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Synthesis of metal shell on metal oxides nanowires forming composite core/branch arrays with enhanced electrochemical properties

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ABSTRACT

In this work, we develop a facile electro-deposition method to assemble Co ultrathin shell on the Co_3O_4 nanowires forming Co_3O_4@Co core/branch arrays (CBAs). Co nanoshell of 5–10 nm is homogeneously connected with each other and forms a conductive "armor" on the Co_3O_4 nanowires. Attractive advantages including high electronic conductivity and large porosity are combined in the designed core/branch architecture. Compared with the unmodified Co_3O_4 nanowires, the Co_3O_4@Co CBAs have been demonstrated with higher capacity and better cycling stability. A specific capacity of 649 mAh g^{-1} is obtained for the Co_3O_4@Co electrode at 3 A g^{-1}, much higher than that (431 mAh g^{-1}) of the Co_3O_4 nanowires counterpart. In addition, after 300 cycles at 0.25 A g^{-1}, the Co_3O_4@Co electrode delivers a stable capacity of 863 mAh g^{-1}, better than the pristine Co_3O_4 counterpart (686 mAh g^{-1}) owing to better conductive networks and more stable electrode structure.

1. Introduction

The growing demand for high energy/power applications has encouraged great research efforts to develop cost-effective and high-performance electrode materials for lithium ion batteries (LIBs) [1–4]. However, commercial graphite anodes have a relatively low theoretical capacity of ~372 mAh g^{-1}, and can not meet the large-scale energy applications. Therefore, it is highly critical to explore alternative anode materials with both higher energy density and better high-rate performance [5–9]. Particularly, Co_3O_4 is one of promising anodes and can deliver as high as three times the capacity of graphite due to 8e reactions [10]. However, the poor electrical conductivity of Co_3O_4 electrodes results in slow reaction kinetics and insufficient Li storage performance [11], especially at high rates requiring fast ion/electron transportation.

There has been a variety of reports on different Co_3O_4 nanostructures (nanoparticles, nanowires, nanoflakes and so on) for LIBs application [12–17]. These works can be classified into two basic types: (1) binder-enriched electrodes [18], and (2) binder-free electrodes [19,20]. For the first case, the Co_3O_4 powder needs to be mixed with polymer binders and additives to form testing electrodes for electrochemical measurement. But the insulating binder will greatly decrease the electrical conductivity of the electrode and undermine the nanoscale advantage. For the second case, nanostructured Co_3O_4 arrays and films are directly grown on conductive substrates forming binder-free electrodes. This integrated electrode architecture avoids the use of binders and exhibit good electrochemical properties due to better conductive network with tailored porosity and good mechanical stability [21,22]. In addition, to further increase electrical conductivity of Co_3O_4 electrode, the popular approach is to rationally combine Co_3O_4 with various conductive matrixes (e.g., graphene [23,24], carbon nanotube [25], carbon nanofibre [26]) to forming hybrid conductive nanostructure. In recent years, construction of metal shell/coating on the metal oxides arrays is considered as an effective strategy to enhance the performance of LIBs [21]. 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 on metal oxides core still remains challenge, and needs to be further explored.

In this paper, different from previous modified works, herein we

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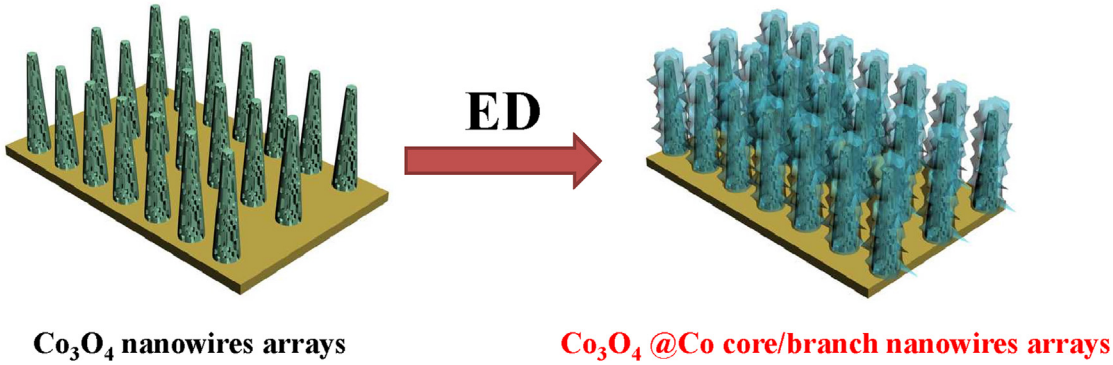

Fig. 1. Schematics of fabrication process of Co_3O_4@Co core/branch nanowires arrays.

report a facile electro-deposition method for controllable synthesis of ultrathin Co shell on the Co_3O_4 nanowires forming composite core/branch arrays. High electrical conductivity and large porosity are combined together in the Co_3O_4@Co CBAs. The electrochemical properties of the Co_3O_4@Co CBAs for Li ion storage are investigated in detail and enhanced performance is 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@Co core/branch arrays

The Co_3O_4@Co core/branch nanowire arrays were prepared by the combined hydrothermal and electro-deposition methods. First, nickel foils were cleaned and then used as the substrates. In a typical synthesis of Co_3O_4 nanowire arrays, 2.5 mmol of $Co(NO_3)_2 \cdot 6H_2O$, 5 mmol of NH_4F, and 12.5 mmol $CO(NH_2)_2$ were dissolved in 100 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 argon for 2 h. Then, the self-supported Co_3O_4 nanowire arrays were used as the backbone for the growth Co shell by a simple electro-deposition method, which was performed in a two-electrode glass cell at 25 °C in 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 Co_3O_4@Co core/branch nanowire arrays. In our case, the ammonium chloride was used to control the pH value. The pH value of the electrolyte was about 4 to control the deposition of Co. The reactions for the deposition of Co shell can be expressed as follows: $CoSO_4 + NH_4Cl + 2e^- \rightarrow Co + NH_4^+ + Cl^- + SO_4^{2-}$. The load weight of Co_3O_4 and Co is about 2.2 and 0.25 mg cm^{-2}, respectively.

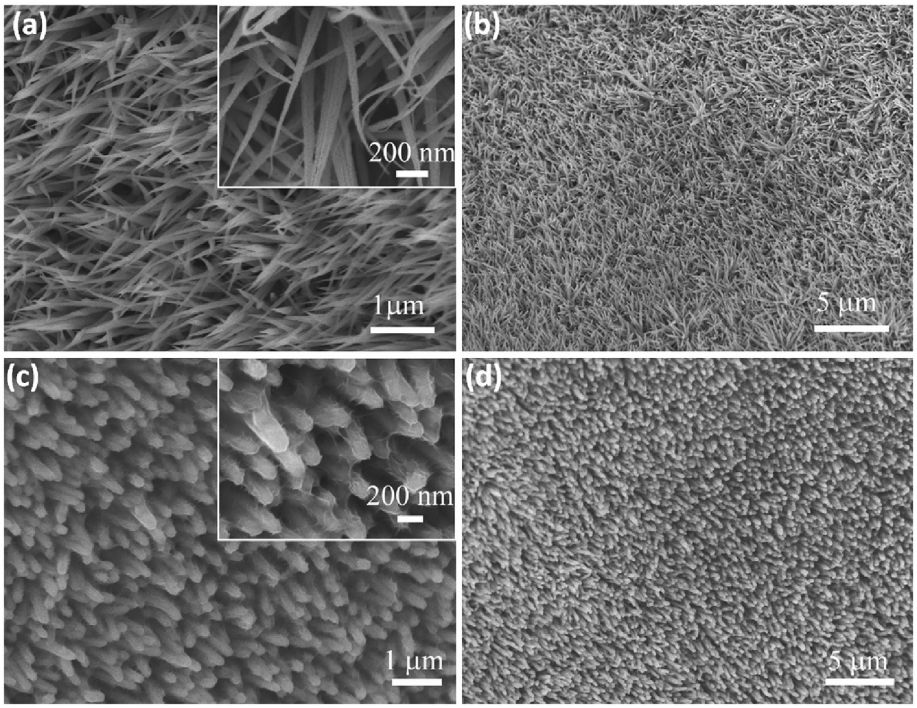

Fig. 2. SEM images of (a, b) Co_3O_4 nanowires and (c, d) Co_3O_4@Co core/branch nanowires arrays.