Fe$_2$O$_3$ Nanoparticles Wrapped in Multi-walled Carbon Nanotubes With Enhanced Lithium Storage Capability

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We have designed a novel hybrid nanostructure by coating Fe$_2$O$_3$ nanoparticles with multi-walled carbon nanotubes to enhance the lithium storage capability of Fe$_2$O$_3$. The strategy to prepare Fe$_2$O$_3$@MWCNTs involves the synthesis of Fe nanoparticles wrapped in MWCNTs, followed by the oxidation of Fe nanoparticles under carbon dioxide. When used as the anode in a Li-ion battery, this hybrid material (70.32 wt% carbon nanotubes, 29.68 wt% Fe$_2$O$_3$) showed a reversible discharge capacity of 515 mAh g$^{-1}$ after 50 cycles at a density of 100 mAg$^{-1}$ and the capacity based on Fe$_2$O$_3$ nanoparticles was calculated as 1147 mAh g$^{-1}$. Three factors are responsible for the superior performance: (1) The hollow interiors of MWCNTs provide enough spaces for the accommodation of large volume expansion of inner Fe$_2$O$_3$ nanoparticles, which can improving the stability of electrode; (2) The MWCNTs increase the overall conductivity of the anode; (3) A stable solid electrolyte interface film formed on the surface of MWCNTs may reduce capacity fading.

With a fast-developing technology in electric energy storage, Li-ion batteries (LIBs) have become the predominant power source for portable electronics due to their high energy density, long lifespan and environment benignity$^{1,2}$. Up to now, although great progress have been achieved by using graphite as anode material for commercial LIBs, the lower theoretical capacity (372 mAhg$^{-1}$) of graphite limits its further practical application$^{3-9}$. Transition metal oxides, as anode materials for LIBs, have gained significant momentum due to their higher theoretical capacities than graphite by the formation of metal simple substance through a chemical conversion mechanism$^{10}$. Among these transition metal oxides materials, Fe$_2$O$_3$ is believed to be a promising candidate to replace graphite because of its high theoretical capacity (1007 mAhg$^{-1}$), low cost, ease of fabrication and environmental benignity$^{10-14}$. In principle, the lithium storage capacity of Fe$_2$O$_3$ is attributed to the reversible conversion reaction between Li$^+$ ions and Fe$_2$O$_3$, leading to the formation of Fe NPs in a Li$_2$O matrix. Generally, the conversion reaction will result in fast capacity fading of Fe$_2$O$_3$ due to the drastic volume variation and severe destruction of the electrode upon electrochemical cycling. In addition, the low conductivity of Fe$_2$O$_3$ also induces additional performance degradation, especially at high current densities$^{15}$. Furthermore, during the cycle process, the solid electrolyte interface (SEI) films formed at the interface between Fe$_2$O$_3$ and liquid electrolyte can be broken owing to the shrink of Fe$_2$O$_3$ anode materials. When the fresh Fe$_2$O$_3$ is exposes to the electrolyte again, the thicker of SEI film will increase with each charge/discharge cycle, which obviously leads to a degradation in battery performance$^{16}$. In order to solve puzzle of Fe$_2$O$_3$ anode materials, all kinds of approach including the synthesis of hollow-structured Fe$_2$O$_3$ have been attempted$^{17-19}$. Although the hollow structure can provide high surface area, short lithium diffusion length to enhance the rate capacity and extra free space to alleviate the volume variation, it is still a challenge to deal with low conductivity and unstable SEI films of Fe$_2$O$_3$ anode materials$^{20}$.

Fabrication of hybrid nanomaterials with carbon coating has been considered as one of the most effective ways towards high-performance electrode materials for LIBs, especially for the electrode materials with volume variation during the charge-discharge process$^{21}$. Under the stimulus of their special properties, various carbon-mixed Fe$_2$O$_3$ anode materials have been reported$^{22-24}$. Due to their porous structure and excellent electrical conductivity, carbon nanotubes (CNTs) are widely used in the filed of preparation of hybrid electrode materials. For example, Zhou et al. have prepared a nanosized Fe$_2$O$_3$ decorated single-walled carbon nanotube (SWCNT)
membrane as a high-performance flexible anode for LIBs, showing a discharge capacity of 801 mAh g\(^{-1}\) after 90 cycles. The highly conducting SWCNT network in membrane not only facilitates electron conduction of Fe\(_2\)O\(_3\), but also buffers the strain of Fe\(_2\)O\(_3\)\(^{22}\). Lou's group have synthesized carbon-coated Fe\(_2\)O\(_3\) hollow nanohorns on the CNTs backbone for superior lithium storage capability. The CNTs backbone and the outmost continuous carbon nanocoating may serve as a structural buffering layer to cushion the internal strain. This hybrid nanomaterial demonstrates a discharge capacity of 820 mAh g\(^{-1}\) after 100 cycles, while CNT@Fe\(_2\)O\(_3\) without carbon coating has a discharge capacity of 660 mAh g\(^{-1}\). In addition to the well conductivity, CNTs have other advantages in the application of electrode for LIBs. The hollow interior of CNTs is an ideal carrier for metal oxide NPs, which could provide enough inner space for the large volume expansion of metal oxide NPs in charge/discharge cycling of batteries. Furthermore, a stable SEI film could be formed during lithiation and delithiation because the electrolyte will contact with the outer surface of CNTs. Therefore, the purpose of this work is to design a novel hybrid material with discontinuous Fe\(_2\)O\(_3\) NPs wrapped in MWCNTs and investigated its potential application as an anode material in lithium ion batteries.

**Results**

Fig. 1 schematically illustrates the procedure to generate Fe\(_2\)O\(_3\)@MWCNTs. First, Fe@MWCNTs are synthesized by placing dried ferrocene in a vacuum tube, which has been reported by our group\(^{24,25}\). Firstly, Fe NPs are generated in the decomposition process of ferrocene, then the chemical bonds of C–H are ruptured and the fragment of ferrocene, then the chemical bonds of C–H are ruptured and the fragment of ferrocene, then the chemical bonds of C–H are ruptured and the fragment of ferrocene, then the chemical bonds of C–H are ruptured and the fragment of ferrocene, then the chemical bonds of C–H are ruptured and the fragment of ferrocene. Afterwards, Fe NPs are formed and for protection of MWCNTs, this volume change of Fe\(_2\)O\(_3\) NPs only occurs in the hollow interior of MWCNTs, which can provide the enough inner space for accommodation of the large volume variation. The larger inner space for enhanced lithium storage capability have been confirmed by previous papers including tin-NPs encapsulated in elastic hollow carbon spheres\(^{26}\), Si NPs encapsulated in continuous hollow carbon tubes\(^{28}\) and hollow carbon nanofiber-encapsulated sulfur\(^{29}\). However, compared with above the amorphous carbon coating, MWCNTs will have a relatively stronger conductivity, which obviously enhance conductivity of Fe\(_2\)O\(_3\) as anode materials.

The crystallographic structure of the hybrid material was analyzed by X-ray diffraction (XRD), shown in Fig. 2(a). In black line (Fe@MWCNTs), a relatively strong peak centred at 44.8\(^{\circ}\) and a weak peak centred at 65.2\(^{\circ}\) are observed, which can be indexed as crystalline Fe (110) and (200) diffractions (JCPDF 89-4186), respectively. A weak broadening diffraction peak at 26.3\(^{\circ}\) is well indexed as the (002) reflection of graphite (JCPDF 75-2078). After high temperature oxidation of Fe@MWCNTs using carbon dioxide as oxidant, the sharp diffraction peak at 18.4\(^{\circ}\), 30.3\(^{\circ}\), 35.7\(^{\circ}\), 37.3\(^{\circ}\), 43.3\(^{\circ}\), 53.8\(^{\circ}\), 57.3\(^{\circ}\), 62.9\(^{\circ}\) can be obviously found, which correspond well to the (111), (220), (311), (222), (400), (422), (511) and (440) crystal planes of iron oxide (JCPDS file 19-0629, Fe\(_3\)O\(_4\), or JCPDS file 39-1346, Fe\(_2\)O\(_3\)), respectively. However, it is hard to identify the iron oxides Fe\(_2\)O\(_3\) or gamma-Fe\(_2\)O\(_3\) due to their same spinel structure and similar lattice parameter a (0.8346 nm for gamma-Fe\(_2\)O\(_3\) and 0.8396 nm for Fe\(_2\)O\(_3\))\(^{11}\). Simultaneously, the diffraction peaks of Fe disappear and the peak of graphite still remain, which means the completely conversion from Fe@MWCNTs to iron oxide@MWCNTs.

Because of the similar XRD pattern of gamma-Fe\(_2\)O\(_3\) and Fe\(_2\)O\(_3\), the Raman spectrum was used to further confirm the composition of the hybrid material. Fig. 2(b) shows the Raman spectrum of Fe\(_2\)O\(_3\)@MWCNTs at the range of 100–1900 cm\(^{-1}\). According to the previous report, the peaks located at 216 cm\(^{-1}\), 280 cm\(^{-1}\) and 390 cm\(^{-1}\) should result from one A\(_{1g}\) mode and two E\(_g\) modes of Fe\(_2\)O\(_3\), respectively\(^{32}\). Meanwhile, compared with standard Fe\(_2\)O\(_3\) Raman spectrum, a small blue-shift may attribute to the interaction between Fe\(_2\)O\(_3\) and MWCNTs\(^{33}\). Moreover, the peak at around 1576 cm\(^{-1}\) involves the in-plane bond stretching motion of pairs of carbon sp\(^2\) atoms, which also exists in the G mode with E\(_{2g}\) symmetry. The D mode of graphite around 1346 cm\(^{-1}\) is related to the degree of disorder in carbon sp\(^2\) bonded clusters in graphite\(^{23}\). Therefore, the two peaks indicate the existence of carbon in the products. In addition, the two peaks can be used to evaluate the extent of carbon-containing defects. From the Raman spectrum, it can be seen that the MWCNTs contain graphitic structures and defects, which may be helpful to enhance the diffusion rate of Li\(^+\) ions and electronics.

The morphology and microstructure of Fe@MWCNTs were examined by SEM and TEM, shown in Fig. S1 and Fig. S2. As shown in Fig. S1, the as-obtained Fe@MWCNTs display standard 1D nanotubes. From the SEM image shown in Fig. 2(c), it can be clearly seen from the TEM image shown in Fig. 2(d) the two peaks can be used to evaluate the extent of carbon-containing defects. From the Raman spectrum, it can be seen that the MWCNTs contain graphitic structures and defects, which may be helpful to enhance the diffusion rate of Li\(^+\) ions and electronics.
illustrates that the Fe₂O₃ NPs are still wrapped in MWCNTs without injuring the wall of MWCNTs. The energy-dispersive X-ray spectrum (Fig. S3) of a single MWCNT indicates the existence of Fe, C and O without other impurity elements. A high-resolution TEM (HRTEM) image shown in Fig. 2(e) clearly demonstrates the graphite layer of carbon nanotube and a 10 nm pore diameter of single MWCNT. Another HRTEM image shown in Fig. 2(f) displays the lattice fringes with a space of 0.209 nm, which can be indexed as (400) lattice plane of Fe₂O₃. The result of the electron microscopy characterization is of good agreement with XRD and Raman characterizations, confirming the successful preparation of Fe₂O₃@MWCNTs.

For further investigation of the chemical composition of the as-prepared Fe₂O₃@MWCNTs, the XPS measurements were carried out. Fig. S4 exhibits a wide scan XPS survey spectrum of Fe₂O₃@MWCNTs between 0 and 1100 eV. The characteristic peaks of C, Fe, and O can be indexed clearly. Meanwhile, the spectrum of Fe 2p is shown in Fig. S5, and the peaks at 710.9 eV and 724.5 eV correspond to the Fe 2p₃/2 and Fe 2p₁/2, respectively. The N₂ absorption/desorption isotherms at 77 K are shown in Fig. S6 and a characteristic of a type IV with type H3 hysteresis loop. The specific surface area calculated with the BET model is 42.55 m²g⁻¹. The pore size distribution (Fig. S7) has a relatively wide peak of 10 nm, corresponding well with the previous microscopy findings. The mass fraction of Fe₂O₃ and MWCNTs is 29.68% and 70.32% according to the ICP characterization.

**Discussion**

To investigate the electrochemical performance of Fe₂O₃@MWCNTs, two-electrode 2032 coin cells with Fe₂O₃@MWCNTs anodes were fabricated with Li metal as the counter electrode. The electrochemical performance of Fe₂O₃@MWCNTs was firstly
evaluated by cyclic voltammetry (CV) in the 0–3.0 V voltage window at the scan rate of 0.1 mV s$^{-1}$ (Fig. 3(a)). It is clearly seen from the CV curves that there is a substantial difference between the first and the subsequent cycles. There is obviously one reduction peak in the potential of 0.6 V, which appears only in the first cycle. This peak corresponds to the Li$^+$ ions insertion into Fe$_2$O$_3$ and the formation of Li$_2$O. The first anodic scan shows an extended peak between 1.6 V and 1.9 V, which corresponds to oxidation of Fe to Fe$^{3+}$ ions to reform Fe$_2$O$_3$. For the second and third curves, a broad reduction peak at 0.85 V is observed, which indicates the reversibility and capacity stability. This broadening is due to the amorphous nature/crystal structure destruction of the electrode material$^{34}$. Fig. 3(b) shows the discharge and charge voltage profiles of different cycles at a current density of 100 mAg$^{-1}$, in good agreement with the CV measurements. A plateau at 0.75 V can be observed only in the first discharge voltage profile, which means the formation of Fe and Li$_2$O, corresponding to the peaks in CV curves. In the subsequent discharge profiles, the plateau moves to 0.9 V because of the change of crystalline structure in the first cycle$^{35}$. When the discharged electrode has been charged to 3.0 V, a smooth voltage profile is observed until 1.5 V which is followed by sloping voltage plateau up to 2.0 V and a steep rise up to 3.0 V, implying the regeneration of Fe$_2$O$_3$. The discharge and charge capacities of the 1st cycle are 870 and 573 mAhg$^{-1}$, respectively, with an initial coulombic efficiency of 65.9%. The discharge capacity of the 2nd cycle is 580 mAhg$^{-1}$. Such an irreversible capacity (290 mAhg$^{-1}$) is attributed to the formation of SEI layer and irreversible electrochemical reactions between lithium ions and electrode material.

To investigate the impact of unique structure of Fe$_2$O$_3$@MWCNTs on lithium storage capability, the coin cells based on MWCNTs, commercial Fe$_2$O$_3$, the composite of Fe$_2$O$_3$ and MWCNTs (same mass ratio with Fe$_2$O$_3$@MWCNTs) have been assembled and test under the same condition with Fe$_2$O$_3$@MWCNTs. The curves of capacity versus cycle number at a current density of 100 mAg$^{-1}$ were shown in Fig. 3(c). Compared with the contrast, Fe$_2$O$_3$@MWCNTs exhibited a reasonable cycle performance. Despite the capacity decayed in the first cycle, even after 50 cycles, the discharge capacity can retain a value of 515 mAhg$^{-1}$. Simultaneously, the initial coulombic efficiency of 47% recovered to 96% in the second cycle, and maintained almost 95% in the subsequent cycles (Fig. S8). As a comparison, MWCNTs, commercial Fe$_2$O$_3$ and the composite only exhibited the 50th discharge capacities of 248 mAhg$^{-1}$, 130 mAhg$^{-1}$ and 192 mAhg$^{-1}$, respectively. Although the discharge capacity of Fe$_2$O$_3$@MWCNTs is not larger than the previous reports of Fe$_2$O$_3$/CNTs composite anode owing to the relatively low loading ratio of Fe$_2$O$_3$ nanoparticles. However, according to the discharge capacity (Fe$_2$O$_3$@MWCNTs: 515 mAhg$^{-1}$, MWCNTs: 248 mAhg$^{-1}$) and mass ratio (Fe$_2$O$_3$: 29.68%, MWCNTs: 70.32%), the discharge capacity contributed by Fe$_2$O$_3$ NPs can be calculated as 1147 mAhg$^{-1}$ (Fig. S9), which is higher than the previous reports$^{8–11,13–15,18–21}$. This high value is even larger than the theoretical capacity of Fe$_2$O$_3$ (1007 mAhg$^{-1}$), suggesting that such a MWCNTs wrapping structure can enhance the lithium storage capability of Fe$_2$O$_3$ and ensure the complete reaction between Fe$_2$O$_3$ and Li$^+$ ions. As mentioned above, Fe$_2$O$_3$ NPs react with Li$^+$ ions and cause volume change inside MWCNTs.

Figure 3 | (a) Cyclic voltammetry of Fe$_2$O$_3$@MWCNTs between 3 and 0 V at a scan rate of 0.1 mVs$^{-1}$, (b) Galvanostatic discharge/charge voltage profiles of Fe$_2$O$_3$@MWCNTs at a current density of 100 mAg$^{-1}$, (c) Discharge capacities versus cycle number of Fe$_2$O$_3$@MWCNTs, MWCNTs, the composite and commercial Fe$_2$O$_3$ at the current density of 100 mAg$^{-1}$ between 3 and 0 V, (d) Discharge and charge capacity of Fe$_2$O$_3$@MWCNTs at different current densities between 3 and 0 V.
According to the Raman spectrum shown in Fig. 3(d). Even cycled at a high rate of 2000 mAg⁻¹ (3.6 C), this material can still deliver an average discharge of 320 mAhg⁻¹. When the current rate is restored to 100 mAg⁻¹, a stable capacity of 520 mAhg⁻¹ is resumed.

For revealing the structural evolution of Fe₂O₃@MWCNTs, the electrode after 50 cycles was examined by TEM, which is shown in Fig. 4(a). The structure of a single MWCNT is well preserved, implying the excellent stability of the graphite wall. It has been reported that CNTs can enhance the electrical conductivity transition metal oxide. Because of the existence of large amount of MWCNTs, Fe₂O₃@MWCNTs exhibit much lower resistance than the bare Fe₂O₃ as evidenced by the drastically reduced diameter of the semicircle at high-frequency region in the electrochemical impedance spectroscopy (EIS) patterns (Fig. 4(b)). Moreover, Waki’s group has proven that the defects on MWCNTs had positive effects on Li storage property. In a typical synthesis, dried ferrocene (0.02 g) were placed into a quartz tube with the inner diameter of 12 mm and effective heating length 150 mm. After being vacuumed, the quartz tube containing ferrocene was sealed. After that, the quartz tube was placed into a tube furnace and heated to 200 °C and maintained for 1 h so that the ferrocene can be slowly sublimed in the quartz tube. Subsequently, in order to gradually decompose ferrocene into the quartz tubes, the tube furnace was heated to and maintained at 400 °C for 1 h. Finally, the tube furnace was heated to and maintained at 950 °C. After 4 h, the tube furnace was naturally cooled to room temperature.

The electrochemical behavior of the as-prepared Fe₂O₃@MWCNTs was dissolved in 50 mL hydrochloric acid (concentration: 1 molL⁻¹, after 50 cycles as anode electrode for LIBs, while the capacity is calculated as 1147 mAhg⁻¹ based on the mass ratio of Fe₂O₃ NPs. Such an enhanced property could be attributed to the unique structure of MWCNTs wrapping, which not only accommodates the large volume variation but also enhances the overall conductivity. Moreover, a stable SEI film formed on the surface of MWCNTs also reduces capacity fading. This hybrid structure can be also applied to enhancing other electrode materials.

Methods
Synthesis. All chemicals are of analytical grade and used without purification. The synthesis of Fe₂O₃ nanoparticles wrapped in multi-walled carbon nanotubes (Fe₂O₃@MWCNTs) contains two steps: Synthesis of Fe nanoparticles wrapped in multi-walled carbon nanotubes (Fe@MWCNTs) and Oxidation of Fe nanoparticles to Fe₂O₃ NPs. The synthesis method of Fe@MWCNTs has been reported by our group. In a typical synthesis, dried ferrocene (0.02 g) were placed into a quartz tube with the inner diameter of 12 mm and effective heating length 150 mm. After being vacuumed, the quartz tube containing ferrocene was sealed. After that, the quartz tube was placed into a tube furnace and heated to 200 °C and maintained for 1 h so that the ferrocene can be slowly sublimed in the quartz tube. Subsequently, in order to gradually decompose ferrocene into the quartz tubes, the tube furnace was heated to and maintained at 400 °C for 1 h. Finally, the tube furnace was heated to and maintained at 950 °C. After 4 h, the tube furnace was naturally cooled to room temperature.

2. Electrochemical measurements. The electrochemical behavior of the as-prepared Fe₂O₃@MWCNTs was examined using CR2032 coin type cells vs. Li with 1 M LiPF₆ in a Japan Rigaku D/MAX-2500 X-ray diffractometer equipped with Cu Ka radiation over the 20 range of 10–80°. Scanning electron microscopy (SEM) images were performed on a JEOI JSM-6700M scanning electron microscope. Transmission electron microscopy (TEM) images were obtained on a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200 kV. High-resolution transmission electron microscopy (HRTEM) images were taken on a JEOI-1020 transmission electron microscope, which was operated at 200 kV. Energy-dispersive X-ray (EDX) analysis was obtained with an EDAX detector installed on the same HRTEM. The Raman spectrum was taken on a LABRAM-HR Confocal Laser Micro-Raman spectrometer using an Ar⁺ laser with 514.5 nm at room temperature. X-ray Photoelectron Spectrum (XPS) was performed on an ESCALAB 250 X-ray Photoelectron Spectrometer with Al Ka radiation. Specific surface areas were calculated from the results of N₂ physisorption at 77 K (Micrometitics ASAP 2020) by using the BET (Brunauer–Emmet–Teller) and BJH (Barrett–Joyner–Halenda) methods. 1 mg Fe₂O₃@MWCNTs was dissolved in 50 mL hydrochloric acid (concentration: 1 molL⁻¹). After intense sonication for 10 min, the mixed solution was transferred into a 75 mL Teflon-lined stainless steel autoclave and maintained at 120 °C for 8 h and then naturally cooled to room temperature. After centrifuging, the concentration of iron ions in solution was measured using inductive coupled plasma-atomic emission spectroscopy (Atomscan Advantage).

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in ethylene carbonate and diethyl carbonate (EC:DEC = 1:1, v/v) as the electrolyte. The working electrode was fabricated by compressing a mixture of the active materials, conductive material (acetylene black), and binder (polyvinylidene fluoride) in a weight ratio of Fe2O3@MWCNTs/carbon/PVDF = 7:1:2 onto a copper foil current collector, then drying at 60°C for 12 h. The cells were assembled in a argon-filled glove box (MBraun Labmaster 130). The electrode capacity was measured by a galvanostatic discharge-charge method in the voltage range between 3 V and 0 V at a current density of 100 mA g⁻¹ on a battery test system (Neware CT-3008W). Cyclic voltammetry was performed using an electrochemical workstation (CHI 660C) between 0–3 V at a scan rate of 0.1 mV s⁻¹. The impedance spectra of the cells were measured on an electrochemical workstation (CHI 660C) in the frequency range of 0.001–100 kHz.

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