'Isfacet' Anatase TiO₂ Microcages: Topotactic Synthesis and Ultrastable Li-Ion Storage

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ABSTRACT: A new type of anatase TiO_2 microcages assembled by oriented nanocrystals have been successfully fabricated through a topotactical conversion from CaTiO_3 microcage precursor. The anatase microcages have all their six side faces dominated by anatase $\{001\}$ facets, as revealed by detailed electron microscopy characterization. When used as the anode material for Li-ion storage, the unique microcages have the advantage of remarkable structural stability, high surface areas, and facile electronic conduction path. As a result, the TiO_2 microcages-based anode achieves a high lithium storage performance especially at high current rates and long cycling stability, giving 175 mAh g^{-1} at 5C (850 mA g^{-1}) after 800 cycles and 95 mAh g^{-1} at 50 C after 5000 cycles. Our comparison to the literature shows that this is a competitive and promising material for Li-ion battery and potentially also photocatalyst applications.

In recent years, hierarchical micro- and/or nano-scale materials assembled by primary building blocks (PBBs) in distinct three-dimensional (3D) arrangement have attracted many attentions for versatile applications such as photonic crystals,^[1] catalysts,^[2] and energy storages.^[3-6] Particularly, mesocrystals assembled by crystallographically oriented nanocrystals have achieved rapidly increasing attention. Due to their good crystallinity, high porosity, and oriented PBBs, mesocrystals are considered to be promising substitutes for single-crystalline or porous polycrystalline materials.^[7, 8] Titanium dioxide (TiO_2) is one of the most investigated materials for its unique properties and great importance in many areas ranging from photocatalysis, solar cells and lithium ion batteries.^[9-13] Anatase TiO_2 mesocrystals were first obtained through topotactic conversion from NH_4TiOF_3 mesocrystals reported by O'Brein and co-workers.^[14, 15] After that, a flourishing emergence of various anatase mesocrystals is observed, like spindle-shaped nanoporous anatase TiO_2 mesocrystals,^[16] single-crystal-like titania mesocages,^[13] hollow anatase TiO_2 mesocrystals with dominant $\{101\}$ facets.^[17] Anatase TiO_2 mesocrystals with uniform pores and large surface area have been proved to have excellent performance in many applications.^[7, 12, 16] It is noteworthy that anatase TiO_2 crystals exposed some specific

facets such as $\{001\}$ generally show higher photocatalytic activity and superior lithium ion storage properties.^[11, 18, 19] In this regard, considering the single crystal-like properties of conversional mesocrystals, the PBBs of one mesocrystal are monotonously oriented and the whole mesocrystal, just like their single crystals, is generally anisotropic. Despite the reduced primary particle size, increased pores and surface area, mesocrystals do not optimize the exposure percentage of specific facets too much compared with single crystals. On the other hand, mesoporous single crystals of TiO_2 were fabricated using mesoporous silica as templates. High surface areas were achieved, but the exposed surfaces were not specific.^[20, 21] Therefore, it remains a great challenge to synthesize TiO_2 mesocrystals with larger percent of specific facets exposed and more active access.

In this study, we successfully obtained a oriented nanocrystals constructed anatase TiO_2 microcage with all its six side faces dominated by the $\{001\}_A$ facets (subscript A is denoted as anatase TiO_2), by using our previously reported hierarchical CaTiO_3 microcage as a precursor and self-template. We name such structural property of a whole microcage as ‘*isofacet*’. As evidenced by detailed crystallographic analyses, this novel structure is perfectly inherited from the CaTiO_3 template due to the well matched lattice spacings between CaTiO_3 and TiO_2 .^[22, 23] Due to its unique crystallographic property and highly porous structure, such hierarchical ‘*isofacet*’ anatase TiO_2 microcages show outstanding cycling stability, rate performance as anode materials for Li-ion batteries.

Results and discussion

Formation of hierarchical TiO_2 microcages. Anatase microcages (*mc*- TiO_2 , before annealing at 400 °C) were fabricated by a hydrothermal treatment of CaTiO_3 precursor with an acetic acid solution. The typical scanning electron microscopy (SEM) images of prepared *mc*- TiO_2 were shown in Figures 1a and 1b. No obvious morphology change was observed compared to the pre-synthesized CaTiO_3 precursor (Supporting Information, Figure S1a), which has a walnut-like morphology constructed by numerous nanocrystals.^[23] The powder X-ray diffraction (XRD) patterns of CaTiO_3 precursor, as-prepared *mc*- TiO_2 and *mc*- TiO_2 -400 (after annealing *mc*- TiO_2 at 400 °C) are presented in Figure S1b. The results confirm that the as-prepared TiO_2 samples are phase-pure tetragonal anatase (JCPDS card No. 21-1272, unit cell $a = b = 3.785 \text{ \AA}$ and $c = 9.514 \text{ \AA}$).

Figure 1. (a) Low and (b) high magnification SEM images of *mc*-TiO₂. (c) Low and (d) high magnification TEM images taken from an individual microcage. (e) HRTEM image recorded from the selected square area in (d) with the corresponding FFT pattern (inset). (e1) and (e2) are FFT patterns from the upper left and lower right individual nanocrystals in (e). The principal d-spacings and diffraction spots are marked and indexed onto the anatase unit cell.

The detailed microstructure and crystalline construction of the product were further revealed by structural characterization using transmission electron microscopy (TEM) and high resolution TEM (HRTEM). As shown in Figure 1c, the clear contrast in TEM image of an individual cage reveals its nanocrystals constructing structure. This structural feature gives a high Brunauer-Emmett-Teller (BET) surface area of 114.7 m²/g (Supporting Information, Figure S2). Moreover, it can be seen that the well-defined shells are built up by an assembly of numerous nanorods with

a diameter of about 14 nm in an excellent alignment (Figure 1d). A HRTEM image of the selected surface area in Figure 1d is shown in Figure 1e. The marked lattice spacings and the corresponding fast Fourier transform (FFT) patterns (Figures 1e1 and 1e2) reveal that these nanorods are single crystalline anatase TiO_2 grown along the $[001]_A$ axis with a perpendicular relationship. The FFT pattern in the inset of Figure 1e taken from the whole area can be recognized as a combination of the FFT patterns in Figures 1e1 and 1e2. Further analysis of cross section TEM image (Figure 2) reveals that the nanorods only appear at the microcage surface. Underneath the surface nanorod layer, major part of the microcage still consists of nanocubes. Consequently, nanocubes are more typical building units, same as that in the precursory CaTiO_3 microcages. The surface nanocubes would undergo further growth along the $[001]_A$ zone axis into nanorods.

Figure 2. (a) A thin cross-section TEM image of an individual *mc*- TiO_2 microcage with the corresponding selected area electron diffraction SAED pattern (b). (c) HRTEM image of a selected nanocube marked in (a) with the corresponding FFT pattern (d).

A selected area electron diffraction (SAED) pattern (Figure 3b) taken from the entire *mc*- TiO_2 microcage shown in Figure 3a reveals that all the nanocrystals (both inner nanocubes and outer nanorods) are perfectly oriented in a unique 3D perpendicular arrangement. As illustrated in Figures S3, this single crystal-like SAED pattern can be regarded as a combination of three sets of diffraction patterns, and only three patterns, derived from three oriented anatase TiO_2

nanoarrays projected along their zone axes of $[100]_A$, $[010]_A$, and $[001]_A$ (Figures 3c and 3c1–3c3), respectively. Furthermore, based on three dark-field TEM images obtained from three different non-overlapped diffraction spots, we found three nanocrystal arrays (Figure 3d1-d3). They agree well with the corresponding schematic illustrations shown in Figures 3c1–3c3. All these evidences confirm that the entire microcage is assembled by 3D perpendicularly arranged anatase TiO_2 nanocubes and nanorods. Moreover, such 3D perpendicular arrangement makes all the six side faces of a single microcage equal and dominated by anatase $\{001\}_A$ facets, indicating an ‘*isofacet*’ feature. As far as we know, such a unique ordered hierarchical architecture has not been discovered in either natural or synthetic anatase TiO_2 materials before.

Figure 3. (a) TEM image of an individual *mc*- TiO_2 microcage and (b) corresponding SAED pattern from the whole microcage, which is combined by three patterns as illustrated by three different colors. (c) A hierarchical network with three perpendicularly arranged anatase TiO_2 nanocrystal arrays (c1-c3). (d1-d3) Three dark field TEM images taken by selecting three diffraction spots 1-3 marked in (b), showing three different sets of the aligned nanorods.

It is well known that the epitaxial growth and topotactic conversion are strongly dependent on the crystallographic relationships between the desired products and templates or substrates.^{[24] [12]}

[24] [12] [24] From the earlier reports,^[25-27] we learned that Ca^{2+} would easily leach out from the perovskite Ti-O frameworks during the hydrothermal treatment in an acidic solution. In the present work, CaTiO_3 microcages were chosen to act as self-templates for the formation of anatase TiO_2 microcages. As described in our previous report,^[23] the porous template is assembled by single crystalline orthorhombic perovskite CaTiO_3 nanocubes in a 3D perpendicular arrangement (Supporting Information, Figures S4a). The lattice spacings of $\{100\}_A$ and two $\{205\}_A$ in anatase TiO_2 perfectly match with $\{110\}_P$ and $\{112\}_P$ (subscript P is denoted as orthorhombic perovskite CaTiO_3) in CaTiO_3 when $[001]_A$ and $[100]_A$ are parallel to $[001]_P$ and $[1-10]_P$, respectively (Supporting Information, Figure S4b). Therefore, if taking a $\sqrt{2}/2 \times \sqrt{2}/2 \times 1$ subunit cell of CaTiO_3 , which contains double perovskite cells, we can find a great similarity between these two structures (Supporting Information, Figure S4c and S4d). Both their $\{001\}$ planes are constructed by corner-sharing TiO_6 octahedra, leading to a square pattern. Therefore, an *in situ* topotactic conversion of CaTiO_3 to anatase TiO_2 is allowed with the crystal growth direction changing from the $[001]_P$ of CaTiO_3 to the $[001]_A$ of TiO_2 .^[26, 27] As a result, the 3D perpendicular arrangement of the CaTiO_3 nanocube building blocks can be almost perfectly inherited to form the anatase TiO_2 microcages with the same hierarchical architecture. Such a crystal intergrowth gives a strong mechanical stability of the microcage structure in comparison with non-orientated aggregation of nanoparticles.

Lithium ion storage properties of TiO_2 microcages. TiO_2 has been widely studied as a very promising anode material in Li-ion batteries.^[7, 10] Herein, the lithium ion storage properties of the TiO_2 microcages (both *mc*- TiO_2 and *mc*- TiO_2 -400) are investigated. The *mc*- TiO_2 can deliver an initial lithium storage capacity of 208 mAh g⁻¹ at 5 C (Li_xTiO_2 , $x=0.5$ corresponding to a theoretical capacity of 170 mAh g⁻¹)^[4, 11] within a cut-off window of 1.0–3.0 V (Supporting Information, Figure S5a). However, compared with *mc*- TiO_2 -400 which was annealed at 400 °C for 2 h, the non-annealing *mc*- TiO_2 delivers a relatively lower capacity. This can be attributed to the electrolyte decomposition resulting from the presence of water-bearing solvent residue tightly adsorbed on the surface of *mc*- TiO_2 as detected by Thermal gravimetric analysis (TGA) (Supporting Information, Figure S5b). As a result, although the annealing process causes a nearly one fourth decrease of surface area to 86 m²/g for *mc*- TiO_2 -400 (Supporting Information, Figure S2), the increased crystallinity of *mc*- TiO_2 -400 and removal of impurities still ensure a better

capacity performance. Similar phenomenon has been observed from other hydrothermally synthesized titania anode materials.^[11] Therefore, proper annealing process is necessary for a better lithium ion battery performance, besides, the annealing process has little influence on its anatase phase, and the 3D microcage morphology (Supporting Information, Figure S6).

Figure 4a shows cyclic voltammograms (CV) of *mc*-TiO₂-400 at a scan rate of 0.5 mV s⁻¹ in the voltage range from 3.0 to 0.8 V. The clear cathodic/anodic peaks at about 1.7/2.1 V could be attributed to the reversible biphasic transition between tetragonal anatase and orthorhombic Li_{0.5}TiO₂, as consistent with other anatase TiO₂.^[16, 28] For comparison, random 20 nm anatase TiO₂ nanoparticles (donated as *np*-TiO₂-400, Supporting Information, Figure S7), transformed from acetic acid treated CaTiO₃ nanoparticles and annealed at 400 °C for 2 h, were also characterized under the same conditions. *np*-TiO₂-400 has a similar surface area to *mc*-TiO₂-400 as 65 m²/g (Supporting Information, Figure S2). As seen in Figure 4b, apparently, compared with those random nanoparticles, ‘*isofacet*’ *mc*-TiO₂-400 constructed by 3D perpendicularly arranged anatase nanocrystals has much better rate capabilities. The stable discharge capacities of *mc*-TiO₂-400 at current densities of 0.5, 1, 2, 5, 10, 20, and 50 C are about 224, 208, 194, 173, 151, 125 and 92 mAh g⁻¹, respectively, which are about 50 mAh g⁻¹ higher than *np*-TiO₂-400 at each corresponding current density.

Figure 4. Electrochemical properties of *mc*-TiO₂-400. (a) Cyclic voltammograms (CV) of *mc*-TiO₂-400 at a scan rate of 0.5 mV s⁻¹ between 3.0 and 0.8 V. (b) Rate capability of *mc*-TiO₂-400 compared with *np*-TiO₂-400 from 0.5 C to 50 C. (c) Corresponding first five discharge/charge voltage profiles of *mc*-TiO₂-400 at 0.5 C in (b). (d) Cycling performance of *mc*-TiO₂-400 and *np*-TiO₂-400 at 5 C. (e) Long cycling performance of *mc*-TiO₂-400 at a high rate of 50 C.

The rate performance of *mc*-TiO₂-400 was further compared with some previous reported anatase anode materials (see Figure S8).^[9, 16, 28-39] The results reveal that this novel 3D '*isofacet*' nanostructure has a better rate capability than most reported nanostructure anatase. Those displaying ultra-high capacities were mostly due to their ordered porous structure,^[34] large amount of conductive carbon added (up to 45%),^[39] or just using carbon nanostructures as supporters with increased conductivity.^[29, 33] We propose that the good rate capability of *mc*-TiO₂-400 can be attributed to its '*isofacet*' property with anatase {001} facets dominated all six side faces. As shown in Figure S4a, the microcage is comprised of 3D perpendicular arranged nanocrystals and all its six side faces are dominated by the {001}_A facets. According to previous research, lithium insertion is favored on the anatase (001)_A surface, because a higher Li⁺ diffusion coefficient ($4 \cdot 10^{-13}$ vs $2 \cdot 10^{-13}$ cm²/s) and standard charge transfer rate constant (10^{-8} vs $2 \cdot 10^{-9}$ cm/s) are observed when lithium ions are propagating along the *c* axis.^[19] Therefore, the special anatase '*isofacet*' {001}_A facets dominated structure will greatly maximize the chance of lithium ions intercalating along the anatase *c*-axis from any direction, and accounts for the good rate capability of *mc*-TiO₂-400. It is reported that when TiO₂ is transformed to Li_{0.5}TiO₂, the *c*-axis contracts and *b*-axis expands. Thus, strain invariant planes between TiO₂ and Li_{0.5}TiO₂ within an individual particle will be generated in the direction parallel to the 1D lithium diffusion direction in Li_{0.5}TiO₂. As a result, additional Li ions are required to diffuse through the original TiO₂ phase.^[40] In our work, the small primary nanocrystals could avoid the TiO₂@Li_{0.5}TiO₂ core-shell growth and the whole particle being covered by Li_{0.5}TiO₂. In our work, the small primary nanocrystals could successfully avoid the core-shell growth mechanism and Li_{0.5}TiO₂ covering the whole particle, enable an exposure of fresh TiO₂ surface for additional Li entering the crystal. Meanwhile, the 3D perpendicular '*isofacet*' structure also has the ability to buffer the shape variation of the primary nanocrystals and maintain the whole microcage framework. Moreover, highly oriented nanocrystals with well-connected grains and abundant pores generally have improved lithium insertion property due to their improved contact with electrolyte.^[16, 33] Thus, the 3D micro/nano structure also enables a facile electron conduction and fast Li ion transport between porous electrode and electrolyte, which further enhances the rate performance of *mc*-TiO₂-400.

Figure 4c presents discharge/charge voltage profiles of the initial five cycles of *mc*-TiO₂-400 at the rate of 0.5 C. The first discharge and charge capacities of *mc*-TiO₂-400 are 287 and 236 mAh

g^{-1} , respectively, corresponding to a first cycle coulombic efficiency of 82.2%. This is a relatively high reversible capacity as most previous reported nanostructured electrode materials or low temperature-treated TiO_2 materials usually show a first irreversible capacity loss of 20–40%.^[38, 41] Figure 4d compares long cycling performance of *mc*- TiO_2 -400 and *np*- TiO_2 -400 at 5 C. After a decrease of the initial cycles, *mc*- TiO_2 -400 is able to deliver a reversible capacity of 175 mAh g^{-1} over 800 cycles, while *np*- TiO_2 -400 shows a much lower discharge capacity of 130 mAh g^{-1} . To further demonstrate the superior long cycling performance of *mc*- TiO_2 -400, especially at high rates, the *mc*- TiO_2 -400 electrode was tested at 50 C (8500 mA g^{-1}) up to 5000 cycles. A stable reversible capacity of 95 mAh g^{-1} is maintained. This performance is better than many TiO_2 nanostructures reported previously, as very few of them could hold comparable capacities at this situation.^[38, 42–45] Figure S9 shows the EBSD (Electron Back-Scattered Diffraction) and TEM images of *mc*- TiO_2 -400 after 2000 cycles at 10 C. The microcage morphology with the 3D perpendicular nanocrystals was well preserved. Therefore, we propose that this 3D perpendicular nanocrystals constructed microcage has a high structure stability, which renders its superior long cycling performance.

Conclusion

In conclusion, ‘*isofacet*’ anatase TiO_2 mesoporous microcages which are comprised of 3D perpendicularly arranged nanocrystals have been successfully synthesized *via* a facile *in situ* topotactic conversion from the pre-fabricated CaTiO_3 precursor. Due to the ideal lattice matching between anatase and the perovskite CaTiO_3 , the obtained mesoporous TiO_2 microcages perfectly inherit the crystallographic features of the CaTiO_3 precursor, namely, all the six side faces of each microcage are dominated by anatase {001} facets. As a result, the as-annealed microcages (*mc*- TiO_2 -400) exhibit much better rate capacity performance than the anatase nanoparticles. Moreover, the microcages are proved to have high structure stability for long cycling discharging/charging at high rates. Combining these advantages, *mc*- TiO_2 -400 is able to deliver capacities of 175 mAh g^{-1} at 5C after 800 cycles and 95 mAh g^{-1} at 50 C after 5000 cycles. The results presented here provide a new and facile approach for the synthesis of the technically important TiO_2 micro/nano structures, and may also be extendable to other hierarchical nanostructured materials with desirable functions by choosing suitable precursors

Experimental section

Preparation of precursory CaTiO_3 microcages. All chemicals were commercially available and used without further purification. The synthetic method is according to our previous report.^[23] In a typical process, 0.236 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was directly dissolved into 19.67 mL of polyethylene glycol 200 (PEG-200) solvent with the aid of ultrasonic treatment. 0.33 mL of $\text{Ti}(\text{OC}_4\text{H}_9)_4$ was then added dropwise into the solution under vigorous stirring, followed by addition of 0.88 g of NaOH powder under stirring to serve as a mineralization reagent. Subsequently, the mixture feedstock was transferred into a 30 mL Teflon autoclave for solvothermal treatment at 180 °C for 15 h. The vessel was then cooled down to ambient temperature. The precipitate was recovered by centrifugation, washed with acetone, diluted acetic acid, and distilled water, and then dried in a desiccator at ambient temperature.

Preparation of TiO_2 microcages. 0.15 g of as-prepared CaTiO_3 was dispersed into 20 mL of acetic acid solution by vigorous stirring. After thorough mixing, the suspension was then transferred into a 30 mL Teflon autoclave and heated at certain temperature for several hours. After reaction, the white product was collected by centrifugation, washed with distilled water several times, and then dried in a desiccator at ambient temperature. The obtained TiO_2 microcages (*mc-TiO₂*) was annealed at 400 °C in air for 2 h to get *mc-TiO₂-400*.

Preparation of TiO_2 nanoparticles. First, CaTiO_3 nanoparticles were synthesized through a sol-gel method reported by Yang and co-workers.^[46] Then they were converted to TiO_2 nanoparticles (*np-TiO₂*) using the same way as preparing TiO_2 microcages. The *np-TiO₂-400* was obtained by annealing *np-TiO₂* at 400 °C for 2 h.

Materials characterization. The powder X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance with Cu K_α radiation (40 kV, 40 mA). The particle morphology was characterized using a FEI Quanta 400 Thermal FE Environmental scanning electron microscope (SEM). The structural characterization was performed by using transmission electron microscopy (TEM) and high resolution TEM (HRTEM) on a JEOL JEM-2010HR microscope operating at 200 kV and a FEI Tecnai G2 F30 microscope operating at 300 kV. The Brunauer-Emmett-Teller (BET) surface areas of the samples were calculated from Nitrogen adsorption-desorption isotherms operating at 77 K under vacuum on an Autosorb-iQ2-MP (Quanta Chrome). Thermal gravimetric analysis (TGA) was conducted in a temperature range of 40–800 °C with air flow on a Netzsch STA 409 PC thermal analyzer.

Electrochemical measurement. To prepare the working electrodes, active material was mixed with acetylene black and polyvinylidene fluoride binder (PVDF) in a weight ratio of 70:20:10 in N-methyl-2-pyrrolidinone (NMP) to form slurry. This slurry was then coated onto copper foil using doctor blade and dried under vacuum at 120 °C over night to form the working electrode. Electrochemical performance was evaluated using a standard CR2032 coin cell composed of as-prepared cathode, a lithium foil as an anode, a polypropylene separator, and LiPF₆ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with a volume ratio of 1:1 as the electrolyte. Cells were assembled in an argon-filled glovebox. The galvanostatic charge/discharge tests were performed using a Neware battery tester at different current densities with a cut-off voltage window of 1–3 V. Cyclic voltammetry (CV) was performed using an electrochemical workstation (Autolab PGSTAT302N) between 0.8–3 V at a scan rate of 0.5 mV s⁻¹. Electrochemical impedance spectra (EIS) were collected using the same workstation from 100 kHz to 100 mHz, with a perturbation of 10 mV applied.

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A new type of hierarchical anatase TiO₂ microcages has been obtained via an *in situ* topotactic transformation from pre-fabricated CaTiO₃ microcages. The interesting microcage is composed of 3D perpendicular nanocrystals, and all its six side faces are ‘isofacet’ and dominated by anatase {001}_A facets. These unique anatase TiO₂ microcages exhibit excellent lithium ion storage properties as an anode material.

Keywords: *Isofacet, Anatase, Topotactic synthesis, 3D perpendicularly arrangement, Lithium ion battery*

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