Multiwalled carbon nanotubes anchored with maghemite nanocrystals for high-performance lithium storage

Ping Wu [*], Kongwei Xie, Xiali Xu, Jianping Li, Yawen Tang, Yiming Zhou [*], Tianhong Lu

Jiangsu Key Laboratory of New Power Batteries, Jiangsu Collaborative Innovation Center of Biomedical Functional Materials, School of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210023, PR China

A B S T R A C T

In this paper, we have anchored maghemite (γ-Fe$_2$O$_3$) nanocrystals compactly and uniformly on multiwalled carbon nanotubes (MWCNT) *via* a polyelectrolyte-assisted layer-by-layer assembly approach based on electrostatic attraction. When evaluated as an anode for lithium-ion batteries (LIBs), the as-synthesized MWCNT-γ-Fe$_2$O$_3$ nanohybrid displays high reversible capacities, remarkable cycling stability, and magnificent high rate capability, facilitating its application as an advanced anode for high-energy, long-life, and high-power LIBs.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Owing to the high theoretical capacities and safety, 3d transition-metal oxides (M$_x$O$_y$, M = Mn, Fe, Co, Ni, and Cu) have been regarded as one of the most promising candidates to replace the commercial graphitic carbon anodes for lithium-ion batteries (LIBs) [1–10]. Among them, iron oxides including magnetite (Fe$_3$O$_4$) [7], hematite (α-Fe$_2$O$_3$) [8], maghemite (γ-Fe$_2$O$_3$) [9], and wustite (FeO) [10] have attracted significant attention due to their low cost, natural abundance, and environmental friendliness. However, the practical application of iron oxide anodes in advanced LIBs has been largely hampered by their poor cycling stability and rate capability, which are caused by the low electrical conductivity and large volume variations upon cycling [7–10].

Various nanostructures of iron oxides, such as nanocrystals [11], nanotubes [12], nanobelts [13], hierarchitectures composed of nanosized building blocks [14], and so forth with large surface area and short charge transport length, have been designed to improve their lithium storage performance to a large extent. However, the application of single-component nanostructured anodes still faces the challenges of poor intrinsic electronic/ionic conductivity and structural instability during lithium insertion/extraction, resulting in poor rate capability, particle agglomeration, pulverization and considerable capacity fading upon cycling. To address these issues,

extensive work has concentrated on constructing iron oxide-based hybrid nanostructures to improve the electrical conductivity and accommodate the volume variations [15–26]. Among various hybrid matrixes, carbon materials especially carbon nanotubes (CNT) have been considered as ideal conducting and buffering matrixes owing to their high electrical conductivity and structural stability [16–26]. Therefore, CNT supported iron oxides are expected to demonstrate further enhanced Li-storage performances [23–26].

Herein, we have anchored γ-Fe$_2$O$_3$ nanocrystals compactly and uniformly on multiwalled carbon nanotubes (MWCNT) *via* a polyelectrolyte-assisted layer-by-layer assembly approach based on electrostatic attraction, as illustrated in Scheme 1. The as-synthesized MWCNT-γ-Fe$_2$O$_3$ nanohybrid has been applied as a potential anode for LIBs, which displays superior lithium storage capabilities in terms of reversible capacities, cycling stability, and rate capability.

2. Experimental

2.1. Synthesis of MWCNT-γ-Fe$_2$O$_3$ nanohybrid

MWCNT synthesized by chemical vapor deposition (CVD) was purchased from Chengdu Organic Chemistry Co., Ltd., Chinese Academy of Science. The polyelectrolytes including poly (allyl-amine hydrochloride) (PAH, M_W = 60,000 Da) and poly (sodium 4-styrenesulfonate) (PSS, M_W = 70,000 Da) were purchased from *Alfa Aesar Co. Ltd.* Typically, the pristine MWCNT was first modified by polyelectrolytes (PAH/PSS/PAH) in sequence through
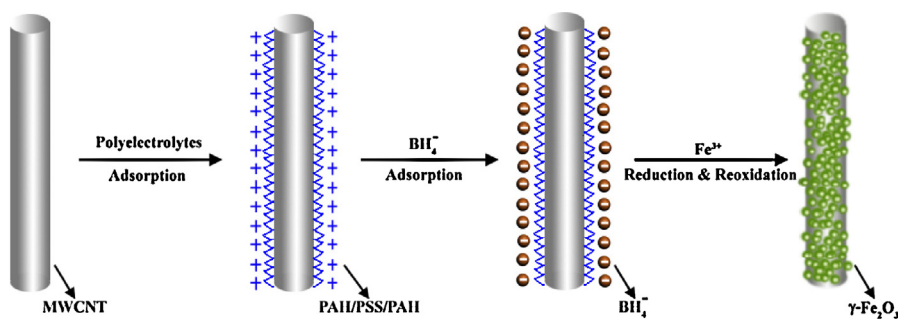
Scheme 1. Schematic illustration for the formation of the MWCNT-γ-Fe$_2$O$_3$ nanohybrid.

layer-by-layer technique according to the previous report [27]. Subsequently, 20 mg PAH/PSS/PAH modified MWCNT was dispersed in 40 mL deionized water, and then 0.5 mmol NaBH$_4$ was added. After sonication for 10 min, a 20 mL aqueous solution containing 0.25 mmol FeCl$_3$ and 0.75 mmol trisodium citrate was added dropwise into the above-mentioned solution, and the mixture was further sonicated for 1 h. After the reaction was finished, the resulting solid product was centrifuged and then dried at 80 °C under vacuum. Finally, the product was kept in a tube furnace at 500 °C for 3 h under N$_2$ at a ramping rate of 5 °C min^{-1}. For comparison, bare γ-Fe$_2$O$_3$ nanocrystals were prepared through the same approach but without MWCNT matrix.

2.2. Characterization

The morphology, composition, and structure of the product were characterized by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010F, 200 kV) equipped with energy-dispersive X-ray spectrometer (EDX, Thermo Fisher Scientific, NORAN System 7). X-ray powder diffraction (XRD) measurements were performed with Model D/max-rC diffractometer using Cu-Kα radiation ($\lambda = 0.15406$ nm) and operating at 45 kV and 100 mA. The differential scanning calorimetry and thermogravimetric analysis (DSC–TGA) was carried out on a PerkinElmer Diamond instrument at a heating rate of 10 °C min^{-1} in air (100 mL min^{-1}). X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo VG Scientific ESCALAB 250 spectrometer with a monochromatic Al Kα X-ray source (1486.6 eV photons).

2.3. Electrochemical measurements of MWCNT-γ-Fe$_2$O$_3$ nanohybrid

Electrochemical measurements were carried out by 2025-type coin cells which were assembled in an argon-filled IL-2GB glove box (Innovative Technology). The anode was made as follows: 70 wt% active material (MWCNT-γ-Fe$_2$O$_3$ nanohybrid), 15 wt% conductive material (Super P carbon black), and 15 wt% binder (polyvinylidene fluoride, PVDF) in N-methyl-2-pyrrolidene (NMP) were mixed, then the slurry was coated on the surface of Cu foam current collectors at room temperature and dried under vacuum at 120 °C for 12 h. MWCNT matrix was considered as part of active material when calculating the specific capacity of MWCNT-γ-Fe$_2$O$_3$ nanohybrid. The counter electrode was lithium metal foil, and the electrolyte was 1 M LiPF$_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume). Finally, the cells were aged for 12 h before measurements. A galvanostatic cycling test of the assembled cells was carried out on a Land CT2001A system in the potential range of 0.01–3 V at different current densities. Cyclic voltammetry (CV) measurements were recorded on a CHI 660B electrochemical analyzer (Shanghai CH Instrument Company) in the potential range of 0.0–3.0 V at a scan rate of

0.1 mV s^{-1}. The voltages mentioned herein were referred to Li$^+$/Li redox couple.

3. Results and discussion

Layer-by-layer assembly, pioneered by Decher et al., has now been widely used to synthesize hybrid materials with structural and functional diversity [28–30]. Herein, iron oxide nanocrystals have been anchored on MWCNT matrix *via* a polyelectrolyte-assisted layer-by-layer technique based on electrostatic attraction between charged species. Fig. 1 displays the XRD patterns of products before (curve *a*) and after (curve *b*) the annealing process. As observed from curve *a*, the diffraction peak at $2\theta = 26°$ can be assigned to (0 0 2) reflection of MWCNT, whereas the deposited iron oxides are poorly crystallized. After annealing at 500 °C under N$_2$, the crystallinity of the nanocrystals is obviously improved, and the observed crystalline phase from curve *b* could be indexed to cubic γ-Fe$_2$O$_3$ (JCPDS: 39-1346) with average crystallite size of *ca.* 6 nm.

Fig. 2a and b reveals the TEM images of MWCNT-γ-Fe$_2$O$_3$ nanohybrid with different magnifications. As observed, a rough coating layer consisting of numerous γ-Fe$_2$O$_3$ nanocrystals is homogeneously deposited onto the surface of MWCNT matrix, whereas no isolated γ-Fe$_2$O$_3$ nanocrystal can be observed in the sample except for the matrix surface. The phenomenon can be explained as follows. Owing to the strong adsorption of negatively charged reductants (BH$_4^-$ ions) to positively charged PAH/PSS/PAH modified MWCNT, the reduction of Fe^{3+} ions to metallic Fe occurs
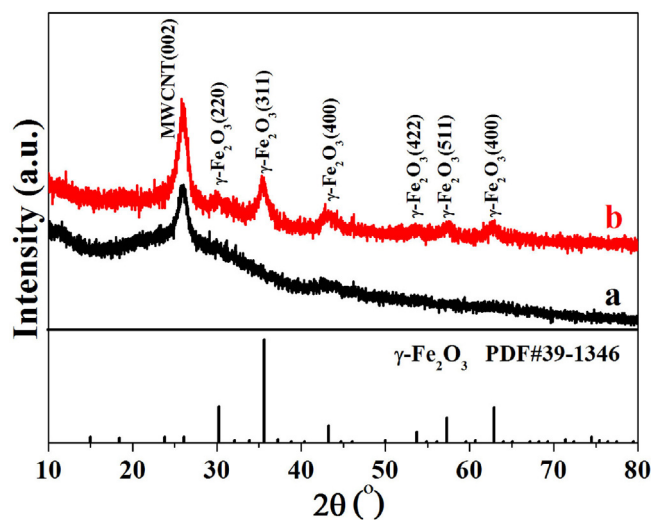
Fig. 1. XRD patterns of MWCNT-γ-Fe$_2$O$_3$ nanohybrid before (curve *a*) and after (curve *b*) the annealing process.