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# Core/shell $\text{Fe}_3\text{O}_4@Fe$ encapsulated in N-doped three-dimensional carbon architecture as anode material for lithium-ion batteries

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## ABSTRACT

Core-shell  $\text{Fe}_3\text{O}_4@Fe$  nanoparticles embedded into porous N-doped carbon nanosheets were prepared by a facile method with NaCl as hard-template. The three-dimensional carbon architecture built by carbon nanosheets enhance the conductivity of the encapsulated  $\text{Fe}_3\text{O}_4@Fe$  nanoparticles and strengthen the structure stability suffering from volume expansion during extraction and insertion of lithium ions. Rich Pores enhance the surface between electrode and electrolyte, which short the transmission path of ions and electrons. The core-shell structure with Fe as core further improves charge transferring inside particles thus lead to high capacity. The as-prepared  $\text{Fe}_3\text{O}_4@Fe/NC$  composite displays an irreversible discharge capacity of  $839 \text{ mAh g}^{-1}$  at  $1 \text{ A g}^{-1}$ , long cycling life ( $722.2 \text{ mAh g}^{-1}$  after 500th cycle at  $2 \text{ A g}^{-1}$ ) and excellent rate performance ( $1164.2$  and  $649.2 \text{ mAh g}^{-1}$  at  $1$  and  $20 \text{ A g}^{-1}$ , respectively). The outstanding electrochemical performance of the  $\text{Fe}_3\text{O}_4@Fe/NC$  composite indicates its application potential as anode material for LIBs.

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## Introduction

Lithium-ion batteries hold on its irreplaceable status since the first commercial LIBs were developed due to its environment friendly, excellent cycle/rate electrochemical performance and high energy density [1–3]. Over past decade, with the

development of hybrid electric vehicles (HEVs) and electric vehicles (EVs), there is an urgent requirement to develop rechargeable LIBs with high energy density and power density [4–6]. However, the commercial graphite anode materials deliver a theoretical capacity of  $372 \text{ mAh g}^{-1}$  which cannot meet enormous demands of energy consumptions with high energy density and power density [7–11]. It is necessary to

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explore alternative anode materials with higher charge-discharge rate and reversible capacity as well as long cycle life, low cost, and the ability to produce in large scale. Transition metal oxides ( $\text{MO}_x$ ) possess high capacity and have been extensively investigated as anode materials for high performance LIBs [12,13]. However, the unstable connection of active materials with current collector and SEI film forming on the surface of  $\text{MO}_x$  lead to poor rate performance and rapid capacity fading during cycling [13].

In order to overcome these issues of  $\text{MO}_x$  materials, some designed structures (such as nanoparticles, nanowires and core-shell et al.) assembled with carbon materials show effective performances [5,14–17]. These composites refined to nanometer size lead to improved conductivity and speed up charge/discharge rate. Additionally, compared with bare bulk materials, the coating with carbon enhances mechanical strength during rapid lithium ion insertion/extraction process. In these  $\text{MO}_x$  materials,  $\text{Fe}_3\text{O}_4$  shows high capacity, low cost, eco-friendliness, and natural abundance, thus has attracted considerable attention [18]. Yang et al. designed a  $\text{Fe}_3\text{O}_4/\text{CNTs}/\text{rGO}$  composite [19], the CNT and rGO improved the conductivity and thus exhibit an excellent rate and cycling performances (540 mAh  $\text{g}^{-1}$  at 10 A  $\text{g}^{-1}$ , 1080 mAh  $\text{g}^{-1}$  at 1 A  $\text{g}^{-1}$  after 450 cycles). Shun Li's group constructed the  $\text{Fe}_3\text{O}_4\text{-TiO}_2$ -carbon composite by using the natural cellulose substance as both the frame and the carbon source [20]. When it as an anode for lithium ion battery, it shows a stable reversible discharge capacity of 525 mAh  $\text{g}^{-1}$  after 100 cycles at 100 mA  $\text{g}^{-1}$ .

Herein, a core/shell  $\text{Fe}_3\text{O}_4/\text{Fe}$  encapsulated in N-doped 3D carbon architecture was prepared by a controllable and facile method using NaCl particles as hard-template. In the designed structure, the N-doped carbon framework as base material consisted of nanosheets improve the conductivity, strengthens stability and increase contact area with electrolyte, which is beneficial to cycling and rate performances. The Fe cores speed up transferring of charges inside the bulk, which enhance the capability of the oxide. The  $\text{Fe}_3\text{O}_4/\text{Fe}/\text{NC}$  composite working as anode material in lithium ion battery exhibits excellent electrochemical performances, suggesting promising application potential as anode material for LIBs.

## Experimental

### Synthesis of $\text{Fe}_3\text{O}_4/\text{Fe}/\text{NC}$ composites

The  $\text{Fe}_3\text{O}_4/\text{Fe}/\text{NC}$  composite was synthesized by a simple in situ synthesis strategy under the NaCl particles as the hard-template. In order to prepare  $\text{Fe}_3\text{O}_4/\text{Fe}/\text{NC}$  composites, 2.00 g of  $\text{FeC}_6\text{H}_5\text{O}_7$  (99.99%, aladdin), 10 g citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ), 2 g urea ( $\text{CH}_4\text{N}_2\text{O}$ ) and 75 g sodium chloride were dissolved in 400 mL of deionized water. The result mixed solution was dried in a drying oven at 80 °C for 48 h and then collect composite powders. After that, the composite powders were heated to 750 °C under Ar atmosphere for 2 h with the heating rate of 2 °C  $\text{min}^{-1}$ . After natural cooled to room temperature at the Ar atmosphere, the black powder was soaked in amount of deionized water for 2 h to dissolve the sodium chloride completely and then collect the black powers of 2D Fe/NC composite by filtering. Finally, the pure  $\text{Fe}_3\text{O}_4/\text{Fe}/\text{NC}$

nanosheets were obtained by heating the Fe/NC black power at 250 °C for 6 h under the air atmosphere. For comparison, at the same conditions, the Fe/NC nanosheets was also obtained, then the oxidation time of Fe/NC was heated at 250 °C under the air atmosphere for 10 h to achieved the pure  $\text{Fe}_3\text{O}_4/\text{NC}$  composite.

### Characterization

The morphology and microstructure of the composites materials were characterized by scanning electron microscopy (SEM: Philips, FEI Quanta 200 FEG) and transmission electron microscope (TEM, JEOL 2010). The crystal structures of the  $\text{Fe}_3\text{O}_4/\text{NC}$  and  $\text{Fe}_3\text{O}_4/\text{Fe}/\text{NC}$  composite were investigated by powder X-ray diffraction (XRD, Rigaku D/max 2500) using Cu  $K\alpha$  radiation under the scanning speed of 10°  $\text{min}^{-1}$  from 10° to 90°. X-ray photoelectron spectra (XPS) were collected on a physical electronics PHI5400 using Mg K radiation, which tested the elements composition of  $\text{Fe}_3\text{O}_4/\text{Fe}/\text{NC}$  composite. TGA (NETZSCH STA 409 PC) was performed up to 1000 °C at air atmosphere with the heating rate of 5 °C  $\text{min}^{-1}$ .

### Electrochemical characterization

The working electrodes were prepared by mixing 70 wt % composite materials ( $\text{Fe}_3\text{O}_4/\text{Fe}/\text{NC}$  or  $\text{Fe}_3\text{O}_4/\text{NC}$  composite) with 10 wt % Super P as a conductive agent and 20 wt % PVDF (polyvinylidene fluorides) as a binder dissolved in N-methylpyrrolidone (NMP) to form a black slurry, which was then coated on Cu foils. Then the coated Cu foil was dried at 80 °C for 12 h in a vacuum oven to remove the solvent. Coin cells (CR2025) were assembled under the argon filled glove box with the metal lithium foil was used as the counter electrode. The electrolyte was consists of  $\text{LiPF}_6$  (1 mol  $\text{L}^{-1}$ ) and a mixed organic solvent (ethylene carbonate (EC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC) with a volume ratio EC-DEC-EMC = 1:1:1). The cycling/rate performance of these two work electrodes were tested with a LAND System (BT2013A, China) within the voltage of 0–3 V. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out over the potential range of 0.01V–3.0 V at a scan rate of 0.1 mV  $\text{s}^{-1}$  with an IM6 electrochemical workstation (Germany).

## Results and discussion

The synthesis process of the  $\text{Fe}_3\text{O}_4/\text{Fe}/\text{NC}$  composite is shown in Fig. 1. The ferric citrate, citric acid, urea and sodium chloride was dissolved in deionized water. Then, the reddish brown mixture was dried to obtain solid precursor. During the first step the formed  $\text{FeC}_6\text{H}_5\text{O}_7\text{-C}_6\text{H}_8\text{O}_7\text{-urea}$  complex was evenly coated on the surface of sodium chloride particles. After heat treatment under the Ar atmosphere, the iron source turned into iron oxide which was then reduced to iron by the carbon source of  $\text{C}_6\text{H}_8\text{O}_7$ . In addition, the urea introduce N element into carbon from decomposition of  $\text{C}_6\text{H}_8\text{O}_7$ , the N-doped carbon layer with rich pores encapsulating Fe nanoparticles (Fe/NC) was left after the NaCl template was removed when soaking in deionized water. In the following step, the Fe/NC composite was calcined in air and partial Fe

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