

Controllable Synthesis of Hollow Bipyramid β -MnO₂ and Its High Electrochemical Performance for Lithium Storage

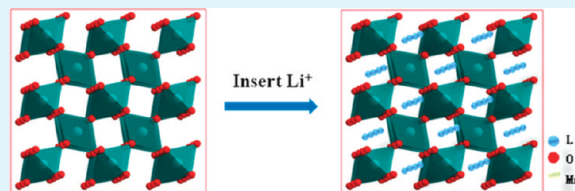
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ABSTRACT: Three types of MnO₂ nanostructures, viz., α -MnO₂ nanotubes, hollow β -MnO₂ bipyramids, and solid β -MnO₂ bipyramids, have been synthesized via a simple template-free hydrothermal method. Cyclic voltammetry and galvanostatic charge/discharge measurements demonstrate that the hollow β -MnO₂ bipyramids exhibit the highest specific capacity and the best cyclability; the capacity retains 213 mAh g⁻¹ at a current density of 100 mA g⁻¹ after 150 cycles. XRD patterns of the lithiated β -MnO₂ electrodes clearly show the expansion of lattice volume caused by lithiation, but the structure keeps stable during lithium insertion/extraction process. We suggest that the excellent performance for β -MnO₂ can be attributed to its unique electrochemical reaction, compact tunnel-structure and hollow architecture. The hollow architecture can accommodate the volume change during charge/discharge process and improve effective diffusion paths for both lithium ions and electrons.

KEYWORDS: MnO₂, nanotubes, bipyramids, lithium storage



INTRODUCTION

In recent years, nanoscaled electrode materials have attracted great interest for lithium-ion batteries because they can effectively improve specific capacity and cycle life due to their high surface area and size effect.^{1–3} Among the numerous nanostructures, one-dimensional (1D) hollow nanostructure like nanotube or hollow sphere is particularly attractive since it shows short diffusion path lengths for ions and electrons, which facilitates excellent electrochemical performance. Several methodologies such as sol–gel, hydrothermal route, template-assisted or template-free synthesis have been employed to fabricate various hollow nanostructures.⁴ However, developing a facile, low-cost, and readily controllable method to attain 1D hollow nanostructure is still a challenge.

Various transition-metal oxides have been investigated as electrode materials for lithium storage, such as MnO₂,^{5–7} SnO₂,^{8–10} TiO₂,¹¹ and MoO_x.^{12,13} Among them, MnO₂ has attracted tremendous research interest due to its low cost, high energy density and environmental friendliness.¹⁴ Up to now, various polymorphs of MnO₂, such as α -, β -, γ -, δ -, and ϵ -types with different morphologies, have been reported.^{15–20} Wang et al. reported that β -MnO₂ nanorods or α -MnO₂ nanowires can be selectively prepared by simply changing the amount of ammonium sulfate.²¹ Hill et al. synthesized all the α -, β -, and γ -MnO₂, and investigated their Li-ion insertion behaviors.^{22,23} It is especially noted that the electrochemical performance of MnO₂ strongly depends on its crystal structure, morphology and particle size. The specific capacity of MnO₂ is generally limited by its poor electrode kinetics because only the molecules located within a very thin layer at outside surface

participate in the charge-storage process while the rest remain inactive. How to insert more lithium ions into the lattice of MnO₂ is crucial to achieve a high capacity. On the other hand, because MnO₂ is irreversibly transformed to lithium manganese oxide during charge/discharge process, the cycle performance of MnO₂ is usually poor.¹⁷ Among the MnO₂ polymorphs, much attention has been paid to β -MnO₂ because of its high specific capacity,^{6,24} although β -MnO₂ has the narrowest (1 × 1) tunnel among the tunnel-type manganese oxide family. Nevertheless, further improvement in cyclic stability and rate capability for β -MnO₂ is still necessary. Moreover, the mechanism for the electrochemical properties of β -MnO₂ is not very clear, which needs to be identified.²⁵

In this work, we report a facile hydrothermal process to prepare three different α -MnO₂ and β -MnO₂ nanostructures with controllable crystal structure and morphology. The formation of three types of MnO₂ (nanotube, hollow bipyramid, solid bipyramid) was achieved by simply varying hydrothermal reaction temperature without any template or surfactant. Electrochemical measurements show that the as-synthesized hollow β -MnO₂ bipyramids exhibit the best discharge performance. Structural change and electrochemical mechanism of β -MnO₂ during lithiation process have been carefully investigated.

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EXPERIMENTAL SECTION

Synthesis of MnO₂. All chemical reagents used were of analytical grade. To prepare nanostructured MnO₂, we mixed 2.8 mmol of KMnO₄ and 1.5 mL HCl (36 wt %) in 40 mL of deionized water and magnetically stirred the mixture for about 30 min to form a precursor solution. The solution was then transferred into a Teflon-lined stainless steel autoclave (70 mL) and heated at 160–200 °C in an oven for 12 h. After the autoclave was cooled to room temperature, the solid precipitate was centrifuged and rinsed for several times with deionized water and absolute ethanol to remove impurities, and finally dried in a vacuum at 80 °C for 12 h.

Characterization. The phase and structure were examined by X-ray diffraction (XRD) on a X'Pert PRO diffractometer (PANalytical B.V., Holland) with high intensity Cu K α irradiation ($\lambda = 1.5406 \text{ \AA}$). The operation voltage and current were 40 kV and 40 mA, respectively. The morphologies of the samples were characterized by field-emission scanning electron microscopy (FE-SEM, FEI, Sirion 200) and their elemental compositions were measured with an energy-dispersive X-ray spectrometer (EDX, Oxford Instrument) attached to the FE-SEM. High-resolution transmission electron microscopy (HRTEM) observations were carried out on a JEM-2100F microscope (JEOL). X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG MultiLab 2000 system with a monochromatic Al K α X-ray source (ThermoVG Scientific). The specific Brunauer–Emmett–Teller (BET) surface area was determined by N₂ adsorption/desorption on a BelSorp-Mini instrument (Ankersmid Co. Ltd.).

Electrochemical Measurement. The working electrodes were prepared by mixing 70 wt % of the as-synthesized MnO₂, 20 wt % acetylene black, and 10 wt % polyvinylidene difluoride (PVDF) to form a slurry with N-methylpyrrolidone (NMP) as solvent. Then the slurry was coated onto an aluminum foil substrate and dried in a vacuum oven for 12 h. The electrochemical test was performed with CR2032 coin-type cells assembled in glovebox under argon atmosphere. The commercial electrolyte was composed of 1 mol L⁻¹ LiPF₆ in a 1:1 solvent mixture of ethylene carbonate and diethyl carbonate (EC/DEC). The galvanostatic charge–discharge tests were carried out using the Land battery measurement system (Wuhan, China) with a cutoff voltage of 1.5–4.3 V vs Li/Li⁺ at the controlled temperature of 25 °C. Cyclic voltammetry (CV) curves were recorded on a PARSTAT 2273 potentiostat at a scan rate of 0.2 mV s⁻¹.

RESULTS AND DISCUSSION

The phase and crystallinity of the resulting materials were tested by powder XRD. As shown in Figure 1, the product

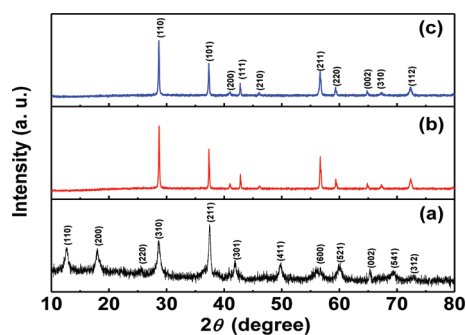


Figure 1. Power XRD patterns of the MnO₂ prepared at different temperatures: (a) 160 °C, (b) 180 °C, and (c) 200 °C.

prepared at 160 °C is identified to pure α -MnO₂ (JCPDS No. 44–0141, tetragonal, $I4/m$, $a = b = 9.78 \text{ \AA}$, $c = 2.86 \text{ \AA}$). When the temperature increases to 180 or 200 °C, the product is pure β -MnO₂ which diffraction peaks are narrow and strong (JCPDS No. 24–0735, tetragonal, $P42/mnm$, $a = b = 4.39 \text{ \AA}$, $c = 2.87 \text{ \AA}$). For α -MnO₂, the broad diffraction peaks indicate that its

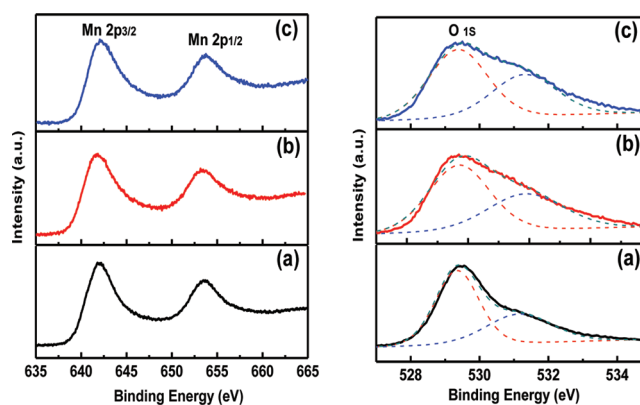


Figure 2. XPS of Mn 2p and O 1s for the MnO₂ samples prepared at different temperatures: (a) 160 °C, (b) 180 °C, and (c) 200 °C.

crystalline size is smaller and the crystallinity is worse as compared with β -MnO₂. No impurity peaks are observed, indicating that high-purity α -MnO₂ and β -MnO₂ can be attained by simply changing the hydrothermal reaction temperature.

Figure 2 shows XPS spectra of Mn 2p and O 1s for α -MnO₂ and β -MnO₂. The peaks of Mn 2p_{3/2} and Mn 2p_{1/2} are centered at 641.8 and 653.6 eV respectively, and their difference in binding energy is 11.8 eV. The data are in good agreement with those of MnO₂.²⁶ The binding energy centered at 530 eV is attributed to O 1s, which can be deconvoluted into two peaks: one sharp peak at 529.5 eV and one broad peak at 531.4 eV. The peak at 529–530 eV responds to the lattice oxygen, while that at 531–532 eV can be assigned to defect oxygen or the surface oxygen ions.²⁷ It can be seen that there is no obvious difference in chemical composition on the surface between α -MnO₂ and β -MnO₂.

The morphologies and compositions of the MnO₂ samples prepared at different temperature were examined by FE-SEM and EDX. The sample obtained at 160 °C is tetragonal α -MnO₂ that mainly consists of nanotubes (Figure 3a). The nanotubes show a square cross-section, with a diameter of 30–40 nm and length of several micrometers. The BET surface area of the nanotubes is 29 m² g⁻¹, slightly larger than that of α -MnO₂ nanotubes prepared at low temperature.¹⁹ When the hydrothermal temperature increases to 180 °C, β -MnO₂ phase is formed. Most of the β -MnO₂ particles show a shape of hexagonal prism containing two pyramid ends with hollow interior, which can be regarded as hollow bipyramids. The unique morphology of β -MnO₂ should be formed because of some cracks or defections induced by the high hydrothermal temperature (Figure 3b). When the temperature increases to 200 °C, the product is still β -MnO₂, but the morphology becomes solid bipyramid (Figure 3c). EDX analysis was employed to determine chemical composite of the α -MnO₂ and β -MnO₂ samples (Figure 3d). The observed Si signal is due to the glass substrate. A small amount of K element is introduced into the sample; the atomic ratio of K to Mn in α -MnO₂ is 9.3%. The incorporation of K is important for the formation of (2 × 2) + (1 × 1) tunnel structure in α -MnO₂. For β -MnO₂, all of the peaks can be ascribed to Mn and O, which demonstrates that no K or any other elements are detected. The results are consistent with the XPS spectra for both α - and β -MnO₂ samples.

Figure 4 shows SEM images of the MnO₂ samples prepared at different temperatures with various amounts of HCl. Figure

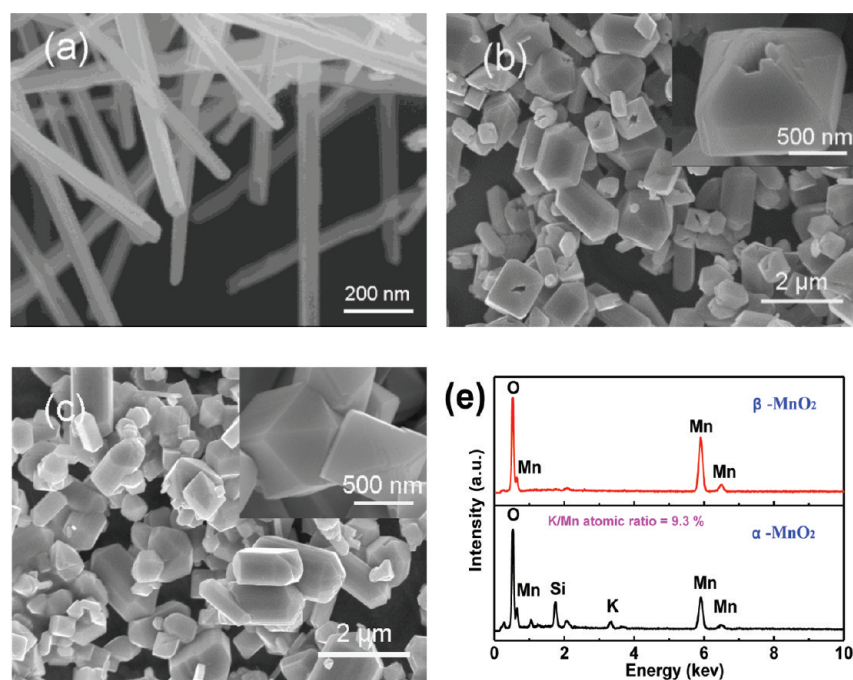


Figure 3. (a–c) FE-SEM images of the MnO₂ prepared at different temperatures: (a) 160 °C, (b) 180 °C, and (c) 200 °C; (d) EDX of the as-prepared α -MnO₂ and β -MnO₂.

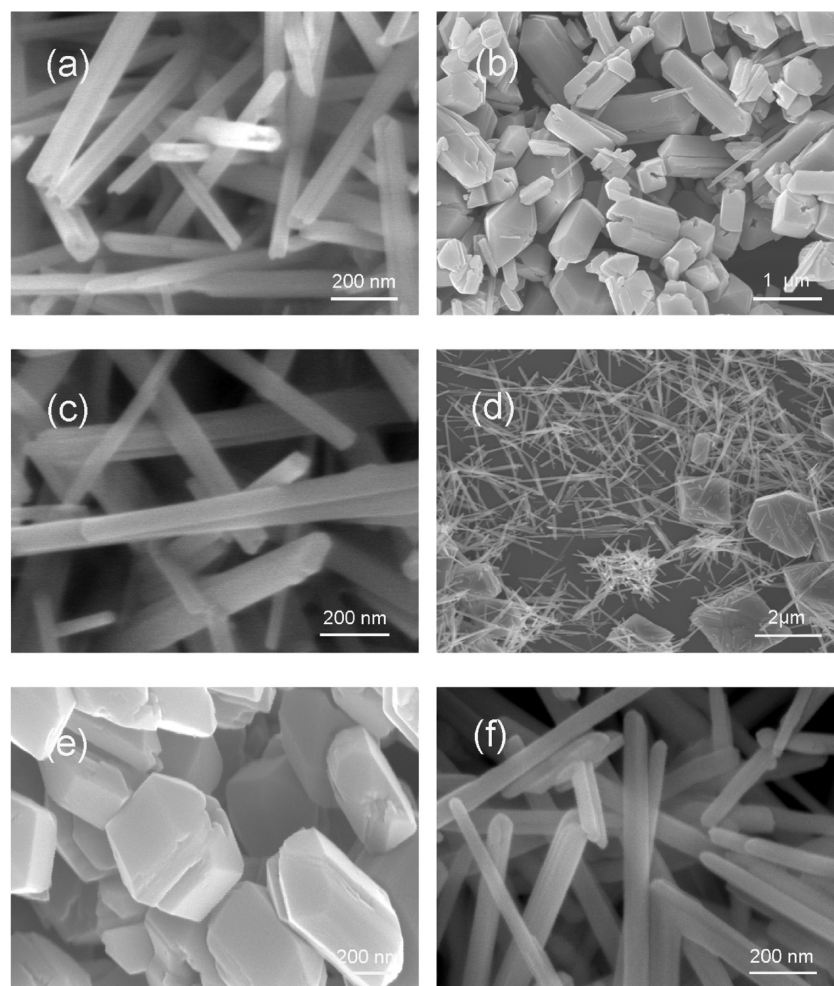


Figure 4. (a–f) FE-SEM images of the MnO₂ samples prepared at different conditions: (a) 1.0 mL HCl, 160 °C; (b) 2.0 mL HCl, 160 °C; (c) 1.0 mL HCl, 180 °C; (d) 1.3 mL HCl, 180 °C; (e) 2.0 mL HCl, 180 °C; (f) 1.0 mL HCl, 200 °C.

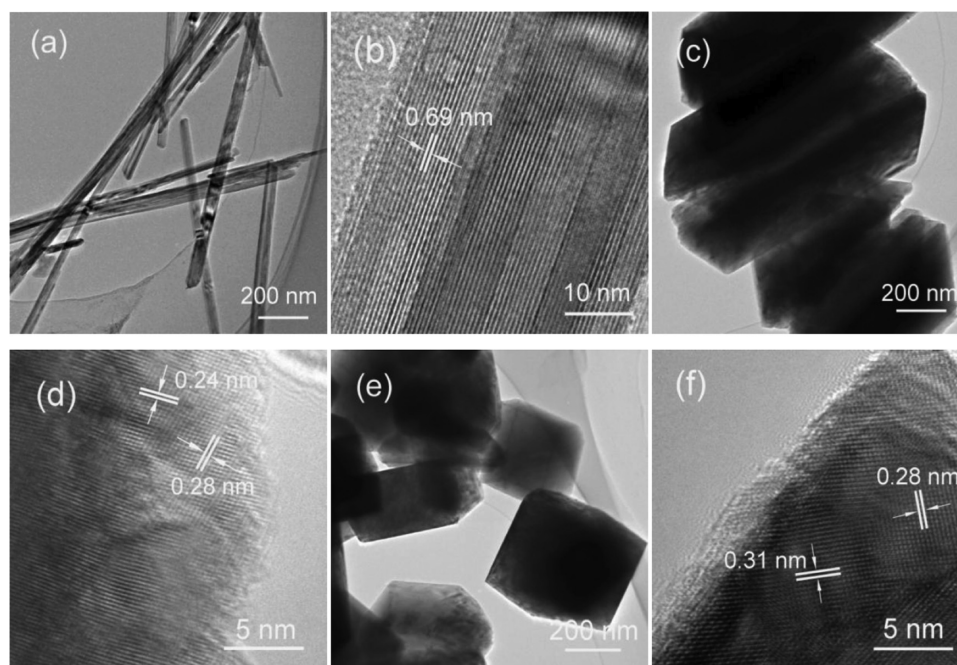


Figure 5. (a, c, e) TEM and (b, d, f) HRTEM images for the MnO_2 samples prepared at different temperatures: (a, b) 160 °C, (c, d) 180 °C, and (e, f) 200 °C.

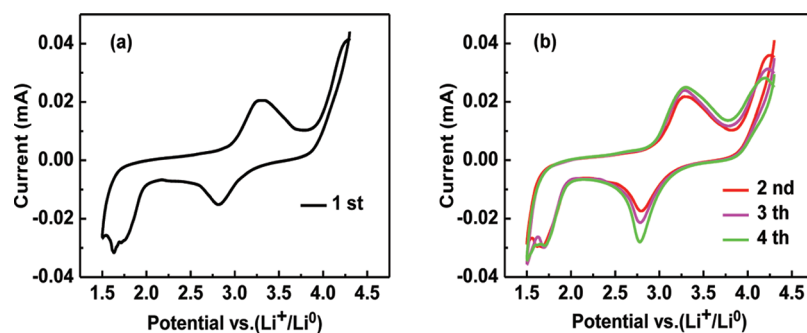


Figure 6. CV curves of the hollow $\beta\text{-MnO}_2$ bipyramids at a scan rate of 0.2 mV s^{-1} in the voltage range from 1.5 to 4.3 V.

4a, c, and f reveals that 1D MnO_2 nanotubes or nanorods are attained at 160, 180, and 200 °C with only adding 1.0 mL HCl. With increasing HCl concentration, the amount of 1D nanostructured MnO_2 decreases while nanorod and bipyramid crystals are observed (Figure 4b, d). If the HCl concentration is high, all MnO_2 crystals become bipyramids with uniform size and rough surface (Figure 4e). It can be seen that high HCl concentration and high reactant temperature favor the formation of MnO_2 bipyramids. The rough surface should be due to the corrosion caused by the excess used acid. The pH is believed to have a large influence on the crystal growth and morphology of MnO_2 .²³ At the same time, since Cl^- can react as a reducer with MnO_4^- to form MnO_2 , it certainly affects the formation of MnO_2 crystals. With changing the HCl concentration, the amount of Cl^- ions varies synchronously with that of H^+ ions. We believe that Cl^- and H^+ ions have cooperative effect on the growth of MnO_2 .

Further information of microstructure for the $\alpha\text{-MnO}_2$ and $\beta\text{-MnO}_2$ was provided by TEM characterization. Figure 5a displays a typical TEM image of $\alpha\text{-MnO}_2$ nanotubes with homogeneous hollow structure. HRTEM analysis (Figure 5b) shows a lattice spacing of 0.69 nm, which agrees well with (110) interplanar distance of $\alpha\text{-MnO}_2$. The HRTEM pattern

demonstrates that the nanotubes grow along [002] direction. TEM images c and e in Figure 5 indicate that the two types of $\beta\text{-MnO}_2$ both have tetragonal bipyramid morphologies. It is notable that the $\beta\text{-MnO}_2$ prepared at 180 °C clearly shows a hollow structure, whereas the $\beta\text{-MnO}_2$ prepared at 200 °C consists of inner solid framework. These results are consistent with those observed by SEM. Images d and f in Figure 5 show the HRTEM images taken from the edge of the $\beta\text{-MnO}_2$ bipyramids, which give more detailed structural information. The marked lattice fringes with the spacings of 0.24, 0.28, and 0.31 nm are ascribed to the interplanar spacings between (101), (001), and (110) planes, respectively, for the tetragonal $\beta\text{-MnO}_2$. All of the well-resolved lattice fringes further indicate the high crystallinity for the two types of $\beta\text{-MnO}_2$ bipyramids.

In general, MnO_2 can form several polymorphs since the MnO_6 octahedral units are linked in different ways. Structurally, $\alpha\text{-MnO}_2$ is constructed from the double chains of edge-sharing MnO_6 octahedra that are linked at the corners to form $(2 \times 2) + (1 \times 1)$ tunnel structure, while $\beta\text{-MnO}_2$ shows 1D channel (1×1) structure composed of individual chains of the MnO_6 octahedral units. Synthesis conditions, such as starting reagents, concentration and pH value of the precursor solution, play important roles in determining the morphology and tunnel

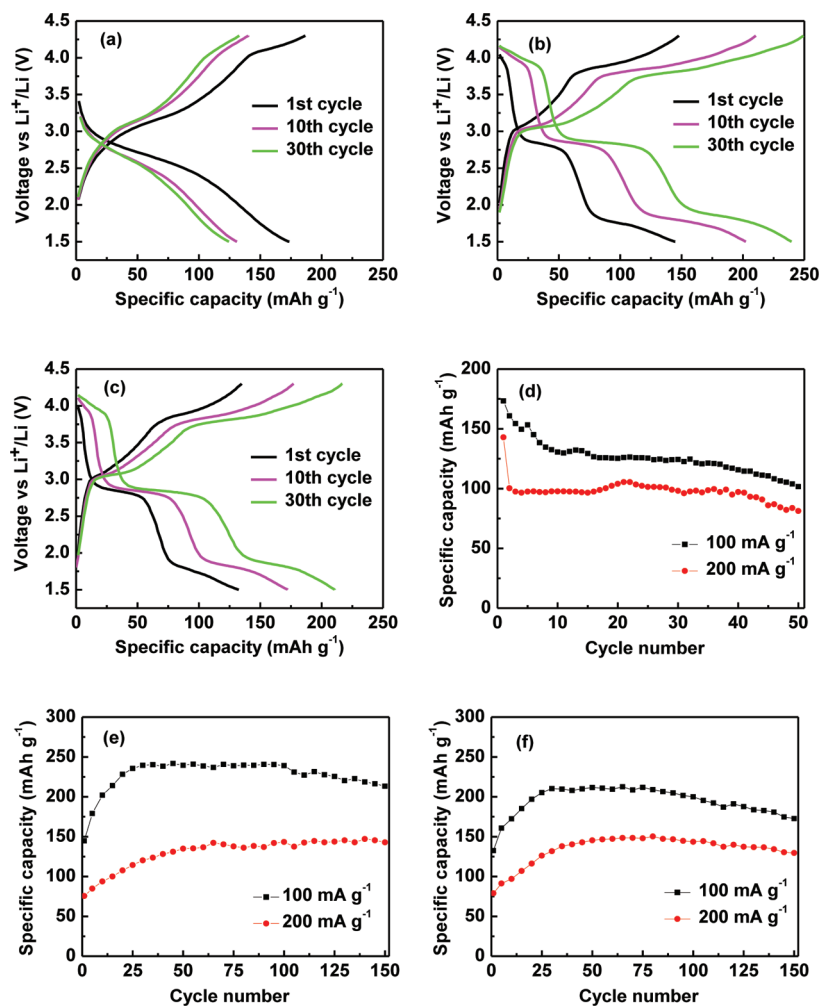


Figure 7. Galvanostatic charge and discharge curves and cycling performance for the MnO_2 prepared at different temperatures: (a, d) 160 °C, (b, e) 180 °C, and (c, f) 200 °C.

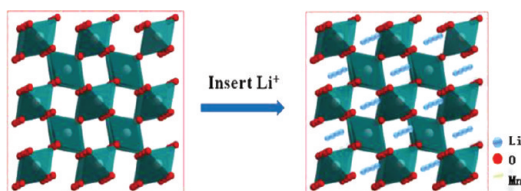


Figure 8. Schematic illustration for the insertion process of lithium ions into the crystal structure of $\beta\text{-MnO}_2$.

structure of MnO_2 . A small amount of guest cations are usually required for the formation of tunnel structure.²⁸ The guest cations are commonly incorporated between the layers or inside the tunnels. Although the growing mechanisms for the three types of MnO_2 nanostructures are difficult to be completely understood, we believe that K^+ ions serve as the crucial guest cations. When the reaction takes place at 160 °C, a certain number of K^+ ions direct the precursor to form (2×2) tunnel structure of $\alpha\text{-MnO}_2$. XPS and EDX results have confirmed the existence of K^+ ions in the $\alpha\text{-MnO}_2$ phase. The formation of the nanotubes can be proposed as “etching” of the nanomaterials caused by HCl in the solution.¹⁹ For the MnO_2 crystals, since the end is metastable while the inner core has a higher surface energy, they are easily attacked by the acidic solution. The etching process is fast once the cracks or

defections are formed at the ends of MnO_2 nanorods. As a result, the MnO_2 nanorods are etched from outside to inside, and then hollow MnO_2 nanotubes are formed so that the end metastable area is reduced and the lateral area with stable surface is enhanced. Since $\alpha\text{-MnO}_2$ is a metastable phase, reaction at temperatures higher than 180 °C will promote the transformation of $\alpha\text{-MnO}_2$ to more stable (1×1) tunnel-structured $\beta\text{-MnO}_2$ phase with compact framework. The (1×1) tunnel of $\beta\text{-MnO}_2$ is too small to accommodate K^+ ions, which demonstrates that the guest ions cannot exist inside the tunnel. In fact, no K^+ ions have been detected in $\beta\text{-MnO}_2$ by both XPS and EDX, which confirms our suggested mechanism. After acidic “etching”, the tetragonal bipyramids uniformly become hollow. When the temperature is raised up to 200 °C, the high activity of KMnO_4 and HCl leads to form large number of nuclei rapidly. As a consequence, solid tetragonal bipyramids with dense cores are formed via Ostwald ripening process. Therefore, it is feasible to control the morphology and structure of MnO_2 by changing the reaction condition.

For insight into the electrochemical properties of the $\alpha\text{-MnO}_2$ and $\beta\text{-MnO}_2$, CV and galvanostatic charge–discharge performance were tested. Figure 6 shows the CV curves of the hollow $\beta\text{-MnO}_2$ bipyramids obtained at a scan rate of 0.2 mV s^{-1} in the voltage range from 1.5 to 4.3 V. Clearly, the first scan cycle is slightly different from the other subsequent cycles. A

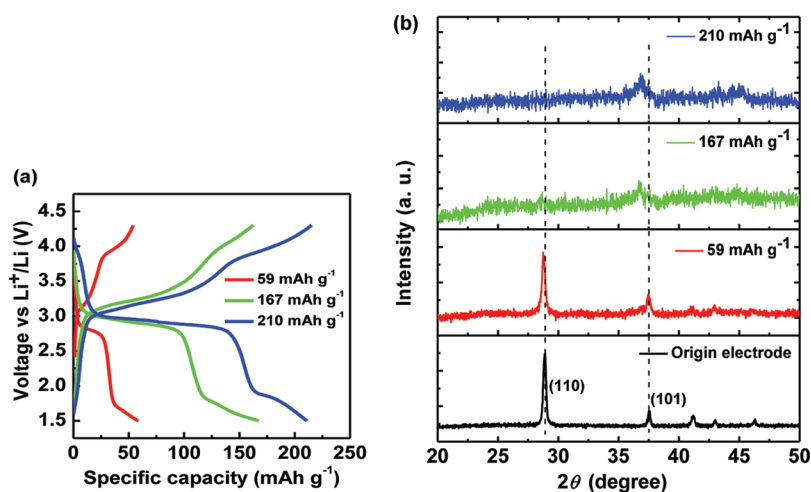


Figure 9. (a) Galvanostatic charge and discharge curves indexed to insertion of different amounts of lithium ions; (b) XRD patterns of the β -MnO₂ electrodes after insertion of different amounts of lithium ions.

broad peak in the first cathodic scan centers at about 1.6 V and it shifts to 1.75 V after the first cycle. With increasing scan cycle, the peak currents of the two redox peaks at 2.8 and 3.4 V clearly increase. The redox peaks should correspond to the absorption/desorption of lithium ions at the electrode surface and Li⁺ insertion/extraction process in the lattice framework of MnO₂, which agrees well with the previous reports.^{5,24}

The first, 10th and 30th charge and discharge curves of the three types of MnO₂ between 1.5–4.3 V at a current density of 100 mA g⁻¹ are displayed in Figure 7. The charge/discharge curves for α -MnO₂ and β -MnO₂ are obviously different. For α -MnO₂ nanotubes, the specific charge and discharge capacities are 187 and 173 mA h g⁻¹, respectively, for the first cycle (Figure 7a). However, the corresponding capacities drop to only 133 and 124 mA h g⁻¹ after 30 cycles, and no obvious potential plateau appears in all the cycles. In Figures 7b and c, the two types of β -MnO₂ bipyramids exhibit observable discharge plateaus at around 1.75 and 3.4 V, giving rise to higher discharge capacities than that of α -MnO₂. Moreover, the discharge capacity for β -MnO₂ increases gradually with cycling, which matches well with the CV curves. The hollow β -MnO₂ bipyramids show the best electrochemical performance with discharge capacity as high as 240 mA h g⁻¹ even after 30 cycles (Figure 7b). From both CV (Figure 6) and discharge curves (Figure 7b, c), it can be seen that β -MnO₂ shows a reaction at the potential of about 1.7 V, which gives additional capacity of about 70–90 mA h g⁻¹. But for α -MnO₂, this reaction does not exist (Figure 7a). The electrochemical reaction at \sim 1.7 V can be ascribed to the process $\text{MnO}_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow \text{Mn} + \text{Li}_2\text{O}$. The unique electrochemical reaction for β -MnO₂ is the main reason for the better electrochemical performance than α -MnO₂.

Figure 7d–f presents long-term stability of the electrodes examined by galvanostatic charge/discharge cycling at current densities of 100 and 200 mA g⁻¹. Apparently, bipyramid β -MnO₂ exhibits much better cyclability than that of nanotube α -MnO₂. For nanotube α -MnO₂, the discharge capacity after 50 cycles is only 102 mA h g⁻¹ at 100 mA g⁻¹ and 81 mA h g⁻¹ at 200 mA g⁻¹ (Figure 7d). For the two β -MnO₂ bipyramids, the specific capacity increases during the initial 40 cycles, and then remains stable. For the hollow β -MnO₂ bipyramids, the capacity and cyclability are superior to those for the solid β -MnO₂ bipyramids. The specific capacity retains 213 mA h g⁻¹

at 100 mA g⁻¹ and 143 mA h g⁻¹ at 200 mA g⁻¹ after 150 cycles (Figure 7e), which is much higher than those reported previously.^{17,29} Except for the unique electrochemical reaction mechanism, the compact (1 × 1) tunnel-structure and hollow architecture also account for the high capacity and excellent cyclability for the hollow β -MnO₂ bipyramids. β -MnO₂ has a 1D structure containing (1 × 1) tunnels with size of 0.189 nm.¹⁹ Although the structure is not desirable for cation accommodation,³⁰ it is feasible for Li⁺ insertion/extraction since the radius of Li⁺ (0.068 nm) is much smaller than the (1 × 1) tunnel size (Figure 8). Moreover, for β -MnO₂, the compact (1 × 1) structure can effectively relieve structural collapse and local volumetric variation during the charge/discharge process, which facilitates the enhancement in structural stability and cycling performance. However, for α -MnO₂, the two-tunnel structure is not stable and the incorporated K⁺ ions may block the transportation of Li ions, resulting in low capacity and poor cyclability. As compared with the solid β -MnO₂ bipyramids, the hollow β -MnO₂ can provide more active sites for penetration of electrolyte and electrochemical reaction, and hence the kinetics of Li⁺ and electron diffusion is highly improved. This effect has also been observed in other hollow or porous materials.^{24,26}

To further understand the mechanism of lithium insertion in the β -MnO₂ bipyramids, we checked the XRD patterns of the β -MnO₂ electrodes after insertion of different amounts of lithium. As shown in Figure 9b, the diffraction peaks of the β -MnO₂ are similar to that of the origin electrode when the capacity reaches 59 mA h g⁻¹. This indicates that insertion of a small amount of lithium does not change the structure of β -MnO₂, and the framework of β -MnO₂ still remains high crystallinity. When the capacity reaches 167 mA h g⁻¹, the discharge plateau at about 2.8 V broadens and the XRD peaks become weak, which means that insertion of large amount of lithium influences the crystallinity of β -MnO₂ phase. In addition, the 2θ corresponding to (101) peak shifts to a lower angle with insertion of lithium, indicative of increase in lattice spacing and expansion in lattice volume. In other words, the increase in lattice spacing demonstrates that lithium ions are inserted into the lattice of β -MnO₂. Further lithiation to 210 mA h g⁻¹, the diffraction peaks become very weak and the peak at 2θ = 28.6° almost disappears. This indicates that the crystallinity of β -MnO₂ degrades continuously and the lattice

volume further expands. It is thus concluded that insertion of Li ions leads to the increase in lattice spacing and cell volume for the nanocrystal β -MnO₂. On the other hand, the crystallinity degradation to an amorphous-like structure for β -MnO₂ may lead to the enhancement of active points for the electrode materials, and hence improve the electrochemical performance. Similar phenomenon has been observed in other MnO₂-based electrode materials.²⁶ The XRD patterns also show that there is no other phase formed during the charge/discharge cycling, which confirms that no irreversible structural change occurs when the oxygen atoms rearrange from tetragonal packing to cubic close-packing. Therefore, the excellent cyclic performance for β -MnO₂ can be ascribed to the reversible insertion/extraction reaction of lithium ions.

CONCLUSIONS

A facile hydrothermal method has been developed to synthesize three types of MnO₂ nanostructures, viz., α -MnO₂ nanotubes, hollow β -MnO₂ bipyramids and solid β -MnO₂ bipyramids, by simply adjusting the reaction conditions. As the cathode material for lithium-ion batteries, hollow β -MnO₂ bipyramids exhibit superior electrochemical performance as compared to α -MnO₂ nanotubes and solid β -MnO₂ bipyramids. The specific capacity of the hollow β -MnO₂ bipyramids reaches 213 and 143 mAh g⁻¹ at current density of 100 and 200 mA g⁻¹, respectively, after 150 charge/discharge cycles. The high specific capacity and excellent cycling stability for the β -MnO₂ can be ascribed to its unique electrochemical reaction mechanism, compact (1 × 1) tunnel structure and hollow architecture. The tunnel structure and hollow architecture can effectively accommodate the volume change and improve diffusion paths for both lithium ions and electrons.

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Notes

The authors declare no competing financial interest.

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