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## The Effect of Crystal Face of Fe<sub>2</sub>O<sub>3</sub> on the Electrochemical Performance for Lithium-ion Batteries

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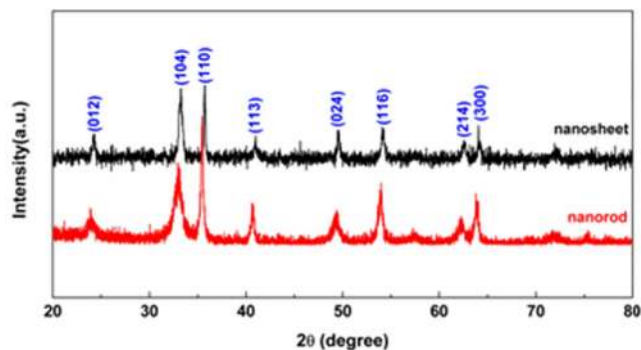
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Fe<sub>2</sub>O<sub>3</sub> nanorods exposing (001) and (010) plane as well as Fe<sub>2</sub>O<sub>3</sub> nanosheets exposing (001) plane have been successfully synthesized. Fe<sub>2</sub>O<sub>3</sub> nanosheets exhibit better cycle performance and rate capabilities than that of Fe<sub>2</sub>O<sub>3</sub> nanorods. The discharge capacity of Fe<sub>2</sub>O<sub>3</sub> nanosheets can stabilize at 865 mAh/g at the rate of 0.2C (1C = 1000 mA/g) and 570 mAh/g at the rate of 1.2C after 80 cycles, which increased by 90% and 79% compared with 456 mAh/g and 318 mAh/g of Fe<sub>2</sub>O<sub>3</sub> nanorods. In comparison with (010) plane, the (001) plane of hematite possesses larger packing density of Fe<sup>3+</sup> and O<sup>2-</sup>, which is responsible for the superior electrochemical performances of Fe<sub>2</sub>O<sub>3</sub> nanosheets than that of Fe<sub>2</sub>O<sub>3</sub> nanorods. In addition, potentiostatic intermittent titration (PITT) results show the diffusion coefficients of Li<sup>+</sup> (D<sub>Li</sub>) of Fe<sub>2</sub>O<sub>3</sub> nanosheets is higher than that of Fe<sub>2</sub>O<sub>3</sub> nanorods. The higher diffusion coefficients of Li<sup>+</sup> is favorable for the excellent lithium-storage capabilities and rate capability of Fe<sub>2</sub>O<sub>3</sub> nanosheets. Inspired by our results, we can design and synthesize Fe<sub>2</sub>O<sub>3</sub> or other electrodes with high performances according to their structure features in future.

3d transition-metal oxides, which can be used as anode materials, such as iron oxide, cobalt oxide, and nickel oxide have attracted a great deal of attentions for their much higher capacity than that of conventional graphite (372 mAhg<sup>-1</sup>)<sup>1-12</sup>. For instance, the theoretical capacity of Co<sub>3</sub>O<sub>4</sub> is about 890 mAhg<sup>-1</sup>, which is almost two and a half times higher than that of graphite. However, high price and toxicity of Co limit the application of Co<sub>3</sub>O<sub>4</sub><sup>13,14</sup>. Interestingly, Fe<sub>2</sub>O<sub>3</sub> also exhibits high capacity (1007 mAhg<sup>-1</sup>) like Co<sub>3</sub>O<sub>4</sub>. More importantly, due to its low cost, nontoxicity and high resistance to corrosion, Fe<sub>2</sub>O<sub>3</sub> has attracted special attentions in recent years<sup>15,16</sup>. For example, various morphologies of Fe<sub>2</sub>O<sub>3</sub> such as nanoparticles, nanotubes, hollow structure and thin films have been studied as electrodes for lithium-ion batteries<sup>17-25</sup>. Lou *et al.* prepared a series of hollow microspheres of iron oxides which showed significantly improved lithium-storage capabilities<sup>24,25</sup>. In addition to the above-mentioned methods, many studies have proved that the crystal plane structure of electrode materials has a significant effect on the electrochemical properties. Islam *et al.* reported that the (010) plane of LiFePO<sub>4</sub> is a favorable plane for fast Li<sup>+</sup> transport<sup>26</sup>. Wei *et al.* found that the electrochemical performance of lithium rich material Li(Li<sub>0.17</sub>Ni<sub>0.25</sub>Mn<sub>0.58</sub>)O<sub>2</sub> with (010) and (100) planes have been greatly increased, exhibiting not only a high reversible capacity but also an excellent cycle stability<sup>27</sup>. Huang *et al.* found the facet-dependent electrochemical properties of Co<sub>3</sub>O<sub>4</sub> toward heavy metal ions and found that the Co<sub>3</sub>O<sub>4</sub> nanoplates with (111) facet performed better electrochemical sensing capability than the Co<sub>3</sub>O<sub>4</sub> nanocubes with (001) facet<sup>28</sup>. Not long ago, we also reported the facet-dependent electrochemical capability of Co<sub>3</sub>O<sub>4</sub> as anode material for Li-ion batteries and proved the Co<sub>3</sub>O<sub>4</sub> octahedron with exposed (111) plane exhibited more excellent electrochemical properties than that of Co<sub>3</sub>O<sub>4</sub> cube with exposed (001) plane and Co<sub>3</sub>O<sub>4</sub> truncated octahedron with exposed (001) and (111) planes<sup>29</sup>. Therefore, studies on the crystal plane controllable synthesis of nanomaterials are of great interest and are actively being pursued. So, controlling the exposed crystal plane of Fe<sub>2</sub>O<sub>3</sub> might also be an effective strategy to further improve the electrochemical performance of Fe<sub>2</sub>O<sub>3</sub> as anode materials for lithium-ion batteries.

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**Figure 1.** Powder X-ray diffraction patterns of  $\text{Fe}_2\text{O}_3$  nanorods and nanosheets in a  $2\theta$  range of  $10\text{--}80^\circ$ .

In this article, we successfully synthesized two kinds of  $\text{Fe}_2\text{O}_3$  with exposed different crystal plane, including nanorods with (001) and (010) plane and nanosheets with the (001) plane. Interestingly, when used as anode materials in lithium-ion batteries,  $\text{Fe}_2\text{O}_3$  nanosheets exhibit better cycle performance and rate capabilities than that of  $\text{Fe}_2\text{O}_3$  nanorods. To be specific, the discharge capacity of  $\text{Fe}_2\text{O}_3$  nanosheets could stabilize at  $865\text{ mAhg}^{-1}$  at the rate of  $0.2\text{C}$  ( $1\text{C} = 1000\text{ mAhg}^{-1}$ ) and  $570\text{ mAhg}^{-1}$  at the rate of  $1.2\text{C}$  over 80 cycles, which increased by 90% and 79% compared with  $456\text{ mAhg}^{-1}$  and  $318\text{ mAhg}^{-1}$  of  $\text{Fe}_2\text{O}_3$  nanorods. Herein, the outstanding electrochemical performance of  $\text{Fe}_2\text{O}_3$  nanosheets can be attributed to the highly exposed (001) planes. Crystal structure have revealed that the (001) plane possesses larger packing density than that of (010) plane, and the crystal effect is the crucial reason for the differences of electrochemical performance<sup>30</sup>. On the other hand, potentiostatic intermittent titration (PITT) results show that  $\text{Fe}_2\text{O}_3$  nanosheets have higher diffusion coefficient of  $\text{Li}^+$  ( $D_{\text{Li}}$ ) and are more favorable for the diffusion of lithium ion.

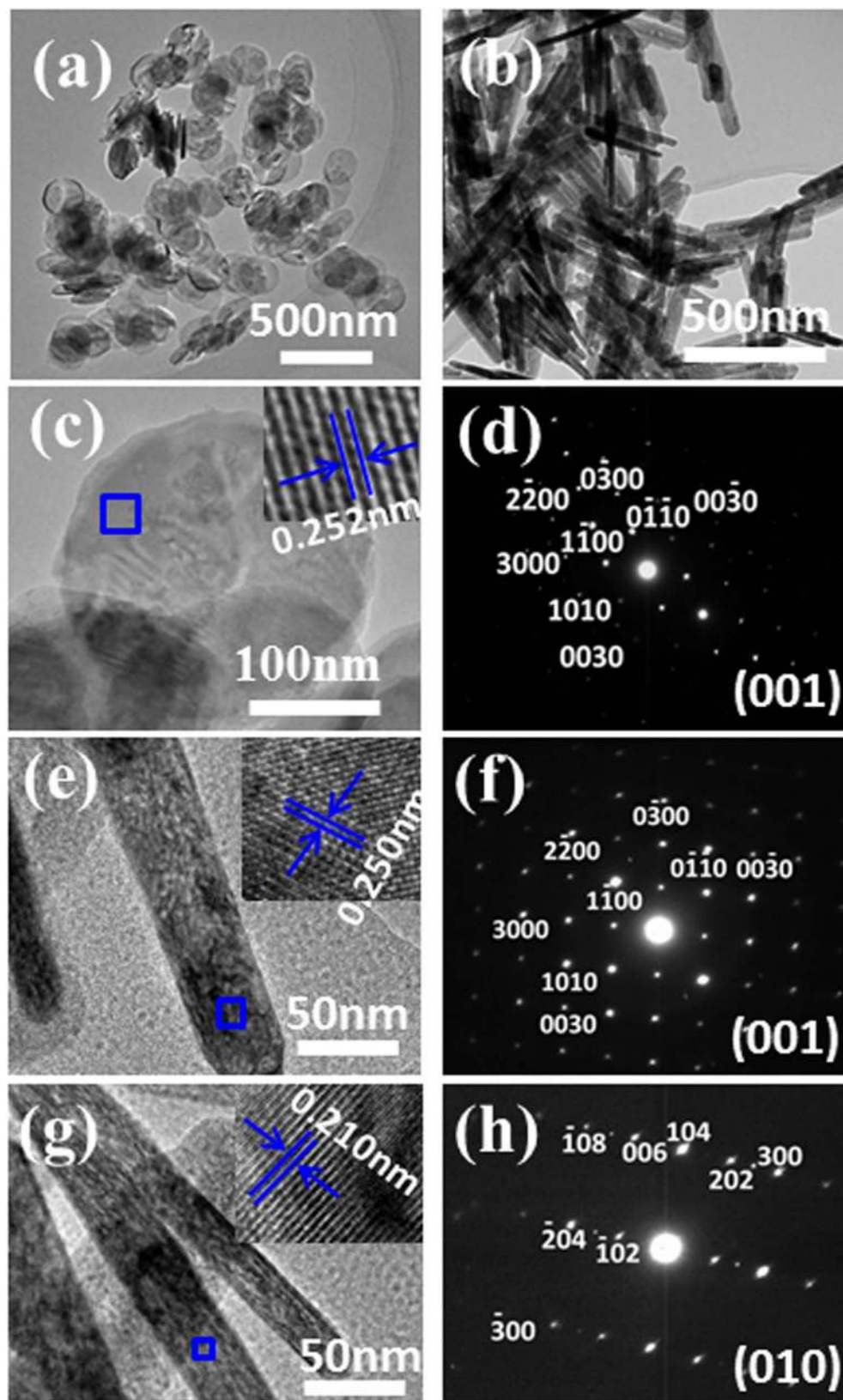
To the best of our knowledge, we, for the first time, combined electrochemical experiment and crystal structure analysis to elucidate exposed crystal plane-electrochemical properties relationship of  $\text{Fe}_2\text{O}_3$  as anode for rechargeable lithium ion batteries. Our results indicate the superior electrochemical performances of  $\text{Fe}_2\text{O}_3$  nanosheets can be attributed to (1) the larger packing density of  $\text{Fe}^{3+}$  and  $\text{O}^{2-}$  of (010) plane and (2) the higher diffusion coefficient of  $\text{Li}^+$  ( $D_{\text{Li}}$ ) of  $\text{Fe}_2\text{O}_3$  nanosheets during discharge-charge process. Furthermore, our results provide a idea which we can design and synthesize electrode materials with high performances according to their structure features in future.

## Results

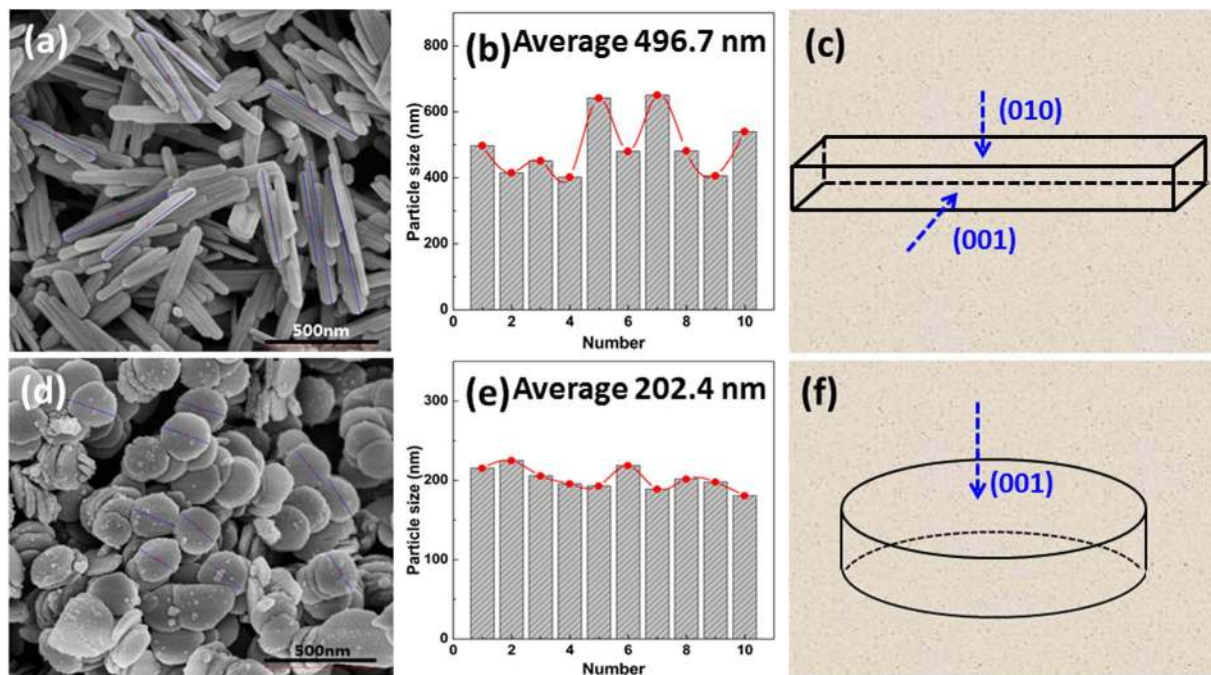
In Fig. 1, the indexed X-Ray Diffraction (XRD) patterns of  $\text{Fe}_2\text{O}_3$  samples show that the diffraction peaks match well with the standard PDF card (JCPDS no. 86–2368), indicating the purity of the products and the two kinds of  $\text{Fe}_2\text{O}_3$  belong to the same space group. The exposed facets of nanosheets and nanorods have been determined by high resolution transmission electron microscopy (HRTEM) characterization in Fig. 2c–h. The clear lattice spacing and fast Fourier transform selected-area electron diffraction (FFT-SAED) patterns indicate that  $\text{Fe}_2\text{O}_3$  nanosheets and nanorods are single crystalline. Figure 2c shows the TEM image of a  $\text{Fe}_2\text{O}_3$  nanosheet, and the corresponding SAED pattern is shown in Fig. 2d. It can be clearly seen that the exposed crystal facet is perpendicular to the (3000), (0300) and (0030) facets of  $\text{Fe}_2\text{O}_3$  nanosheets, and the interlayer spacings of  $0.252\text{ nm}$  inserted in Fig. 1c correspond to the (110) plane of the  $\text{Fe}_2\text{O}_3$ . Thus it can be concluded that the exposed facets of the nanosheets are (001). Figure 2e and f show the similar interlayer spacings and SAED pattern compared with the  $\text{Fe}_2\text{O}_3$  nanosheets, which indicate that one of the exposed facets of the  $\text{Fe}_2\text{O}_3$  nanorods are (001). Figure 2g shows the TEM image of another facet of  $\text{Fe}_2\text{O}_3$  nanorods and the corresponding SAED pattern is shown in Fig. 2h. The SAED pattern in Fig. 2h shows that the exposed crystal facet is perpendicular to the (300), (006) and (202) facets of the  $\text{Fe}_2\text{O}_3$ , and the interlayer spacings of  $0.210\text{ nm}$  inserted in Fig. 2g correspond to the (202) plane of the  $\text{Fe}_2\text{O}_3$ .

So another exposed facets of the nanorods are (010). The structural models of  $\text{Fe}_2\text{O}_3$  nanorod is displayed in Fig. 3c, the exposed (001) and (010) crystal facets can be clearly shown and the models of  $\text{Fe}_2\text{O}_3$  nanosheet is showed in Fig. 3f. Figure 3a,d show the SEM images of  $\text{Fe}_2\text{O}_3$  nanorods and nanosheets, respectively. It can be seen that the average length of  $\text{Fe}_2\text{O}_3$  nanorods is about  $500\text{ nm}$ , the width and thickness is about  $50$  and  $15\text{ nm}$ , respectively. The average diameter and thickness of  $\text{Fe}_2\text{O}_3$  nanosheets is about  $200\text{ nm}$  and  $15\text{ nm}$ , respectively. The  $\text{Fe}_2\text{O}_3$  nanosheets and nanorods of nanosize can reduce the diffusion length of  $\text{Li}^+$  ions and increase reactivity of the material, which are very favorable for excellent electrochemical performances.

Subsequently, the comparison galvanostatic discharge capacities of  $\text{Fe}_2\text{O}_3$  nanorods and nanosheets in a potential range of  $0.1\text{--}3.0\text{ V}$  (vs  $\text{Li}/\text{Li}^+$ ) at a rate of  $0.2\text{C}$  were comprehensively investigated and illustrated in Fig. 4a–c. It can be seen from Fig. 4a that  $\text{Fe}_2\text{O}_3$  nanorod and  $\text{Fe}_2\text{O}_3$  nanosheet electrodes deliverer approximately a discharge capacity of  $1135\text{ mAhg}^{-1}$  and  $1210\text{ mAhg}^{-1}$  in the first cycle, respectively. After that the discharge capacity decreases rapidly, and the reason can be ascribed to the change of structure during the initial charge-discharge process. From the beginning of the second cycle, two kinds of  $\text{Fe}_2\text{O}_3$  electrodes exhibit good cycle stability until to the 20 cycles. Surprisingly, after 20 cycles, the discharge capacity of the  $\text{Fe}_2\text{O}_3$  nanorods monotonically decline, while the discharge capacity of  $\text{Fe}_2\text{O}_3$  nanosheets slightly increase. Similar phenomenon also has been found in the case of  $\text{CoO}$  and  $\text{Co}_3\text{O}_4$  as well as other  $\text{Fe}_2\text{O}_3$  reports in the literature, though a clear understanding has not



**Figure 2.** TEM images of  $\text{Fe}_2\text{O}_3$  nanosheets (a) and  $\text{Fe}_2\text{O}_3$  nanorods (b); (c,d) The TEM image of a  $\text{Fe}_2\text{O}_3$  nanosheet, inset shows the lattice fringes and the corresponding SAED pattern; (e,f) The TEM image of  $\text{Fe}_2\text{O}_3$  nanorod with {001} plane, inset shows the lattice fringes and the corresponding SAED pattern; (g,h) The TEM image of  $\text{Fe}_2\text{O}_3$  nanorod with {010} plane, inset shows the lattice fringes and the corresponding SAED pattern.



**Figure 3.** The SEM images and crystal size distribution histogram of (a,b)  $\text{Fe}_2\text{O}_3$  nanorods and (d,e)  $\text{Fe}_2\text{O}_3$  nanosheets; Structural models of (c)  $\text{Fe}_2\text{O}_3$  nanorods and (f)  $\text{Fe}_2\text{O}_3$  nanosheets.

been obtained<sup>31–33</sup>. As shown in Fig. 4a, the discharge capacity of the  $\text{Fe}_2\text{O}_3$  nanosheets maintains at  $865 \text{ mAhg}^{-1}$  with a capacity retention of 95.3% after 80 cycles, in contrast, the discharge capacity of  $\text{Fe}_2\text{O}_3$  nanorods maintains at  $456 \text{ mAh/g}$  with a capacity retention of 50.7% after 80 cycles.

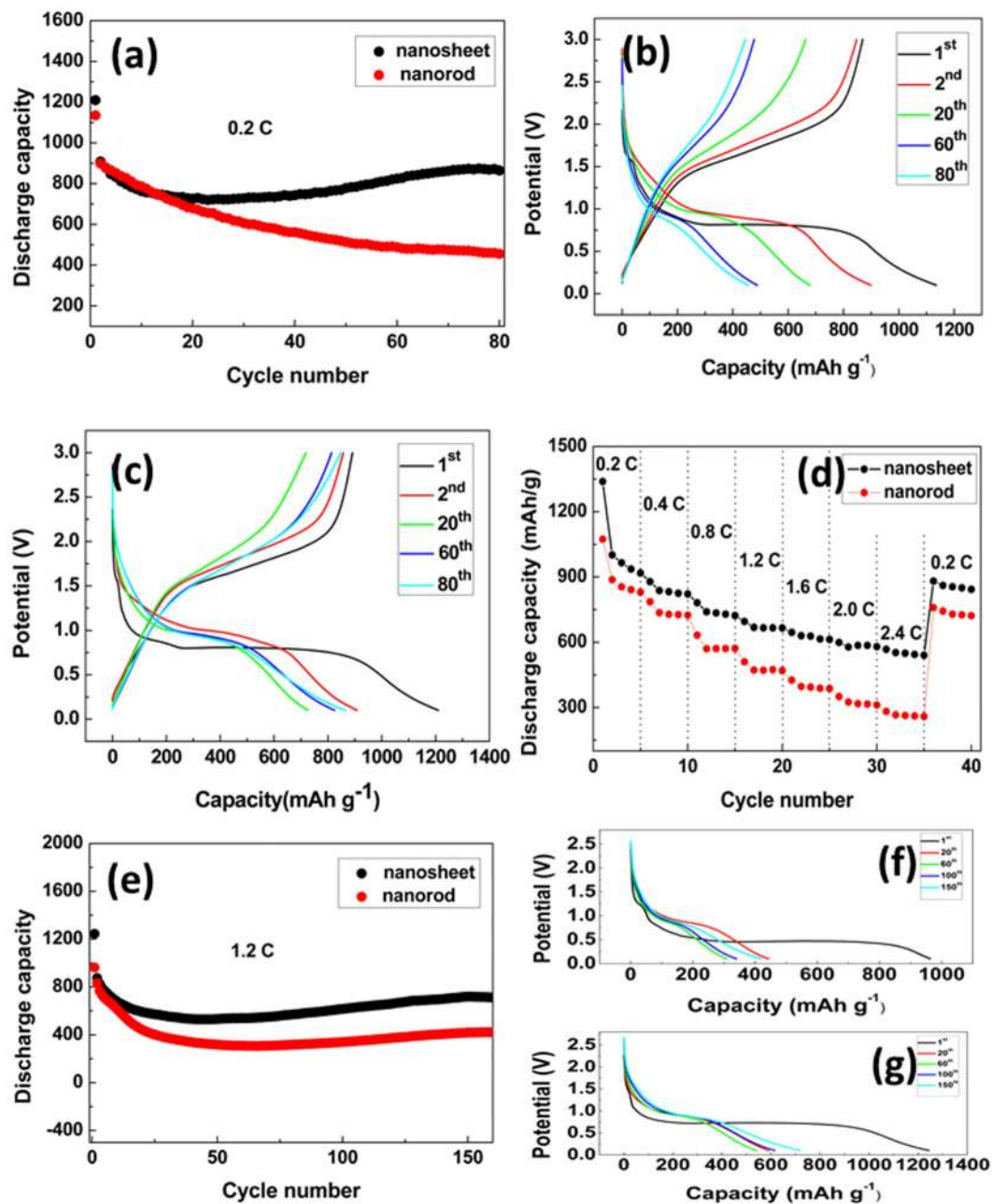
Figure 4d shows the rate performance of  $\text{Fe}_2\text{O}_3$  nanorods and nanosheets. Specifically, the discharge capacity of  $\text{Fe}_2\text{O}_3$  nanorods at 0.2, 0.4, 0.8, 1.2, 1.6, 2.0 and 2.4 C are 896, 763, 627, 544, 478, 430 and  $385 \text{ mAhg}^{-1}$ , respectively. The corresponding values for the  $\text{Fe}_2\text{O}_3$  nanosheets were 966, 832, 734, 667, 628, 586 and  $550 \text{ mAhg}^{-1}$ , respectively. By comparing the discharge capacity of the two samples,  $\text{Fe}_2\text{O}_3$  nanosheets display higher capacity than  $\text{Fe}_2\text{O}_3$  nanorods at various charge–discharge rates from 0.2 to 2.4 C. Meanwhile, as the growth of charge–discharge current density, the gap between the discharge capacities of the  $\text{Fe}_2\text{O}_3$  nanorods and nanosheets samples became larger. For instance, the discharge capacity of  $\text{Fe}_2\text{O}_3$  nanosheets increase by 8% compared with that of  $\text{Fe}_2\text{O}_3$  nanorods at 0.2 C, while the discharge capacity increase by 43% at the rate of 2.4 C. In addition, it should be noted when the rate was returned back to the 0.2 C,  $\text{Fe}_2\text{O}_3$  nanosheets still show higher discharge capacity than that of  $\text{Fe}_2\text{O}_3$  nanorods. At the recovery rate of 0.2 C, both  $\text{Fe}_2\text{O}_3$  nanosheets and nanorods display lower discharge capacity compared with the initial capacity at 0.2 C. The phenomenon is due to the destruction of crystal structure of  $\text{Fe}_2\text{O}_3$  during discharge-charge cycle process.

In order to research the cycle stability under high current density, the  $\text{Fe}_2\text{O}_3$  nanorods and nanosheets are tested at the rate of 1.2 C, as shown in Fig. 4e–g. Obviously, the electrode of  $\text{Fe}_2\text{O}_3$  nanosheets shows much higher discharge capacity than that of  $\text{Fe}_2\text{O}_3$  nanorods at high rate. Especially, the discharge capacity of  $\text{Fe}_2\text{O}_3$  nanosheets can reach  $719 \text{ mAhg}^{-1}$  after 150 cycles. This value is 71% higher than that of  $\text{Fe}_2\text{O}_3$  nanorods, which only shows  $419 \text{ mAhg}^{-1}$  after 150 cycles.

SEM and TEM images of  $\text{Fe}_2\text{O}_3$  nanosheets and nanorods samples after extensive cycling are shown in Fig. 5. It can be clearly seen in Fig. 5a,c that  $\text{Fe}_2\text{O}_3$  nanosheets keep relatively complete sheet structure after extensive charge-discharge cycling. Similar to nanosheets,  $\text{Fe}_2\text{O}_3$  nanorods also show well virgulate shape which can be seen in Fig. 5b,d. In addition, there is no significant change of the  $\text{Fe}_2\text{O}_3$  particle size after charge-discharge cycling.

It is reported that the Brunauer–Emmett–Teller (BET) surface areas of electrode materials play a important role on the electrochemical performance of lithium ions batteries<sup>34</sup>. Our nitrogen-sorption analysis reveals that the BET specific surface areas of  $\text{Fe}_2\text{O}_3$  nanorods and  $\text{Fe}_2\text{O}_3$  nanosheets were 26.81 and  $18.25 \text{ m}^2/\text{g}$ , respectively (Fig. 6). The BET specific surface areas of  $\text{Fe}_2\text{O}_3$  nanorods is larger than that of  $\text{Fe}_2\text{O}_3$  nanosheets, whereas, the  $\text{Fe}_2\text{O}_3$  nanosheets exhibit better electrochemical properties compared with  $\text{Fe}_2\text{O}_3$  nanorods. So it can be concluded that the effect of specific surface areas of electrodes on the difference of electrochemical properties between  $\text{Fe}_2\text{O}_3$  nanosheets and nanorods can be overlooked.

Evidently, the electrochemical performances of lithium ion batteries are related to the intrinsic crystal structure<sup>35</sup>. So the crystal structure of  $\text{Fe}_2\text{O}_3$  is analyzed. For  $\text{Fe}_2\text{O}_3$  samples, the (001) plane has been found possessing the larger packing density, in which  $\text{Fe}^{3+}$  and  $\text{O}^{2-}$  ions pack layer by layer. Specifically, the packing densities of the  $\text{Fe}^{3+}$  and  $\text{O}^{2-}$  are  $9.11 \text{ nm}^{-2}$  and  $13.8 \text{ nm}^{-2}$ , respectively. In contrast, the packing densities of the (010) facets for ions are  $2.89 \text{ nm}^{-2}$  and  $5.78 \text{ nm}^{-2}$ . Due to the high atomic density, more  $\text{Fe}^{3+}$  ions participate in the reaction, and lead to a high specific capacity<sup>28</sup>. The detailed crystal structure of  $\text{Fe}_2\text{O}_3$  have been displayed in Fig. 7. Meanwhile, it can be seen from the model of  $\text{Fe}_2\text{O}_3$  nanosheets and nanorods in Fig. 7, that the proportion of (001) plane in

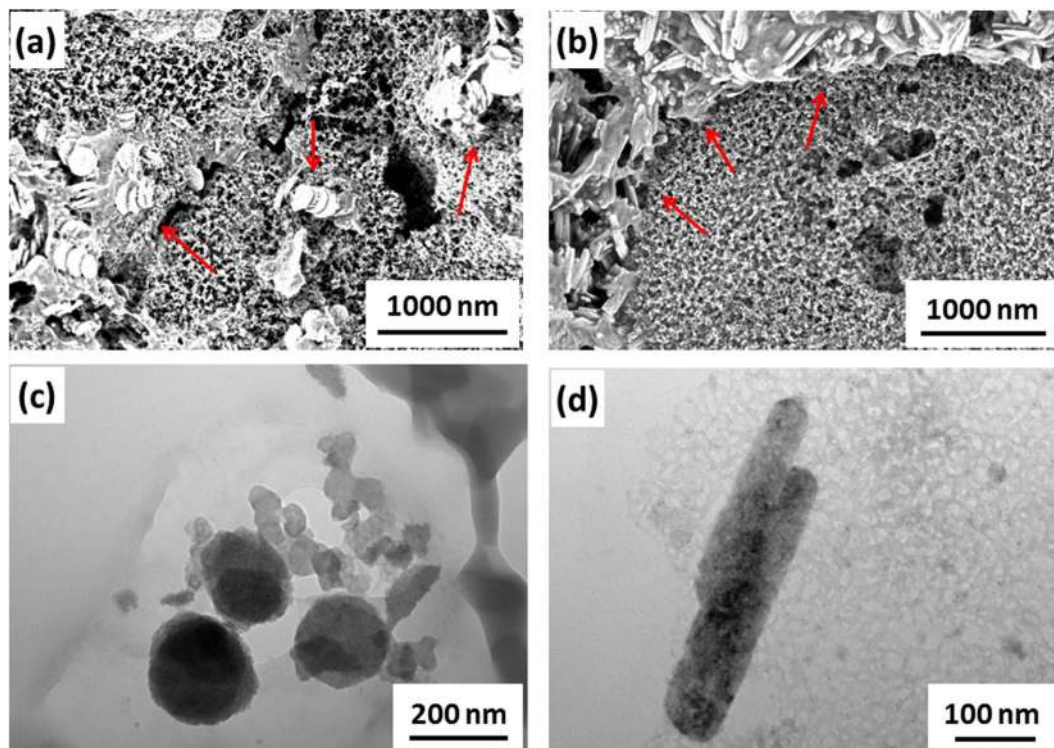


**Figure 4.**  $N_2$  absorption curves of  $Fe_2O_3$  nanosheets and  $Fe_2O_3$  nanorods. (a) Comparison of cycling performance of the two kinds of  $Fe_2O_3$  at the rate of 0.2 C; The charge/discharge curves of (b)  $Fe_2O_3$  nanorods and (c)  $Fe_2O_3$  nanosheets in the 1st, 2nd, 20th, 60th and 80th cycles at the rate of 0.2 C, respectively. (d) The rate performances of  $Fe_2O_3$  nanorods and  $Fe_2O_3$  nanosheets. (e) Plots of the specific discharge capacity vs. cycle number for the  $Fe_2O_3$  nanostructure electrode at the rate of 1.2 C; The discharge curves of (f)  $Fe_2O_3$  nanorods and (g)  $Fe_2O_3$  nanosheets in the 1st, 20th, 60th, 100th and 150th cycles at the rate of 1.2 C, respectively.

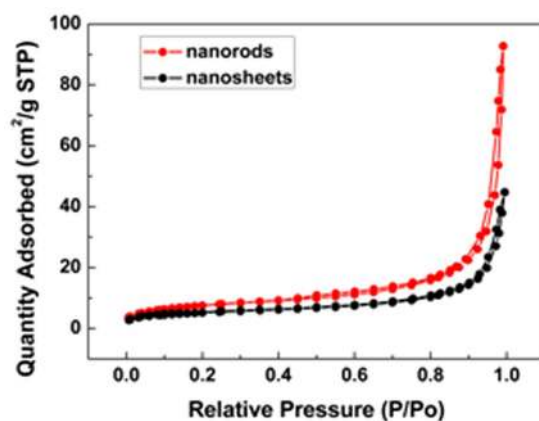
nanosheet is almost 100%, while in nanorods is about 23%. And the mainly exposed crystal plane is (010) facet in nanorods, in which the proportion of (010) plane is about 77%. The results indicate that the  $Fe_2O_3$  samples which exposed more (001) plane show a superior electrochemical capability.

Figure 8 shows Nyquist plots of the two kinds of  $Fe_2O_3$  electrode measured at the open circuit potential and an equivalent circuit proposed to fit the spectra. As can be seen from Table 1, the charge transfer resistances ( $R_{ct}$ ) for  $Fe_2O_3$  nanosheets (53  $\Omega$ ) is much smaller than that obtained from the  $Fe_2O_3$  nanorods (179  $\Omega$ ) electrode. The electrochemical impedance spectroscopy (EIS) data indicates that  $Fe_2O_3$  nanosheets possesses smaller lithium ion migration resistance and is more conducive to the rapid migration of lithium ions.

For the sake of confirming  $D_{Li}$  in electrode materials, PITT measurement was performed. Figure 9a–c display the PITT results of  $Fe_2O_3$  samples before discharge-charge cycle. It can be seen the  $D_{Li}$  of  $Fe_2O_3$  nanosheets is about one time higher than that of  $Fe_2O_3$  nanorods. Figure 9d–f display the PITT results of  $Fe_2O_3$  samples after a



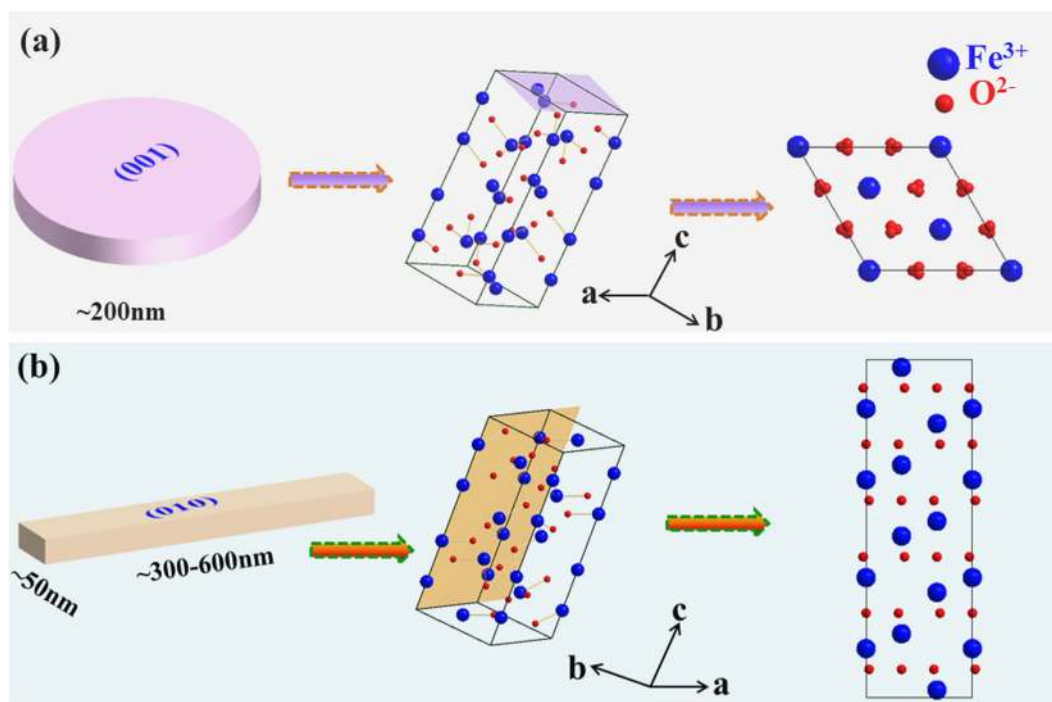
**Figure 5.** SEM and TEM images of (a,c)  $\text{Fe}_2\text{O}_3$  nanosheets and (b,d)  $\text{Fe}_2\text{O}_3$  nanorods after 30 cycles at 0.2 C.



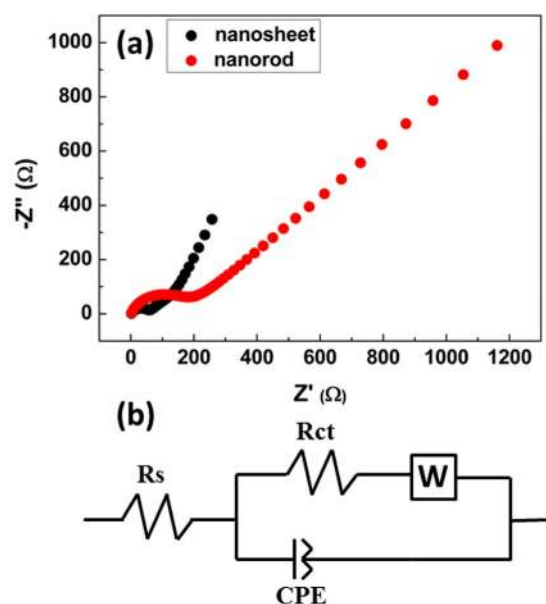
**Figure 6.**  $\text{N}_2$  adsorption curves of  $\text{Fe}_2\text{O}_3$  nanosheets and  $\text{Fe}_2\text{O}_3$  nanorods.

circle of discharge-charge cycle at the current density of 200 mA/g. It is obviously that  $D_{\text{Li}}$  of  $\text{Fe}_2\text{O}_3$  nanosheets are higher than that of  $\text{Fe}_2\text{O}_3$  nanorods. For instance, the  $D_{\text{Li}}$  average value of  $\text{Fe}_2\text{O}_3$  nanosheets is  $2.2 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$  which increased by 15.7%, compared to  $1.9 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$  of  $\text{Fe}_2\text{O}_3$  nanorods. The improved kinetic parameters  $D_{\text{Li}}$  indicate that  $\text{Fe}_2\text{O}_3$  nanosheets possess higher lithium diffusion coefficient. For this reason,  $\text{Fe}_2\text{O}_3$  nanosheets show better rate capability, as shown in Fig. 4d. Figure 4d show that  $\text{Fe}_2\text{O}_3$  nanosheets with (001) planes possess higher discharge capacity not only at the low rate of 0.2 C but also at the high rate of 1.2 C. Additional, the  $\text{Fe}_2\text{O}_3$  nanosheets with (001) planes exhibit better cycle stability and rate ability. Generally, the  $\text{Fe}_2\text{O}_3$  nanosheets with (001) plane exhibit better electrochemical properties than that of the  $\text{Fe}_2\text{O}_3$  nanorods with (010) and (001) planes.

In conclusion, we successfully synthesized two kinds of morphology of single crystal  $\text{Fe}_2\text{O}_3$  with exposed different crystal plane, including nanorods with (001) and (010) plane and nanosheets with the (001) plane.  $\text{Fe}_2\text{O}_3$  nanosheets exhibit better cycle performance and rate capabilities than that of  $\text{Fe}_2\text{O}_3$  nanorods. The reasons can be attributed to that (1) the larger packing density of  $\text{Fe}^{3+}$  and  $\text{O}^{2-}$  of (010) plane and (2) the higher diffusion coefficient of  $\text{Li}^+$  ( $D_{\text{Li}}$ ) of  $\text{Fe}_2\text{O}_3$  nanosheets during discharge-charge process. Our studies indicate that the crystal structure has a very important influence on the electrochemical performances, which may be helpful for developing high performance lithium ion batteries.



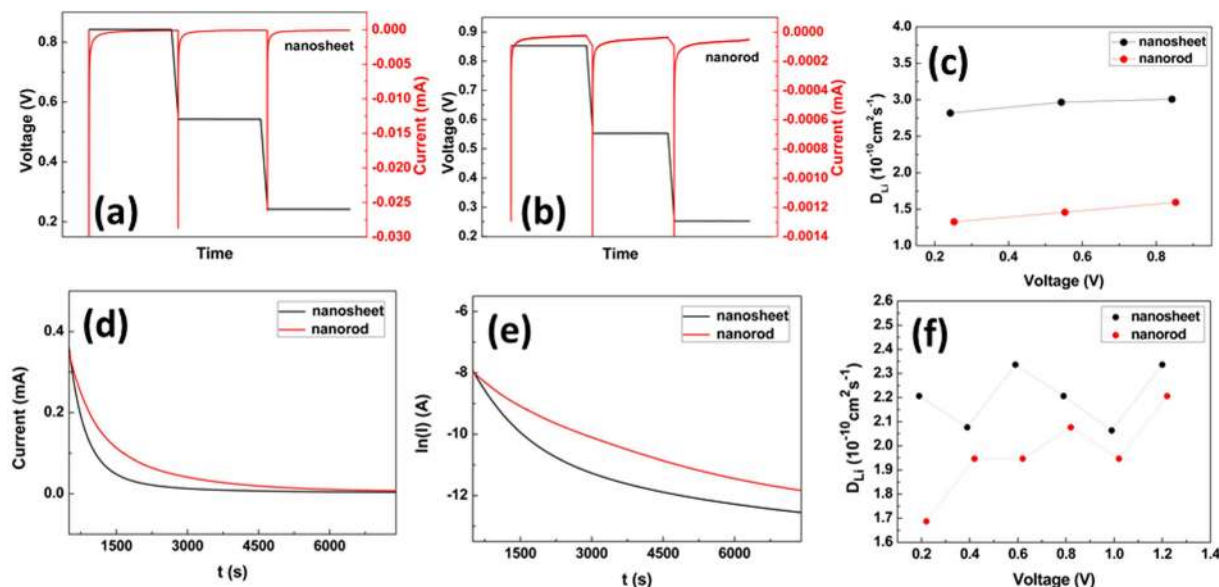
**Figure 7.** The surface atomic configurations in (a) the (001) plane and schematic hematite structure projected along {001}, (b) the (010) plane and schematic hematite structure projected along {010}. The  $\text{Fe}_2\text{O}_3$  Crystallographic Information File (CIF) was taken from the NIST/FIZ FindIt Inorganic Crystal Structure Database.



**Figure 8.** (a) Nyquist plots for  $\text{Fe}_2\text{O}_3$  nanorods and  $\text{Fe}_2\text{O}_3$  nanosheets; (b) The corresponding equivalent circuit.

Sample	$R_s$		$R_{ct}$	
	Value ( $\Omega$ )	Error %	Value ( $\Omega$ )	Error %
$\text{Fe}_2\text{O}_3$ nanorods	1.2388	26.4	178.7	4.346
$\text{Fe}_2\text{O}_3$ nanosheets	1.7051	6.436	53.337	2.482

**Table 1.** The fitted solution resistances ( $R_s$ ) and charge transfer resistances ( $R_{ct}$ ) for the Nyquist plots of  $\text{Fe}_2\text{O}_3$  nanorods and nanosheets.



**Figure 9.** PITT curves of (a)  $\text{Fe}_2\text{O}_3$  nanosheets and (b)  $\text{Fe}_2\text{O}_3$  nanorods and (c) diffusion coefficients of  $\text{Li}^+$  ( $D_{\text{Li}}$ ) before discharge-charge cycle; Current-time transient plots of PITT for a potential step of 1.0–0.8 V after one cycle, (d)  $I$  vs.  $t$  and (e)  $\ln(I)$  vs.  $t$ ; (f)  $D_{\text{Li}}$  of  $\text{Fe}_2\text{O}_3$  nanorods and  $\text{Fe}_2\text{O}_3$  nanosheets during discharge process.

## Methods

**Materials synthesis.** The  $\text{Fe}_2\text{O}_3$  nanorods were synthesized by  $\text{FeOOH}$  nanorods template. To prepare  $\text{FeOOH}$  nanorods precursors, 1.9 mmol of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was put into 15 ml of deionized water to form a homogeneous solution, then added 15 ml of 0.8 M  $\text{NaOH}$  solution under stirring, quickly. After stirring for 10 min, the total solution was transferred into a 50 ml Teflon-lined stainless steel autoclave, sealed and heated at  $180^\circ\text{C}$  for 4 h. The result product was collected by centrifugation, washed with deionized water and ethanol, then was dried at  $80^\circ\text{C}$  and calcined at  $250^\circ\text{C}$  for 2 h. The  $\text{Fe}_2\text{O}_3$  nanosheets were synthesized based on the previous work<sup>28</sup>. 5.1 mmol of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was dissolved in 35 ml of anhydrous ethanol, and 38.4 mmol of  $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$  was rapidly added into the solution with stirring. After about 5 min of stirring, all of the reactants were transferred into a 50 ml Teflon-lined stainless steel autoclave, sealed and heated at  $200^\circ\text{C}$  for 22 h. The result product was collected by centrifuge, washed with deionized water and ethanol. Then dried at  $80^\circ\text{C}$  and calcined at  $250^\circ\text{C}$  for 2 h.

**Characterization.** XRD measurements were performed on a Persee XD2 X-ray diffractometer with  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5418$ ). The size and morphology of all of the samples were measured with a S-4800 HITACHI scanning electron microscope (SEM) and a JEM-2100 transmission electron microscope (TEM). The specific surface areas of the powders were collected by a Gemini V Brunauer-Emmett-Teller (BET).

**Electrochemical Measurement.** For electrochemical studies, working electrode was fabricated with mixing active material, acetylene black and polyvinylidene fluoride (PVDF) with weight ratio 2:1:1 using  $N$ -methylpyrrolidone (NMP) as solvent. The slurry was fully ground and pasted onto copper foil, and then the loaded copper foil was dried in a vacuum oven at  $120^\circ\text{C}$  for 12 h. Lithium metal, celgard 2300 membrane and 1 M  $\text{LiPF}_6$  solution in DMC/EC (1: 1 in volume) were used as counter electrode, separator and electrolyte respectively to assemble coin cells in an  $\text{Ar}$ -filled glove box. The galvanostatic charge/discharge performance of the cells were tested on a battery testing system (BTS-5 V 5 mA, Neware) with the voltage between 0.1 and 3.0 V at the current density of 200, 400, 800, 1200, 1600, 2000, 2400 mA/g. The electrochemical spectroscopy (EIS) was tested with an (PGSTAT302N, Metrohm-Autolab) instrument using an amplitude of 5 mV and a frequency range from 100 KHz to 0.1 Hz. The PITT tests were also performed on the same instrument with EIS.

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## Author Contributions

X.X. designed the experiments. M.C. and E.Z. performed the experiments, D.C. supervised the experiments, X.X., M.C. and E.Z. collected and analyzed the data, and wrote the paper. Z.H. gave suggestion to revise the manuscript. All authors analyzed data, discussed the results, and reviewed the manuscript.

## Additional Information

**Competing financial interests:** The authors declare no competing financial interests.

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