M. Lieber, Science 279 (1998) 208.
[8] T.J. Trentler, K.M. Hickman, S.C. Goel, A.M. Viano, P.C. Gibbons, W.E. Buhro, Science 270 (1995) 1791.
[9] J.D. Holmes, K.P. Johnston, R.C. Doty, B.A. Korgel, Science 287 (2000) 1471.
[10] (a) M.H. Huang, A. Choudrey, P. Yang, Chem. Commun. 12 (2000) 1603.
(b) J. Zhu, S. Fan, J. Mater. Res. 14 (1999) 1175.
[11] Y. Li, G.W. Meng, L.D. Zhang, F. Phillipp, Appl. Phys. Lett. 76 (2000) 2011.
[12] B. Cochet-Muchy, J. Portier, in: P. Hagenmuller (Ed.), Inorganic Solid Fluorides, Academic Press, Orlando, 1985, p. 565.
[13] E. Carnall, S.E. Hatch, L.S. Ladd, W.F. Parsons, US Patent 3, 294, 878, 1967.
[14] (a) T. Kobayasi, S. Mroczkowski, J.F. Owen, J. Lumin. 21 (1980) 247.
(b) G. Blasse, A. Bril, Philips Technol. Rev. 31 (1970) 304.
[15] A.R. West, Solid State Chemistry and its Applications, Wiley, New York, 1984, p. 338.
[16] C.Y. Zhao, S.H. Feng, Z.C. Chao, C.S. Shi, R.R. Xu, J.Z. Ni, Chem. Commun. (1996) 1641.
[17] (a) C.M. Bender, J.M. Burlitch, Chem. Mater. 12 (2000) 1969.
(b) J.W. Stouwdam, F.C.J.M. van Veggel, Nano Lett. 2 (2002) 733;
(c) X.M. Sun, Y.D. Li, Chem. Commun. (2003) 1768.
[18] J. Zhang, L.D. Sun, H.Y. Pan, C.S. Liao, C.H. Yan, New J. Chem. 26 (2002) 33.
[19] L.M. Qi, J.M. Ma, H.M. Cheng, Z.G. Zhao, J. Phys. Chem. B 101 (1997) 3460.
[20] J.D. Hopwood, S. Mann, Chem. Mater. 101 (1997) 3460.
[21] P. Zhang, L. Gao, Langmuir 19 (2003) 208.
[22] S. Kwan, F. Kim, J. Akana, P.D. Yang, Chem. Commun. (2001) 447.
[23] X.H. Zhang, S.Y. Xie, Z.Y. Jiang, L.C. Zhou, Z.X. Xie, R.B. Huang, L.S. Zheng, Chem. Commun. (2002) 2032.
[24] (a) M.H. Cao, C.W. Hu, G. Peng, Y.J. Qi, E.B. Wang, J. Am. Chem. Soc. 125 (2003) 4982;
(b) M.H. Cao, C.W. Hu, Y.H. Wang, Y.H. Guo, C.X. Guo, E.B. Wang, Chem. Commun. (2003) 1884
(c) M.H. Cao, C.W. Hu, E.B. Wang, J. Am. Chem. Soc. 125 (2003) 11196.
[25] L.F. Gou, C.J. Murphy, Nano Lett. 3 (2003) 231.