Facile one-pot fabrication of α -Fe₂O₃ nano-coffee beans by etching along [001] direction for high lithium storage

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ABSTRACT It is a great challenge to finely tune the morphology of iron oxides for energy storage. In this work, we introduced a facile hydrothermal method to obtain single crystalline hematite (α -Fe₂O₃) nano-coffee beans (NCBs) with the assistance of acetic acid. Interestingly, α -Fe₂O₃ nanostructures with this special morphology were formed under the effect of Ostwald ripening and oriented etching of H⁺ ions along [001] direction, which could be proved by the scanning electron microscope /transmission electron microscope and X-ray diffraction. After calcination at high temperature, the as-prepared α -Fe₂O₃ NCBs were used as potential anode materials, showing a very high reversible capacity of 810 mA h g⁻¹ (0.2 C), excellent cycling stability, and high-rate performance for lithium storage. Hence, in virtue of the good performances, the structural design of nanomaterials would be promoted in the fabrication of electrode materials for lithium-ion batteries.

Keywords: hematite, etching, hydrothermal, lithium storage, designed nanostructures

INTRODUCTION

Nanostructured materials with properly engineered morphology have attracted a lot of attention for many years, due to their great importance for both fundamental study and technological development in various fields, such as catalysis [1], sensors [2], biomedical applications [3], energy conversion and storage [4]. As a result, innovative methods for efficiently fabricating nanomaterials with unique morphology and tuning their structure for desirable properties are imperative. In the past years,

many techniques have been explored, including template-assisted, solvothermal, microwave-assisted, sol-gel, mechanical milling and chemical etching [5–7]. However, it is still a challenge to find a facile synthesis method of nanomaterials with designed structures.

Hematite (α -Fe₂O₃), the most stable iron oxide under ambient conditions, has received great interest [8–10], which can be mainly ascribed to its versatile synthetic chemistry and various applications, such as catalysts, pigments, sensors and as the raw material for the synthesis of maghemite (γ -Fe₂O₃) [11,12]. In a practical point of view, α -Fe₂O₃ possesses many attractive properties, such as the favorable band gap (1.9–2.1 eV), chemical stability, natural abundance, nontoxicity and low cost [6,11,13,14]. Moreover, as considering for the application in the field of energy storage, owing to much higher capacity than that of conventional graphite (372 mA h g⁻¹), α -Fe₂O₃ has been regarded as an appealing candidate of the anode electrode in lithium-ion batteries (LIBs), which have been the predominant power source for the portable electronics for many years [15–18]. The high specific capacity is mainly delivered by the reversible conversion reaction between Li ions and α -Fe₂O₃. However, the hematite usually shows poor cyclability, due to drastic volume change and severe destruction of the electrode during charge-discharge process [8,14,19–21]. So far, for addressing these issues, an enormous amount of effort has been made to develop advanced synthesis methods for preparing α -Fe₂O₃ with designed sizes and shapes, such as nanoparticles, nanorods, nanotubes and hollow nanospheres [1,16,17,19,22,23]. For better rate and cy-

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clinging capabilities in lithium batteries, Lu *et al.* [22] prepared two-dimensional hematite nanodiscs with preferentially exposed (001) facets through the precipitation-dissolution-growth mechanism. Chen *et al.* [13] obtained single-crystal α -Fe₂O₃ nanodiscs using top-down fabrication *via* selective oxalic acid etching. Cao *et al.* [17] fabricated 3D hierarchical porous α -Fe₂O₃ nanosheets on copper foil using FeOOH as precursor. However, the fabrication of truly durable iron oxide electrodes with satisfactory high-rate capability and high specific capacity is still a great challenge [24,25].

Motivated by these purposes, in this work, we firstly reported a facile hydrothermal approach to synthesize single crystalline α -Fe₂O₃ nano-coffee beans (NCBs) with the assistance of acetic acid *via* an orientated H⁺ etching process. Acetic acid acted as the agent to control the growth of nanoparticles (NPs) and provided enough H⁺ ions in the hydrothermal process. Scanning electron microscope (SEM), transmission electron microscopes (TEM) analysis and X-ray diffraction (XRD) measurement were performed to investigate the formation of NCBs. The reaction time had an important influence on the morphology of the product. Furthermore, such well-defined nanostructures were evaluated as an anode electrode material in lithium battery, showing significantly improved Li storage capability in the electrochemical evaluation.

EXPERIMENTAL SECTION

Materials

Iron chloride hexahydrate (FeCl₃·6H₂O, 99%) was supplied by Aladdin Inc. Acetic acid (99.7%) was purchased from Alfa Aesar Ltd. Ethanol was bought from Shenzhen Chemical Reagent Company. All of the chemicals were analytical grade and used without further purification. Deionized (DI) water was used throughout.

Synthesis of α -Fe₂O₃ nano coffee beans

The single crystal Fe₂O₃ powders were obtained through a simple but effective method as follows. 3 mL of FeCl₃ solution (0.5 mol L⁻¹) was dropwise added into 28 mL of acetic acid solution with a series of concentration (0, 0.007, 0.015, 0.03 and 0.06 mol L⁻¹) under continuous magnetic stirring. After stirring for 30 min, the mixture was transferred into 100 mL-Teflon lined stainless steel autoclave, and then maintained at 180°C for different times (1, 2, 4, 8, 12 and 24 h). The dark red precipitate was washed with DI water and ethanol for three times to remove ions possibly remnant in the final products. After

being dried at 60°C for 12 h, these red powders were calcined at 600°C for 4 h under the protection of argon, improving crystallinity and removing the residue completely.

Characterization

The SEM images and elements distribution of NPs were taken on a field emission SEM (Merlin, Zeiss), equipped with an energy-dispersive X-ray spectrum (EDX, EDAX, Octane Pro). The morphology of the NPs was observed on field emission TEM (Tecnai G2 F30 U-TWIN). XRD analysis was performed using Bruker-AXS Micro-diffractometer (D8 Advance X-ray diffractometer, Cu K α , λ = 1.5046 Å, 40 kV and 40 mA). X-ray photoelectron spectrum (XPS) measurements were carried out with an ESCALab220i-XL spectrometer by using a twin-anode Al K α (1486.6 eV) X-ray source, equipped with a homemade heater. All the spectra were calibrated to the binding energy of the adventitious C1s peak at 284.6 eV. Fourier transform infrared (FT-IR) spectra were recorded on a FT-IR spectrometer (Spectrum Two, PerkinElmer).

Electrochemical evaluation

To prepare the electrodes, active materials (70 wt.%), acetylene black (20 wt.%), and acrylonitrile copolymer (LA133, 5 wt.%) were mixed together after adding isopropanol/water (3:1, v:v) solution in mortar. After the above slurries were uniformly spread onto an aluminum foil, the electrodes were dried at 80°C in vacuum for 12 h. Then the electrodes were pressed and cut into disks. Coin cells (CR2016) were laboratory-assembled using lithium metal as the counter electrode, Celgard 2400 membrane as the separator and LiPF₆ (1 mol L⁻¹) in ethylene carbonate/dimethyl carbonate (EC/DMC, 1:1 v%) as the electrolyte. The galvanostatic charge-discharge tests were carried out on a Neware Battery Testing System (Neware technology limited, China) in a potential range between 0.01 and 3.00 V. Cyclic voltammogram (CV) measurements were performed on a Bio-logic VMP3 electrochemical workstation with a voltage range from 0.01 to 3 V at a scan rate of 0.05 mV s⁻¹.

RESULTS AND DISCUSSIONS

The dark red NCBs powders were obtained through a simple but effective hydrothermal process, as described in the experimental section. Compared with the samples obtained with the solution of NaOH (Fig. S1), Fig. 1 clearly demonstrates that acetic acid has a great influence on the morphology and size of these NCBs. Fig. 1a shows that the NCBs obtained without acetic acid are in-

Figure 1 SEM images of single crystalline α - Fe_2O_3 NCBs synthesized at 180°C for 12 h in the presence of (a) DI water only, and different concentrations of acetic acid: (b) 0.007 mol L^{-1} ; (c) 0.015 mol L^{-1} ; (d) 0.03 mol L^{-1} and (e) 0.06 mol L^{-1} ; (f) EDX spectrum of α - Fe_2O_3 NCBs.

homogeneous, with sizes range from 150 to 600 nm. However, these NCBs become more uniform with the diameter of ca. 600 nm after adding acetic acid. In the reaction, the small organic additives (acetic acid) could act as a capping agent to occupy Fe^{3+} ions [26,27]. Then, these Fe-acetic acid complexes control the growth of the NPs, leading to the formation of uniform NCBs. Moreover, with the increase of the amount of acetic acid, the line-like dents in the middle of NCBs become deeper and more obvious, accompanied by smoother and flatter surfaces (Fig. 1b–e). Moreover, as shown in Fig. S2, FT-IR analysis was conducted for the sample, demonstrating the existence of acetic acid on the NCBs after washing with water/ethanol and desiccation. The strong band around 3440 cm^{-1} can be attributed to the O–H stretching vibrations in H_2O molecules. Two characteristic peaks at ~ 1634 and $\sim 1040\text{ cm}^{-1}$ can be ascribed to C=O and C–O stretching vibrations of acetic acid molecules, respectively. The weak peaks around 2925 and 1384 cm^{-1} correspond to O–H stretching vibration and C–H deformation, respectively [26]. Additionally, two peaks around 0.704 and 6.398 keV in the EDX spectrum are attributed to the existence of Fe element in the particles

Figure 2 SEM images of the samples synthesized with acetic acid (0.03 mol L^{-1}) at 180°C for a series of time: (a) 1 h; (b) 2 h; (c) 4 h; (d) 8 h; (e) 12 h; and (f) 24 h.

[28].

In order to get an entire view of the formation process of the unique nanostructures and their growth mechanism, a time-dependent morphology revolution study was carried out. The mixtures, containing FeCl_3 and acetic acid, were kept at 180°C for various reaction times (1, 2, 4, 8, 12 and 24 h), leaving other conditions unchanged. And these products are named Fe-1h, Fe-2h, Fe-4h, Fe-8h, Fe-12h, and Fe-24h, respectively. SEM images in Fig. 2 clearly display the effect of reaction time on the progressive growth of the NPs. As seen from Fig. 2a, there are all spindle-like nanostructures (length: $(270 \pm 20)\text{ nm}$) without any NPs of other shapes. What is more, the marked selected area with red dashed box (inset in Fig. 2a) reveals that these nano-spindles consist of self-assembling of nanorods with diameter of ca. 20 nm. By extending the reaction time to 2 h, these nano-spindles become smoother and shorter with the appearance of some NCBs ($246 \pm 16\text{ nm}$), which can be attributed to the Ostwald ripening (Fig. 2b). Under the ripening effect, the samples synthesized under 4 h are all turned into NCBs with the diameter of ($596 \pm 15\text{ nm}$), accompanied with the disappearance of nano-spindles (Fig. 2c). However, as

Figure 3 XRD patterns of the samples synthesized with acetic acid (0.03 mol L^{-1}) at 180°C for a series of time: 1, 2, 4, 8, 12 and 24 h, accompanied with standard PDF card.

shown in the SEM images of Fe-8h, Fe-12h and Fe-24h samples (Fig. 2d–f), continuously extending reaction time cannot induce further changes in the diameter of NCBs, but makes line-like dents deeper and the surfaces of NCBs smoother. Furthermore, visible cracks turn up instead of dents, forming broken coffee beans-like morphology in the Fe-24h NCBs (Fig. 2f).

XRD analysis was carried out on these samples to further investigate the intrinsic mechanism for this morphology change and orientated etching. The XRD patterns of the powders with different reaction time are exhibited in Fig. 3. The nano-spindles obtained with 1 h are all akaganeite $\text{FeO}(\text{OH})$, in good accordance with the standard PDF card (JCPDS No. 34-1266) without any other detected characteristic peaks from other impurities. After 2 h hydrothermal reaction, two weak peaks (marked with blue ball) come out, which are ascribed to hematite ($\alpha\text{-Fe}_2\text{O}_3$, JCPDS No. 89-0596). This fact demonstrates that a small quantity of $\alpha\text{-Fe}_2\text{O}_3$ starts to appear in Fe-2h. Furthermore, all the peaks of akaganeite disappear in the pattern of Fe-4h, illustrating the completed transformation from akaganeite to $\alpha\text{-Fe}_2\text{O}_3$. Moreover, the continuously prolonging reaction time cannot introduce any changes in the XRD pattern, as shown in Fig. 3.

To understand the chemical states of Fe in these NPs with two different shapes, XPS was performed. As seen from these two spectra, the Fe $2p_{3/2}$ and $2p_{1/2}$ peaks are located at around 711.5 and 724.6 eV (Fig. S3), respectively, with associated satellite shoulders about 8 eV higher than the main peaks. The fact indicates that the Fe ions in both compounds are trivalent [4,29], in good agreement with the results of XRD.

For the sake of further insight into the nanostructures

Figure 4 TEM and HRTEM images of the samples prepared with acetic acid (0.03 mol L^{-1}) at 180°C for different time: (a, b) 1 h; (c, d) 2 h and (e–g) 12 h (observed from the front of a $\alpha\text{-Fe}_2\text{O}_3$ particle); (h) SAED pattern of a single $\alpha\text{-Fe}_2\text{O}_3$ NCB.

of these nano-spindles and NCBs, Fe-1h, Fe-2h and Fe-12h were selected to be characterized with TEM as displayed in Fig. 4 and Fig. S4. Fig. 4a shows a low-resolution TEM image of the sample Fe-1h and Fig. 4b is the typical high resolution TEM (HRTEM) image of a single akaganeite nano-spindle. As seen from the HRTEM image, the clear lattice indicates the high crystallinity of the nano-spindles. The measured interplanar spacings of 0.152 nm between the adjacent lattice fringes is in good agreement with the d_{002} spacing of akaganeite $\text{FeO}(\text{OH})$ (JCPDS No. 34-1266), revealing the nano-spindles growth along [001] direction. The inset in Fig. 4b is a HRTEM image from the top of one nano-spindle. It is clearly seen that the nano-spindle consists of smaller nanorods (marked with dashed boxes). When the reaction time is extended to 2 h, these nano-spindles become shorter with the smoother surface, and the appearance of some NPs (Fig. 4c). What is more, a HRTEM image of the dashed box-marked area exhibits that the NPs consist of many nanorods (Fig. 4d). The lattice spacing is measured to be

Scheme 1 Schematic diagram of the formation of single crystal $\alpha\text{-Fe}_2\text{O}_3$ NCBs through a hydrothermal process under 180°C .

0.230 nm, which can be attributed to the (006) planes of the hematite structures ($\alpha\text{-Fe}_2\text{O}_3$, JCPDS No. 89-0596), according to the XRD analysis. In the light of these observed changes, the NPs possibly grow by centering on some nano-spindles and the Ostwald ripening effect, with the transformation from FeO(OH) to $\alpha\text{-Fe}_2\text{O}_3$. Fig. 4e–g are the TEM/HRTEM images of a NCB with 12 h reaction time. As observed from two etched sides of a NCB, these two HRTEM images clearly show that the measured interplanar spacings of ca. 0.230 nm is consistent with the d_{006} spacing of $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS No. 89-0596), demonstrating the NCBs are possibly etched along the [001] direction. Additionally, their single crystal nature is confirmed by the selective-area electron diffraction (SAED) in Fig. 4h.

Based on those above time-dependent morphology and crystalline type evolution evidences, an assumption of the mechanism for the formation process of NCBs can be proposed as described in Scheme 1. According to the Equation 1, Fe^{3+} ions are inclined to form $\text{Fe}^{3+}(\text{CH}_3\text{COO}^-)_3$ complex. During the whole reaction, the complex can steadily and slowly release Fe^{3+} to control the crystal growth of NPs, improving the uniformity and tuning the morphology, which have been reported in other small organic molecules, such as glycerol [26] and citric acid [27]. Undergoing hydrothermal process, akaganeite FeO(OH) nano-spindles with the [001] growth direction and rough surface are formed at the initial stage. Then, during

the continuous reaction, some nano-spindles serve as nuclei to form NPs with rough surface by the main force of Ostwald ripening. Some FeO(OH) nano-spindles with smaller sizes re-dissolve slowly along [001] direction and release Fe^{3+} ions into solution, due to their higher surface energy. Simultaneously, the ones with bigger sizes grow to be NPs, accompanied by the transformation from FeO(OH) to $\alpha\text{-Fe}_2\text{O}_3$ under high temperature and high pressure. The [001] direction (c axis) of $\alpha\text{-Fe}_2\text{O}_3$ NPs is marked with yellow arrow. At the stage III, continuously driven by Ostwald ripening, all FeO(OH) nano-spindles disappear, leaving only the bigger NPs. Meanwhile, according to the Equations 1–3 (Scheme 1), H^+ ions release into the solution during a series of reactions, which would etch the $\alpha\text{-Fe}_2\text{O}_3$. According to the previous reports, the preferred etching along the [001] direction will take place with the help of selective adsorption of phosphate ions at different faces, due to the more surface hydroxyl functional groups on the planes of [001] crystal axis [11,13,22]. Hence, the (006) planes, which place on [001] direction (c axis), may be preferentially attacked by H^+ ions, resulting in the selective etching along [001] direction and leading to the formation of NCBs. At the stage IV, with the extended reaction time, the NCBs become broken, as the consequence of continuous etching of H^+ ions along [001] direction.

According to the assumption, the TEM image in Fig. 4e obtained by observing at the front of a NCB shows the

Figure 5 Electrochemical evaluations of single crystalline $\alpha\text{-Fe}_2\text{O}_3$ NCBs in the range of 0.01–3 V. (a) CVs at a scan rate of 0.05 mV s^{-1} ; (b) discharge-charge profiles of different cycles (1^{st} , 5^{th} , 100^{th} , 200^{th} , 300^{th} , and 400^{th}) at 0.2 C ($1\text{ C}=1000\text{ mA g}^{-1}$); (c) cycling performance and Coulombic efficiency at 0.2 C ; (d) rate performance at different current densities (0.2 , 0.5 , 1 , 1.5 and 2 C).

third stage of hydrothermal process. In order to further support the above possible mechanism for the formation of NCBs, TEM measurement was carried out to selectively observe two NCBs from the top and the left which are exhibited in Fig. S4a–c, S4d, respectively. As seen from the top, it is clear that the cross-section of the NCB is regular hexagon. Since the edges of side 1 and 4 are rougher than those of other sides, the two parallel sides (side 1 and 4) should lie on the $[001]$ direction and be preferentially etched by H^+ ions, according to our hypothesis. With this purpose, each side was analyzed by HRTEM test. Notably, both HRTEM images of the red dashed box marked areas in side 1 and 4 (Fig. S4b, c, respectively) distinctly display that the lattice spacing are measured to be 0.231 nm , which is consistent with the d_{006} spacing of $\alpha\text{-Fe}_2\text{O}_3$. These clear lattice fringes demonstrate that $[001]$ direction on this NCB is from side 1 to side 4 (yellow arrow), firmly proving our previous assumption for the formation of NCBs. Moreover, as exhibited in Fig. S3d, another NCB has also been observed from the left as described in Scheme 1. The inset is a HRTEM image of the red dashed box marked area, presenting two sets of clear lattice fringes with the interplanar distance of 0.270 and 0.370 nm for (140) and $(1\bar{2}0)$

planes, respectively. Consequently, it is easy to calculate that the crystal axis of these two planes is $[001]$, in agreement with the description in stage IV of Scheme 1.

Since hematite has been considered as a promising candidate for lithium-ion battery, we further carried out the electrochemical evaluations for lithium storage capability of these single crystalline $\alpha\text{-Fe}_2\text{O}_3$ NCBs as potential anode material. These measurements were performed in coin cells (CR 2016), and the results are exhibited in Fig. 5. The representative CV measurements were carried out at a scan rate of 0.05 mV s^{-1} in the voltage window of $0.01\text{--}3.0\text{ V}$. The CV curves for the first six cycles are displayed in Fig. 5a, clearly identifying the distinct redox current peaks. In the first cathodic sweep, two apparent reduction peaks located at 1.62 and 0.66 V can be generally attributed to the stepwise reduction of Fe^{3+} to Fe^{2+} and Fe^0 with the lithium insertion. Especially, the latter peak (0.66 V) is partly owing to the formation of solid electrolyte interface (SEI) film. On the other hand, two peaks are clearly observed at 1.57 and 1.87 V during the anodic polarization process, which are ascribed to the oxidation of Fe^0 to Fe^{2+} and further complete oxidation to Fe^{3+} [17,18,20,30,31]. The overall Li-ion reactions with Fe_2O_3 anodes can be described by Equation (5):

From these CV curves, the full lithiation voltage in the subsequent cycles (~ 0.92 V) is higher than that in the first cycle (~ 0.66 V), because of the improved kinetics of the $\alpha\text{-Fe}_2\text{O}_3$ NCBs electrode resulting from a microstructural alteration after the first lithiation, which has been discussed in terms of the surface energy and the amorphization effect in RuO_2 [18,32]. Hence, the CV curves not only exhibit the good overlapping in the following cycles, but also indicate nice reversibility of the electrochemical reactions, which is further proved by the cycling performance.

Fig. 5b shows the discharge-charge voltage profiles of the NCBs Fe-12h for the selected cycles (1st, 5th, 100th, 200th, 300th, and 400th) at a current density of 0.2 C (1 C = 1000 mA g⁻¹) with a potential window of 0.01–3.0 V. A distinct voltage plateau at ca. 0.8 V can be obviously observed in the initial discharge process, and then shifts to ca. 1.0 V in the subsequent cycles. A high first-cycle discharge capacity of 1334 mA h g⁻¹ is found in the initial cycle, together with a charge capacity of 999 mA g⁻¹. The irreversible capacity loss of 25.1% is ascribed to the irreversible processes including the formation of SEI film and electrolyte decomposition [16–18,31]. The charge-discharge cycling performance and Coulombic efficiency of the $\alpha\text{-Fe}_2\text{O}_3$ NCBs is evaluated at a constant current density of 200 mA g⁻¹ between 0.01 and 3.0 V (Fig. 5c). From the second cycle, the $\alpha\text{-Fe}_2\text{O}_3$ NCBs exhibit stable capacity retention with a high Coulombic efficiency over 98%. Even in the 400th cycle, the NCBs deliver a reversible discharge capacity as high as 810 mA h g⁻¹, proving the good charge-discharge cycling stability. Moreover, it is interesting that the specific capacity of the electrode decreases during the first 35 cycles and then increases to a stable value. This capacity vibration has been reported in previous studies about various nanostructured metal oxide electrodes, which is ascribed to pseudo-capacitive interfacial storage and the reversible reactions between generated LiOH and Li, or forming oxidation state products [8,17,30,33]. Fig. 5d shows the investigation for the rate capability of the $\alpha\text{-Fe}_2\text{O}_3$ NCBs at different current densities within 0.01–3.0 V, displaying a remarkable high-rate performance. During the first six cycles, the $\alpha\text{-Fe}_2\text{O}_3$ NCBs show the decrease from 1300 to 750 mA h g⁻¹ at a current density of 0.2 C, which is in good agreement with the results in Fig. 5c. After deep cycling at 2 C, a constant capacity around 850 mA h g⁻¹ can be restored when cycling at a lower current density of 0.2 C, revealing the good rate capability of the $\alpha\text{-Fe}_2\text{O}_3$

NCBs.

CONCLUSIONS

In summary, single crystalline and uniform coffee beans-like $\alpha\text{-Fe}_2\text{O}_3$ NPs were synthesized through a facile and effective hydrothermal method with the assistance of acetic acid. In the hydrothermal process, it is interesting that the $\alpha\text{-Fe}_2\text{O}_3$ NPs with special morphology are formed by the effect of Ostwald ripening and oriented H⁺ etching along [001] direction, which was proved by the SEM/TEM and XRD analysis. Additionally, it is found that the reaction time has a great important influence on the morphology of the product. As an anode material, the as-prepared $\alpha\text{-Fe}_2\text{O}_3$ NCBs show significantly improved Li storage capability with a very high reversible capacity of 810 mA h g⁻¹ at a current density of 0.2 C even after 400 cycles. It is believed that the structural design of electrodes will have important implications on the fabrication of good performance electrode materials for lithium-ion batteries.

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Author contributions Zhou L designed and synthesized these NCBs, and completed this paper; Yi Z carried out SEM and XRD analysis of these samples, and revised this paper; Lyu F evaluated the electrochemical performance of these NCBs; Wang Z characterized these NCBs by using TEM. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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[001]晶向定向刻蚀介导 α - Fe_2O_3 纳米咖啡豆的一步合成及其高储锂性能研究

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摘要 目前,对铁氧化物的形貌进行有效调控,并使其更好地应用于能量储存领域,是一项巨大的挑战.本工作成功地利用醋酸通过简单有效的水热合成法,得到了单晶赤铁矿 α - Fe_2O_3 纳米咖啡豆.这种特殊的纳米结构是在奥斯瓦尔德熟化(Ostwald ripening)和氢离子沿着[001]晶向定向刻蚀的共同作用下形成的.利用扫描电子显微镜、透射电子显微镜和X射线衍射测试等手段证明了这一假设的可信性.通过高温煅烧之后,作为负极材料,这些纳米咖啡豆展现了良好的锂离子性能.其在0.2 C倍率下的可逆容量为 810 mA h g^{-1} ,且具有良好的循环稳定性和倍率性能.因此,该纳米材料的结构设计将为合成具有更好表现的锂离子电池正极材料提供借鉴.