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Self-supported hierarchical hollow-branch cobalt oxide nanorod arrays as binder-free electrodes for high-performance lithium ion batteries

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ABSTRACT

In this work, hierarchical hollow-branch CoO nanorod arrays are synthesized by an electrodeposited template method. Interestingly, the as-prepared hierarchical CoO arrays possess combined properties of hollow core and interconnected nanosheet branches. As anode for lithium ion batteries, the hollow-branch CoO nanorod arrays exhibit impressive electrochemical performances with good cyclability and high-rate capability due to the unique hollow-branch architecture with fast ion/electron transfer path and sufficient contact between active materials and electrolyte. The developed methodology enables a new fabrication of hierarchical hollow metal oxides with applications in electro-catalysis, optical and electrochemical devices.

1. Introduction

The pursuit for better performing, longer lasting lithium ion batteries (LIBs) is driven by the rising demand of battery-powered devices, and machinery [1]. In order to increase the energy output and reduce the battery weight, exploring anode materials with high specific capacities to substitute the commercial graphite is an attractive route [2]. To date, transitional metal oxides have been widely studied as promising candidates because of their high specific capacity, typically 2–3 times higher than that of the carbon based materials [3–5]. Among them, CoO has attracted increasing attention due to its high theoretical capacity (718 mAh g^{-1}) [6], arising from the reversible electrochemical reaction with Li ion ($CoO+2Li^{+}+2e \leftrightarrow Co+Li_2O$). However, similar to other metal oxides, the practical application of CoO as anode for LIBs is still hampered by two main issues: pulverization problem and fast capacity fading [7,8]. To overcome these problems, integrated binder-free arrays electrodes have been developed to improve the power/energy densities and cycling stability. The integrated arrays electrodes possess three main advantages. First, no extra preparation process of electrode and avoid undesirable supplementary interfaces. Second, it offers better electrical contact. Third, the open space between the adjacent porous arrays allows for better accommodation of large volume changes and stress. All these favorable characteristics accelerate the reaction kinetics leading to higher capacity and energy/power density.

In this work, we report hierarchical hollow-branch CoO nanorod arrays directly on the nickel foil by a facile electrodeposited template method. Highly porous structure with hollow core and interconnected branch nanosheets is obtained by the combination of electro-deposition and dissolving sacrificial ZnO template. As an integrated anode for LIBs, the CoO nanorod arrays exhibit high capacity and noticeable high-rate capability due to the porous array structure. The proposed method is applicable for preparation of other metal oxide arrays for applications in catalysis and energy storage and conversion.

2. Experimental

Firstly, the nickel foil was coated with a ZnO seed layer (thickness ~10 nm) by atomic layer deposition (ALD Beneq TFS 200) with Diethyl zinc (DEZ, 99.99%, Sigma Aldrich) and H_2O as the Zn and O precursors, respectively. Afterwards, the sample was placed into autoclave liners with 50 mL solution containing 0.75 g $Zn(NO_3)_2$ and 0.35 g hexamethylenetetramine and kept at 95 °C for 9 h to obtain ZnO nanorod arrays. Then, CoO was assembled on the ZnO nanorod arrays through a simple cathodic electrodeposition method, which was performed in a standard three-

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electrode cell at 25 °C, the above self-supported ZnO nanorod arrays electrode as the working electrode, saturated calomel electrode (SCE) as the reference electrode and a Pt foil as the counter-electrode. The electrolyte consisted of 0.5 M $Co(NO_3)_2$+0.1 M $NaNO_3$. The electro-deposition was conducted at a current density of 0.5 mA cm^{-2} for 15 min. Then, the sample was immersed into the 0.5 M KOH for 10 min to remove the ZnO template and followed by annealing at 350 °C for 2 h in Ar to obtain self-supported hierarchical hollow-branch nanorod arrays. The load weight of CoO is about 1.1 mg cm^{-2}.

The morphology and microstructure of the samples were characterized by X-ray power diffraction (XRD, Rigaku D/max 2550PC, Cu Kα), a scanning electron microscopy (SEM, Hitachi S-4700 and FESEM, FEI Sirion-100) and transmission electron microscopy (TEM, JEM 200CX at 160 kV, Tecnai G2 F30 at 200 kV).

The electrochemical tests were performed using a coin-type half cell (CR 2025). Test cells were assembled in an Ar-filled glove box with pure lithium foil as both the counter and the reference electrodes. The separator was polypropylene (PP) micro-porous film (Cellgard 2300), 1 M $LiPF_6$ in ethylene carbonate (EC)-dimethyl carbonate (DME) (1:1 in volume) as the electrolyte. The cyclic voltammetry was scanned at 0.1 mV s^{-1} using an electrochemistry system (CHI660E). The galvanostatic charge/discharge tests were conducted on a LAND battery program-control test system at room temperature.

3. Results and discussion

Fig. 1a shows that the skeletons of the nickel foil are uniformly covered by the ZnO nanorods with diameters of ~100 nm. The ZnO nanorods are hexagonal-shaped and their outer surfaces are very smooth. Fig. 1b presents the TEM images of a single ZnO nanorod. Selected area electron diffraction (SAED) pattern reveals that the ZnO nanorod belongs to hexagonal ZnO phase (JCPDS 36-1451) with single crystal nature. After electro-deposition and etching the ZnO temple, notice that hierarchical porous CoO nanorod arrays are formed and the 3D array architecture is well preserved. The CoO nanorods have diameters of 250–300 nm, and consist of interconnected nanosheets. Moreover, there are lots of open pores ranging from 20–100 nm between interconnected nanosheets. TEM result of the CoO nanorods (Fig. 1d) verifies that their structure is composed of randomly self-stacked sheet-like CoO building-blocks. Moreover, a hollow center structure is confirmed. All

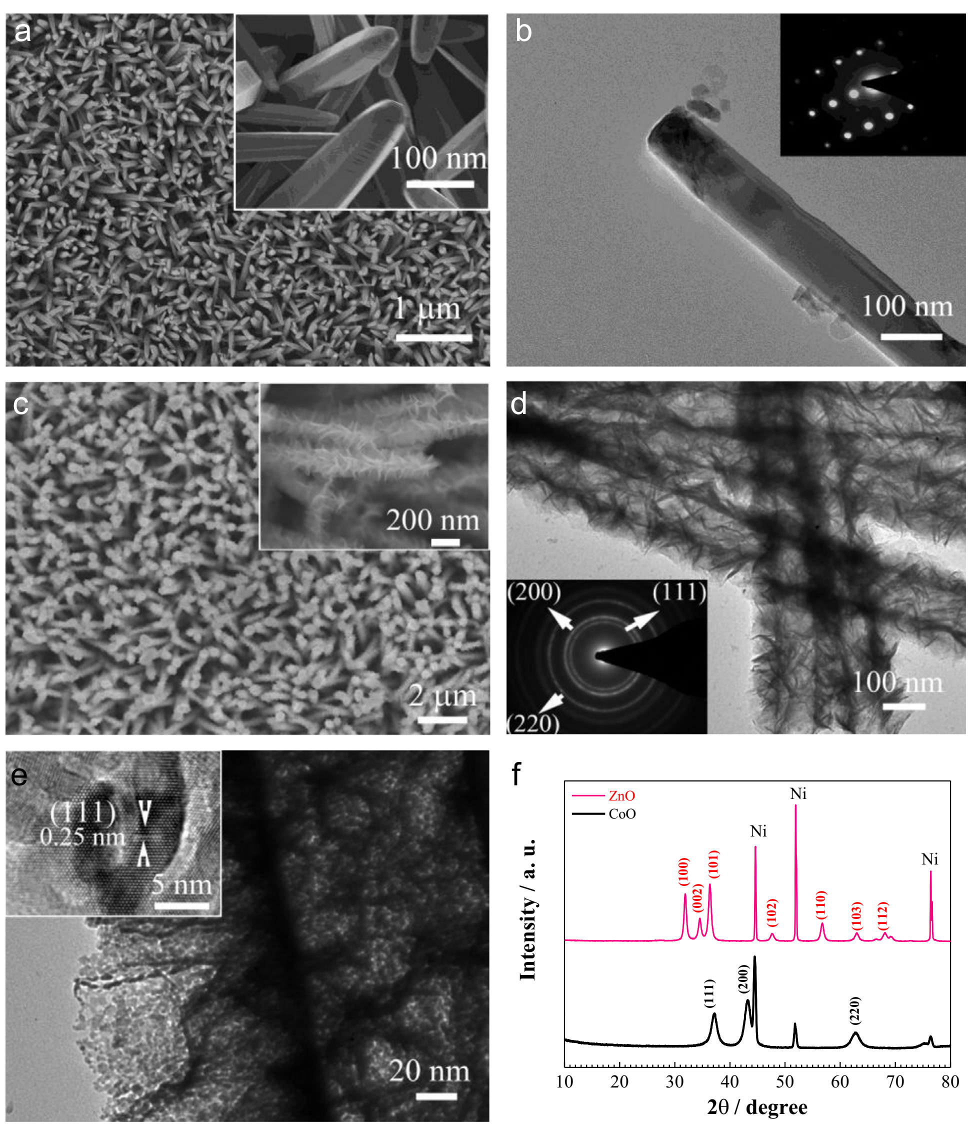

Fig. 1. (a) SEM image and (b) TEM image of ZnO nanorod arrays (SAED pattern in inset); (c) SEM image and (d, e) TEM images of CoO nanorod arrays (SAED pattern in inset); and (f) XRD patterns of CoO and ZnO nanorod arrays.