



Short communication

Morphologically controlled Co_3O_4 nanodisks as practical bi-functional catalyst for rechargeable zinc–air battery applications

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ABSTRACT

The morphological control of Co_3O_4 by polyvinylpyrrolidone during precipitation reaction has resulted in the formation of two-dimensional nanodisks with surface porosity. As a bi-functional catalyst, Co_3O_4 nanodisks are active towards both the oxygen reduction and evolution reactions. The electrocatalytic activity is evaluated by preparing air electrodes for rechargeable zinc–air batteries utilizing ambient air to emphasize practicality. The galvanodynamic charge and discharge behaviors are far superior than Co_3O_4 nanoparticle counterparts particularly at high applied current densities. Electrochemical impedance spectroscopy reveals that Co_3O_4 nanodisk electrode results in significantly less internal, solid-electrolyte interface, and charge transfer resistances which lead to highly efficient electrochemical reactions. Superior rechargeability has also been confirmed where virtually no voltage drops are observed over 60 pulse cycles. The practicality of Co_3O_4 nanodisks is highlighted by demonstrating comparable discharge voltages and greatly outperforming charge voltages with excellent electrochemical stability than commercial Pt/C catalyst.

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1. Introduction

With rising price of fossil fuels and its limited nature, the need for advanced energy conversion and storage devices has never been higher. Metal–air batteries, such as zinc–air and lithium–air batteries, are promising candidates for the next generation energy storage device, which have extremely high theoretical specific energy density for applications such as electric vehicles [1–4]. In addition, metal–air batteries utilize oxygen in the air as the source of fuel, which eliminate on-board fuel reservoir and the use of expensive intercalation materials to generate energy [1]. In particular, zinc–air batteries are interesting and are being highly investigated for their cost competitiveness, environment benignity, and low operation risks [5,6].

For rechargeable zinc–air batteries, the two primary electrochemical reactions required are oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), which correspond to the discharge and charge processes, respectively. However, the intrinsic kinetics of these reactions are sluggish, hence electrocatalysts are used to lower the activation energy to progress them at practical rates [7]. Bi-functional catalysts are extremely beneficial as they are capable of catalyzing both ORR and OER on a single electrode, greatly simplifying the battery

architecture and cost of the battery [8,9]. The most effective catalysts currently available are those based on noble metals, such as platinum and iridium [10,11], however the high costs and electrochemical instability limit their use in zinc–air batteries and hamper wide commercialization. Having said this, non-precious transition metal oxides such as cobalt based spinels are being actively investigated to develop cost competitive, stable, and efficient bi-functional catalyst [7,8,12]. Herein, we introduce two-dimensional nanodisk morphology of cobalt oxide (Co_3O_4) with surface porosity as highly efficient and stable bi-functional electrode material for rechargeable zinc–air battery applications.

2. Materials and methods

2.1. Preparation of Co_3O_4 nanodisks

In a typical synthesis, a solution of 10 mL mixture of double deionized (DDI) water and ethanol in a 1:1 volume ratio containing 1.65 g of 24,000 molecular weight polyvinylpyrrolidone (PVP) and 1.252 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is dissolved by magnetic stirring and bubbled with N_2 for 30 min. Then, 0.213 mL of 1.0 M NaOH solution is added drop-wise at a rate of 0.56 mL min^{-1} resulting in color change of the solution from pink to dark blue as the precipitation reaction proceeds. The mixture is transferred to a sealed Teflon-lined autoclave and heated at 120°C for 6 h. The resulting precipitate is centrifuged three times with DDI water and another three times with acetone at 5000 rpm then freeze-dried for 24 h. Finally, the obtained black powder is calcined in air at 300°C for 3 h to obtain Co_3O_4 nanodisks.

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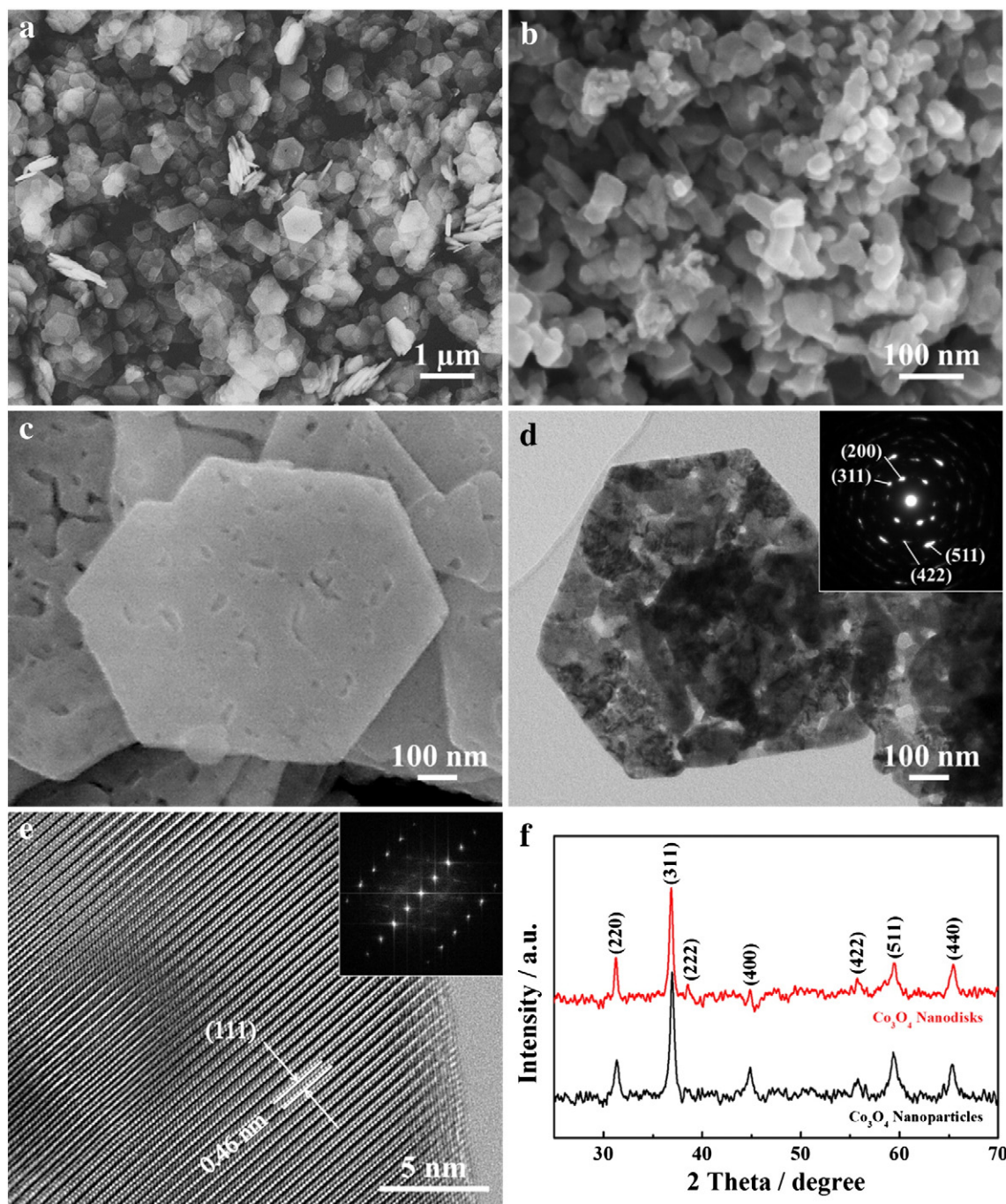


Fig. 1. SEM images of Co_3O_4 (a) nanodisks, (b) nanoparticles, and (c) surface morphology of Co_3O_4 nanodisks. (d) TEM image of Co_3O_4 nanodisks. Inset: SAED pattern. (e) HR-TEM of (111) crystal plane of Co_3O_4 nanodisk. Inset: FFT pattern. (f) XRD patterns of Co_3O_4 nanodisks (red) and nanoparticles (black).

2.2. Materials characterization

Scanning electron microscopy (SEM) (Leo FESEM 1530) and transmission electron microscopy (TEM) (Phillips CM300) are conducted to reveal the morphology and surface features, and high resolution TEM (HR-TEM), fast Fourier transform (FFT) pattern, and selected area electron diffraction (SAED) patterns are used to reveal the crystallinity. X-ray diffraction (XRD) (Bruker AXS D8 Advance) is utilized to confirm the spinel crystal structure of Co_3O_4 nanodisks and nanoparticles.

2.3. Single-cell practical zinc-air battery fabrication

The single-cell catalytic activity is tested by fabricating a home-made zinc-air battery and a multichannel potentiostat (Princeton Applied Research, VersaSTAT MC). For the anode and cathode of the battery, a polished zinc plate (Zinc Sheet EN 988, OnlineMetals) and a catalyst-deposited gas diffusion layer (GDL) (SGL Carbon 10 BB, Ion Power Inc.) are used, respectively. The GDL is prepared by spray-coating a catalyst ink consisting of 10 mg of Co_3O_4 nanodisks and 67 μL of 5 wt.% Nafion (LIQUion™ solution, Ion Power Inc.) dispersed in 1.0 mL

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