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An effective three-dimensional ordered mesoporous $CuCo_2O_4$ as electrocatalyst for Li-O_2 batteries

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ABSTRACT

Three-dimensional ordered mesoporous (3DOM) $CuCo_2O_4$ materials have been synthesized via a hard template and used as bifunctional electrocatalysts for rechargeable Li-O_2 batteries. The characterization of the catalyst by X-ray diffractometry and transmission electron microscopy confirms the formation of a single-phase, 3-dimensional, ordered mesoporous $CuCo_2O_4$ structure. The as-prepared $CuCo_2O_4$ nanoparticles possess a high specific surface area of 97.1 $m^2\ g^{-1}$ and a spinel crystalline structure. Cyclic voltammetry demonstrates that mesoporous $CuCo_2O_4$ catalyst enhances the kinetics for either oxygen reduction reaction (ORR) or oxygen evolution reaction (OER). The Li-O_2 battery utilizing 3DOM $CuCo_2O_4$ shows a higher specific capacity of 7456 mAh g^{-1} than that with pure Ketjen black (KB). Moreover, the $CuCo_2O_4$-based electrode enables much enhanced cyclability with a 610 mV smaller discharge–recharge voltage gap than that of the carbon-only cathode at a current rate of 100 mA g^{-1}. Such excellent catalytic performance of $CuCo_2O_4$ could be associated with its larger surface area and 3D ordered mesoporous structure. The excellent electrochemical performances coupled with its facile and cost-effective way will render the 3D mesoporous $CuCo_2O_4$ nanostructures as attractive electrode materials for promising application in Li-O_2 batteries.

1. Introduction

Rechargeable lithium-oxygen (Li-O_2) batteries have received much research attention recently due to its much higher theoretical energy density (3505 Wh kg^{-1}) compared to current state-of-the-art lithium-ion batteries and have been considered to be one of the most promising systems as high-energy storage in the electric vehicle field [1–3]. A typical nonaqueous rechargeable Li-oxygen battery is composed of Li metal as the negative electrode, a Li-ion conducting nonaqueous electrolyte, and porous oxygen diffusion cathode. During the discharge process, oxygen is reduced in pores of the positive electrode and then combines with the Li-ions to form Li_2O_2 (oxygen reduction reactions, ORRs), the reverse reaction occurs during the charging process (oxygen evolution reactions, OERs) [4–5]. However, before their practical applications, there are many obstacles to overcome such as low round-trip efficiency, low rate capability, and poor cycling stability [6–8].

Recently, great efforts have been made to improve the charge performance of Li-oxygen batteries by employing bifunctional catalyst in oxygen electrode. These catalysts mainly include noble metals [5,9–11], metal nitrides [12,13], and also various classes of metal oxides [14–16]. Among those catalysts, covalent hybrids of spinel metal oxides have higher electrochemical activities as catalysts for Li-O_2 batteries [17,18]. Spinel oxides, having a general formula of AB_2O_4 (A, metal cation occupying tetrahedral sites; B, metal cation occupying octahedral sites), are a family of important technological materials because they have intriguing properties and widespread applications in many fields such as drug delivery, catalysts, energy storage and conversion, and so on [19–22]. Among spinel-type oxides, cobalt oxides have drawn the most potential because of reasonably good catalytic activity, low cost, ease of preparation, and good chemical stability. However, due to the toxicity and high cost of cobalt, one of the worthwhile efforts is to partially replace the Co in Co_3O_4 by cheaper and more eco-friendly alternative metals. For example, Dai's group developed a covalently coupled $MnCo_2O_4$-graphene hybrid as an oxygen cathode catalyst [17]. The hybrid catalyst exhibited much better cycling stability of the Li-O_2 battery than Pt/C through charge and discharges with a capacity cutoff of 1000 mAh g^{-1} over 40 cycles, with little change in the discharging and charging potentials. Cui et al. [23] reported mesoporous $NiCo_2O_4$ nanoflakes as electrocatalysts for rechargeable Li-O_2 batteries. The as-

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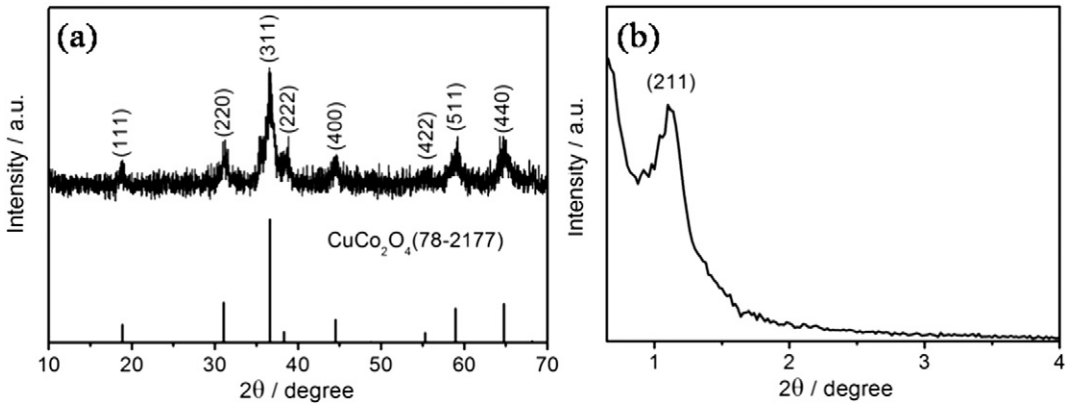

Fig. 1. Wide-angle (a) and low-angle (b) XRD patterns of the 3DOM $CuCo_2O_4$ samples.

prepared $NiCo_2O_4$ has a specific nanostructure with numerous catalytic active sites. The battery with a $NiCo_2O_4$-based cathode exhibited an improved performance, including lower overpotential than pure carbon, reasonable specific capacity (1560 mAh g^{-1}), and enhanced cyclability with 10 stable cycles. Recently, spinel $CuCo_2O_4$ nanocrystals have been investigated as a cathode material in Li-oxygen batteries [24]. The authors found that the $CuCo_2O_4$/KB electrode exhibits much lower polarization, better rate capability, and longer cycling life. In the simulated air conditions, the battery delivers a high capacity of 7962 mA h g^{-1} with a discharge–recharge voltage gap of 0.95 V at 50 mA g^{-1}.

Mesoporous materials, which not only provide more electrocatalytic sites but also promote mass transport (oxygen and ions) in the electrolyte, have been reported as electrocatalysts for rechargeable Li-O_2 batteries [23,25–29]. In this work, we report 3-dimensional (3D), ordered mesoporous $CuCo_2O_4$ (3DOM $CuCo_2O_4$) electrocatalyst synthesized via a hard-template method. In contrast with the reported $CuCo_2O_4$ nanocrystals, our as-prepared $CuCo_2O_4$ has an ordered 3D mesoporous structure with many more electrocatalytic active sites, which would lead to an excellent bifunctional electrocatalytic performance for the ORR/OER in nonaqueous Li-O_2 batteries. When used as cathodes in Li-O_2 batteries with nonaqueous electrolytes, 3DOM $CuCo_2O_4$ electrocatalyst alleviated polarization and improved the cyclability of batteries.

2. Experimental

2.1. Synthesis of materials

All the chemical reagents were analytical grade and used without further purification. KIT-6 was purchased from Nanjing Xfnano Materials Tech Co., Ltd., China. In a typical procedure [28,29], 0.3 g KIT-6 mesoporous silica template was impregnated with 1 mmol $Cu(NO_3)_2 \cdot 3H_2O$ and 2 mmol $Co(NO_3)_2 \cdot 6H_2O$ dissolved in 3.0 mL ethanol by stirring at room temperature until ethanol was totally volatilized; the sample was then heated slowly to 300 °C and calcined at the same temperature for 2 h to pyrolyze the nitrate. The impregnation procedure was repeated twice with 0.6 and 0.3 times the amounts for $Cu(NO_3)_2 \cdot 3H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$, respectively, and then the samples were calcined at 380 °C for 5 h in a muffle under an air atmosphere for crystallization of the metal oxide. Subsequently, the silica matrix was removed with a 2 M NaOH solution at 60 °C for 24 h under magnetic stirring. Finally,

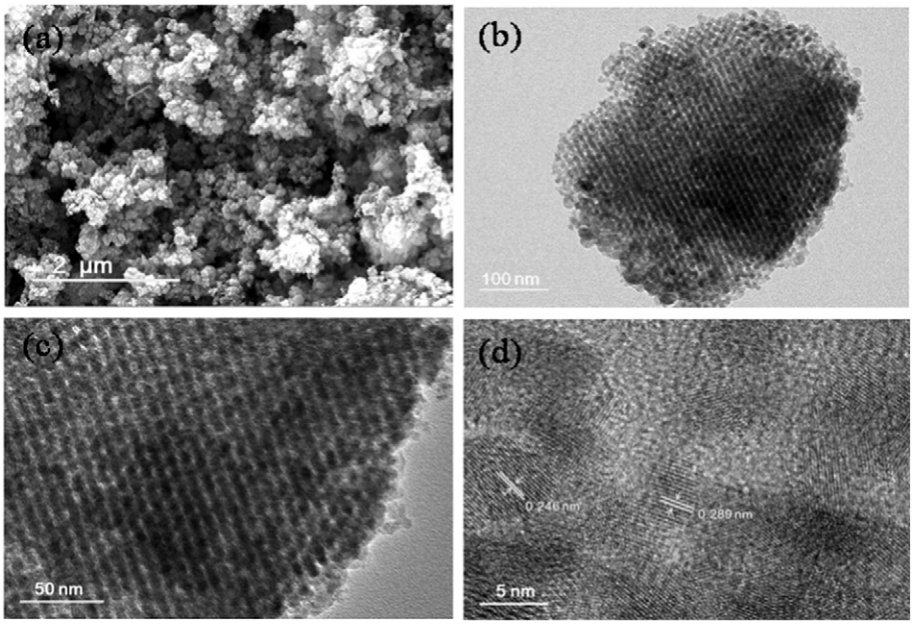

Fig. 2. (a) SEM, (b, c) TEM, and (d) HRTEM images of as-prepared ordered 3D mesoporous $CuCo_2O_4$.