Synthesis of mesoporous r-Fe2O3 nanostructures for highly sensitive gas sensors and high capacity anode materials in lithium ion batteries

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Synthesis of Mesoporous $\alpha$-Fe$_2$O$_3$ Nanostructures for Highly Sensitive Gas Sensors and High Capacity Anode Materials in Lithium Ion Batteries

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Mesoporous $\alpha$-Fe$_2$O$_3$ materials were prepared in large quantity by the soft template synthesis method using the triblock copolymer surfactant F127 as the template. Nitrogen adsorption—desorption isothermal measurements and transmission electron microscope observation revealed that the as-prepared mesoporous $\alpha$-Fe$_2$O$_3$ nanostructures have large mesopores in a wide size range of 5–30 nm. It has been found that the Morin transition depends on thermal history of mesoporous $\alpha$-Fe$_2$O$_3$, which is driven by surface anisotropy. Superparamagnetic behavior of mesoporous $\alpha$-Fe$_2$O$_3$ is also associated with surface spins with blocking temperature around 50 K. When applied as gas sensors, mesoporous $\alpha$-Fe$_2$O$_3$ nanostructures exhibited high gas sensitivity toward acetic acid and ethanol gas. As anodes in lithium ion cells, mesoporous $\alpha$-Fe$_2$O$_3$ materials show a high specific capacity of 1360 mAh/g with excellent cycling stability and high rate capacity.

1. Introduction

As an n-type semiconductor, hematite ($\alpha$-Fe$_2$O$_3$) has attracted a great deal of attention from researchers in different fields because of its nontoxicity, low cost, high stability under ambient conditions, and multiple functions. It has been intensively investigated for applications in lithium batteries, sensors, catalysts, pigments, and magnetic devices. The performance of $\alpha$-Fe$_2$O$_3$ strongly depends on the particle size, morphology, and structure. For use as anode material in the lithium ion battery, the reversibility of lithium intercalation in $\alpha$-Fe$_2$O$_3$ depends strongly on the structure and particle size. Nanosize $\alpha$-Fe$_2$O$_3$ exhibits better performance than microscale samples as the smaller particle size can greatly reduce the diffusion length of the lithium ions. From the investigations on gas-sensing performance, the sensitivities of $\alpha$-Fe$_2$O$_3$ nanospheres are much higher than those of microcrystalline $\alpha$-Fe$_2$O$_3$ powders. The interconnected pores in the nanospheres are of benefit for the diffusion of gas and have been proved to offer more active sites for gas chemisorption. There is growing interests in the preparation of nanomaterials with specially designed structures. Nanostructured $\alpha$-Fe$_2$O$_3$ with one-dimensional nanowire/nano-tube structures, have already been synthesized by a variety of methods, such as the sol—gel method, electrostatic spray deposition, and hydrothermal treatment. Since the discovery of MCM-41 mesoporous silica in 1992, mesoporous materials have been developed into an important class of materials and occupy a very important position in materials science. The mesopore structure can dramatically increase the surface area/volume ratio, which makes the mesoporous materials very useful in the surface-related applications. There is intense interest in preparing mesoporous transition-metal oxides because of their unique catalytic, magnetic, adsorptive, and electrochemical properties in applications as catalysts, magnetic materials, absorbents, and energy conversion and storage materials. Several mesoporous transition-metal oxides have already been synthesized, such as Co$_3$O$_4$, Mn$_3$O$_4$, Fe$_3$O$_4$, TiO$_2$, and V$_2$O$_5$; however, it is still much more difficult to synthesize mesoporous transition-metal oxides than mesoporous silica. The materials with three-dimensional mesoporous architectures are normally obtained through template-directed methods, which can be simply classified into the hard template method and the soft template method. The hard templates (usually mesoporous silica or carbon) normally possess well-confined channels and pores, which strongly influence the structure of the resulting solid product. Soft templates are usually surfactants, long-chain polymers, and viruses, which function as structure-directing agents that assist in the assembly of reacting species. Yang et al. first reported the synthesis of a series of metal oxides by employing nonionic polymer surfactants as templates, which could be easily removed by solvent extraction or thermal treatment. The hard template methods usually involve a multistep synthesis process. Mesoporous silica or carbon must be prepared first. Then, the inorganic precursors are combined with the templates by impregnation or incorporation. The final product can be obtained by template removal after the solid species has formed through reaction, nucleation, and growth. However, for the soft template methods, the templates can form by self-assembly in liquid solution and can be easily removed by solvent or calcination. Therefore, the soft template method is generally easier to be scaled up for large-scale production than the hard template method.
template method. However, it is difficult to control the regularity, pore size, and pore structure using the soft template method. In this paper, we report the synthesis of mesoporous α-Fe₂O₃ nanostructures with large mesopores by using a soft template method in nonaqueous solution. The as-prepared mesoporous α-Fe₂O₃ materials exhibit unique magnetic properties, high gas sensitivity, and high reversible lithium storage capacity in lithium ion cells.

2. Experimental Section

2.1. Preparation of Mesoporous α-Fe₂O₃. In a typical synthesis, the triblock copolymer (H₂O(CH₂CH₂O)₇₀(CH₂(CH₃)O)₁₀(CH₂CH₂O)₇₀H) (F127) and iron nitrate were used as the template and inorganic source, respectively. F127 block copolymer (1 g) was dissolved in a mixture of propanol (5 g) and ethylene glycol (EG; 5 g). To this solution, 0.01 mol Fe(NO₃)₃·9H₂O was added with vigorous stirring over 2 h. The resulting sol solution was then aged in air at 40 °C for 7 days and then was gradually heated to 150 °C (1 °C/min) and was maintained at 150 °C for 24 h. Finally, the samples were further sintered at 400 °C for 5 h to remove the block copolymer surfactant (heating rate: 1 °C/min).

2.2. Structural, Optical, and Magnetic Characterization. The crystal structure and phase of the as-prepared mesoporous α-Fe₂O₃ were characterized by X-ray diffraction (XRD, GBC MMA) using Cu Kα radiation with 2θ ranging from 20° to 70°. Raman spectra were collected on a JOBIN Yvon Horiba Confocal Mico Raman spectrometer model HR 800 with 632.8 nm diode laser excitation on a 300 lines/mm grating at room temperature. The band gap energy of the as-prepared mesoporous α-Fe₂O₃ was calculated via ultraviolet-visible (UV-Vis) spectroscopy on a Shimadzu UV-1700 spectrophotometer. The morphology and microstructures were characterized by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM, JEOL 2011). N₂ adsorption–desorption measurements were conducted using a Quantachrome Autosorb analyzer at 77 K with the samples degassed at 120 °C overnight under vacuum before measurements. The magnetic moment of mesoporous α-Fe₂O₃ was measured with a vibrating sample magnetometer (VSM) option of a Quantum Design Physical Properties Measurement System (PPMS). The temperature dependence of the magnetic moments was measured in three different consecutive regimes: during warming after zero-field-cooling of the sample (ZFCW), during subsequent field cooling (FC), and finally, during warming after field cooling (PCW). For the ZFCW measurements, the sample was cooled in zero field from 305 to 5 K, a magnetic field was applied, and the magnetic moment was measured in constant field as the temperature was swept to 305 K. The FCW measurements were performed by subsequently cooling the sample to 5 K without changing the field. The FCW measurements were performed during a further sweep of the temperature from 5 to 305 K without changing the field after the FC measurement. The sweep rate of the temperature was 2 K/min. Several temperature scans were performed at different magnetic fields. Magnetic hysteresis loops were measured at selected temperatures with a sweep rate of the field of 50 Oe/s.

2.3. Gas-Sensing Measurement. Gas-sensing properties of the as-prepared mesoporous α-Fe₂O₃ were measured by a computer-controlled WS-30A gas-sensing measurement system. The schematics of the device and its operating principles are shown in Figure S-1 of the Supporting Information (SI).

2.4. Electrochemical Characterizations. To prepare the working electrode, the as-prepared mesoporous α-Fe₂O₃ powder (50 wt %), acetylene black (40 wt %), and poly(vinylidene fluoride) (PVDF, 10 wt %) were mixed in N-methyl-2-pyrrolidone (NMP) to form a slurry. The resultant slurry was pasted onto copper foil with a blade and was dried at 100 °C for 12 h under vacuum conditions followed by pressing at 200 kg cm⁻². Electrochemical measurements were carried out using two-electrode coin cells with lithium metal as the counter and reference electrode. The CR2032-type cells were assembled in an argon-filled glovebox. The electrolyte solution was 1 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of 1:1. Cyclic voltammetry (CV) was carried out on a CHI 660C electrochemistry workstation with a scan rate of 0.1 mV s⁻¹ from 0.005 to 3.0 V in a two-electrode system. The charge–discharge measurements were carried out at ambient temperature at different current densities in the voltage range from 0.005 to 3.0 V.

3. Results and Discussion

3.1. Structure and Morphological Analysis. Figure 1a shows the powder X-ray diffraction (XRD) pattern of the as-prepared mesoporous α-Fe₂O₃ and the commercial α-Fe₂O₃ powder (Sigma-Aldrich). All diffraction peaks can be indexed to the standard hematite (α-Fe₂O₃) crystal structure (JCPDS card number 33-0664) indicating that a pure and highly crystalline product has been obtained by calcining iron oxide precursor. The average crystal size of mesoporous α-Fe₂O₃ was calculated to be about 20.6 nm on the basis of the broadening of the (104) diffraction peak using the Scherrer formula. Raman spectroscopy is a powerful tool to identify the crystal phase of Fe₂O₃. Figure


1b shows the Raman spectrum of the as-prepared mesoporous α-Fe₂O₃ along with a hematite reference spectrum (RRUFF ID R050300). The spectrum indicates a typical α-Fe₂O₃ crystal structure showing Raman peaks at 224, 292, 410, 496, and 613 cm⁻¹, which matches well with the hematite reference spectrum. Compared to the previous report on α-Fe₂O₃ microcrystalline powders, all Raman peaks of our mesoporous α-Fe₂O₃ are slightly blue-shifted. This may be due to the small size of the component nanocrystals. The Raman peak around 660 cm⁻¹ in the spectrum has been reported in several published papers and is attributed to a large amount of defects and local lattice disorder at the interfaces and interior faces, which leads to the reduction of space symmetry and the appearance of the new peak. Both the XRD and Raman spectroscopy measurements confirmed the pure phase nature of mesoporous α-Fe₂O₃. The optical absorption property of the as-prepared mesoporous α-Fe₂O₃ was investigated at room temperature by UV–vis spectroscopy (Figure 2). The band gap of hematite can be calculated by the following equation:

\[(\alpha h \nu)^2 = B \times (h \nu - E_g)\]  

where \(\alpha\) is the absorption coefficient, \(h\) is the photon energy, \(B\) is a constant, and \(E_g\) is the band gap. The \((\alpha h \nu)^2\) versus \(h \nu\) curve is shown as the inset in Figure 2. The band gap of the as-prepared mesoporous α-Fe₂O₃ calculated from eq 1 is 2.14 eV, which agrees well with previously reported values of 1.9–2.2 eV for n-type semiconductor α-Fe₂O₃. The absorption spectrum of the as-prepared mesoporous α-Fe₂O₃ calculated from eq 1 is 1.8 eV.

Figure 3 shows the TEM and HRTEM images of the as-prepared mesoporous α-Fe₂O₃ powders. The prepared material exhibits an ordered porous structure with different shapes of pores as shown in Figure 3a. Pores in the iron oxide materials originate from the regions previously occupied by the polymer surfactants. After the removal of the surfactant, some walls of the porous structure collapse and form a wormhole-like morphology. The selected area electron diffraction (SAED) pattern of the HRTEM image in Figure 3b clearly presents the lattice fringes of the (110) and (102) planes of α-Fe₂O₃ corresponding to d-spacings of 0.250 and 0.388 nm. Both the HRTEM images and the SAED pattern confirm the formation of single-crystalline mesoporous α-Fe₂O₃. In addition, regular mesopore structures were extensively observed by TEM analysis, but we also found a large amount of mesoporous spheres (as shown in Figures S2 and S3 of the SI).

To examine the specific surface area and the pore size distribution, N₂ adsorption–desorption isotherm measurements were carried out. The curve shown in Figure 4a depicts a typical H₂-type hysteresis loop, which makes it clear that the distribution of the pore sizes and shapes is heterogeneous. This further confirmed the TEM results shown in Figure 3. The pore size distribution, obtained from the Barrett–Joyner–Halenda (BJH) method, is shown in Figure 4b. The plot shows that the dominant peaks are in the mesoporous range with a wide main peak around 7 nm and a small narrow peak at 15 nm. The two main peaks in pore size distribution suggest that the mesopores are distributed over a wide range of sizes. The surface area estimated from the Brunauer–Emmett–Teller (BET) method is 128 m² g⁻¹. The high surface area of the mesoporous structures will be of benefit for improvement of the sensitivity in gas sensors and for increased reversible lithium storage capacity as anode material in lithium ion batteries.

3.2. Magnetic Properties of Mesoporous α-Fe₂O₃. Figure 5 shows temperature dependence of magnetic moment in the applied field of 1 T. For ZFCW regime, the moment increases strongly with temperature up to 50 K. This is followed by a weak decrease of the moment with temperature for temperatures up to 180 K. There is an abrupt increase of magnetic moment with temperature between 180 and 228 K. This steep increase corresponds to Morin transition, a characteristic feature of α-Fe₂O₃. Magnetic moment decreases with temperature above 228 K. Similar features are also obtained for FCC and FCW
measurements, however, there is no increase of the moment with temperature for $T < 50$ K. Instead, the magnetic moment slightly decreases with temperature up to 50 K followed by a further decrease with a different rate. There is no overlap of ZFCW, FCC, or FCW branches in any measured temperature range. The Morin transition occurs at lower temperature for the FCW and FCC measurements than for the ZFCW ones. The width of the Morin transition of $\sim 40$ K indicates a wide distribution of the crystal properties in the mesoporous samples.

The Morin transition occurs at Morin temperature $T_M$, because of competition between different anisotropy terms in $\alpha$-Fe$_2$O$_3$ as described by Artman et al. Antiferromagnetically ordered spins in macroscopic $\alpha$-Fe$_2$O$_3$ crystals are oriented along trigonal $[111]$ axis below $T_M$. The sample has no net magnetic moment at these temperatures. The spins are flipped into the basal (111) plane above $T_M$ and are also antiferromagnetically ordered. However, they are slightly canted out of the perfect antiferromagnetic alignment. This canted component of the spins couples ferromagnetically, which gives rise to a small net magnetic moment of $\alpha$-Fe$_2$O$_3$ above $T_M$.

The transition between the ferromagnetic (FM) and antiferromagnetic (AFM) state is the first-order magnetic transition. Although the bulk free energy of the AFM and FM states are the same at $T_M$, there is an energy barrier associated with the transition between the two states. Chow and Keffer showed that surface anisotropies and their interaction with the bulk states have to be considered to explain these transitions. The surface states do not contribute appreciably to the net magnetic moment because they are confined to a thin surface layer. However, they define the way the energy barrier is overcome upon the transition between the two states. In the case of weak surface anisotropy, the transition from AFM to FM state during warming occurs at $T_M$ of the bulk spins. However, FM to AFM transition during cooling occurs at a lower temperature than $T_M$. For strong surface anisotropy, it is the opposite: FM to AFM transition occurs at bulk $T_M$ upon cooling and AFM to FM transition occurs at a $T > T_M$ upon warming.

Our measurements are consistent with the model of Chow and Keffer. The transitions between AFM and FM states upon warming occur at higher temperatures than upon cooling (Figure 5). The difference between ZFCW and FCW could be associated with irreversibilities of surface states. Magnetic anisotropy is defined by coupling of spins to the crystal lattice order. In the absence of a strong crystal order, magnetic anisotropy decreases. Because surface of our nanoparticles is associated with a crystal disorder that results in unpaired spins, it is reasonable to assume that magnetic anisotropy on the surface is weaker than deeper inside the nanoparticles. According to the model of Chow and Keffer, $T_M$ is then obtained from the transition in ZFCW measurements.

The value of $T_M$ for macroscopic $\alpha$-Fe$_2$O$_3$ is 263 K, and it depends on the crystal size when the crystals are smaller than $\sim 100$ nm. Using the data reported by Zysler et al., the value of $T_M$ of 209 K for our samples suggests the average crystal size of about 20–40 nm, which is consistent with the result of XRD analysis. These crystallites agglomerate into lumps of a few hundred nanometers in size as observed by TEM and HRTEM analysis. This is similar to the report on $\alpha$-Fe$_2$O$_3$ particles obtained by reaction of $2 \times 10^{-2}$ M FeCl$_3$ and $3 \times 10^{-4}$ M NaH$_2$PO$_4$.

The transition temperature between AFM and FM states is field-dependent, which was also reported by Qian et al. The transition temperature in our FCC measurements decreases with the field at a rate of 9 K/T from its value of 191 K at 0.01 T. This field dependence of transition temperature points to magnetic irreversibilities associated with ferromagnetic ordering in $\alpha$-Fe$_2$O$_3$ that was not destroyed by warming the sample to 305 K. This is due to existence of the intrinsic ferromagnetic ordering above $T_M$ of Artman-type but is also due to the unpaired spins on the surface of $\alpha$-Fe$_2$O$_3$ crystals. There is also interaction between nanoparticles of agglomerates, which will depend on thermal history due to reorientation of the nanoparticles within the agglomerates.

The other features of the observed temperature dependence of the magnetic moment can be explained in terms of ferromagnetic ordering of unpaired surface spins on the top of the antiferromagnetic moment of the bulk hematite. The magnetic
moment of our sample at 1 T and 200 K is about 0.6 emu/g. Hematite single crystal has magnetic susceptibility at 200 K for parallel and perpendicular direction to the easy axis of about 3 × 10^{-6} and 18 × 10^{-6} emu/(g Oe), respectively. This results in a magnetic susceptibility for powder with randomly oriented crystals of 13 × 10^{-6} emu/(g Oe). Taking into account this antiferromagnetic susceptibility, surface spins contribute 0.47 emu/g to the magnetic moment at 200 K and 1 T (Figure 5). This is substantially more than the additional ~0.15 emu/g contributed by the Morin transition just above 200 K. The Artman-type magnetic moment in macroscopic hematite crystals is 0.4 emu/g, which is substantially higher than the increase by 0.15 emu/g at the Morin transition for our sample. This is probably because our sample consists of some crystallites smaller than the particular size $d_0$ at which $T_M$ vanishes if the particle sizes are smaller than $d_0$. The value of $d_0$ can be estimated from the report by Zysler et al. to be about 10 nm. The Morin temperature $T_M$ decreases with particle size and strains in the particles. Therefore, particles smaller than $d_0$ do not undergo Morin transition at the measured temperatures. Instead, these particles have the Artman-type ferromagnetic component at all measured temperatures as shown by Bodker et al. As a result, the increase of the magnetic moment upon Morin transition, normalized to the total sample mass, is smaller than for the samples where all the particles undergo Morin transition. Therefore, these sub-$d_0$ particles contribute to the superparamagnetic behavior because of their Artman-type magnetic moment. There are also unpaired surface spins. For particles smaller than $d_0$, these surface spins will contribute to superparamagnetic behavior because they are coupled to the canted Artman-type bulk magnetic moment at all temperatures. Coupling of the unpaired surface spins to the antiferromagnetic bulk order is also likely to contribute because this coupling is disturbed by the surface disorder for particles of any sizes. Thus, both surface spins and Artman-type magnetic moment of sub-$d_0$ particles contribute to the magnetic moment of 0.47 emu/g just below 200 K at 1 T. The mesoporous $\alpha$-Fe$_2$O$_3$ seems to be in superparamagnetic state for 50 K < $T$ < 200 K as indicated by magnetic hysteresis loops (Figure 6). The unpaired surface spins and the Artman-type contribution of sub-$d_0$ particles are responsible for this superparamagnetic state. There is a strong increase of magnetic irreversibility for $T$ < 50 K (Figure 5) indicating yet another magnetic transition. A similar effect was also reported by Jiao et al.

Most likely this can be ascribed to the blocking transition at 50 K, where superparamagnetic spins freeze-in upon cooling and give an almost constant magnetic moment. This moment is zero if cooling is in zero field. With warming up in ZFCW measurements, the magnetic moment rises with temperature as an increasing number of spins gets unfrozen by thermal excitation and gets aligned in the direction of the field. Finally, above blocking temperature, superparamagnetic system occurs. Measurements in Figure 5 are consistent with this picture as ZFCW magnetic moment increases from a low value at 5 K up to its maximum value at the blocking temperature of 50 K. Above 50 K, the sample is in superparamagnetic state for $H = 1$ T showing a very small coercive field and S-shaped hysteresis loops typical of superparamagnetic particles (Figures 6 and 7). This transition temperature is field-dependent. It increases from 53 K at 1 T to 96 K at 0.01 T. This is also consistent with the picture of unfreezing spins as the temperature increases in ZFCW measurements. A higher magnetic field exerts larger force on misaligned spins, and a lower energy of thermal excitation is required to align them in the direction of the field. With the lower field, higher thermal excitations are required for the same effect.

The ZFC, FCC, and FC curves do not overlap above 200 K. The reason for this could be the irreversibilities associated with the ordering of surface spins that are still not suppressed at these temperatures as well as Artman-type ferromagnetic order above $T_M$. However, there is also a possibility of magnetic nanoparticles rotating upon thermal cycling within the agglomerates in a different way for FCC, FCW, and ZFCW measurements. This changes the interaction between the nanoparticles and results in additional irreversibilities that depend on the way the measurements are performed. A good indication for this effect is that the magnetic moment for $T > 200$ K in Figure 5 measured upon warming decreases with temperature with the same rate for ZFCW and FCW measurements. However, magnetic moment measured upon cooling (FCC) in the same temperature range and the same field decreases with temperature at a higher rate.

The coercive field of our nanoparticles at room temperature is much larger than for bulk crystals (Figure 7). The coercive field can be strongly affected by distribution of sizes of nanoparticles as well as by their interaction within the agglomerates. $H_c$ of similar magnitude to our samples was obtained for hematite nanoparticles that were densely packed into agglomerates. Loosely packed nanoparticles gave ~10 times lower $H_c$. This supports our argument on the importance of nanoparticle interaction to their magnetic properties.

Magnetic hysteresis loops are in agreement with the above description (Figure 5). The hysteresis loop measured at 5 K strongly differs from the ones measured above 50 K. It has much larger coercive field, $H_c$, than the hysteresis loops measured between 50 and 200 K (Figures 6 and 7). The hysteresis loops between 50 and 200 K are distinctly S-shaped with vanishingly low coercive field as expected for superparamagnetic particles. $H_c$ starts increasing with the onset of Artman-type ferromag-
netism for nanoparticles larger than $d_0$ at $\sim$200 K (Figure 7). Superparamagnetic behavior seems to be suppressed for $T > 200$ K because of an additional magnetic moment arising from Artman-type of ordering. The interaction between the nanoparticles within the mesoporous structures probably plays an important role in these processes even though its magnitude and the exact mechanisms are still unknown. The increase of $H_c$ and the appearance of ferromagnetic order at temperatures higher than the blocking temperature may sound confusing. However, there are two families of spins contributing to the measured magnetic moment: unpaired surface spins and bulk spins due to Artman-type transition. When both of them are ordered ferromagnetically, the net magnetic moment may be large enough to give the observed ferromagnetic behavior. Nanoparticle agglomeration probably also plays a role here through magnetic coupling of nanoparticles.

Therefore, surface spins and Artman-type magnetic moment of sub-$d_0$ nanoparticles dominate the magnetic behavior of mesoporous $\alpha$-Fe$_2$O$_3$ below 200 K. There is evidence for superparamagnetic behavior of this system with blocking temperature around 50 K at 1 T. Morin transition of particles larger than $d_0$ occurs at 200 K giving additional ferromagnetic contribution above 200 K. The magnetic moment of the surface spins and sub-$d_0$ particles with Artman-type ordering is about 3 times higher than the one due to Morin transition of particles larger than $d_0$ at 200 K and 1 T. There seems to be an effect of orientation of the nanoparticles within the mesoporous structures on the net magnetic moment. As this orientation changes with field and temperature, so does the magnetic interaction between the nanoparticles giving a magnetic moment that depends on history of thermal cycling in magnetic field.

3.3. Gas-Sensing Performance. The gas-sensing performance of the as-prepared mesoporous $\alpha$-Fe$_2$O$_3$ was investigated toward a variety of flammable, toxic, and corrosive gases such as ethanol, acetone, gasoline, heptane, formaldehyde, acetic acid, 1-butanol, and 2-propanol. Figure 8a displays the real-time sensing response characteristics toward ethanol of a sensor based on the as-prepared mesoporous $\alpha$-Fe$_2$O$_3$ at a working temperature of 150 °C and 30% relative humidity (RH). It can be seen that the value of the output voltage increased abruptly after the injection of ethanol and recovered its initial value after release of the gas. The response and recovery times (defined as the time required to reach 90% of the final equilibrium value) of the as-prepared mesoporous $\alpha$-Fe$_2$O$_3$ based sensor were only 1−3 s each indicating their rapid response and good reversibility. From Ohm’s law, the electric resistance of the sensor underwent a decrease (increase) when the ethanol was injected (released), which is the typical sensor behavior of n-type semiconductor sensors. In the ambient environment, n-type $\alpha$-Fe$_2$O$_3$ is expected to adsorb both oxygen and moisture. The adsorbed $O^2-$ and $OH^-$ groups trap electrons from the conduction band of the $\alpha$-Fe$_2$O$_3$ nanocrystals and increase the resistance of the sensor. When the sensor is exposed to ethanol, the test gas molecules are chemiadsorbed at the active sites on the surface of the as-prepared mesoporous $\alpha$-Fe$_2$O$_3$. These molecules will be oxidized by the adsorbed oxygen and the lattice oxygen (O$^2-$) of $\alpha$-Fe$_2$O$_3$, at the sensor working temperature (150 °C). In this process, electrons will be transferred to the surface of the as-prepared mesoporous $\alpha$-Fe$_2$O$_3$ to lower the number of trapped electrons inducing a decrease in the resistance. The magnitude of the response for a sensor based on the as-prepared mesoporous $\alpha$-Fe$_2$O$_3$ improved dramatically with increasing the concentration of the ethanol from 5 ppm to 1000 ppm suggesting that the as-prepared mesoporous $\alpha$-Fe$_2$O$_3$ has good sensitivity toward ethanol. After eight cycles between the ethanol and fresh air, the output voltages could still recover to their initial states indicating excellent reversibility. Figure 8b presents the sensitivity of a sensor based on the as-prepared mesoporous $\alpha$-Fe$_2$O$_3$ toward a variety of gases at different concentrations. The gas sensitivity (S) is defined as the ratio of the stationary electrical resistance of the sensor in air ($R_{\text{air}}$) to its resistance in the test gas ($R_{\text{gas}}$), that is, $S = R_{\text{air}}/R_{\text{gas}}$. The as-prepared mesoporous $\alpha$-Fe$_2$O$_3$ exhibited a very impressive sensitivity toward ethanol at high concentration (1000 ppm), which is better than the performance of its nanosphere and nanowire counterparts as we previously reported. The improvement of the sensing performance of the as-prepared mesoporous $\alpha$-Fe$_2$O$_3$ may be attributed to the mesoporous structure. The highly porous structure leads to high specific surface area, which is measured to be 128 m$^2$/g resulting in more active sites for gas chemisorption. The abundant open pores distributed in the three-dimensional space can facilitate the diffusion of the test gas and can improve the kinetics of both the reaction of the test gas with surface adsorbed oxygen and the replacement of the latter from the gas phase. From Figure 8b, we can also note that the as-prepared mesoporous $\alpha$-Fe$_2$O$_3$ sensor also has high sensitivity toward some other flammable and explosive gases such as 92° gasoline, 2-propanol, 1-butanol, heptane, and acetone. However, the sensor could barely detect heptane even at high concentration (e.g., 1000 ppm). For application in air quality monitoring, we also investigated the sensing performance of the as-prepared mesoporous $\alpha$-Fe$_2$O$_3$ to some toxic, corrosive,
and irritating gases, such as formaldehyde and acetic acid. It is interesting that the as-prepared mesoporous α-Fe2O3 displayed the highest responsiveness to acetic acid (Figure 8b) with S reaching as high as S = 185 in the presence of 1000 ppm of acetic acid vapor. This ultrahigh sensitivity may be caused by the strong chemisorption of acetic acid on the surface of the as-prepared mesoporous α-Fe2O3 owing to the strong coordination of carboxyl to Fe3+. For comparison, Figure 9 presents a bar graph of the sensitivity of the mesoporous α-Fe2O3 sensor toward eight types of gases or vapors at a concentration of 1000 ppm. We can clearly identify that the as-prepared mesoporous α-Fe2O3 showed the highest sensitivity and selectivity toward acetic acid as opposed to any other gas. On the other hand, the as-prepared mesoporous α-Fe2O3 can selectively detect alcohol in the presence of other flammable and explosive gases, such as acetone, 92° gasoline, and heptane. However, the sensor could barely detect heptane indicating that the as-prepared mesoporous α-Fe2O3 based sensor has a degree of selectivity to different gases.

3.4. Electrochemical Performance in Lithium Ion Battery.

The electrochemical behavior of the electrode made from the as-prepared mesoporous α-Fe2O3 was evaluated by cyclic voltammetry (CV) and galvanostatic charge/discharge cycling. Figure 10 shows the CV curves of the mesoporous α-Fe2O3 anode. During the cathodic polarization in the first cycle, a spiky peak was observed at 0.65 V with two small peaks appearing at 1.0 and 1.6 V indicating the following three lithiation steps:

\[
\begin{align*}
\alpha-Fe_2O_3 + xLi^+ + xe^- & \rightarrow \alpha-Li_xFe_2O_3 & \quad (2) \\
\alpha-Li_xFe_2O_3 + (2-x)Li^+ + (2-x)e^- & \rightarrow Li_2FeO_3(cubic) & \quad (3) \\
\alpha-Fe_2O_3 + 6Li^+ + 6e^- & \rightarrow 2Fe^0 + 3Li_2O & \quad (4)
\end{align*}
\]

At the initial stage of lithium intercalation (peak I), a small amount of lithium can be inserted into the crystal structure of the as-prepared mesoporous α-Fe2O3 without change in the structure. In the next step of lithium intercalation (peak II), the hexagonal α-Li_xFe_2O_3 is transformed to cubic Li_2FeO_3. The spiky peak (peak III) corresponds to the complete reduction of iron from Fe^{3+} to Fe^{0} and the decomposition of electrolyte. On the other hand, in the anodic polarization process, two broad overlapping peaks were recorded at about 1.7 and 1.85 V corresponding to the oxidation of Fe^{0} to Fe^{2+} and further oxidation to Fe^{3+}. The curves of the subsequent cycles are significantly different from that of the first cycle as only one cathodic peak appears at about 0.8 V with decreased peak intensity, while the anodic polarization only showed one broad peak with a little decrease in peak intensity. The difference between the first and the second cathodic curves is due to an irreversible phase transformation during the process of lithium insertion and extraction in the initial cycle. After the first discharge process, α-Fe2O3 was completely reduced to iron nanoparticles and was dispersed in a Li2O matrix. The disappearance of the peaks at 1.6 V and 1.0 V from the second cathodic process indicates that the lithium insertion reaction and phase transformation from hexagonal α-Li_xFe_2O_3 to cubic Li_2FeO_3 are irreversible. The decrease of the redox peak intensity implies that the capacity is decreased during cycling. After the second cycle, the CV curves are very stable for the mesoporous α-Fe2O3 electrode indicating enhanced stability during the lithiation and delithiation processes.

The charge–discharge curves of the mesoporous α-Fe2O3 electrode during the first and second cycles are shown in Figure 11a, and these are typical charge–discharge curves for transition metal anode materials. For the discharge curve in the first cycle, the voltage initially decreased quickly to approximately 1.6 V followed by a weak slope corresponding to the initial lithium insertion into the α-Fe2O3 without any change in the structure. There is also a wide slope located at 1.2–0.85 V, where there is a phase transformation from the hexagonal α-Li_xFe_2O_3 to the cubic Li_2FeO_3. An obvious plateau was observed at 0.85 V indicating the complete reduction of iron from Fe^{3+} to Fe^{0}. This electrochemical behavior is consistent with the results of the CV measurement. The capacity obtained above 0.8 V is 940 mAh g⁻¹ (5.6 mol of Li per mole of α-Fe2O3), which is very close to the theoretical capacity of 1007 mAh g⁻¹ (6 mol of Li per mole of α-Fe2O3). After discharging the voltage to 0.01 V, the total specific capacity of the as-prepared mesoporous α-Fe2O3 is 1730 mAh g⁻¹ corresponding to 10.3 mol of Li per mole of α-Fe2O3, which is much higher than the theoretical capacity. The large excess capacity could...
be ascribed to the decomposition of the electrolyte at low voltage (generally below 0.8 V vs Li+/Li) to form a solid electrolyte interphase (SEI) layer and further lithium storage via interfacial charging at metal/Li2O interface.\textsuperscript{38-39} It has been demonstrated in previous reports that the morphology plays a significant role in the discharge performance.\textsuperscript{2,12}\ The materials that have small particles with high surface area always yield high discharge capacities indicating that high surface area can enhance the interfacial charge storage. During the second cycle, the discharge curve only shows a slope at 1.0–0.8 V, and the capacity is reduced to 1360 mAh g\textsuperscript{−1}. Usually, the slope behavior during the discharge process of metal oxide anode materials is considered to relate to the irreversible formation of a nanocomposite of crystalline grains of metals and amorphous Li2O matrix.\textsuperscript{48,53} For the charge curves of the first and second cycles, no obvious plateau can be observed and the charge capacities are 1200 mAh g\textsuperscript{−1} and 1250 mAh g\textsuperscript{−1}, respectively, corresponding to the oxidation of Fe\textsuperscript{0} to Fe\textsuperscript{3+}, with part of the Fe further oxidized to Fe\textsuperscript{3+}, along with some contribution from the reversible surface layer formed during the discharge process. The cycling performance of mesoporous α-Fe2O3 electrode is shown in Figure 11b, which demonstrates an excellent cycling performance. After 50 cycles at a current rate of 200 mA g\textsuperscript{−1} (0.2C), the specific discharge capacity is 1293 mAh g\textsuperscript{−1}, which is about 95\% of the second cycle discharge capacity and represents a 0.1\% capacity drop per cycle apart from the first cycle. The excellent capacity retention should be related to the mesoporous structure of the materials, which can accommodate the volume change of the Li\textsuperscript{+} insertion/extraction during the charge/discharge processes and which can prevent the active materials from falling off the current collector.\textsuperscript{49,54}

We also investigated the electrochemical performance of mesoporous α-Fe2O3 electrodes at different current densities (as shown in Figure 12). Even at the 2C (2000 mA g\textsuperscript{−1}) rate, we achieved a specific lithium storage capacity of 870 mAh g\textsuperscript{−1}, which is much higher than the theoretical capacity of graphite (372 mAh g\textsuperscript{−1}). The mesoporous structure with high surface area provides high surface contact with the electrolyte and decreases the current density per unit area. To our knowledge, this is the best performance compared with the previously reported electrochemical performance for α-Fe2O3 material.\textsuperscript{2,11,12,14,17,50} The excellent cycling stability and high rate specific capacity of the as-prepared mesoporous α-Fe2O3 indicate its attractive potential for use as an anode material in lithium ion batteries.

4. Conclusions

Herein, we used a soft template synthesis method to successfully prepare mesoporous α-Fe2O3. The as-prepared material shows a highly porous structure with a large surface area of 128 m\textsuperscript{2} g\textsuperscript{−1}. Magnetic property measurement shows that surface spins dominate the magnetic behavior of mesoporous α-Fe2O3 material. The contribution of the surface spins to magnetic moment at 200 K is about 3 times higher than the one due to Morin transition at H = 1 T. Mesoporous α-Fe2O3 materials exhibit superparamagnetic behavior because of small particle size with blocking temperature at 1 T field of 50 K. The Morin transition at ~200 K is also associated with the surface spins. In the gas-sensing experiments, the as-prepared mesoporous α-Fe2O3 exhibits high sensitivities toward acetic acid and flammable gases. For use as anode materials in lithium ion batteries, the as-prepared mesoporous α-Fe2O3 shows a high discharge specific capacity of 1730 mAh g\textsuperscript{−1} for the first cycle and 1293 mAh g\textsuperscript{−1} after 50 cycles. The good cycling stability and high rate specific capacity indicate its potential for application in the lithium ion battery industry.

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Supporting Information Available: Schematic diagram of the gas sensor system and TEM images of mesoporous $\alpha$-Fe$_2$O$_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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