Reduced titanium oxide Ti$_3$O$_5$ powder as a promising conductive additive for LiFePO$_4$-based lithium-ion batteries

Yun Chen · Jian Mao

Abstract Reduced titanium oxide Ti$_3$O$_5$ powder which was fabricated by a sol–gel process was added to lithium iron phosphate (LiFePO$_4$) cathode electrodes for use in lithium-ion batteries and its performance was investigated. First discharging of the cathode electrode with Ti$_3$O$_5$ powder as the conductive additive keeps the capacity of 170.9 mAh g^{-1} at 0.1 C, 150.8 mAh g^{-1} at 0.5 C, 134.6 mAh g^{-1} at 1 C, and 107 mAh g^{-1} at 2 C, respectively, which is higher than that of the cathode electrode with acetylene black as the conductive additive, who keeps the capacity of 162 mAh g^{-1} at 0.1 C, 142.8 mAh g^{-1} at 0.5 C, 126.9 mAh g^{-1} at 1 C, and 105.8 mAh g^{-1} at 2 C, respectively. Over 100 cycles at 0.5 C, the LiFePO$_4$ cathode electrode with Ti$_3$O$_5$ powder can maintain 77.5 % of its initial capacity, and the electrode with acetylene black shows 73.6 % capacity retention. The reason why the electrode with Ti$_3$O$_5$ additive shows better rate capability is that the Ti$_3$O$_5$ powder exhibits a relatively good electrical conductivity and shows a more homogeneous dispersion than acetylene black among the LiFePO$_4$ particles during the cycles, in the investigation, a layer of suspected titanium oxide yarn-like thin film is discovered coating on the LiFePO$_4$ particles of the cathode electrode with Ti$_3$O$_5$ powder after 100 cycles at 0.5 C.

Y. Chen · J. Mao (✉)
School of Materials Science and Engineering,
Sichuan University, Chengdu 610065, Sichuan,
People's Republic of China
e-mail: maojianemail@163.com

1 Introduction

Olivine lithium iron phosphate (LiFePO$_4$) with various advantages, such as high voltages (3.4 V vs. Li/Li$^+$), relatively high theoretical capacity (170 mAh g^{-1}), high thermal stability at high temperature, high safety, low cost and so on, has been considered as a promising candidate for a cathode material of lithium-ion batteries since it was first reported by Padhi et al. [1]. Unfortunately, the poor electronic conductivity and the low tap density have been main obstacles for the practical applications of LiFePO$_4$.

At present, progressive efforts have been made by several research groups to overcome the low electrical conductivity of LiFePO$_4$, including carbon coating [2, 3] and particle size minimization [4]. However, while researchers are focusing on the improvement of low electrical conductivity of LiFePO$_4$, the low tap density of LiFePO$_4$ has usually been overlooked and evaded. To effectively utilize the active material, the ratio of acetylene black often reaches 10 wt% in the blending of the cathode material with the binding polymer and electrically conductive additives. However, due to the low density of carbon, the required amount of acetylene black leads to considerable increase in volume resulting in a great decrease in the tap density and the following lower volumetric energy density of the LiFePO$_4$ cathode electrodes in lithium-ion batteries. One way to improve the volume specific energy is to increase the cathode density by applying more compact and dense conductive additives, because this cell component has the largest volume and the heaviest weight. Therefore, there is a need for alternative conductive additives that may improve the performance and the tap density of the LiFePO$_4$ cathode electrodes in lithium-ion cells.

Reduced titanium oxides materials are a series of substoichiometric oxides of titanium which are identifiable

compounds and not simply doped titanium dioxide or casual mixtures of TiO_x, where x is less than 2 [5]. They can be synthesized by heat-treating titanium dioxide at high temperature in a reducing atmosphere, usually in the presence of hydrogen [6] or carbon [7]. These oxides materials possess several advantages, including narrow band gap enabling absorption of visible light [8, 9], chemical stability, and high electrical conductivity comparable to that of graphite thanks to the mixed Ti^{III}/Ti^{IV} valences [10]. Due to these favorable properties, a lot of academic and industrial laboratories have devoted considerable efforts to applications of these titanium oxides in various cells, for example, reduced titanium oxide Ti_4O_7 as a conductive additive for Zn electrodes in secondary Ni/Zn batteries [11], carbon-coated Ti_9O_{17} nanobelts as anodes for Li-ion batteries and hybrid electrochemical cells [12] and reduced titanium oxides materials as a positive electrode conductive additive in Lead-acid batteries [5]. However, to our knowledge, this type of reduced titanium oxides materials as a conductive additive for Li-ion cells has not yet tested on $LiFePO_4$ cathode electrodes in lithium-ion batteries.

Among the family of these titanium oxides materials, Ti_3O_5 has been considered to be well worth investigating and one of the most concerns for its excellent performance in electrical conductivity which can reach as high as 630 S cm^{-1} [13]. Herein, we adopt reduced titanium oxide Ti_3O_5 powder to replace acetylene black as the conductive additive for $LiFePO_4$ cathode electrodes in lithium-ion cells.

2 Experimental

The $LiFePO_4$ powder was purchased from Unanoergy Technology Co., Ltd, acetylene black was purchased from Shenzhen Poxon Machinery Technology Co., Ltd and Ti_3O_5 powder in this study was fabricated by a sol–gel process using tetrabutyl titanate as a precursor, dehydrated alcohol as an impregnant, and polyethylene glycol (PEG-600) as organic carbon source, and then by calcination at 1,000 °C for 4 h under high pure (99.999 %) argon atmosphere in an evacuated silica tube, as described in previous report [14]. The $LiFePO_4$ cathode electrode contains 80 wt% dry basis $LiFePO_4$ powder, 10 wt% conductive additive Ti_3O_5 or acetylene black, and 10 wt% poly(vinylidene fluoride) (PVDF) using N-methyl-2-pyrrolidone (NMP) as a solvent. The mixture slurry was coated on an aluminum foil and dried at 80 °C for 12 h. The charge and discharge characteristics were examined using a coin cell (CR2025 type), which consisted of a $LiFePO_4$ cathode electrode, an electrolyte of 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DC) with a volume ratio of 1:2, a lithium metal negative electrode, and a Celgard 2500

separator. The CR2025 coin cells were assembled in an argon-filled glove box.

The crystalline structure of the samples was identified by a Rigaku Dmax-2000 XRD diffractionmeter with Cu Kα_1 ($\lambda = 0.154056$ nm) radiation. The surface morphology of the samples was recorded using a Hitachi S-4800 field emission scanning electron microscope (FESEM). TG measurement of $LiFePO_4$ powder was carried out by using a TG 209 F1 (NETZSCH Instrument). The size distribution of $LiFePO_4$ powder was made at a temperature of 25 °C on a ZS90 nano particle and zeta analyzer (Malvern, UK). Brunauer–Emmett–Teller (BET) surface area of Ti_3O_5 powder and acetylene black powder was determined by a NOVA 4200e nitrogen adsorption instrument (Quantachrome Instruments, USA). The tap density of the samples was measured by a JZ-1 powder tap density tester (Shenzhen Sannuo Instrument Co. Ltd, China). The resistivity of Ti_3O_5 powder and acetylene black powder was measured by a FZ-2010 semiconductor powder resistivity meter (Shanghai Yi Yu Instrument Co., Ltd, China). Charge–discharge performances of the cells were evaluated by a LAND-CT2001A battery test system (Jinnuo Wuhan Corp., China) with voltage range from 2 to 4.2 V at room temperature.

To investigate the active material $LiFePO_4$ after the completion of the cycles test, the cycled coin cells were dissembled in a glove box under Ar atmosphere, and the electrodes were rinsed with dehydrated alcohol and dried and stored in the glove box before analysis. Surface and particle morphology were examined by a Hitachi S-4800 FESEM, energy dispersive X-ray spectroscopy was used to analyze the surface compositions of electrodes.

3 Results and discussion

Figure 1a presents the XRD patterns of the cathode active material employed in this experiment and the standard PDF card of pure $LiFePO_4$. The characteristic peaks of the employed cathode active material agree very well with that of pure $LiFePO_4$ and no evidence of impurity phases could be observed, which denotes that the sample is olivine $LiFePO_4$. The FESEM image of the employed $LiFePO_4$ sample is shown in Fig. 1b. As can be seen, the $LiFePO_4$ particles have a rice-like shape and there is a layer of carbon coating on the surface of $LiFePO_4$ particles, and the average carbon-coated $LiFePO_4$ particle size is 567.9 nm, as displayed in Fig. 1c. The carbon content of the employed carbon-coated $LiFePO_4$ sample can be approximately estimated about 3.6 wt% through the TG curve in Fig. 1d.

The XRD pattern of the reduced titanium oxide powder sample is shown in Fig. 2a, almost all the peaks can be

Fig. 1 a XRD patterns of the employed $LiFePO_4$ sample and the standard PDF card of pure $LiFePO_4$, **b** FESEM images of the $LiFePO_4$ particles, **c** particle size distribution of the $LiFePO_4$ sample, **d** TG curve of employed $LiFePO_4$. TG measurement was carried out under N_2 atmosphere, and heating rate was 10 °C min^{-1}
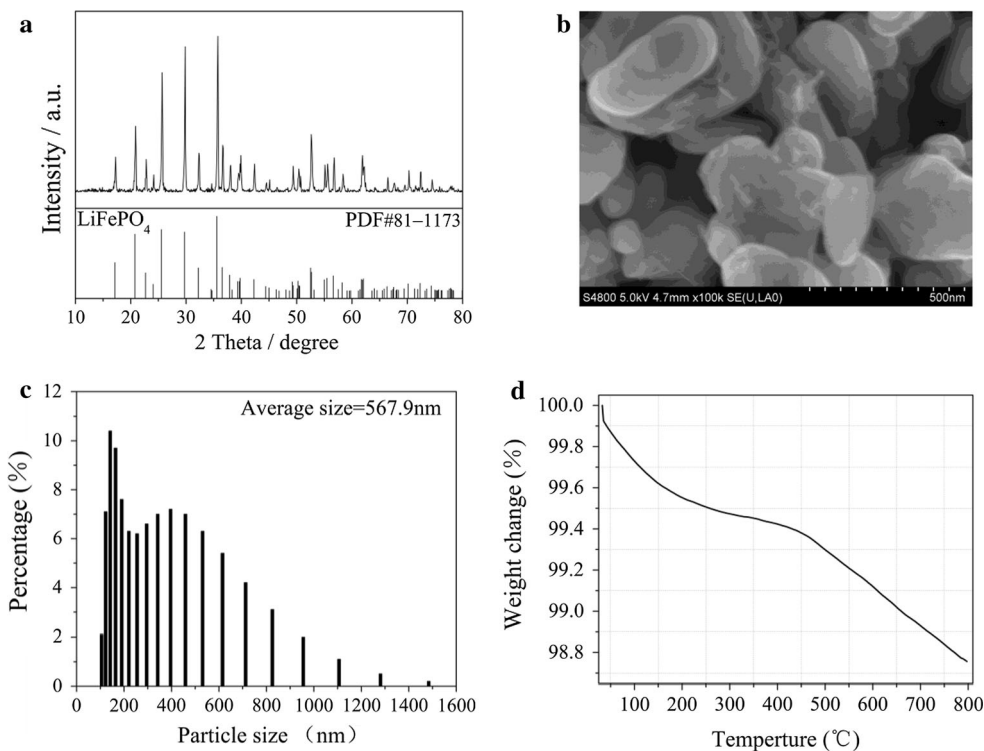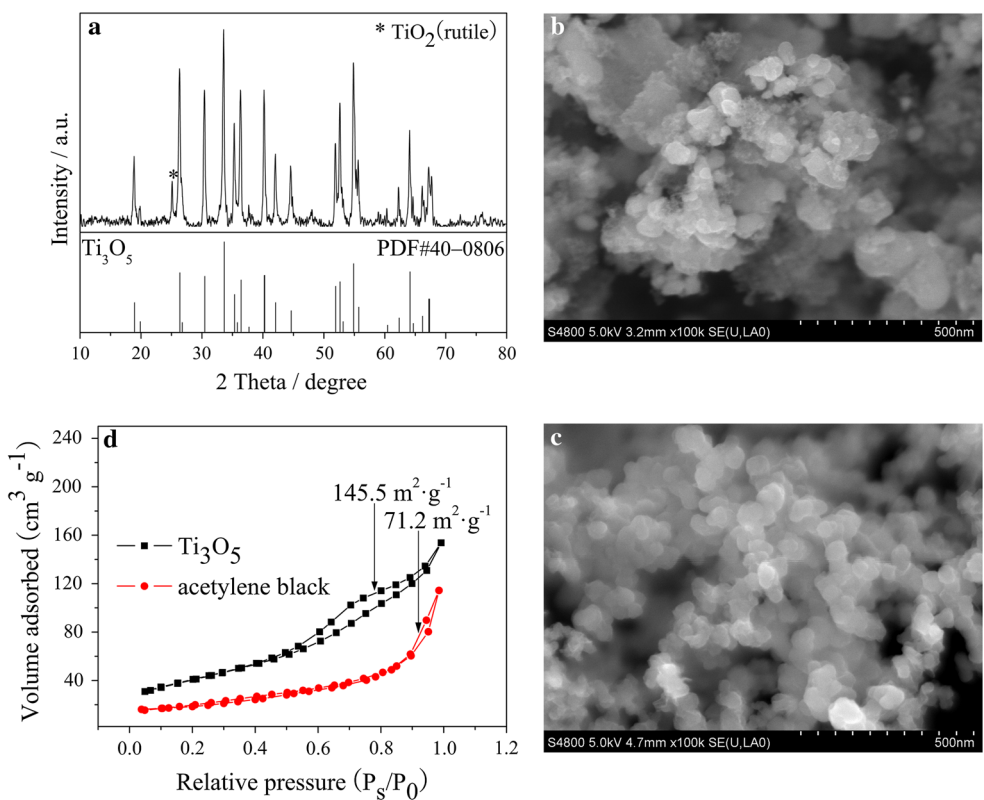

Fig. 2 a XRD pattern of the reduced titanium oxide sample, **b** the FESEM image of Ti_3O_5 sample, **c** the FESEM image of acetylene black, **d** N_2 adsorption/desorption curves of the samples

indexed as monoclinic Ti_3O_5 phase (PDF No.40-0806) except a weak peak of rutile type TiO_2 is observed, illustrating that the reduced titanium oxide powder is relatively pure Ti_3O_5. Figure 2b, c shows the FESEM image of Ti_3O_5 powder and acetylene black powder, respectively. Acetylene black powder is more uniform in shape and size in

Fig. 3 **a** Capacity-rate performance of LiFePO$_4$ cathode electrodes by adding conventional acetylene black and Ti$_3$O$_5$ conductive additives, **b** comparison of the cycle performance of LiFePO$_4$ cathode electrodes using different conductive additives
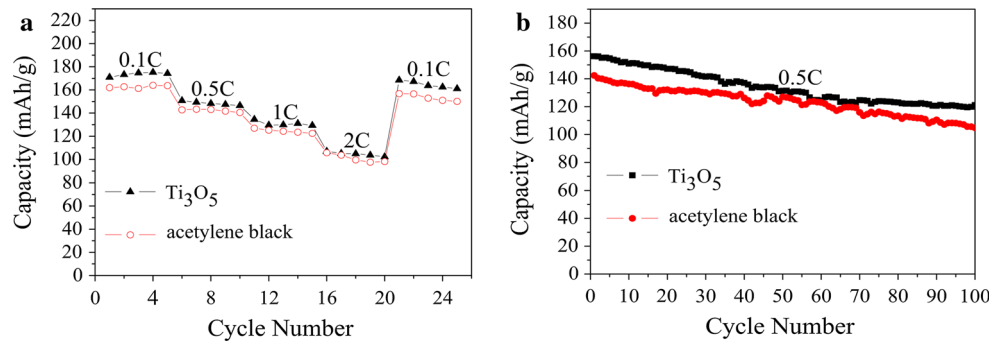
comparison with that of Ti$_3$O$_5$ powder. However, the BET test appears a different result, as presented in Fig. 2d. The BET specific surface area of Ti$_3$O$_5$ particles is 145.5 m^2 g^{-1}, which is much larger than that of acetylene black powder who only exhibits 71.2 m^2 g^{-1}. This probably suggests that the Ti$_3$O$_5$ aggregates in Fig. 2b have a fluffy, porous structure and consist of smaller particles.

The composite electrode with 10 wt% Ti$_3$O$_5$ powder shows good rate capability. As shown in Fig. 3a, first discharging keeps the capacity of 170.9 mAh g^{-1} at 0.1 C, 150.8 mAh g^{-1} at 0.5 C, 134.6 mAh g^{-1} at 1 C, and 107 mAh g^{-1} at 2 C, respectively, which is better than that of the composite electrode with 10 wt% acetylene black, who keeps the capacity of 162 mAh g^{-1} at 0.1 C, 142.8 mAh g^{-1} at 0.5 C, 126.9 mAh g^{-1} at 1 C, and 105.8 mAh g^{-1} at 2 C, respectively. Over 100 cycles at 0.5 C, the LiFePO$_4$ cathode electrode with Ti$_3$O$_5$ powder can maintain 77.5 % of its initial capacity, and the electrode with acetylene black shows 73.6 % capacity retention, as presented in Fig. 3b. The results demonstrate that Ti$_3$O$_5$ powder as the conductive additive is superior to acetylene black for LiFePO$_4$ cathode electrodes in Li-ion cells. Moreover, Ti$_3$O$_5$ powder possesses a tap density of 1.46 g cm^{-3}, which is more than eight times as high as that of acetylene black who only exhibits 0.17 g cm^{-3}. Therefore, Ti$_3$O$_5$ additive can sufficiently increase tap density and volumetric energy density of the LiFePO$_4$ electrode.

Figure 4 compares the FESEM images of the surface and morphology of electrodes with different conductive additives pre and post 100 cycles at 0.5 C. As shown in Fig. 4a, b, the surface and morphology of the electrode with acetylene black as the conductive additive remain unchanged during the cycles test, while, those of the electrode with Ti$_3$O$_5$ additive have been greatly changed after 100 cycles at 0.5 C. The surface of the cathode LiFePO$_4$ substrate with Ti$_3$O$_5$ additive is found to be covered with a uniform thin layer of yarn-like material after the cycles test (Fig. 4d). The inset EDS results of Fig. 4d show the presence of Ti element in the selected rectangle region, which means there maybe exist titanium

oxide film on the LiFePO$_4$ particles, but its special chemical formula of titanium oxide is not sure just by the EDS results.

Based on above analysis, the reasons for Ti$_3$O$_5$ additive improving the rate capability of LiFePO$_4$ cathode electrodes in Li-ion cells can be attributed to that, firstly, Ti$_3$O$_5$ powder sample exhibits a relatively good electrical conductivity, its electrical resistivity is 4.7 × 10^{-3} Ω m, as a contrast, that of acetylene black is 5.6 × 10^{-4} Ω m. Despite the electric conductivity of Ti$_3$O$_5$ powder is lower than that of acetylene black, however, even more important is that Ti$_3$O$_5$ powder displays a more homogeneous dispersion among the LiFePO$_4$ particles during the cycles than that of acetylene black powder, there forms a thin suspected titanium oxide film coating on the LiFePO$_4$ particles after 100 cycles at 0.5 C, while the surface and morphology of the electrode with acetylene black has remained almost unchanged during the cycles test.

4 Conclusions

The analysis results indicate that Ti$_3$O$_5$ powder with a fluffy, porous structure exhibits a much larger BET specific surface area than acetylene black powder. The cathode electrode with Ti$_3$O$_5$ shows higher rate capability and cycling stability in comparison with the electrode with acetylene black. First discharging of the cathode electrode with Ti$_3$O$_5$ powder keeps the capacity of 170.9 mAh g^{-1} at 0.1 C, 150.8 mAh g^{-1} at 0.5 C, 134.6 mAh g^{-1} at 1 C, and 107 mAh g^{-1} at 2 C, respectively, and that of the cathode electrode with acetylene black is 162 mAh g^{-1} at 0.1 C, 142.8 mAh g^{-1} at 0.5 C, 126.9 mAh g^{-1} at 1 C, and 105.8 mAh g^{-1} at 2 C, respectively. Over 100 cycles at 0.5 C, the LiFePO$_4$ cathode electrode with Ti$_3$O$_5$ powder as the conductive additive can maintain 77.5 % of its initial capacity, and the electrode with acetylene black shows 73.6 % capacity retention. The reasons can be summarized that, Ti$_3$O$_5$ powder exhibits a relatively good electrical conductivity and shows a homogeneous dispersion among the LiFePO$_4$ particles during the

Fig. 4 FESEM images of the LiFePO$_4$ electrodes with different conductive additives pre and post 100 cycles at 0.5 C: **a** the electrode with acetylene black before the cycles test, **b** the electrode with acetylene black after the cycles test, **c** the electrode with Ti$_3$O$_5$ before the cycles test, **d** the electrode with Ti$_3$O$_5$ after the cycles test, and the *inset* is the corresponding EDS result of the *rectangle* selection region
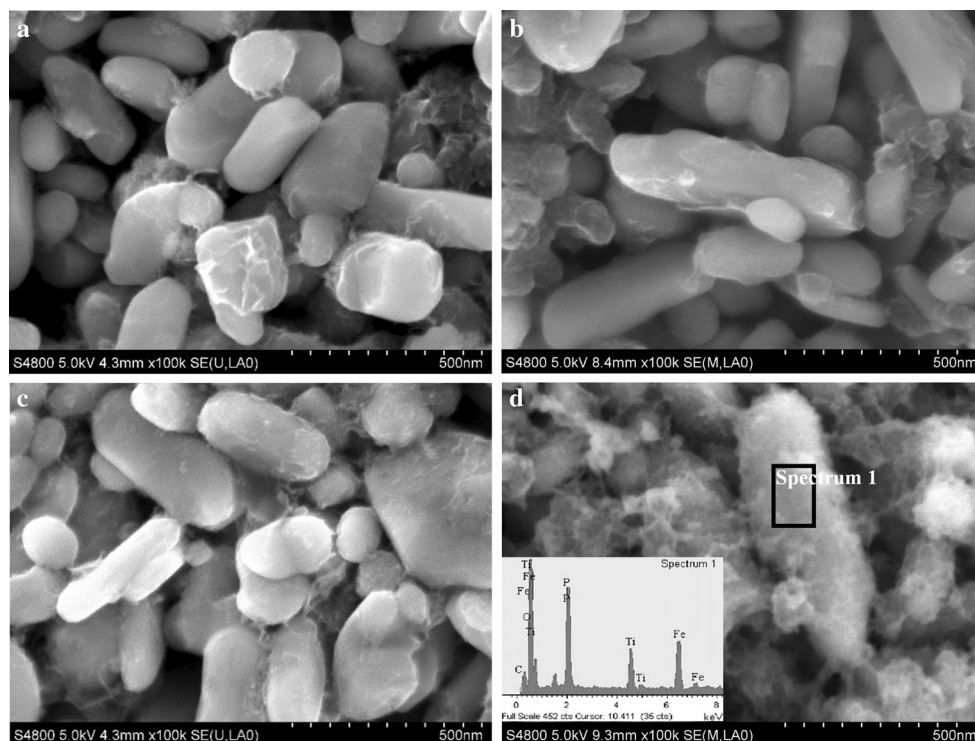
cycles test, in the investigations, there exists a layer of suspected titanium oxide yarn-like thin film coating on the LiFePO$_4$ particles after 100 cycles at 0.5 C.

In addition, Ti$_3$O$_5$ powder possesses a relatively high tap density of 1.46 g cm^{-3}, much higher than that of acetylene black (0.17 g cm^{-3}). Considering this and its relatively better rate capability, Ti$_3$O$_5$ powder has the potential to be applied to LiFePO$_4$ cathode electrodes in lithium-ion batteries as the conductive additive.

References

1. A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, J. Electrochem. Soc. **144**, 1188 (1997)
2. S.W. Oh, S.T. Myung, S.M. Oh, K.H. Oh, K. Amine, B. Scrosati, Y.K. Sun, Adv. Mater. **22**, 4842 (2010)
3. C. Zhu, Y. Yu, L. Gu, K. Weichert, J. Maier, Angew. Chem. Int. Ed. **50**, 6278 (2011)
4. S.-Y. Chung, Y.-M. Kim, S.-Y. Choi, Adv. Funct. Mater. **20**, 4219 (2010)
5. J.R. Smith, F.C. Walsh, R.L. Clarke, J. Appl. Electrochem. **28**, 1021 (1998)
6. X. Li, A.L. Zhu, W. Qu, H. Wang, R. Hui, L. Zhang, J. Zhang, Electrochim. Acta **55**, 5891 (2010)
7. D. Regonini, A.C.E. Dent, C.R. Bowen, S.R. Pennock, J. Taylor, Mater. Lett. **65**, 3590 (2011)
8. H.M. Liu, W.S. Yang, Y. Ma, J.N. Yao, Appl. Catal. A **299**, 218 (2006)
9. W.Q. Han, Y. Zhang, Appl. Phys. Lett. **92**, 203117 (2008)
10. Edmund G. Seebauer, Meredith C. Kratzer, Mater. Sci. Eng. R **55**, 57 (2006)
11. Z. Luo, S. Sang, Q. Wu, S. Liu, ESC Electrochem. Lett. **2**, A21 (2013)
12. W.Q. Han, X.L. Wang, Appl. Phys. Lett. **97**, 243104 (2010)
13. A.A. Gusev, E.G. Avvakumov, AZh Medvedev, A.I. Masliy, Sci. Sinter. **39**, 51 (2007)
14. Yun Chen, Jian Mao, J. Mater. Sci. Mater. Electron. **25**, 1284 (2014)