

Nanometer Cr₂O₃-doped MnO₂ spheres for rechargeable lithium batteries

X. Y. Zhan · J. J. Tang · Z. H. Li · D. S. Gao · P. Chen · Q. Wu

Received: 23 April 2009 / Revised: 2 July 2009 / Accepted: 16 July 2009 / Published online: 5 August 2009
© Springer-Verlag 2009

Abstract Nanometer manganese dioxide spheres were prepared by water/oil microemulsion technology using sodium pyrosulfite and potassium permanganate as the raw materials. The scanning electron microscopy and the transmission electron microscopy images showed that the as-prepared MnO₂ particles aggregated with many nanosize spheres with an average diameter about 100 nm. From the X-ray diffraction patterns, it suggested that the achieved materials had the crystal structure of α -MnO₂. The electrochemical properties of the nanometer MnO₂ spheres doped with various amounts of Cr₂O₃ were studied in detail in this paper. The results revealed that the MnO₂ particles doped with 4 wt.% Cr₂O₃ can maintain more than 150 mAh g⁻¹, which is about 84% of the initial specific capacity, even after 50 cycles indicating a promising application in the rechargeable lithium batteries.

Keywords Manganese dioxide · Microemulsion · Cr₂O₃-doped · Electrochemical property · Rechargeable lithium battery

Introduction

Manganese dioxide is very attractive electrode materials for batteries because of its low cost, environmental friendliness, and convenient preparation, which has been used as a kind of cathode materials for Li primary batteries, the dry batteries, and the rechargeable lithium batteries [1–3]. As cathode materials of the rechargeable lithium battery, the various species of MnO₂ such as α -MnO₂ [4, 5], β -MnO₂ [6], γ -MnO₂ [7], and the layered structure MnO₂ [8, 9] have been reported. Among these manganese dioxides, α -MnO₂ has now received special attention as cathode materials for the rechargeable lithium batteries, since the large 2×2 tunnels, which exist in the crystalline lattice of α -MnO₂, are believed to facilitate the accommodation and transportation of the inserting lithium ions.

It is well known that the kinetics of the intercalation process of Li⁺ ions is of vital to determine the electrochemical performance of the MnO₂ electrode. Therefore, how to accelerate the diffusion of Li⁺ ions becomes an important problem to be solved. Nanosized materials have higher active surface area and smaller diffusion length for the Li⁺ intercalation and therefore should have higher specific capacity and better rate capability than the large size particles. Consequently, much effort has been devoted to the fabrication of 1D MnO₂ nanomaterials [10, 11]. Very recently, MnO₂ nanowires [12, 13] and nanorods [14, 15] have been reported. Some of them showed a relatively high specific capacity up to 200 mAh g⁻¹ but poor cyclic performance [16]. Up to date, a vital drawback of MnO₂ materials, which used as electrode materials of rechargeable lithium batteries as well as rechargeable alkaline batteries, is the poor cyclic property in both nonaqueous and aqueous electrolytes. Some kinds of additives such as Bi₂O₃ [17, 18], TiS₂ [19], TiB₂ [20], CeO₂ [21], and so on were doped

X. Y. Zhan · J. J. Tang · Z. H. Li (✉) · D. S. Gao
Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education & College of Chemistry, Xiangtan University,
Xiangtan 411105, China
e-mail: lzh69@xtu.edu.cn

X. Y. Zhan · P. Chen · Q. Wu
L&F Co. Ltd,
703-13 Hosan-Dong Dalsu-Gu,
Daegu 704-220, South Korea

into the electrode to improve the cyclic property of MnO_2 materials. Nevertheless, few works are devoted to improve the cyclic property of $\alpha\text{-MnO}_2$ materials. Since the bonding energy of Mn–O in MnO_2 is 946 kJ mol^{-1} similar to that of Cr–O ($1,029 \text{ kJ mol}^{-1}$) [22], we choose the Cr_2O_3 as dopant. In our primary intention, it is presumed that Cr_2O_3 compounds should be coated on the surface of the amorphous MnO_2 particles or inserted into their framework. We propose first time to use Cr_2O_3 to modify the amorphous $\alpha\text{-MnO}_2$ nanomaterials with novel shapes so as to improve the electrochemical performances when they are used as the cathode materials for rechargeable lithium batteries.

Here, the nanometer MnO_2 spheres are prepared by water/oil (W/O) emulsions technology, then doped with Cr_2O_3 to enhance their electrochemical performances. The electrochemical properties of the MnO_2 microspheres doped with different amounts of Cr_2O_3 were studied. The results show that the doped MnO_2 should be applied as the electrochemically active materials for the rechargeable lithium batteries.

Experimental

At first, 18 ml *n*-hexane and 9 ml 1.5 M $\text{Na}_2\text{S}_2\text{O}_5$ aqueous solution were mixed with stirring for 30 min forming a stable emulsion, which contained the surfactant 0.28 g TX-100 and 0.14 g Span-80 (the ratio of TX-100 to Span-80 was fixed to 2:1). The resultant emulsion was then dropped slowly to an aqueous solution of permanganate (36 ml, 0.5 M) at 25°C under intensive stirring within 30 min. After stillness 4 h, some black materials precipitated at the bottom of the flask. The obtained precipitates were centrifuged and subsequently washed with the distilled water and ethanol twice. The samples were produced finally by dried at 120°C in an oven overnight.

To obtain the doped samples, a certain amount of the dried MnO_2 samples were added to a solution of $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in ethanol and stirred gently till the ethanol evaporated completely at room temperature (the mass ratio of Cr_2O_3 to MnO_2 was adjusted to 0%, 2%, 4%, 6%). The resultant powders were calcined at 150°C for 2 h and 400°C for another 2 h under air atmosphere finally.

The obtained samples were characterized by X-ray diffraction (XRD; Bruker D8 X-ray diffractometer) with Cu $\text{K}\alpha$ radiation. Their morphologies were observed with the scanning electron microscope (SEM; Philips XL-60) and the transmission electron microscope (TEM; JOEL JEM2010).

A three-electrode cell using Li foil as the counter and reference electrode was employed to measure the electrochemical properties of the samples. The rechargeable

lithium batteries were constructed with the MnO_2 electrode (the mass ratio of the MnO_2 , polytetrafluoroethylene, and acetylene black was 75:15:10), the lithium electrode, and the nonaqueous electrolyte 1.0 M LiClO_4 in the mixture of ethyl carbonate and dimethyl carbonate (volume ratio of 1:1, denoted as LIB315). Charge–discharge tests were performed at a current rate of 45 mA g^{-1} in the potential range of 4.0–1.5 V on the Land battery system (Wuhan, People's Republic of China). Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) measurements were carried out by using a CHI-660C electrochemical analysis system.

Result and discussion

Figure 1 shows the XRD patterns of the various amounts Cr_2O_3 -doped MnO_2 . It finds that the undoped sample exhibits no sharp diffraction peaks except for a weak and broad peak at 36.03° , indicating that this sample seems amorphous. The result is similar to the previous reports [23–27]. Little amount of Cr_2O_3 -doped samples display the scarcely same patterns as the undoped sample suggesting that the doping with little amount of Cr_2O_3 hardly changes the crystalline structure of the as-prepared MnO_2 .

Figure 2 shows the SEM images of the undoped and doped MnO_2 particles. Both of them display the morphology of aggregation by many nanometer spherical particles ranged from 60 to 150 nm in diameter. From the TEM images (Fig. 3), it can be seen that these particles exhibit a coarse surfaces. The size of the undoped samples is larger than that of the doped samples because the decomposed

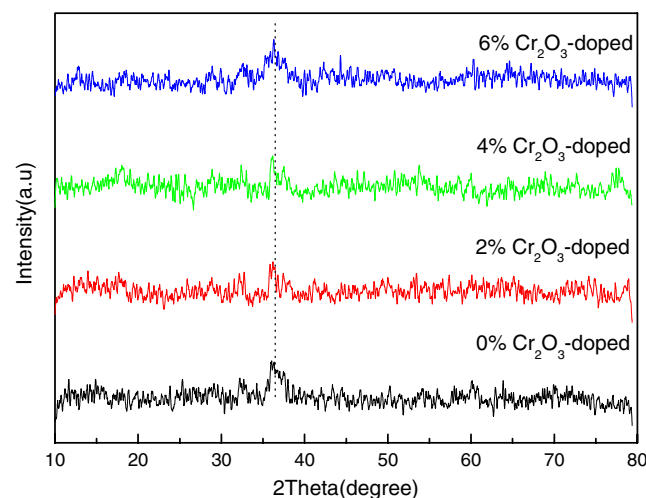


Fig. 1 X-ray diffraction patterns of the MnO_2 doped with various amounts of Cr_2O_3

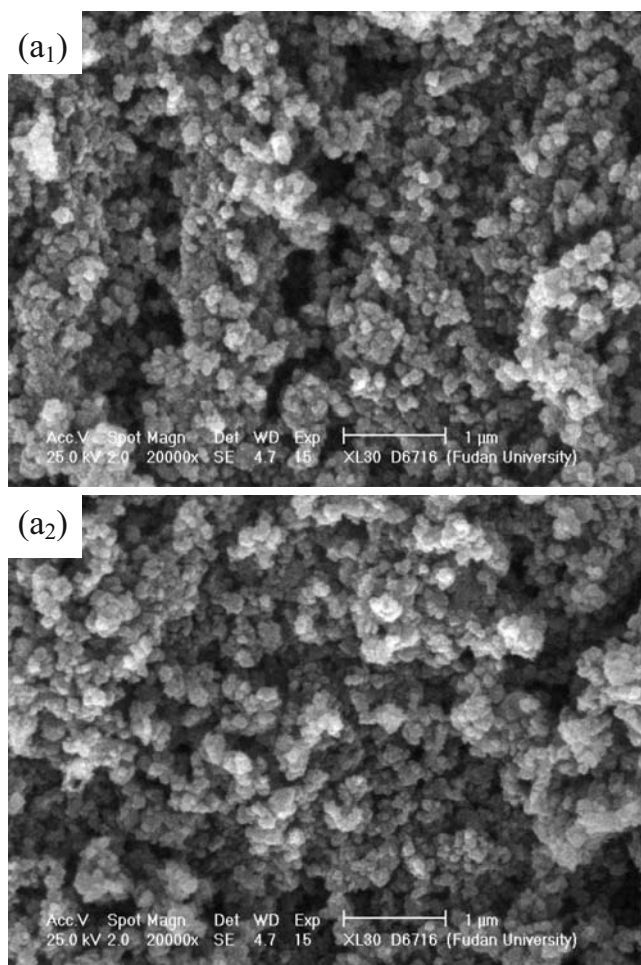


Fig. 2 SEM micrographs of *a*₁ the undoped and *a*₂ the 4-wt.% Cr₂O₃-doped MnO₂

Cr₂O₃ on the surface of MnO₂ microspheres may prevent the MnO₂ particles from further enlargement.

Figure 4 shows the cyclic performances and charge–discharge plots of the MnO₂ particles doped with different amounts of Cr₂O₃ at a current density of 45 mA g⁻¹. It finds that, from Fig. 4a, the samples doped with 2 and 4 wt.% Cr₂O₃ exhibit higher discharge capacity and better cyclic performance than the undoped MnO₂ spheres. The specific capacity of the 4-wt.% Cr₂O₃-doped sample reaches the highest value 180.8 mAh g⁻¹. After 50 cycles, the 4-wt.% Cr₂O₃-doped sample can deliver 152.0 mAh g⁻¹, which is about 84% of the initial specific capacity of this sample. In case of the undoped sample, it can only deliver 76.9 mAh g⁻¹ corresponding to 51% of its initial specific capacity. The variation of the specific capacity for the different MnO₂ samples may be ascribed to the integration of their structural characteristics, such as morphology, Cr existing in the cavity, and specific surface area, which may provide more active sites and affect the diffusion kinetics of Li⁺ ions [28]. The charge–discharge plots of the various

samples, shown in Fig. 4b, display that the discharge voltage plateau of the 4 wt.% is about 2.5 V (vs. Li/Li⁺) while those of the undoped and 6 wt.% samples disappear.

The cyclic voltammograms (CV) plots recorded at 0.1 mV s⁻¹ in the LIB315 electrolyte for the different MnO₂ samples are shown in Fig. 5. It exhibits a pair of redox peaks at 2.6 and 3.6 V vs. Li/Li⁺ with a similitude shape for the different Cr₂O₃-doped MnO₂ samples except for 6 wt.% Cr₂O₃-doped sample. The existing of the excessive Cr in MnO₂ crystal lattice may lead to the structural disorder and affect the deintercalation–intercalation reaction of lithium ions. The reaction corresponding to the redox peak can be expressed by the equation $x \text{Li}^+ + \text{MnO}_2 + x \text{e}^- \leftrightarrow \text{Li}_x\text{MnO}_2$ [29]. In addition, the integral area of the CV plots of the samples increases firstly with the increasing amount of Cr₂O₃ not more than 4 wt.% then decreases with further doping with Cr₂O₃. At 4 wt.% doping amount, the sample displays the largest integral area of the CV plot indicating that this sample can deliver more

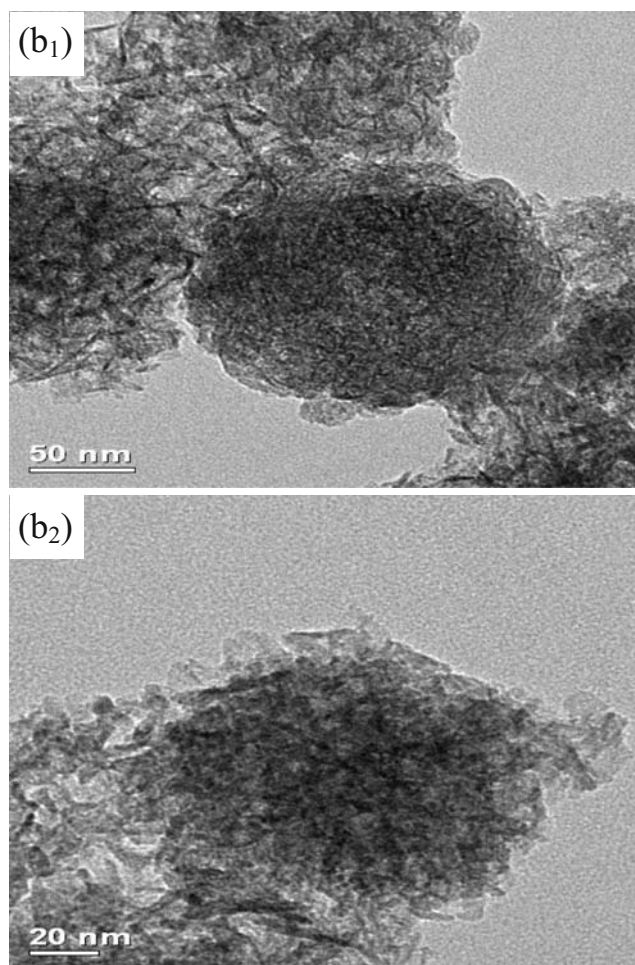


Fig. 3 TEM micrographs of *b*₁ the undoped and *b*₂ the 4-wt.% Cr₂O₃-doped MnO₂

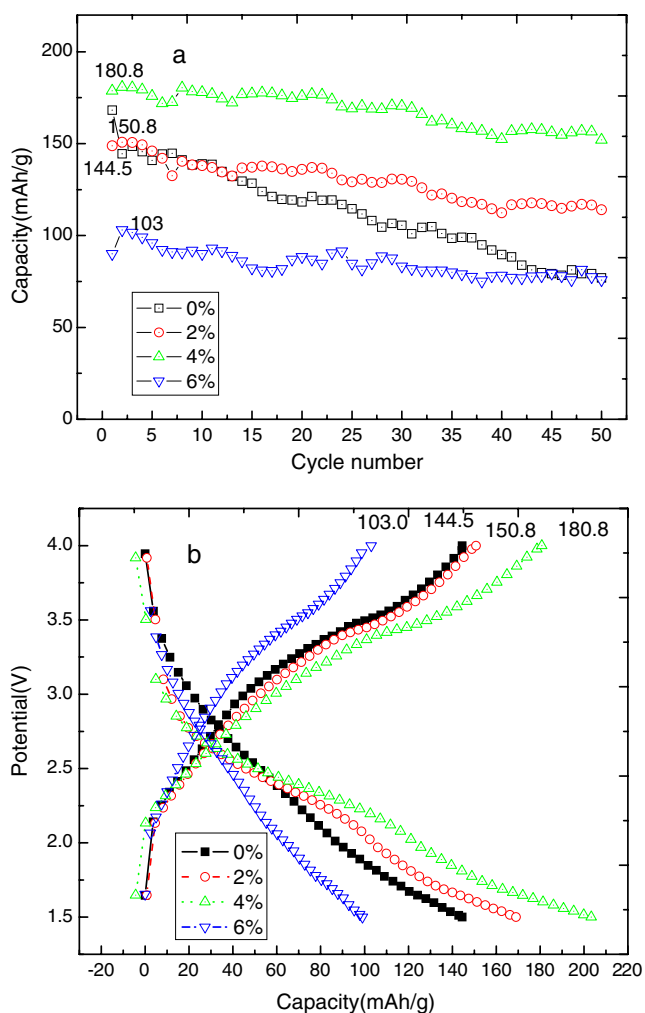


Fig. 4 Cyclic properties (a) and charge–discharge plots (b) of the MnO₂ doped with different amounts of Cr₂O₃ at a current density of 45 mA g⁻¹ in a voltage range of 4.0–1.5 V

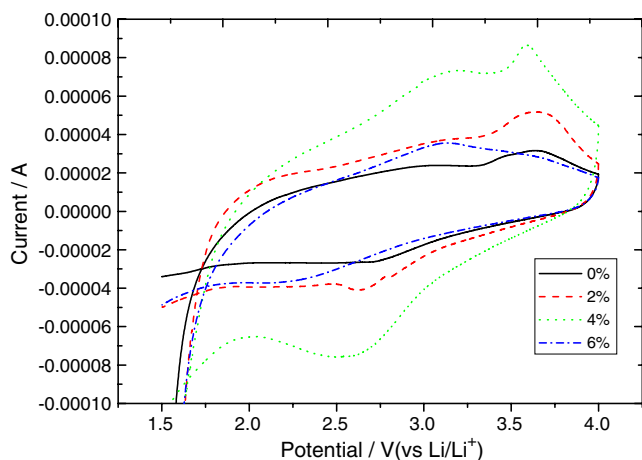


Fig. 5 Cyclic voltammogram plots of the MnO₂ samples doped with different amounts of Cr₂O₃ at a scanning rate of 0.1 mV s⁻¹

capacity than other samples. It is consistent with the results of the discharge–charge tests of the samples.

The effect of the spherical structure on the ion diffusion of the samples was further investigated by the EIS technology, which has been considered a powerful method to obtain the dynamic information of ion diffusion [30]. The Nyquist plots (Fig. 6) in the high frequency range appear as a semicircle indicating the existence of certain charge transportation resistances, R_{ct} . The diameter of the semicircle decreases firstly with the increasing amount (≤ 4 wt.%) of doped Cr₂O₃ and increases with further Cr₂O₃-doped. Unfortunately, the 6-wt.% Cr₂O₃-doped sample shows a relatively low specific capacity (Fig. 4). As a coating layer, the doped Cr₂O₃ influences the electrochemical performance of the as-prepared MnO₂ particles.

Conclusions

In conclusion, nanometer MnO₂ microspheres have been successfully prepared by W/O emulsions technology. The products consist of a large quantity of floccule spheres with a diameter of 100 nm or so. The results of the electrochemical measurements suggest that the 4-wt.% Cr₂O₃-doped MnO₂ microspheres show a higher discharge capacity and better cyclic performance than other MnO₂ microspheres. The as-prepared nanometer MnO₂ microspheres may be applied in not only the rechargeable lithium batteries but also the super electrochemical capacitors.

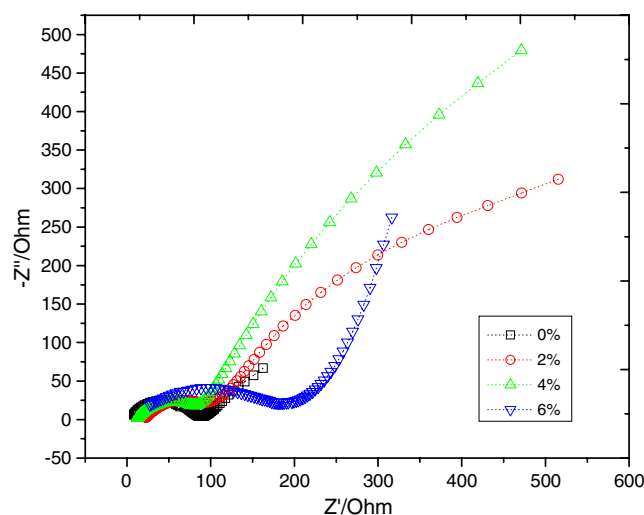


Fig. 6 Typical Nyquist plots of the MnO₂ samples doped with different amounts of Cr₂O₃ at an open circuit potential (3.0 V vs. Li/Li⁺) within a frequency range from 10 mHz to 10 kHz

Acknowledgments Financial support from the National Basic Research Program of China (973 Program No: 2007CB209702), the Natural fund from Hunan Province (09JJ5008), and the Doctoral Starting Fund from Xiangtan University (05QDZ18) is acknowledged.

References

1. Yagi H, Ichikawa T, Hirano A, Imanishi N, Ogawa S, Takeda Y (2002) *Solid State Ionics* 154:273
2. Wang Y, Cao GZ (2008) *Adv Mater* 20:2251
3. Fu LJ, Liu H, Wu YP, Rahm E, Holze R, Wu HQ (2005) *Prog Mater Sci* 50:881
4. Li ZQ, Ding Y, Xiong YJ, Yang Q, Xie Y (2005) *Chem Commun* 7:918
5. Wang HE, Qian D (2008) *Mater Chem Phys* 109:399
6. Liu DW, Garcia BB, Zhang QF, Guo Q, Zhang YH, Sepelri S, Cao GZ (2009) *Adv Funct Mater* 19:1015
7. Jung WI, Sakamoto K, Pitteloud C, Sonoyama N, Yamada A, Kanno R (2007) *J Power Sources* 174:1137
8. Yuan JQ, Liu ZH, Qiao SF, Ma XR, Xu NC (2009) *J Power Sources* 189:1278
9. Nakayama M, Kanaya T, Lee JW, Popov BN (2008) *J Power Sources* 179:361
10. Kijima N, Sakata Y, Takahashi Y, Akimoto J, Kumagai T, Igarashi K, Shimizu T (2009) *Solid State Ionics* 180:616
11. Feng ZP, Li GR, Zhong JH, Wang ZL, Ou YN, Tong YX (2009) *Electrochem Commun* 11:706
12. Kim JH, Ayalasomayajula T, Gona V, Choi D (2008) *J Power Sources* 183:366
13. Débart A, Paterson AJ, Bao JL, Bruce PG (2008) *Angew Chem Int Ed* 47:4521
14. Yang YY, Xiao LF, Zhao YQ, Wang FY (2008) *Int J Electrochem Sci* 3:67
15. Wang GL, Tang B, Zhuo LH, Ge JC, Xue M (2006) *Eur J Inorg Chem* 11:2313
16. Yoo HN, Park DH, Hwang SJ (2008) *J Power Sources* 185:1374
17. Bach S, Ramos JPP, Baffier N, Messina R (1995) *Electrochim Acta* 40:785
18. Minakshi M (2009) *J Solid State Electrochem* 13:1209
19. Minakshi M, Mitchell DRG, Singh P (2007) *Electrochim Acta* 52:3294
20. Minakshi M, Mitchell DRG, Prince K (2008) *Solid State Ionics* 179:355
21. Minakshi M, Mitchell DRG, Carter ML, Appadoo D, Kalaiselvi N (2009) *Electrochim Acta* 54:3244
22. Wu YP, Rahm E, Holze R (2002) *Electrochim Acta* 47:3491
23. Kobayashi S, Kottegoda IRM, Uchimoto Y, Wakihara M (2004) *J Mater Chem* 14:1843
24. Zhan H, Zhou YH, Wang CG, Guo WY, Peng ZH (2005) *Mater Chem Phys* 90:353
25. Yang X, Wang Y, Xiong HM, Xia YY (2007) *Electrochim Acta* 53:752
26. Chen R, Zavaliji P, Whittingham MS (1996) *Chem Mater* 8:1275
27. Ching S, Landrigan JA, Jorgensen ML, Duan N, Suib SL, OYoung C (1995) *Chem Mater* 7:1604
28. Cheng FY, Zhao JZ, Song WN, Li CS, Ma H, Chen J, Shen PW (2006) *Inorganic Chemistry* 45:2038
29. Luo JY, Zhang JJ, Xia YY (2006) *Chem Mater* 18:5618
30. Yuan CZ, Gao B, Su LH, Zhang XG (2008) *J Colloid Int Science* 322:545