



# A general approach towards carbon nanotube and iron oxide coaxial architecture and its lithium storage capability



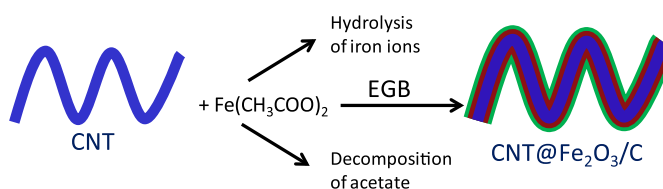
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## HIGHLIGHTS

- A general synthetic approach is developed to construct coaxial materials.
- Coaxial CNT@Fe<sub>2</sub>O<sub>3</sub>/C architecture is readily fabricated through this approach.
- Coaxial CNT@Fe<sub>2</sub>O<sub>3</sub>/C exhibits a remarkable electrochemical Li-storage activity.
- Coaxial architecture holds potential in the manipulation of battery materials.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Coaxial architectures consisting of metal oxide and carbon nanotube are promising for many energy applications due to their synergetic interaction. The engineering and development of coaxial structures through a simple approach are highly desirable but remain a challenge. Herein, we present a general and facile ethylene glycol bath approach to fabricate coaxial architectures in which the metal oxide component is sandwiched by carbon nanotube and amorphous carbon. These unique architectures can serve as efficient electrode for lithium storage. The internal carbon nanotube allows rapid electron transport, while the external amorphous carbon acts as flexible buffer to accommodate volume variation upon lithium uptake. When evaluated in lithium cells, the carbon nanotube and iron oxide coaxial material exhibits a remarkable electrochemical lithium storage. It affords a capacity of 1083 mAh g<sup>-1</sup> over 60 cycles, and retains 529 mAh g<sup>-1</sup> at a high rate of 5 A g<sup>-1</sup>, drastically outperforming the pure iron oxide counterpart. This facile approach is in principle applicable to constructing other coaxial electrodes, and thus holds great potential in the manipulation of battery materials for lithium storage application.

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## 1. Introduction

Nanostructured transition metal oxides can be explored as alternative Li-storage electrodes, as they can reversibly store

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substantial amount of Li ions beyond graphite anode [1]. In addition, they usually store and release Li storage at a potential around 0.5 V (vs. Li, unless otherwise denoted), thus eliminating the risk of Li dendrites [2,3]. Among these oxides, hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) has received a great deal of attention owing to its abundant resource, low cost, high theoretical capacity (1007 mAh g<sup>-1</sup>), and environmental compatibility [4]. However, the low electronic and ionic conductivities present a significant challenge resulting in poor Li-storage capability [5]. To mitigate this issue, numerous Fe<sub>2</sub>O<sub>3</sub>

nanomaterials such as nanorods [6], nanotubes [7], nanosheets [8], and hierarchical porous assemblies [9,10] have been designed. In these systems, the mobility of both electron and ion has been remarkably enhanced as the transport length is reduced to nanoscale [11].

Recently, nanocarbons such as carbon nanotubes (CNTs) and graphenes have emerged as efficient conductive supports for energy-related application. In viewing of production, scalability, cost, and reliability, CNT is currently the ideal support for Li-storage materials [12], as it is featured with superior conductivity, fast charge transport, and unique dimensionality [13,14]. Integrating CNT into electrode materials could be an alternative and particularly promising solution towards efficient Li storage [15,16]. In this regards, our group has made substantial efforts on several active materials and drastically boosted their energy and power capability [17–20]. Among possible integration configurations based on CNT, formation of one-dimensional coaxial structure might be the most promising one. This is because the coaxial structure offers the advantage of both the high electronic conductivity of the core and high lithium-ion transportation in the shell [21]. During the last decade, numerous CNT-based coaxial structures have been engineered and fabricated, and shown intriguing Li-storage behaviors [22–28]. For instance, Ajayan group has fabricated  $\text{MnO}_2/\text{CNT}$  coaxial inside AAO template using a combination of vacuum infiltration and chemical vapor deposition techniques [23]. Fan group has developed coaxial  $\text{Fe}_3\text{O}_4/\text{CNT}$  using magnetron sputtering process [24]; Liu et al. obtained coaxial  $\text{MoO}_3/\text{CNT}$  using electrodeposition [25]. However, these fabrications are either equipment-intensive or procedure-tedious, and consequently less accessible to scalable production and application. In addition, as the coaxial structures only deal with the conducting issue, their long-term lithiation stability is not satisfactory. A simple but efficient solution is surface wrapping by carbon or graphene, as recently proposed by Mai et al. [29].

In this work, we present a general and scalable approach to prepare coaxial  $\text{CNT@Fe}_2\text{O}_3/\text{C}$  nanostructures. This approach is based on one-pot thermal decomposition of precursor (i. e. iron(II) acetate) under ethylene glycol bath (EGB). The obtained coaxial structure is composed of iron oxides nanocrystallites sandwiched by the internal CNT and external carbon layer derived from the decomposed acetate. The CNT network serves as a highly conducting and porous network facilitating electron and ion transport, while the carbon coating layer provides flexible space for accommodating lithiation-induced volume expansion. As a consequence, the  $\text{CNT@Fe}_2\text{O}_3/\text{C}$  exhibits excellent electrochemical Li-storage capability. It affords a reversible capacity of 1083 mAh  $\text{g}^{-1}$  with stable cycling over 160 cycles, and retains 529 mAh  $\text{g}^{-1}$  at a high rate of 5 A  $\text{g}^{-1}$ , significantly outperforming the pure  $\text{Fe}_2\text{O}_3$  counterpart.

## 2. Experimental

### 2.1. Synthesis

$\text{CNT@Fe}_2\text{O}_3/\text{C}$  coaxial structure was synthesized through one-pot EGB approach. In a typical attempt, 20 mg CNTs were ultrasonically dispersed in 20 ml EG and heated to 150 °C using oil bath. To this suspension, an aqueous solution containing 1 mmol  $\text{Fe}(\text{CH}_3\text{COO})_2$  was added dropwise. The suspension was further bathed at 150 °C for 3 h. After the reaction, the resulting precipitation was collected by centrifugation, washed repeatedly with water and ethanol, and vacuum dried at 60 °C overnight.

### 2.2. Characterization

X-ray diffraction (XRD) pattern was recorded on a Rigaku Dmax-2400 automatic diffract meter equipped with Cu  $K\alpha$  radiation. Morphologies were observed by scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, FEI Tecnai G2 T20). Raman spectroscopy measurements were conducted on a JY HR800 spectrometer using an excited HeNe laser (633 nm). Thermogravimetric analysis (TGA) was performed on a TG/DTA-7300 thermal analyzer (Seko). Nitrogen adsorption and desorption isotherms were measured on a Tristar 3020 micropore analyzer (Micromeritics).

### 2.3. Electrochemical evaluations

Prior to electrochemical test, the powder was further heated at 350 °C for 2 h with a ramping rate of 1 °C  $\text{min}^{-1}$  in air. 70 wt% as-prepared  $\text{CNT@Fe}_2\text{O}_3/\text{C}$  material, 20 wt% carbon black, and 10 wt% binder polyvinylidene fluoride (PVDF) were thoroughly blended in N-methyl pyrrolidone. The homogeneous slurry was then coated on a copper foil using a doctor-blade technique. After drying overnight, the electrode sheet was roll pressed, tailored to disks shape, and vacuum dried at 120 °C overnight. The typical loading of active material is 2.5  $\text{mg cm}^{-2}$ . Galvanostatic Li-storage performance was evaluated by assembling coin-type 2032 two-electrode cells in an argon filled glove box (Mikrouna) with  $\text{O}_2$  and  $\text{H}_2\text{O}$  concentration below 0.1 ppm. The working electrode is the composite disks, the counter electrode and reference electrode are Li metal foil, the electrolyte is 1 M  $\text{LiPF}_6$  solution in ethylene carbonate/dimethyl carbonate (1:1, v/v), and the separator is glass microfiber filters (Whatman). Galvanostatic charge and discharge tests were performed on a CT2001A battery test system (LAND) in the voltage range of 0.01–3.0 V at room temperature. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were measured on an RST electrochemical workstation.

## 3. Result and discussion

As schematically illustrated in Fig. 1, fabrication of  $\text{CNT@Fe}_2\text{O}_3/\text{C}$  involves two simultaneous processes (i) hydrolysis of iron oxide and subsequent depositing onto CNT and (ii) the carbonization of acetates. The attachment and growth of oxides on CNT are probably owing to the strong interaction between iron ions and oxygen-containing groups of CNTs, which were introduced by acid treatment in advance [30].

The coaxial  $\text{CNT@Fe}_2\text{O}_3/\text{C}$  structure via the EGB process can be confirmed by SEM and TEM imaging (Fig. 2). These coaxial cables are rather uniform, having diameter of 60–70 nm (Fig. 2a). As the diameter of the used CNTs is about 30–40 nm (Fig. S1), the thickness of  $\text{Fe}_2\text{O}_3$  precursor overlayer is 10–20 nm. After annealing at 350 °C in air, the  $\text{CNT@Fe}_2\text{O}_3/\text{C}$  well retains the coaxial structure, although the thickness of the overlayer is reduced to 5–10 nm (Fig. 2b and c). A high-resolution TEM image presented in Fig. 2d suggests that  $\text{Fe}_2\text{O}_3$  nanocrystals 5–10 nm in size are tightly anchored onto the CNT to form a coaxial structure. A close observation reveals a 1–2 nm amorphous layer, which can be identified as carbon by energy dispersive X-ray spectroscopy (EDX). The interplanar spacing of 0.27 nm correlates well with the (104) face of the hematite  $\text{Fe}_2\text{O}_3$ . The selected area electron diffraction shown in Fig. 2e reveals clear diffraction ring due to (002) face of CNT and spots due to (024) and (006) faces of hexagonal  $\text{Fe}_2\text{O}_3$  (space group R-3C). The composition of the  $\text{CNT@Fe}_2\text{O}_3/\text{C}$  is identified by EDX (Fig. 2f), in which Fe, O, C elements are revealed. These results suggest that coaxial  $\text{CNT@Fe}_2\text{O}_3/\text{C}$  is readily fabricated through this one-pot approach. Note that this EGB approach is general and can

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