



Short communication

Synthesis of spherical porous vanadium pentoxide and its electrochemical properties

C.Q. Feng^{a,b}, S.Y. Wang^a, R. Zeng^b, Z.P. Guo^{b,c,d,*}, K. Konstantinov^b, H.K. Liu^{b,c}^a Faculty of Chemistry and Chemical Engineering, Hubei University, Wuhan 430062, China^b Institute for Superconducting & Electronic Materials, University of Wollongong, NSW 2522, Australia^c ARC Centre of Excellence for Electromaterials Science, University of Wollongong, NSW 2522, Australia^d School of Mechanical, Materials & Mechatronic Engineering, University of Wollongong, NSW 2522 Australia

ARTICLE INFO

Article history:

Received 20 December 2007

Received in revised form 13 February 2008

Accepted 9 April 2008

Available online 29 April 2008

Keywords:

Spherical porous vanadium pentoxide

Spray pyrolysis

Lithium-ion battery

Specific capacity

ABSTRACT

Spherical porous vanadium pentoxide (V_2O_5) phase is synthesized by a spray-pyrolysis method followed by heat-treatment, as confirmed by powder X-ray diffraction. Under high-resolution electron microscope observation, the as-prepared particles are spherical and porous, with uniform particle size. On investigation of the electrochemical properties of V_2O_5 synthesized by this method, it is found that the initial specific capacity of the V_2O_5 is 399 mAh g^{-1} , and it exhibits good cycleability during the discharge and charge processes. The experimental results suggest that V_2O_5 synthesized by this method could be a promising electrode material for lithium-ion batteries.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Lithium-ion batteries have become the most popular power sources for consumer electronic devices, such as cell phones and laptop computers, due to their high specific energy and long cycle-life. In addition, lithium-ion batteries are expected to be part of a major breakthrough in the hybrid electric vehicle field. Despite their successful commercial application, further improvement in the performance of the lithium-ion battery is still required for large-scale applications. Vanadium pentoxide (V_2O_5) is often employed as a cathode in lithium-ion batteries to improve capacity, voltage (versus the anode material), reversibility, and stability [1–3]. It has been found that the performance of a V_2O_5 cathode is heavily dependent on its crystallinity and morphology [4–6]. Crystalline V_2O_5 has a high specific capacity, but during deep charge–discharge cycles, it undergoes structural modification which is induced by mechanical stress. This leads to a decrease in specific capacity and specific energy. In addition, the diffusion coefficient of Li^+ in crystalline V_2O_5 is inherently low. Amorphous or low crystallinity V_2O_5 allows faster lithium-ion diffusion and displays remarkable cycleability, as mechanical stress associated with lithium

intercalation/de-intercalation can be more easily absorbed by small crystallites with a high surface area, which also leads to higher ionic conductivity. Therefore, it is quite obvious that structural changes of V_2O_5 during charging/discharging and low ionic diffusion are the two key problems of V_2O_5 cathode.

If a V_2O_5 nanostructure can be obtained with a porous network and a high surface area, it can be expected that the combination of small crystallites and pores in the network may more effectively relax the structural changes, which are caused by volumetric changes due to the electrochemical intercalation/de-intercalation of Li^+ , solvent transport into or out of the material during redox cycling, and changes in the coordination geometry at the metal centres that result from the redox transitions. The porous network also provides electrolyte-filled channels, i.e., pathways for faster transport of the ions to insertion sites, which will favour the diffusion of lithium ions.

V_2O_5 nanostructures have mostly been prepared by wet processes, such as the sol–gel method [7–11]. Vanadium oxide gels are normally made by hydrolysis of organic vanadyl alkoxides in acetone–water solution, followed by thermal treatment [7,12]. The vanadium pentoxide so prepared exhibits high capacity. The whole preparation process takes a long time, however, and the vanadium oxides so obtained have a sloping discharge curve, which is typical of amorphous substances. The synthesis of V_2O_5 porous nanostructures with high surface area has never been reported, because porous structures are not stable during the synthesis process. In this study, the spray-pyrolysis technique is employed to synthesize

* Corresponding author at: Institute for Superconducting & Electronic Materials, University of Wollongong, Northfield Avenue, Wollongong, NSW 2522, Australia. Tel.: +61 2 4221 5225; fax: +61 2 4221 5731.

E-mail address: zguo@uow.edu.au (Z.P. Guo).

V₂O₅ porous nanostructures. The spherical shape of the droplets during the spray process is retained after pyrolysis (transport) in a vertical furnace. The decomposition of oxalic acid (H₂C₂O₄) and citric acid in the precursor solution and the carrier gas induce porous structures, so that spherical porous V₂O₅ is successfully fabricated. The electrochemical properties of the V₂O₅ so obtained are systematically investigated with reference to the suitability of V₂O₅ as a cathode material for lithium-ion batteries.

2. Experimental

2.1. Synthesis and characterization

V₂O₅, H₂C₂O₄, and citric acid in a molar ratio of 1:1:1.2 were dissolved in distilled water by heating to form a precursor solution, in which the concentration of V₂O₅ was 0.1 M. The solution was then fed into a vertical spray-pyrolysis reactor at a rate of 50 ml min⁻¹. An atomizing nozzle was used in combination with compressed air, and the spraying was carried out at a pressure of 2.0 MPa and an atmospheric temperature of 350 °C to produce the oxide precursor. The oxide precursor was heat-treated at different temperatures in air to form spherical porous V₂O₅. Powder X-ray diffraction (XRD; 1730 Philips X-ray diffractometer) using Cu K α radiation was employed to identify the crystalline phases of the synthesized materials. The morphology of the resultant vanadium pentoxide was observed under a scanning electron microscope (SEM; Leica Cambridge Stereoscan 440). A battery testing system (Neware Technology Ltd., China) was used for electrochemical investigation.

2.2. Electrochemical measurements

The cathode was made by mixing 70% active materials with 20% acetylene black as a conducting agent and 10% poly(vinylidene fluoride) (PVDF) powder as a binder. After *N*-methyl-2-pyrrolidone (NMP, Aldrich) was added to the mixture, which was further ground to form a slurry, the slurry was spread on to Al foils at a mass loading of about 1 mg cm⁻², and then dried at 125 °C and pressed under 150 kg cm⁻². The thickness of the electrode after pressing was ~50 μ m, and the V₂O₅ loading was ~1.2 mg. CR2032 coin cells were assembled in an argon-filled glove box. A microporous film (Celgard 2500, Hoechst Celanese) was used as the separator, and the electrolyte was 1 M LiPF₆ in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1, v/v, from Merck). The cells were cycled between 4.0 and 1.5 V at room temperature.

3. Results and discussion

3.1. Reaction process and crystal structure

V₂O₅/H₂C₂O₄/citric acid in a molar ratio of 1:1:1.2 was first dissolved in distilled water to form a precursor solution, and the solution was then transported into a reaction furnace using air as the carrier gas. The droplets were dried, decomposed, reacted and sintered during passage through the reaction furnace, where the following reactions occurred to form spherical porous vanadium pentoxide:

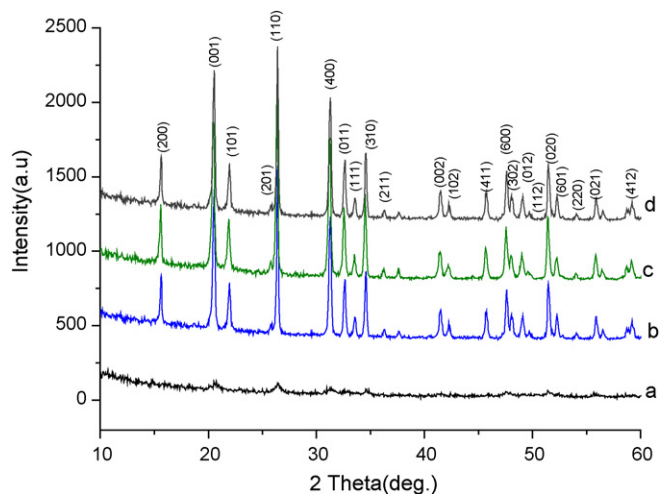
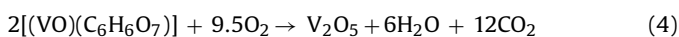
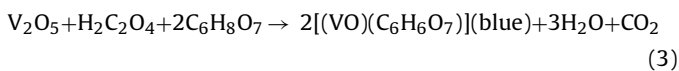
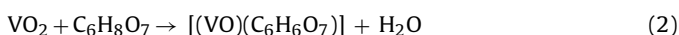
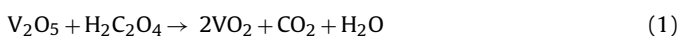


Fig. 1. XRD patterns of V₂O₅ prepared by spray pyrolysis at 350 °C followed by heat-treatment: (a) as-sprayed V₂O₅; (b) heat-treatment at 350 °C for 6 h; (c) heat-treatment at 420 °C for 6 h; (d) heat-treatment at 450 °C for 6 h.

The XRD pattern of the as-sprayed powder is shown in Fig. 1(a). A few broadened peaks can be observed, which correspond to V₂O₅. The XRD patterns of the powders after heat-treatment are also shown in Fig. 1. It is obvious that V₂O₅ was formed after heat-treatment at different temperatures (b: 350 °C; c: 420 °C; and d: 450 °C). All diffraction lines can be indexed as V₂O₅ with an orthorhombic structure (PDF card 41-1426). The lattice parameters of V₂O₅ heat-treated at 420 °C were calculated from the XRD data ($a = 1.1516$ nm, $b = 0.35656$ nm, and $c = 0.43727$ nm). These results are consistent with values previously reported in the literature.

Scanning electron micrographs of as-sprayed V₂O₅ and V₂O₅ samples after heat-treatment at different temperatures are presented in Fig. 2. The as-prepared V₂O₅ materials are spherical particles of uniform size (Fig. 2(a)). After heat-treatment at the lower temperatures (<420 °C), the spherical shape is retained, but the spherical particles appear porous, although some particles have shrunk, and the particle size is distributed over a wide range of 1–8 μ m (Fig. 2(b) and (c)). When the temperature of the heat-treatment is increased to 450 °C, it can be seen from Fig. 2(d) and (e) that the spherical V₂O₅ particles become dense. On further increase to 600 °C, the spherical porous network of sprayed V₂O₅ particles collapses and particles with random shapes are formed. Brunauer–Emmett–Teller (BET) nitrogen-adsorption measurements show that the specific surface areas of the V₂O₅ samples heat-treated at 420 and 450 °C are 114 and 76 m² g⁻¹, respectively. This confirms that the V₂O₅ samples become denser and less porous when the heat-treatment temperature is increased. The crystallite size also increases with increasing heat-treatment temperature.

The electrochemical properties of V₂O₅ were also systematically investigated. The charge/discharge profiles and the delivered cathode capacity for different cycles are shown in Figs. 3 and 4, respectively. The V₂O₅ heat-treated at 420 and 350 °C has an initial capacity of 399 and 330 mAh g⁻¹, corresponding to an intercalation of about 2.7 and 2.2 mol Li⁺ into 1 mol V₂O₅, respectively. This reveals the formation of ω -Li_xV₂O₅ ($x > 2$). It has been reported [13] that the theoretical discharge capacity of 294 mAh g⁻¹ for Li₂V₂O₅ is rarely reached by crystalline V₂O₅. Our results, however, clearly show that high initial discharge capacities are obtained with V₂O₅ spherical porous materials prepared by the spray-pyrolysis technique. In Fig. 3(a), there are four plateaux in the discharge and charge curves that originate from phase transitions between α -V₂O₅, ϵ -Li_xV₂O₅ (0.35 < x < 0.7), δ -Li_xV₂O₅ ($x = 1$), γ -Li_xV₂O₅ ($x < 2$),

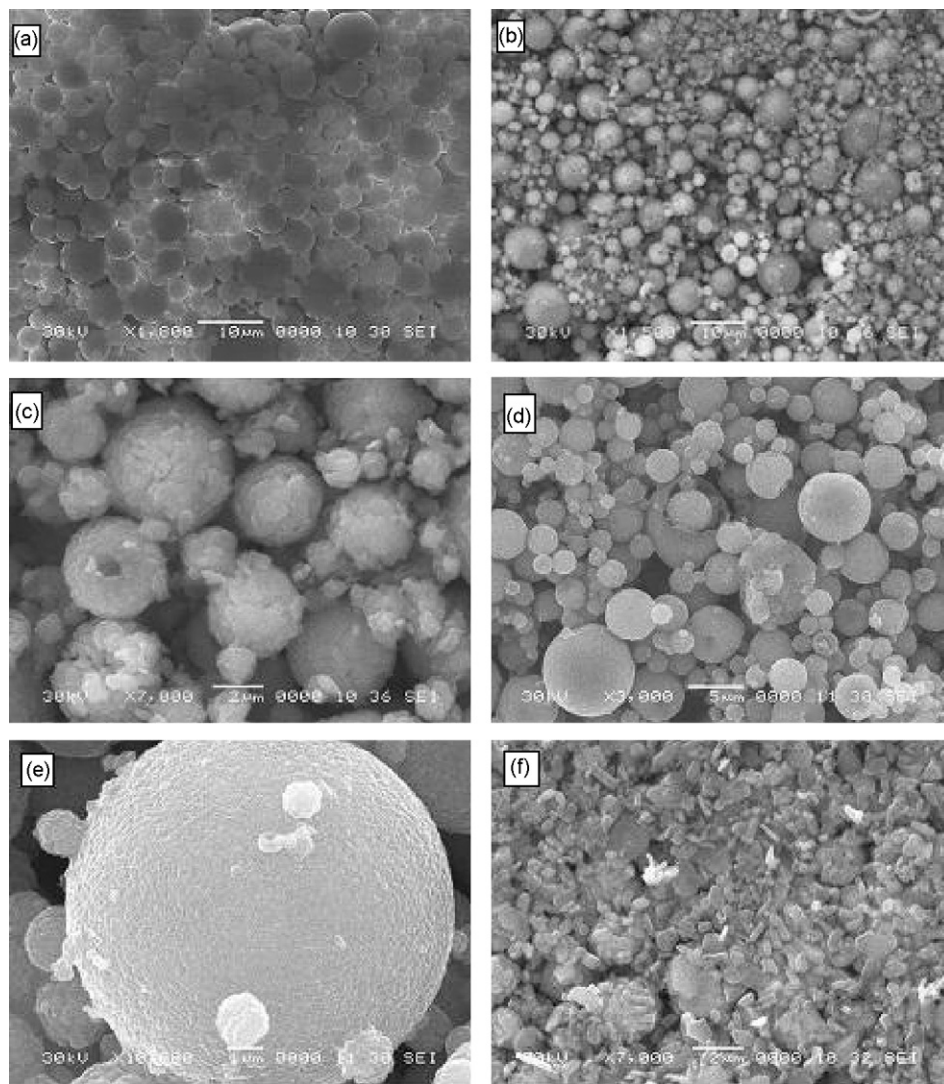


Fig. 2. Scanning electron micrographs of (a) as-sprayed V_2O_5 ; V_2O_5 heat-treated at different temperatures: (b) heat-treated at 350°C ; (c) heat-treated at 420°C ; (d) heat-treated at 450°C at low magnification; (e) heat-treated at 450°C at higher magnification; (f) heat-treated at 600°C .

and $\omega\text{-Li}_x\text{V}_2\text{O}_5$ ($x > 2$), respectively [14,15]. By contrast, for V_2O_5 heat-treated at 420°C (Fig. 3(b)), plateaux exist only in the first cycle, but disappear in the following discharge and charge curves. The V_2O_5 powders treated at 450°C have similar discharge and

charge profiles to those of Fig. 3(b). The disappearance of plateaux after the second cycle in Fig. 3(b) may be due to the larger impedance (larger polarization) of the electrode fabricated using V_2O_5 heat-treated at 420°C compared with that at 350°C . (Several

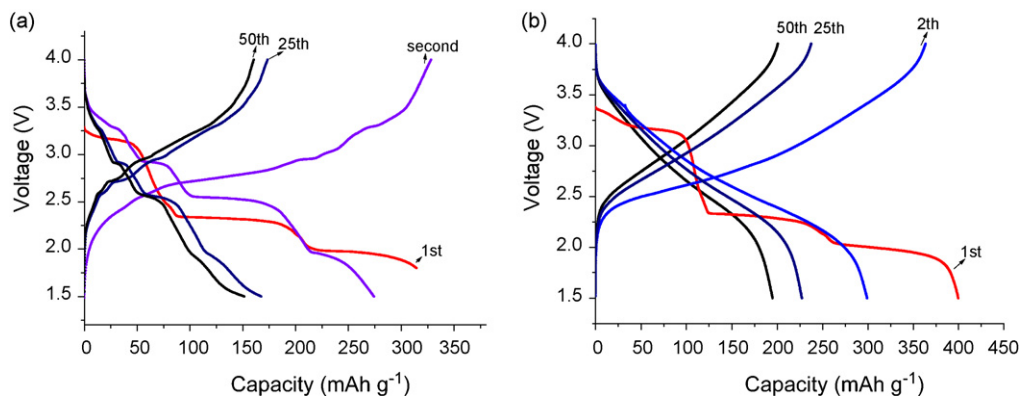


Fig. 3. Typical charge and discharge curves of V_2O_5 electrode at different cycles: (a) spray pyrolysis at 350°C and heat-treatment at 350°C ; (b) spray pyrolysis at 350°C and heat-treatment at 420°C (current density 40 mA g^{-1}).

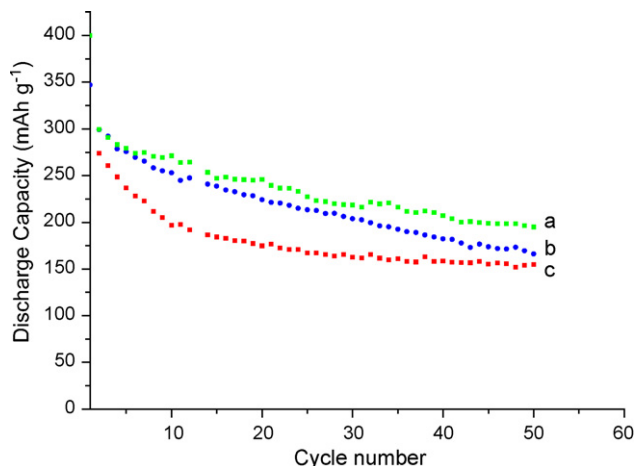


Fig. 4. Capacity as function of cycle number for electrodes made with V_2O_5 prepared under different conditions: (a) spray pyrolyzed at 350°C and heat-treated at 420°C ; (b) spray pyrolyzed at 350°C and heat-treated at 450°C ; (c) spray pyrolyzed at 350°C and heat-treated at 350°C (current density was 40 mA g^{-1}).

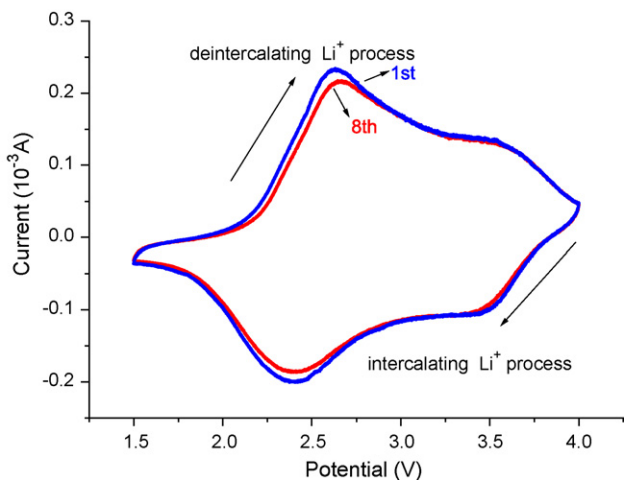


Fig. 5. Cyclic voltammograms for first and eighth cycles of V_2O_5 electrode (spray pyrolyzed at 350°C and heat-treated at 420°C for 6 h) in a coin cell (vs. Li).

plateaux may overlap each other in the case of the sample prepared at 420°C due to the larger polarization.)

From Fig. 4, it can be clearly see that heat-treatment temperatures significantly influence the cycling stability of the V_2O_5 cathodes. V_2O_5 prepared by spray pyrolysis at 350°C , followed by heat-treatment at 420°C , delivers not only a high initial discharge capacity, but also better cycling performance.

In order to investigate further the electrochemical properties of V_2O_5 prepared by spray pyrolysis at 350°C and heat-treatment at 420°C , cyclic voltammograms (CVs) of a cell using the V_2O_5 as the cathode are collected and are shown in Fig. 5.

Cyclic voltammograms of an electrode made from spherical porous V_2O_5 that was spray pyrolyzed at 350°C and then heat-treated at 420°C for 6 h are given in Fig. 5. Two pairs of redox peaks are observed. Two reduction peaks are located at 3.49 and 2.37 V, while the corresponding oxidation peaks are at 3.57 and 2.62 V, respectively. Peak intensities decrease with cycling, but the shape of the CV curve in the eighth cycle remains similar to that in the

first cycle, which suggests the reversible reduction and oxidation of the V_2O_5 electrode materials.

It is obvious that the optimum heat-treatment temperature after spray pyrolysis is 420°C . It is considered that the main reasons for this phenomenon are as follows:

- (i) V_2O_5 particles heat-treated at 420°C maintain their spherical porous structure, i.e., the porous network remains in place after heat-treatment. This porous network provides high surface area and many pathways for lithium-ion diffusion in the material.
- (ii) V_2O_5 particles heat-treated at 420°C are composed of smaller V_2O_5 crystals compared with V_2O_5 heat-treated at higher temperature. The structural changes associated with lithium intercalation/de-intercalation can be easily relaxed in the small crystallites.
- (iii) Spherical porous V_2O_5 particles heat-treated at 420°C have a very advantageous shape, offering a three-dimensional network to provide numerous electrolyte-filled channels for faster transport of lithium ions to the insertion sites.

4. Conclusions

Spherical porous V_2O_5 has been synthesized by a spray-pyrolysis route, followed by heat-treatment. XRD spectra of the product show that the precursor powder is decomposed to form spherical porous V_2O_5 at a suitable temperature (420°C). The V_2O_5 powders formed by this method are clearly porous and take on a perfectly spherical shape, with particle sizes in the range of 1–8 μm . The initial discharge capacity of a spherical porous phase V_2O_5/Li cell between 4.0 and 1.5 V at a current density of 40 mA g^{-1} is 399 mAh g^{-1} , and the cell exhibits good performance during the cycling process. Therefore, spherical porous V_2O_5 prepared by this method is a suitable electrode material for lithium-ion battery applications.

Acknowledgments

This work was supported by the Australian Research Council (ARC) through Linkage Project DP0775456 with industry partner DLG Battery Co. Ltd. The authors also thank Dr. T. Silver for critical reading of the manuscript.

References

- [1] A. Hammou, A. Hammouche, *Electrochim. Acta* 33 (1998) 1719.
- [2] M.S. Whittingham, *Prog. Solid State Chem.* 12 (1978) 41.
- [3] J.M. Tarascon, *Solid State Ionics* 69 (1994) 1.
- [4] G. Pistoia, M. Pasquali, G. Wang, *J. Electrochem. Soc.* 137 (1990) 2365.
- [5] Y. Sato, T. Nomura, H. Tanaka, K. Kobayakawa, *J. Electrochem. Soc.* 138 (1990) L37–L39.
- [6] J.B. Bates, N.J. Dudney, D.C. Lubben, G.R. Gruzalski, B.C. Kwak, X. Yu, R.A. Zuhr, *J. Power Sources* 54 (1995) 58–62.
- [7] K. Salloux, F. Chaput, H.P. Wong, B. Dunn, M.W. Brenner, *J. Electrochem. Soc.* 142 (1995) L191–L192.
- [8] H.K. Park, W.H. Smyrl, M.D. Ward, *J. Electrochem. Soc.* 142 (1995) 1068.
- [9] A.L. Tipton, S. Passerini, B.B. Owens, W.H. Smyrl, *J. Electrochem. Soc.* 143 (1996) 3473.
- [10] F. Leroux, B.E. Koene, L.F. Nazar, *J. Electrochem. Soc.* 143 (1996) L181.
- [11] D.B. Le, S. Passerini, J. Guo, J. Ressler, B.B. Owens, W.H. Smyrl, *J. Electrochem. Soc.* 143 (1996) 2099.
- [12] J. Livage, *Chem. Mater.* 3 (1991) 578.
- [13] D. Sun, C.W. Kwon, G. Baure, E. Richman, J. MacLean, B. Dunn, S.H. Tolbert, *Adv. Funct. Mater.* 14 (2004) 1197.
- [14] K. Takahashi, S.J. Limmer, Y. Wang, G.Z. Cao, *J. Phys. Chem. B* 108 (2004) 9795.
- [15] A.M. Cao, J.S. Hu, H.P. Liang, L.J. Wan, *Angew. Chem. Int. Ed.* 44 (2005) 4391.