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Short communication

# Facile synthesis of carbon layer-entangled $Fe_2O_3$ clusters as anode materials for improved Li-ion batteries

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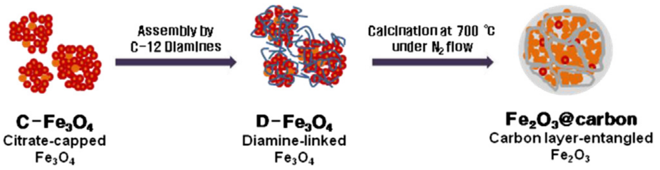
## HIGHLIGHTS

- ► Carbon layer-entangled iron oxides ($Fe_2O_3$@carbon) were facilely prepared.
- ► 1,12-Diaminodedecane (C-12 diamine) induced the assembly of iron oxide clusters.
- ► Entangled carbon layer enhanced the conductivity and structural integrity of $Fe_2O_3$.
- ► Composite electrodes improved the electrochemical performance of Li-ion batteries.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Carbon layer-entangled iron oxides ($Fe_2O_3$@carbon) are facilely prepared through the cross-linking assembly of iron oxides induced by the addition of 1,12-diaminododecane (C-12 diamines). The calcined $Fe_2O_3$@carbon composites exhibit the XRD patterns attributed to hexagonal phase of hematite ($\alpha$-$Fe_2O_3$) with negligible magnetism. As anode electrode materials for Li-ion batteries, the $Fe_2O_3$@carbon exhibits the retained capacity of 614 mAh $g^{-1}$ at 0.1 C after 35 cycles, while the carbon free $Fe_2O_3$ exhibits the retained capacity of 283 mAh $g^{-1}$ at 0.1 C after 35 cycles. The unique formation of carbon layer entanglement within iron oxide clusters contributes the improved capacity retention capability of the composite electrode ($Fe_2O_3$@carbon) by providing buffering space for large volume expansion and enhanced electrical conductivity between the active iron oxides.

## 1. Introduction

Li-ion batteries are widely employed as power sources for mobile electronics due to their high-energy density and long cycling performance [1–3]. The capacity of Li-ion batteries can be improved by increasing the storage amounts of Li-ions in electrode materials [4,5]. Recently, transition metal oxides ($MO_x$, M = Fe, Ti, Co, Mn, etc.) have been intensively investigated as active electrode materials for Li-ion batteries because they have high theoretical specific capacity and good structural stability [6–10]. Among them, iron oxide can be an attractive anode material due to its low cost, low toxicity, and natural abundance [11,12].

Recently, hematite ($\alpha$-$Fe_2O_3$) has been evaluated as an active anode material with the theoretical capacity of 1007 mAh $g^{-1}$ [13–15]. The electrochemical reaction of $Fe_2O_3$ with Li ions is given by '$6Li + Fe_2O_3 \leftrightarrow 2Fe^0 + 3Li_2O$' through the intermediate complex of

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$Li_xFe_2O_3$ [15]. The $Fe_2O_3$ can reversibly intercalate $Li^+$ ions more than 4 mol, thereby providing a higher lithium storage capacity than that of commercial graphite anodes (372 mAh $g^{-1}$) [16]. However, the performance of iron oxide electrode is limited by the slow diffusion of Li ions and poor electrical conductivity of the electrode materials, resulting in rapid capacity fading with prolonged cycling [3,10]. Well-designed nanostructures can solve these problems by providing buffering space which can accommodate the volume expansion of electrode materials during charge–discharge processes. For instance, uniform hematite capsules showed the improved electrochemical performance (retained capacity of 740 mAh $g^{-1}$ after 30 cycles) [17]. Nanoflakes of $\alpha$-$Fe_2O_3$were demonstrated as active anode materials with the stable capacity of ca. 680 mAh $g^{-1}$ up to 80 cycles [18].

Another approach to overcome these problems is to wrap the active $Fe_2O_3$ with carbon materials which can improve the electrochemical properties of the interface between electrodes and electrolytes: i) carbon coating, ii) carbon matrix embedding, iii) carbon-layer entanglement [19–22]. $Fe_3O_4$ nanospheres entangled with polyacrylic acid (PAA) exhibited greatly enhanced lithium storage properties with the retained capacity of 712 mAh $g^{-1}$ after 60 cycles [20]. $Fe_3O_4$ nanoparticles embedded in graphene sheets also exhibited improved cycling stability and rate performance due to homogeneously dispersed $Fe_3O_4$ (ca. 7 nm) in carbon matrix [22]. However, most of the synthetic procedures require complex steps with toxic chemicals under severe conditions.

In this work, carbon layer-entangled iron oxides were facilely prepared as active anode materials for Li-ion batteries through diamine-linked assembly of iron oxides and their subsequent heat-treatment at 700 °C under $N_2$ flow. The resulting nanocomposites exhibited the favorable nanostructure (i.e., iron oxide clusters entangled with conductive carbon layer) which can enhance the electrical conductivity and minimize the pulverization process, consequently leading to the improved electrochemical performance (e.g., high capacity retention and good cycling stability). The characteristic properties of as-prepared samples were analyzed by SEM (Scanning Electron Microscope), TEM (Transmission Electron Microscope), XRD (X-ray Diffraction), and the electrochemical properties of the samples were tested by cyclic voltammetry and galvanostatic cycling techniques.

## 2. Experimental

### 2.1. Preparation of citrate-capped magnetite clusters (C-$Fe_3O_4$)

Aqueous ferrofluid was prepared according to the modified co-precipitation method [23]. $FeCl_3$ and $FeCl_2$ (3:2 mol ratio) were mixed with 25 ml of distilled water, and then 20 ml of ammonium hydroxide (28 wt% $NH_3$) was quickly added into the mixture with vigorous stirring at room temperature. Black precipitates immediately formed and were mixed with 100 ml of citrate solution (1.0 M) for 3 h at room temperature, then the mixture was refluxed for 1 h at 70 °C to obtain citrate-capped magnetites (C-$Fe_3O_4$).

### 2.2. Preparation of carbon-layered entangled iron oxides ($Fe_2O_3$@carbon)

Diamine molecules as a cross-linker were added to the C-$Fe_3O_4$ solution to induce the cross-linked assembly of magnetite clusters. 1,12-diaminododecane (C-12 diamines of 1.0 M) was prepared by adding 2.0 g of C-12 diamines to 10 ml of aqueous solution. An aliquot volume (250 µl, 1000 µl) of diamines was added into the C-$Fe_3O_4$ solution and the mixed solution was stirred vigorously for 2 h at 30 °C. Finally, diamine-linked magnetite clusters (D-$Fe_3O_4$) were purified by removing residual impurities through several centrifugations. The D-$Fe_3O_4$ was subsequently heat-treated under $N_2$ flow at 700 °C for 2 h, consequently leading to the formation of carbon layer-entangled iron oxide clusters ($Fe_2O_3$@carbon).

### 2.3. Electrochemical measurements

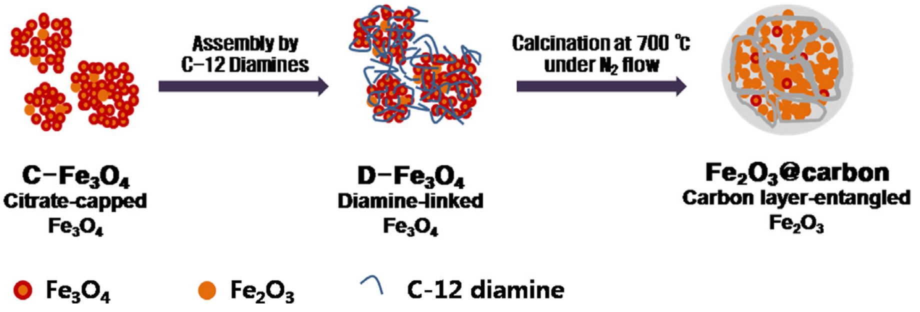
The half-cell electrodes for Li-ion batteries were described in other studies [24,25]. In preparing anode electrode materials, a slurry containing 70 wt% of magnetite powder, 15 wt% of denka black (DB) and 15 wt% of polyvinylidene fluoride (PVDF) dissolved in *N*-methyl-2-pyrrolidone (NMP) was pasted onto a Cu substrate. A half-cell assembled in a dry room with iron oxide composites was used as a working electrode, a metallic lithium foil as a counter electrode, 1.0 M $LiPF_6$ in ethylene carbonate (EC), dimethyl carbonate (DMC), and ethylmethyl carbonate (EMC) as electrolytes, and a polypropylene-based film as a separator. The mass of working and Li counter electrode was 88.4 mg (including cupper plate) and 80.9 mg, respectively. The loading densities of carbon free $Fe_2O_3$ and $Fe_2O_3$@carbon were $3.33 \times 10^{-3}$ and $3.36 \times 10^{-3}$ g $cm^{-2}$, respectively.

Cyclic voltammetry (CV) was measured in the voltage range between 0.05 V and 3.0 V at the scan rate of 0.01 mV $s^{-1}$. Galvanostatic discharge–charge cycling was measured at 0.1 C in the voltage range of 0.05–2.5 V.

## 3. Results and discussion

### 3.1. Nanocomposite preparation and its characterization

Scheme 1 showed the fabrication procedures in which C-12 diamine acted as a cross-linker to assemble iron oxide clusters and the resulting composites were finally transformed into the $Fe_2O_3$@carbon through the heat-treatment process: (1) Diamine-linked magnetite clusters (D-$Fe_3O_4$) were prepared by adding an aliquot volume of 1,12-diaminododecane (C-12 diamine of 1.0 M) into citrate-capped $Fe_3O_4$ (C-$Fe_3O_4$) solution prepared by the co-



**Scheme 1.** Fabrication schemes for carbon-layer entangled iron oxides.