



Electrodeposited thin cobalt branch on cobalt oxides core exhibiting enhanced electrochemical properties



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ABSTRACT

Rational design/fabrication of metal oxide/metal composite arrays is critical for construction of advanced energy storage devices. Herein, we assemble ultrathin Co shell on the preformed Co_3O_4 nanowires core forming porous $\text{Co}_3\text{O}_4/\text{Co}$ core/shell arrays. In such a composite structure, nanowire arrays possess open spaces for shorter ion diffusion length, while ultrathin metal Co shell has high electronic conductivity for fast electron transfer. As an anode of lithium ion batteries, enhanced Li ion storage properties have been demonstrated for the $\text{Co}_3\text{O}_4/\text{Co}$ composite nanowire arrays. At a high current density of 3 A g^{-1} , the specific capacity of $\text{Co}_3\text{O}_4/\text{Co}$ electrode is up to 642 mAh g^{-1} , which is much higher than that (440 mAh g^{-1}) of the pristine Co_3O_4 nanowires electrode. These results indicate that conformal deposition of ultrathin metal shell can efficiently enhance the Li ion storage performance of metal oxides.

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1. Introduction

Lithium ion batteries (LIBs) have become one of the most successful commercialized energy storage devices [1–3]. The growing demands for high energy/power applications have encouraged great research efforts to develop cost-effective and high-performance electrode materials for LIBs [4–7]. However, current commercial graphite based anodes have a relatively low theoretical capacity of $\sim 372 \text{ mAh g}^{-1}$, which is far below large-scale energy applications. Thus, it is highly critical to explore alternative anode materials that could endow LIBs with both higher energy density and better rate performance. Cobalt oxide based materials have attracted great attention as promising anode materials [8,9]. Particularly, Co_3O_4 can theoretically deliver as high as three times the capacity of graphite due to its 8-electron transfer reaction upon cycling [10]. However, the poor ionic and electronic conductivity of Co_3O_4 electrodes results in slow reaction kinetics and insufficient Li storage performance [11], especially at high discharge/charge rates requiring fast ion/electron transportation.

There has been a variety of reports of preparing different Co_3O_4 nanostructures for LIBs application. [12–15] According to the published electrode configurations, these works can be classified into two basic types: (i) binder-enriched [16] and (ii) binder-free

[17,18]. In the former case, the Co_3O_4 powder electrode needs to be fabricated by traditional slurry-coating technique for electrochemical measurement. Despite much progress, the binder involved will greatly decrease the electrical conductivity of the electrode materials and undermine the nanoscale advantage. For the latter case, electro-active Co_3O_4 nanostructures (such as arrays and films) are directly grown on conductive substrates forming binder-free electrodes. This kind of electrode architectures avoids the use of auxiliary components like conductive agents and binders and exhibit good electrochemical properties due to well-defined electrode network with tailored porosity and good mechanical stability [19]. In addition, to further increase electronic conductivity of Co_3O_4 , the typical way is to combine Co_3O_4 with various conductive components (such as graphene [20,21], carbon nanotube [22], carbon nanofibre [23]) for forming a hybrid nanostructure. In recent years, construction of metal shell or coating on the metal oxides arrays is considered as a new type of modification strategy to enhance the performance of LIBs [5]. Typically, ultrathin porous metal shell possesses higher electrical conductivity than the carbon, and meanwhile, will not block the fast transfer of ions. Nevertheless, the conformal deposition of ultrathin metal shell still remains challenge, and needs to be further explored.

In this paper, different from previous metal modified works, herein we report a facile method for controllable synthesis of ultrathin Co on the preformed Co_3O_4 nanowires forming composite nanowire arrays. High electrical conductivity and porosity are

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combined together in this $\text{Co}_3\text{O}_4@\text{Co}$ core/shell arrays. The electrochemical properties of the $\text{Co}_3\text{O}_4@\text{Co}$ core/shell nanowire arrays for Li ion insertion/extraction are investigated in detail and enhanced performance is clearly demonstrated. Our electrode design method can provide a new way for construction of advanced metal shell based electrodes.

2. Experimental

2.1. Synthesis of porous Co_3O_4 nanowire arrays

Commercial nickel foils were cleaned by sonication sequentially in acetone, and ethanol for 15 min, respectively, and then used as the substrates. In a typical synthesis of Co_3O_4 nanowire arrays, 3 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2 mmol of NH_4F , and 6 mmol $\text{CO}(\text{NH}_2)_2$ were dissolved in 80 mL H_2O . The above solution was then transferred into a Teflon-lined stainless autoclave and maintained at 120°C for 9 h. After the autoclave cooled down to room temperature, the product was collected and washed, and then annealed at 350°C in air for 3 h.

2.2. Synthesis of porous $\text{Co}_3\text{O}_4@\text{Co}$ core/shell nanowire arrays

The self-supported Co_3O_4 nanowire arrays were used as the backbone for the growth Co shell by a simple electro-deposition method. The electro-deposition was performed in a two-electrode glass cell at 25°C in the electrolyte consisting of 0.05 mol L^{-1} cobalt sulfate + 0.1 mol L^{-1} ammonium chloride, the above Co_3O_4 nanowire arrays as the working electrode, and a Pt foil as the counter electrode. The electro-deposition was carried out at 2.5 mA cm^{-2} for 10 min to form $\text{Co}_3\text{O}_4@\text{Co}$ core/shell nanowire arrays. The load weight of Co_3O_4 and Co is about 2.2 and 0.25 mg cm^{-2} , respectively.

2.3. Material characterization

The morphology of the samples was characterized by field emission scanning electron microscopy (FESEM; JEOL, Model JSM-7600F) and transmission electron microscopy (TEM; JEOL, Model JEM-2100). The crystal structure of the products was analysed by X-ray diffraction (XRD; Philips PC-APD) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), operating at 40 kV, 60 mA.

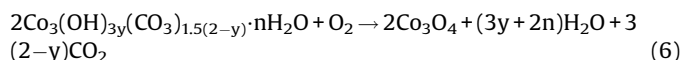
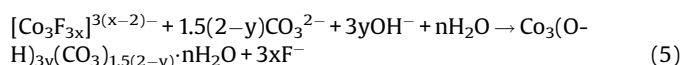
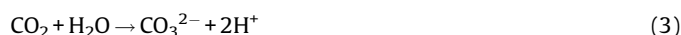
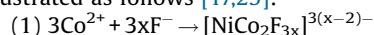
2.4. Electrochemical measurement

Electrochemical performances of the $\text{Co}_3\text{O}_4@\text{Co}$ core/shell nanowire arrays were characterized in a coin-type cell (CR 2025) assembled according to the Ref. [24]. The coin-type cells

were assembled in an argon-filled glove-box, where both moisture and oxygen levels were less than 1 ppm. Lithium foils were used as counter/reference electrodes, Celgard 2400 membrane was used as the separator, and 1 M LiPF_6 dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1/1, wt./wt.) was used as an electrolyte. All the cells were tested by an NEWARE multi-channel battery test system with galvanostatic charge and discharge. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed on CHI660C electrochemical workstation.

3. Results and discussion

The simplified schematic diagram of the formation process of the $\text{Co}_3\text{O}_4@\text{Co}$ core/shell nanowire arrays is shown in Fig. 1. In the first step, porous Co_3O_4 nanowire arrays are prepared by combining hydrothermal method and following thermal treatment. The Co_3O_4 nanowires come from thermal decomposition of basic cobalt carbonate hydroxide nanowires. The reactions involved for Co_3O_4 nanowires have been discussed and can be illustrated as follows [17,25]:



In the second step, ultrathin Co shell is conformably deposited on porous Co_3O_4 nanowires core with the help of electro-deposition method (Fig. 1). The morphology of the as-prepared samples is characterized by FESEM. It is seen that the Co_3O_4 nanowires with sharp tips are grown uniformly on the substrate forming array structure. The low magnification FESEM image (Fig. 2b) demonstrates the large-area growth of Co_3O_4 nanowire arrays. After electro-deposition of Co (Fig. 2c), note that each Co_3O_4 nanowire is interconnected by thin Co shell forming composite

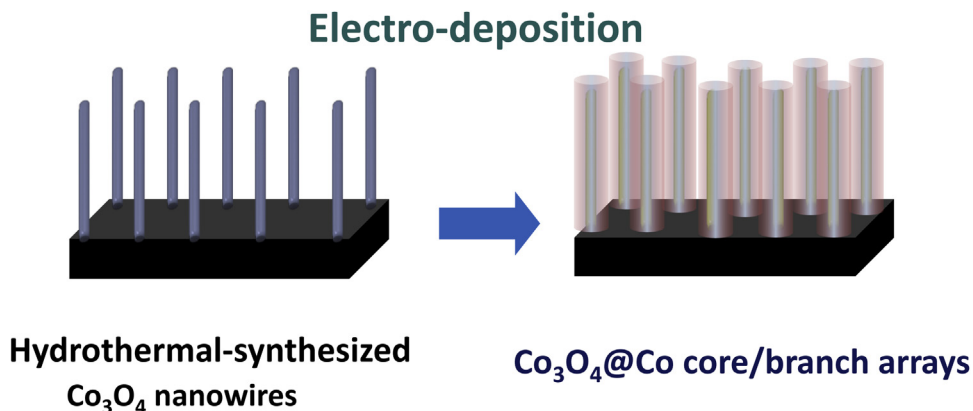


Fig. 1. Synthesis process of $\text{Co}_3\text{O}_4@\text{Co}$ core/branch nanowires arrays.

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