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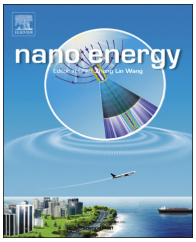

RAPID COMMUNICATION

# High-density iron nanoparticles encapsulated within nitrogen-doped carbon nanoshell as efficient oxygen electrocatalyst for zinc-air battery

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**Abstract**
Exploring highly efficient electrocatalysts toward oxygen reduction and evolution reactions are critical for the development of rechargeable zinc-air batteries. As a novel class of electrocatalyst, transition metal nanoparticles encapsulated within nitrogen-doped carbon have been regarded as competitive alternative to replace noble metal electrocatalysts. Herein, we report successful synthesis of high-density iron nanoparticles encapsulated within nitrogen-doped carbon nanoshell (Fe@N-C) by solid-phase precursor's pyrolysis of dicyandiamide and ammonium ferric citrate. The resulting Fe@N-C material shows excellent bifunctionality for ORR and OER in alkaline medium compared to state-of-the-art commercial Pt/C and $IrO_2$, which demonstrates high performance and cycling durability in zinc-air battery as efficient oxygen electrocatalyst.
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## Introduction

Renewable energy sources, such as solar and wind energy, have been developed rapidly due to the world's growing energy demands and serious environmental threat caused by

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the depletion of natural fossil resources [1,2]. The intermittent and local nature of renewable energy sources make them difficult to merge with the electricity grid. Electrochemical energy storage and conversion technologies provide a promising solution for efficient use of renewable electricity [3-5]. In recent years, rechargeable zinc-air batteries, consisting of a zinc electrode, electrolyte and an air electrode, have attracted increasing attention due to their high energy density, low cost and compact structure [6]. The renewable electricity is stored into rechargeable zinc-air battery by the charge process, and then the zinc-air battery delivers electricity by the discharge process as portable and transportation power sources, accomplished with oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) in the air electrode. There are several challenges in oxygen electrocatalysis for rechargeable zinc-air batteries, such as intrinsically sluggish kinetics of ORR and OER, high overpotential and poor cycling durability, etc [7-9]. Noble metal electrocatalysts containing Pt, Ru or Ir have demonstrated high activity and durability in ORR or OER, however, these electrocatalysts exhibit poor bifunctionality. For example, Pt shows a high ORR activity but a poor OER activity, while $RuO_2$ and $IrO_2$ exhibit high OER activities but poor ORR activities [10-12]. Furthermore, the high cost and terrestrial scarcity of noble metals hinder an extensive use in zinc-air battery. Therefore, development of competent and inexpensive electrocatalysts using earth-abundant elements is highly demanded to address the major issues currently plaguing oxygen electrocatalysis.

Up to now, some transition metal- and nitrogen-functionalized carbon materials have shown remarkable activities in oxygen electrocatalysis [6,13-18], as well as high performances in zinc-air and lithium-oxygen batteries [13,14,16-18]. Among different active sites, transition metal-$N_x$, such as Fe-$N_x$, is considered as the most active species for oxygen electrocatalysis [13,18], however, the acidic and oxidant attacks lead to leaching of iron out of Fe-$N_x$/C catalysts during the electrocatlytic process. Furthermore, the optimum iron content in Fe-$N_x$/C catalysts is usually less than 0.2 wt% [15], therefore, the leaching problem and low active site density cause a poor durability, especially in acidic medium [19]. Very recently, transition metal nanoparticles encapsulated in carbon are being spotlighted as a competitive candidate to replace noble metal electrocatalysts [20-22]. The surface carbon layer in the unique encapsulation structure prevents acid-leaching, oxidation and aggregation of transition metal nanoparticles in the electrocatalytic process, showing excellent durability in a wide pH range [23,24]. Transition metal nanoparticles not only increase the graphitization degree of surface carbon layer during carbonization [25], but also transfer electron to the surface carbon layer [26]. The doping nitrogen in carbon lattice further induces uneven charge distribution of the adjacent carbon atoms [27,28]. A synergetic role of the doped nitrogen in carbon lattice and the encapsulated transition metal nanoparticles stimulates an enhanced intrinsic electrocatlytic activity on the carbon-based materials [21,26]. Therefore, there are urgent demands to synthesize high-density transition metal nanoparticles encapsulated within nitrogen-doped carbon for increased active site density and enhanced electrocatalytic performance.

Various routes have been well developed for preparing high-purity carbon nanomaterials [29,32]. In sharp contrast, synthesis of high-density transition metal nanoparticles encapsulated in carbon is still in their early stages of development. Some encapsulation structures have been successfully synthesized recently [20-22,26,33,34], however, the content of transition metal is low [20,34] and the particle size of encapsulated transition metal is rather large [33], resulting in a low surface area of transition metal and active site density. Therefore, there is still a great challenge to synthesize carbon encapsulated transition metal nanoparticles with high loading and dispersion. Recently, solid phase precursors have been widely used to synthesize carbon nanomaterials due to several advantages such as high yield, convenience of nitrogen doping and low cost using cheap equipment and a simple process [24,35-37]. In this work, we report using dicyandiamide (DCDA) together with ammonium ferric citrate (AFC) as solid-phase precursors to prepare high-density iron nanoparticles encapsulated within nitrogen-doped carbon nanoshell (labeled as Fe@N-C) by pyrolysis and acid-leaching. The carbon structure and morphology show strong dependence on the composition of iron precursor and pyrolysis temperature. With an increased pyrolysis temperature in a range of 600-900 °C, the form of carbon evolves from graphitic $C_3N_4$ into carbon nanoshell and carbon nanotube, while the crystalline size of encapsulated iron nanoparticles increases and content of doped nitrogen decreases. The optimized high-density Fe@N-C material shows excellent bifunctionality for ORR and OER in alkaline medium compared to state-of-the-art commercial Pt/C and $IrO_2$. Furthermore, the high-density Fe@N-C material demonstrates high performance and cycling durability in zinc-air battery as efficient oxygen electrocatalyst.

## Experimental

### Material synthesis

In a typical experiment, 8 g of dicyandiamide ($C_2H_4N_4$, Alfa Aesar, denoted as DCDA) and 1 g of ammonium ferric citrate ($C_6H_{11}FeNO_7$, J&K Chemical Ltd., denoted as AFC) were dissolved in 100 mL of de-ionized water. The solution was continuously stirred and dried at 80 °C. The obtained mixture was placed in a quartz tube of a horizontal furnace. The pyrolysis of the mixture was performed in Ar atmosphere at a flow rate of 50 mL $min^{-1}$. The furnace was heated to the target temperature at a rate of 10 °C $min^{-1}$ and kept at the target temperature for 2 h, then cooled to room temperature. The target temperature was set as 600, 700, 800 and 900 °C, respectively. Then the samples were leached in 0.5 M $HClO_4$ solution at 80 °C for 8 h to remove unstable iron species, and washed thoroughly with de-ionized water. Finally, the samples were dried at 60 °C in an oven. The samples are labeled as Fe@N-C-*X*, in which *X* represents pyrolysis temperature. For highlighting the role of iron precursor, ferric chloride was used instead of AFC, and the mixture of DCDA and ferric chloride was pyrolyzed at 700 °C, followed by acid-leaching and washing, which is denoted as D-FC-700. The weight ratio of DCDA to iron was kept identical in the DCDA-AFC and DCDA-$FeCl_3$ mixtures.

### Physicochemical characterization

The morphology of the samples was investigated by an FEI Tecnai $G^2$ microscope at 120 kV and a JEM-2100 microscope

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