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Short communication

# Cubic spinel cobalt oxide/multi-walled carbon nanotube composites as an efficient bifunctionalelectrocatalyst for oxygen reaction

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ABSTRACT

A facile hydrothermal route has been adopted to fabricate cubic spinel cobalt oxide/multi-walled carbon nanotube composite using acid-functionalized carbon nanotubes as structure directing/oxidizing agents. The composite material demonstrated excellent bifunctionality before and after long periods of cyclic voltammetry cycling. After cycling, the oxygen reduction current density of the composite shows about 4, 34 and 3 times improvements in comparison to multi-walled carbon nanotube, cubic spinel cobalt oxide and their physical mixture, respectively. The oxygen evolution current density of the composite was 49% higher than the physical mixture and even greater than each component alone after 500 CV cycles. The cause of high performance is presumably contributed to the synergistic coupling effects between the multi-walled carbon nanotubes and the cubic spinel cobalt oxide.

## 1. Introduction

Rechargeable zinc–air batteries have attracted enormous attention as alternative energy sources owing to their advantages over traditional batteries in aspects of low-cost, environmental benignity and extremely high energy density [1]. Nevertheless, the most critical issue that hampers large-scale implementations of metal–air batteries is the sluggish kinetics of oxygen evolution and reduction reactions occurring during charge and discharge of a metal–air battery. Aiming to overcome this, scientists have devoted considerable efforts for developing low-cost and efficient bifunctionalelectrocatalysts that are capable of catalyzing both oxygen reduction reactions (ORRs) and oxygen evolution reactions (OERs). Currently, to reach satisfactory performance, precious metal-based bifunctional materials such as Pt-$IrO_2$ and PtIrRu are the best choices [2,3]. Due to the high cost and scarcity of precious metals, it is challenging but highly desirable to develop low-cost and efficient bifunctionalelectrocatalysts.

Spinels are potential candidates as low-cost electrocatalysts for both ORRs and OERs in alkaline environments [4,5]. This is owing to the more tolerant environment and facile reaction kinetics in comparison to acidic electrolytes, allowing for a broader selection of oxygen catalysts [6], especially for non-precious bifunctional catalysts such as $Co_3O_4$. However, very little has been reported to date about utilizing $Co_3O_4$ as bifunctionalelectrocatalyst components for metal–air batteries. Liang et al. [7] brought insights into the synergistic coupling between $Co_3O_4$ and graphene, and demonstrated excellent bifunctionality and stability of the composite material. Inspired by his idea, coupling $Co_3O_4$ and multi-walled carbon nanotubes (MWCNTs) could also display bifunctionality and stability. Furthermore, it is well believed that the electrochemical activities of nanostructured catalysts are closely related to their morphologies [8]. Different shaped $Co_3O_4$ such as nanocubes, nanoplatelets, and so forth has been synthesized with a variety of methods [9,10]. While the impact of morphology on the bifunctionality of $Co_3O_4$ microspheres for lithium–air batteries has been demonstrates by Yang et al. [11], the bifunctional capabilities of morphology controlled $Co_3O_4$ composited with carbon supports has never been reported. As a result, evaluating the ORR/OER activities of cubic $Co_3O_4$ ($cCo_3O_4$) and its MWCNT composite material will be very intriguing and is worth studying, although no techniques have previously been reported to synthesize morphology controlled cubic cCo3O4 directly chemically attached to MWCNTs. Herein, we report a highly active and stable bifunctionalelectrocatalyst synthesized via a facile hydrothermal process. To the best of our knowledge, this is the first reported cubic $Co_3O_4$ and MWCNT composite material ($cCo_3O_4$/MWCNT) with outstanding bifunctionality and stability.

## 2. Experimental procedure

### 2.1. Preparation of $cCo_3O_4$ and $cCo_3O_4$/MWCNT

The $cCo_3O_4$ was prepared via the synthesis method of Feng et al. [12]. The $cCo_3O_4$/MWCNT was prepared through a hydrothermal method with acid-functionalized MWCNT and $Co(CH_3COO)_2\cdot 4H_2O$ (Reagent grade, Sigma-Aldrich) as starting materials. MWCNTs were

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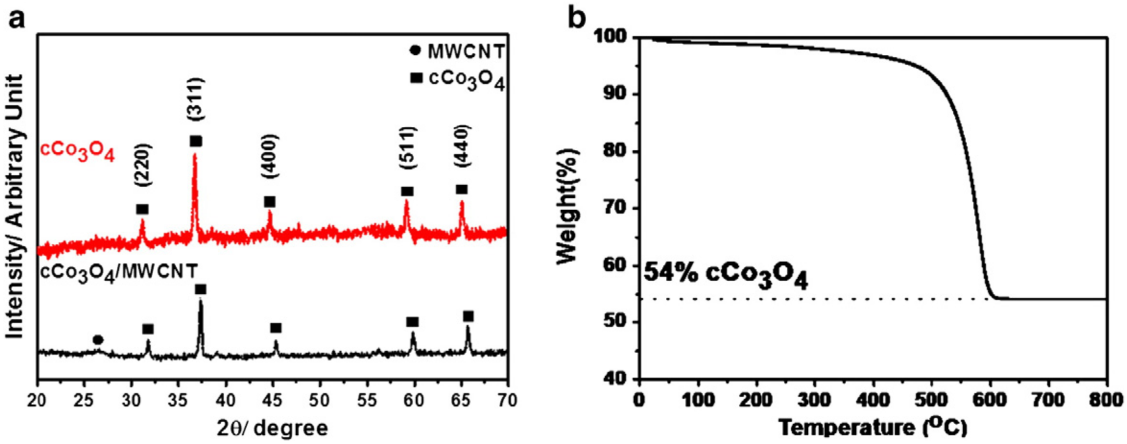

**Fig. 1.** (a) XRD patterns of $cCo_3O_4$ and $cCo_3O_4$/MWCNT and (b) TGA of $cCo_3O_4$/MWCNT.

purchased from MER Corporation., USA. The MWCNTs were treated in 6 M nitric acid at 110 °C for 5 h followed by washing with copious amount water and dried in the oven for further uses. Typically, 45 mg of $Co(CH_3COO)_2 \cdot 4H_2O$ was dissolved in 10 mL of ultrapure water, into which ammonia was added to adjust the pH of solution to 8. Afterwards, 15 mg of the acid-treated MWCNT was dispersed in the above solution by stirring and followed by ultrasonication. The solution was then transferred into an autoclave for 5 h reaction at 150 °C. The resulting black product was collected by centrifuge and dried overnight.

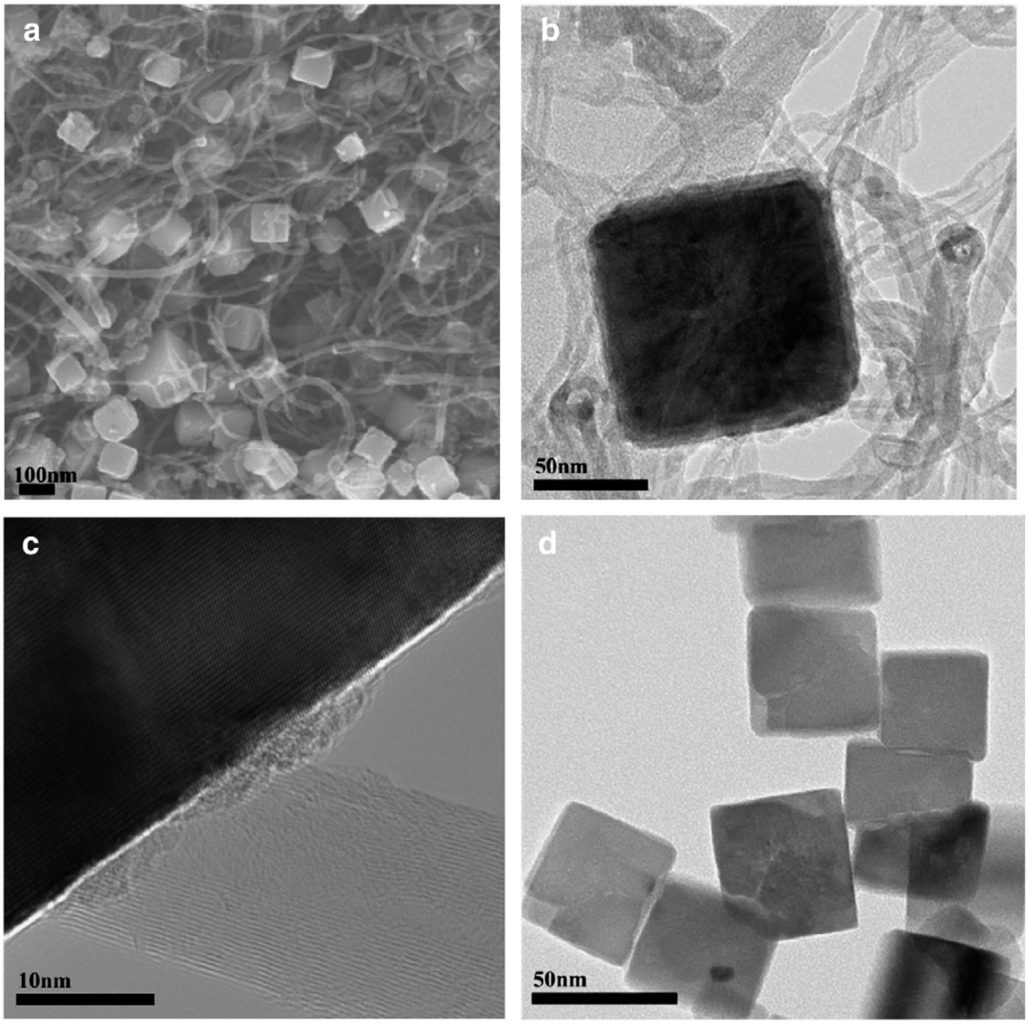

**Fig. 2.** SEM (a) and TEM (b) images of $cCo_3O_4$/MWCNT; HRTEM images of $cCo_3O_4$/MWCNT; and (c) TEM image of pure $cCo_3O_4$ (d).