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Well-shaped Mn$_3$O$_4$ tetragonal bipyramids with good performance for lithium ion batteries

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Abstract:

Well-shaped Mn$_3$O$_4$ tetragonal bipyramids with a high reversible capacity of 822.3 mA h g$^{-1}$ are synthesized by a simple hydrothermal method without any surfactants or coordination compounds. The structural feature and morphology of the final product are investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). The SEM and HRTEM results reveal that all eight exposed facets of the Mn$_3$O$_4$ tetragonal bipyramids are indexed to the high-energy \{101\} planes. The tetragonal bipyramids with high-energy facets provide Mn$_3$O$_4$ anode material with high initial discharge capacity (1141.1 mA h g$^{-1}$). In addition, the anode displays good fast rate
performance, delivering a reversible capacity of 822.3 mA h g\(^{-1}\) (the theoretical capacity: 937 mA h g\(^{-1}\)) at a current density of 0.2 C after 50 cycles. And the coulomb efficiency for the first cycle reaches about 66% and remains at about 100% during the subsequent cycles. A relatively detailed growth mechanism of these tetragonal bipyramids is proposed in this manuscript.

**Keywords:**
Mn\(_3\)O\(_4\) tetragonal bipyramids, \{101\} planes, lithium ion batteries

### 1. Introduction

Lithium ion batteries have captured significant attention because of their high power density (150 Wh kg\(^{-1}\)) and high energy density (400 Wh L\(^{-1}\)).\(^1\)-\(^3\) It exhibits great prospects in small portable applications including mobile phone, notebook computer, digital camera, and other fields such as submarine, aerospace, and electric vehicle. As is known, graphite-based materials as main lithium ion battery anodes have been industrialized. However, graphite-based materials have a limited theoretical specific capacity of 372 mA h g\(^{-1}\) and a quick capacity fade caused by the disintegration, which cannot meet the broad need of the high-energy applications.\(^4\)-\(^6\) Therefore, the alternative anode materials with higher energy capability are urgently needed. Nanomaterials have gradually attracted attention in the application of lithium ion batteries due to a very large specific surface area, a short ion diffusion path, a creep resistant and a high plasticity.

Nano-sized transition metal oxides have been also considered as the promising alternative anode materials owning to their high theoretical specific capacity (450 -
1500 mA h g⁻¹).⁷,⁸ Among the transition oxides, Mn₃O₄ is worthy of exploiting, not only because of its high theoretical capacity of 937 mA h g⁻¹, but also its better properties of low toxic, low cost and abundance in nature.⁹⁻¹¹ In addition, Mn₃O₄ exhibits the better thermo-stability than graphite-based materials as the batteries are overcharged or charged at a high rate.⁹,¹² It is generally accepted that with the lower redox potential renders the higher energy density anode materials. Mn₃O₄ with the lower redox potential (1.2 V), has been conserved to be more fascinating than other transition metals such as cobalt (2 V).¹¹,¹³ Thus, much effort has been put into the area of Mn₃O₄ as anode materials in the past years.

In order to obtain the excellent properties of Mn₃O₄ nanoparticles, many researches focused on the size control and morphology control of Mn₃O₄ nanomaterials. For instance, mesoporous Mn₃O₄ nanotubes delivering a reversible capacity of 641 mA h g⁻¹ at a high current density of 500 mA g⁻¹ were reported by Bai.¹³ Single crystalline Mn₃O₄ nano-octahedras were synthesized by a hydrothermal method and their electrochemical results show a charge capacity of 500 mA h g⁻¹ at a current density of 50 mA g⁻¹ and a charge capacity of 350 mA h g⁻¹ when cycled at 500 mA g⁻¹.¹⁴ Mn₃O₄ nano-octahedras prepared by the calcination of a Zn-Mn citrate complex can exhibit a reversible capacity of about 240 mA h g⁻¹ at a high rate of 1000 mA g⁻¹.¹⁵ Mn₃O₄ octahedral nanocrystals were also prepared by a hydrothermal method and their cycle performances exhibited a discharge capacity of 269 mA h g⁻¹ at a current density of 500 mA g⁻¹.¹⁶ The above-mentioned experimental results showed that there were still a certain distance far from the theoretical capacity of 937
mA h g⁻¹.

In this paper, we report a surfactant-free hydrothermal method to fabricate the well-shaped Mn₃O₄ tetragonal bipyramids with a high reversible capacity using KMnO₄ and H₂C₂O₄·2H₂O as raw materials at 200 ºC for 12 h. High-resolution transmission electron microscope (HRTEM) data indicated that eight exposed facets of the Mn₃O₄ tetragonal bipyramids were the {101} planes. The electrochemical performance of the Mn₃O₄ tetragonal bipyramids as anode material was evaluated by cyclic voltammograms (CV) and galvanostatic discharge-charge tests. The electrochemical results indicate that the Mn₃O₄ tetragonal bipyramids exhibit a high initial discharge capacity (1141.1 mA h g⁻¹) and deliver a reversible capacity of 822.3 mA h g⁻¹ at a current density of 0.2 C after 50 cycles, which reaches ~88% of the theoretical capacity of manganese oxides. The coulomb efficiency for the first cycle reaches about 66% and remains at about 100% during the subsequent cycles. Finally, the formation mechanism of the Mn₃O₄ tetragonal bipyramids was discussed from the view of crystallography.

2. Experimental section

2.1 Synthesis of the Mn₃O₄ tetragonal bipyramids

KMnO₄ and H₂C₂O₄·2H₂O (99 %) were purchased and used without a further purification. In a typical procedure, KMnO₄ (0.50 g) was completely dissolved in the 40mL KOH solution (0.01 M) to form a dark purple solution. H₂C₂O₄·2H₂O (0.86 g) was added to the above solution. Then the mixed solution was transferred into a Teflon-lined stainless steel autoclave (60 mL), which was subsequently sealed and
maintained at 200 °C, for 10 h and then cooled to room temperature. The brownish red product was collected and washed with distilled water and absolute ethanol several times. Finally, the product was dried under vacuum at 60 °C for several hours.

2.2 Characterization

The phase of the products was characterized by an X-ray powder diffraction (XRD) technique using a Bruker D8 advanced X-ray diffractometer equipped with graphite-monochromatized Cu-Kα radiation (Kα = 1.5418 Å). X-ray photoelectron spectroscopy (XPS) spectra of the synthesized Mn₃O₄ tetragonal bipyramids were obtained with an Axis Ultra, Kratos (UK) using monochromatic Al Ka radiation (150 W, 15 kV, and 1486.6 eV). Scanning electron microscopy (SEM) images were taken with a MIRA3 LMH scanning electron microscope. The TEM and HRTEM images were recorded using a JEOL-2100 high-resolution transmission electron microscope at an acceleration voltage of 200 kV.

2.3 Electrochemical measurements

The working electrodes for electrochemical properties were prepared with 70 wt% active materials of the Mn₃O₄ tetragonal bipyramids, 20 wt% conducting acetylene black, and 10 wt% carboxy methyl cellulose (CMC) binder in water. The slurry was pasted on a clean copper foil followed by drying in vacuum at 80 °C for 12 h. The resulting foil was roll-pressed and cut into a disc. The Mn₃O₄ tetragonal bipyramid cells were fabricated using lithium foil as a counter electrode and a reference electrode, celgard 2400 as a separator, and a solution of 1 M LiPF₆ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) as an
electrolyte. The assembly of the cells was carried out in an argon-filled humidity-free glove box. The cells were charged and discharged from 0.01 to 3.0 V at different current rates (Land CT 2001A). CV profiles were obtained in the range of 0.01–3 V at a scanning rate of 0.1 mV s\(^{-1}\) from an electrochemical workstation (CHI-760).

3. Result and discussion

The as-prepared product was characterized by XRD (Fig. 1 and Fig. S1). In Fig. 1, almost all the diffraction peaks of the as-synthesized sample can be well indexed as the tetragonal structure for Mn\(_3\)O\(_4\) with lattice parameters of a = b = 5.763 Å and c = 9.456 Å, which is in good agreement with the data reported in the JCPDS standard card (No. 89-4837, space group I41/amd (141)). The valence of the Mn\(_3\)O\(_4\) was analyzed by X-ray photoelectron (XPS) test. The XPS spectra in Fig. S2 indicate that the Mn2p region consists of a spin-orbit doublet (L-S coupling) with binding energy of 652.9 eV (Mn2p\(_{1/2}\)) and 642.1 eV (Mn2p\(_{3/2}\)) for Mn\(_3\)O\(_4\) tetragonal bipyramids, which is characteristic of a mixed-valence manganese system (Mn\(^{3+}\) and Mn\(^{2+}\)).\(^{17}\)

A SEM image (Fig. 2a) shows that the morphologies of the final sample are the Mn\(_3\)O\(_4\) tetragonal bipyramids. Fig. 2b is a high-magnification SEM image of the Mn\(_3\)O\(_4\) tetragonal bipyramids. It can be clearly observed that the surfaces of the well-defined Mn\(_3\)O\(_4\) tetragonal bipyramids are mostly smooth. The inset in Fig. 2b is an ideal geometrical model of the Mn\(_3\)O\(_4\) tetragonal bipyramids. We defined the vertice of long axis (C\(_4\)) as A and the vertice of minor axis (C\(_2\)) of the Mn\(_3\)O\(_4\) tetragonal bipyramids as B or C. To obtain a closer insight of the inner structure of the well-defined Mn\(_3\)O\(_4\) tetragonal bipyramids, TEM was carried out. Figs. 2c and 2d are
a low-magnification and a high-magnification TEM images, respectively. From Fig. 2c, there are two kinds of morphologies including square and rhombus, which are slightly different from the results observed from SEM. The reason was that these two morphologies were the projections of tetragonal bipyramids from different prospective. The inset in Fig. 2c is an ideal geometrical model of the Mn$_3$O$_4$ tetragonal bipyramids from the view of A, whose projection is a square with a dark crossing (marked with the white arrows). If viewed from the midpoint of AB in the geometrical model of Fig. 2d, the projection of the Mn$_3$O$_4$ tetragonal bipyramid labeled with the white arrows can become a rhombus. Based on our limited SEM observation along with a low resolution survey, it is estimated that up to about 95% of the Mn$_3$O$_4$ tetragonal bipyramids and their average sizes (Heywood diameter) range from 80 to 160 nm.

To further investigate the detailed microstructure of the Mn$_3$O$_4$ tetragonal bipyramids, high-resolution TEM imaging was employed. Fig. 3a is a typical TEM image of a whole Mn$_3$O$_4$ tetragonal bipyramid and Fig. 3c and 3d are the corresponding simulated geometrical model images along different directions. The diffraction spots of SAED pattern in Fig. 3b is in a regular sequence, which is featured of the monocystal. The facets are best revealed by the projection of the Mn$_3$O$_4$ tetragonal bipyramid along [010] orientation, parallel to which 4 of the 8 exposed facets are imaged edge-on Fig. 3a. The Miller indices of exposed faces of the Mn$_3$O$_4$ tetragonal bipyramids can be confirmed by a conjunction of the angles between the facets in Fig. 3a, whose borders can be recognized as the projection of
four \{101\} facets parallel to the [010] orientation.\textsuperscript{18} The HRTEM images in Figs. 3e and 3f recorded from the white rectangle areas of Fig. 3a show continuous lattice fringes with lattice spacing of 0.49 nm, which corresponds to the \{101\} planes of Mn$_3$O$_4$. As shown in Fig. 3e, the angle of two opposite surfaces ((101) and (-101)) of 63$^\circ$ is measured, which is in good agreement with the angle marked with a black double-headed arrow in Fig. 3d. From Fig. 3f, it can be calculated that the angle between (-101) and (-10-1) is 117$^\circ$, in accordance with the angle marked with a white double-headed arrow in Fig. 3f. Based on the above-mentioned crystal data, the crystal orientation relation to the morphology can be determined in Fig. 3c. Therefore, we drew a conclusion that the crystal facets at the surface of the Mn$_3$O$_4$ tetragonal bipyramids accord with \{101\} planes.

As an effort to explore the growth mechanism for this synthetic route, it is necessary to check out the morphology and structure of samples prepared at various reaction times while other conditions were kept the same. Fig. 4a shows a SEM image of the products synthesized at 4 h. From Fig. 4a, two distinct morphologies were observed. One is aggregated micron-sized cubic-shaped nanoparticles, the other is one-dimension nanocrystals. Further SEM structural analysis provides more pronounced evidence to inspect the morphology of the white rectangle area in Fig. 4a. Fig. 4b is the typical SEM image of the one-dimension nanocrystals. Rod-like structures with an average width of 45 nm and an aspect ratio of 4-20 have been clearly observed. Moreover, XRD data also show the presence of two major phases of MnCO$_3$ and MnOOH (Fig. S3). According to the related papers, the chemical
composition of aggregated micron-sized cubic-shaped nanoparticles was MnCO$_3^{19}$ and the chemical constitution of rod-like structures was MnOOH.$^{20,21}$ So the possible chemical reaction pathway involved in the range of 0 to 4 h can be written as follows:

$$\text{KMnO}_4 + \text{H}_2\text{C}_2\text{O}_4 + \text{KOH} \rightarrow \text{MnCO}_3 + \text{MnOOH} + \text{KHCO}_3 + \text{H}_2\text{O} \quad (1)$$

When the reaction time was increased to 6 h, Mn$_3$O$_4$ and MnOOH were indexed in corresponding XRD (Fig. S4). No obvious diffraction peaks of MnCO$_3$ were observed in the XRD pattern, which suggests that MnCO$_3$ phase was an intermediate product. This interesting finding shows that the stability of MnCO$_3$ was not as good as that of MnOOH in our reaction route. It's common knowledge that MnOOH phase was stable in a strong alkali solution (Fig. S5). The SEM image of Fig. S6 also gives evidence that the aggregated cubic-shaped MnCO$_3$ nanoparticles disappeared and the Mn$_3$O$_4$ tetragonal bipyramids emerged. When the reaction time was further increased from 6 to 8 h, the proportion of the Mn$_3$O$_4$ tetragonal bipyramids in the final products was on the increase (Fig. S7). When the reaction time was extended to 10 h, more than 95% Mn$_3$O$_4$ tetragonal bipyramids have been inspected in our sample. Consequently, the chemical reactions involved in the growth from 4 to 10 h could be described as follows:

$$\text{MnCO}_3 + 2\text{MnOOH} \rightarrow \text{Mn}_3\text{O}_4 + \text{CO}_2 + \text{H}_2\text{O} \quad (2)$$

The reaction from 4 to 10 h can be summarized as the reaction diagram (Fig. 5).

The overall reaction can be formulated as follows:

$$\text{KMnO}_4 + \text{H}_2\text{C}_2\text{O}_4 + \text{KOH} \rightarrow \text{Mn}_3\text{O}_4 + \text{CO}_2 + \text{KHCO}_3 + \text{H}_2\text{O} \quad (3)$$

Further on, in order to elucidate the growth mechanism of these Mn$_3$O$_4$
tetragonal bipyramids, we proposed a hypothesis in the frame of a structural transformation from MnCO$_3$ and MnOOH to Mn$_3$O$_4$ on the basis of the above-mentioned reactions (Fig. 4c). As the structure of MnCO$_3$ was destroyed completely along with the escaping of CO$_2$, the dissociative Mn$^{2+}$ entered into the tetrahedral sites of the defective MnOOH cell. Then, the Mn$_3$O$_4$ spinel structure was formed. Fig. 4d presents the crystal structure of the tetragonal Mn$_3$O$_4$ with two unit cells. It is clearly displayed that the Mn$_3$O$_4$ structure has a normal spinel structure with the Mn$^{2+}$ ($4s^03d^5$) in the tetrahedral sites and the Mn$^{3+}$ ($4s^03d^4$) in the elongated octahedral sites, which can be explained by Jahn-Teller effect. In the octahedral complexes of Mn$_3$O$_4$, five 3d orbitals of Mn atom in the Mn$_3$O$_4$ crystal structure are divided into two types: one is $t_{2g}$ orbital ($d_{xy}$, $d_{xz}$ and $d_{yz}$), the other is $e_g^*$ orbital ($d_z^2$ and $d_{x^2-y^2}$). And Mn$^{3+}$ has a high-spin configuration of $(t_{2g})^3(e_g^*)^1$. Every $t_{2g}$ orbital ($d_{xy}$, $d_{yz}$ and $d_{xz}$) has a 3d electron and the $d_z^2$ orbital of the $e_g^*$ orbital is occupied by the remaining 3d electron (Fig. S8). Four O$^{2-}$ of the octahedral Mn$_3$O$_4$ complexes in the XY plane received a smaller repulsive force than two O$^{2-}$ in the Z axe (Fig. S9), resulting in the structure distortion from the octahedrons to the elongated tetragonal bipyramids. Furthermore, there are not the compounds such as the surfactants and the coordination compounds which can affect the growth faces of the tetragonal bipyramids in our hydrothermal system. Accordingly, the final morphology of the as-prepared samples is consistent with its primary framework structure. Based on the HRTEM and SAED results, we can know that the elongated octahedron structure stacked along the $\{101\}$ planes simultaneously.
The electrochemical properties of the as-obtained Mn$_3$O$_4$ tetragonal bipyramids were firstly evaluated by CV. Fig. 6 displays three CV curves of the cell with the Mn$_3$O$_4$ tetragonal bipyramids used as anode material under different cycles. In the first cathodic scan, there were two weak peaks appeared at 1.01V (a) and 0.88V (b), which both vanished in the succeeding cycles. The peak (a) can be attributed to a reduction reaction ($\text{Mn}_3\text{O}_4 + 2\text{Li}^+ + 2e^- \rightarrow \text{MnO} + \text{Li}_2\text{O}$)\(^{27}\) and the peak (b) can be ascribed to the formation of a solid electrolyte interphase (SEI) layer ($\text{electrolyte} + e^- + \text{Li}^+ \rightarrow \text{SEI} (\text{Li})$) on the surface of the Mn$_3$O$_4$ tetragonal bipyramid electrode.\(^{14,28,29}\) In addition, the strong peak located at 0.08V (c) is related to a reduction reaction of MnO ($\text{MnO} + \text{Li}^+ + 2e^- \rightarrow \text{Mn} (0) + \text{Li}_2\text{O}$).\(^{28}\) During the next anodic process, one peak located at 1.33 V (d) was observed due to an oxidation reaction of the former-formed Mn and the decomposition of Li$_2$O.\(^{30}\) In the second cathodic cycle, the reduction peak shifts from 0.08 V (c) to 0.32 V (e) mainly due to an irreversible phase transformation. After the second cycle, the appearance of similar CV curves indicates a good reversibility of the electrochemical reactions of the Mn$_3$O$_4$ tetragonal bipyramid electrode. On basis of the above analysis results and the relative literature,\(^{31-33}\) the entire reversible electrochemical mechanism of Mn$_3$O$_4$ on Li insertion and extraction can be summarized by the following equation:

\[
\text{Mn}_3\text{O}_4 + 8 \text{Li}^+ + 8 e^- \leftrightarrow 3 \text{Mn} + 4 \text{Li}_2\text{O}
\]

Fig. 7 exhibits the discharge and charge curves of the 1$^{\text{st}}$, 2$^{\text{nd}}$, 10$^{\text{th}}$ and 50$^{\text{th}}$ cycles for the Mn$_3$O$_4$ tetragonal bipyramid electrode cycled between 0.01 and 3 V at a current density of 0.2 C. In the first discharge curve (Li insertion), three distinctive
regions (a, b and c) related to different Li storage mechanisms are observed. The first short plateau (a) and the following sloped region (b) can be assigned to the reduction reaction from Mn$_3$O$_4$ to MnO and the formation of the SEI film on the electrode surface, respectively. The long plateau (c) was related to the reduction reaction from Mn$^{2+}$ to Mn$^0$. In the first charge curve, a slight slope recorded between 1.1 and 1.5 V can be regarded as the oxidation reaction from Mn$^0$ to Mn$^{2+}$ or Mn$^{3+}$. All these results were in accord with the CV test results. From the second cycle, the discharge plateau (d) of the Mn$_3$O$_4$ tetragonal bipyramid electrode shifts to about 0.5 V, indicating the irreversible formation of crystalline: metallic Mn and amorphous Li$_2$O matrix. After the second cycle such as 10$^{th}$ and 50$^{th}$ cycle, the discharge and charge curves are similar. However, nearly 7 mol Li is stored per mole Mn$_3$O$_4$ with a total capacity of 822 mA h g$^{-1}$ during the 50$^{th}$ cycle, which is higher than that (760 mA h g$^{-1}$) of the 10$^{th}$ cycle.

Fig. 8 shows the cycling performance and the columbic efficiency of the Mn$_3$O$_4$ tetragonal bipyramid electrode at the rate of 0.2 C from 0.01 to 3.0 V about 56 cycles. As shown in Fig. 8, the Mn$_3$O$_4$ tetragonal bipyramid electrode delivered an initial capacity of 1141.1 mA h g$^{-1}$ and exhibited a first cycle columbic efficiency of 66.7 %. The large irreversible capacity loss (33.3 %) in the first cycle is very common for the transition metal oxides, the main reason is the formation of an SEI film by the degradation of the electrolyte (electrolyte + e$^{-}$ + Li$^+$ → SEI (Li)), the other is the transformation of irreversible phase (Mn nanoparticles and amorphous Li$_2$O matrix).

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In the second cycle, its capacity quickly decreased to 761.1 mA h g\(^{-1}\) with an increased columbic efficiency of nearly 100%. In the subsequent cycles, the capacity and the columbic efficiency both remained steady. However, the capacity from the 20\(^{th}\) to the 56\(^{th}\) cycle increased from 765.7 to 822.3 mA h g\(^{-1}\) gradually. The growing reversible capacity can beexplained by an interfacial mechanism in which extra lithium is accommodated in these boundary regions between nano-sized Mn and Li\(_2\)O (In the reaction process, the size of these two products got smaller and the boundary regions increased.) via charge separation.\(^{34,35}\)

In order to evaluate the power capability of the Mn\(_3\)O\(_4\) tetragonal bipyramid electrode, we investigate its rate performance at different current densities (Fig. 9). From Fig. 9, the reversible capacity gradually decreases as the current density increases. The specific capacities of 869, 798, 708 and 604 mA h g\(^{-1}\) are detected as the current density varies from 0.1, to 0.2, 0.5 and 1 C, respectively. Even at a current density as high as 2 C, the Mn\(_3\)O\(_4\) tetragonal bipyramid electrode can still deliver an average specific capacity of 471 mA h g\(^{-1}\), much higher than the theoretical specific capacity (372 mA h g\(^{-1}\)) of graphite-based anode materials.\(^{37}\) When the current density was back to 0.1 C, an average capacity could be recovered to 883 mA h g\(^{-1}\), which was a little higher than the capacity (856.3 mA h g\(^{-1}\)) at the initial rate of 0.1 C.

The enhanced electrochemical performance of the as-synthesized Mn\(_3\)O\(_4\) tetragonal bipyramids could be ascribed to its special structure. The nanoparticles provide large specific surface area ((101) facets), which improve the utilization of active material, and provide reduced transport pathways for lithium ions to transfer in and out easily.
The structure of the Mn$_3$O$_4$ tetragonal bipyramids lithium ion batteries has the ability to tolerate the volume deformation during discharge-charge process and maintain the stability of the Mn$_3$O$_4$ electrode. These may be responsible to the good performance for LIBs. Therefore, the Mn$_3$O$_4$ tetragonal bipyramid electrode with a good rate capacity can be regarded as a promising alternative anode material for lithium ion batteries.

4. Conclusion:

The Mn$_3$O$_4$ tetragonal bipyramids with a high reversible capacity (up to 822.3 mA h g$^{-1}$) were synthesized by the reaction of KMnO$_4$ and H$_2$C$_2$O$_4$·2H$_2$O in the alkali solution at 200 °C for 12 h without any surfactants or coordination compounds. Inspection of the HRTEM and SAED data of the final products showed that the Mn$_3$O$_4$ tetragonal bipyramids were monocrystal and the elongated octahedron structure of the Mn$_3$O$_4$ tetragonal bipyramids stacked along the {101} planes. The CV and the galvanostatic discharge-charge test results showed that the Mn$_3$O$_4$ tetragonal bipyramid electrode could display a high initial discharge capacity of 1141.1 mA h g$^{-1}$ and deliver a reversible capacity of 822.3 mA h g$^{-1}$, close to the theoretical capacity value of 937 mA h g$^{-1}$, at 0.2 C after 50 cycles. The coulomb efficiency could be nearly 100% after the first cycles. A growth mechanism of the Mn$_3$O$_4$ tetragonal bipyramids was proposed and accounted for the obtained experimental results very well.

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Fig. 1 XRD patterns of the as-prepared product
Fig. 2 A typical large-area SEM image (a) and a partially enlarged SEM image (b) of the Mn$_3$O$_4$ tetragonal bipyramids; A large-area TEM image (c) and an enlarged TEM image (d) of the Mn$_3$O$_4$ tetragonal bipyramids. The insets in b, c and d are the ideal geometrical models of the Mn$_3$O$_4$ tetragonal bipyramids marked with the corresponding white arrows, in which the ratio of AB and BC is about 1.1.
Fig. 3 (a) A typical TEM image of the Mn$_3$O$_4$ tetragonal bipyramids; (b) the corresponding selected area electron diffraction (SAED) pattern; (c) the corresponding simulated 2D geometrical model image along the Y axis; (d) The corresponding 3D geometrical model image; (e) a HRTEM image of the white rectangle marked with e in (a), the angle between two opposite planes is 63°; (f) a HRTEM image of the white rectangle marked with f in (a), the angle between two adjacent planes is 117°.
Fig. 4 (a) A SEM image and (b) a partially enlarged SEM image of the reaction process at 4 h; (c) a schematic illustration of the formation of the Mn₃O₄ tetragonal bipyramids transformed from MnCO₃ and MnOOH; (d) the crystal structure of the tetragonal Mn₃O₄ with two unit cells. The simulated diagrams of MnCO₃, MnOOH and Mn₃O₄ were extracted from the crystal files 1011262.cif, 9007689.cif, and 9009774.cif.
Fig. 5 A schematic illustration of the formation of the Mn$_3$O$_4$ tetragonal bipyramids.
Fig. 6 CV curves of the Mn₃O₄ tetragonal bipyramid electrode at a constant density of 0.2 C in the voltage range 0.01 - 3.0 V. The number a, b, c, d and e denote the peaks.
Fig. 7 The 1st, 2nd, 10th and 50th charge and discharge curves of the Mn$_3$O$_4$ tetragonal bipyramid electrode between 0.01 and 3 V at a current density of 0.2 C. The number a, b, c and d represent the plateaus and the sloped regions.
Fig. 8 Cycle performance and cumbic efficiency versus cycle number of the Mn$_3$O$_4$ tetragonal bipyramid electrode at a current density of 0.2 C.
Fig. 9 The rate performance of the tetragonal bipyramid Mn$_3$O$_4$ electrode (rate= 0.1 - 2 C) and the cell was tested for 5 cycles at each current density.
Abstract:

Well-shaped Mn$_3$O$_4$ tetragonal bipyramids with a high reversible capacity of 822.3 mA h g$^{-1}$ are synthesized by a simple hydrothermal method without any surfactants or coordination compounds. The structural feature and morphology of the final product are investigated by X-ray diffraction, scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). The SEM and HRTEM results reveal that all eight exposed facets of the Mn$_3$O$_4$ tetragonal bipyramids are indexed to the high-energy {101} planes. The tetragonal bipyramids with high-energy facets provide Mn$_3$O$_4$ anode material with high initial discharge capacity (1141.1 mA h g$^{-1}$). In addition, the anode displays good fast rate performance, delivering a reversible capacity of 822.3 mA h g$^{-1}$ (the theoretical capacity: 937 mA h g$^{-1}$) at a current density of 0.2 C after 50 cycles. And the coulomb efficiency for the first cycle reaches about 66% and remains at about 100% during the subsequent cycles. A relatively detailed growth mechanism of these tetragonal bipyramids is proposed in this manuscript.