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Short communication

Ternary core/shell structure of Co_3O_4/NiO/C nanowire arrays as high-performance anode material for Li-ion battery

J.B. Wu*, R.Q. Guo*, X.H. Huang, Y. Lin

School of Physics & Electronic Engineering, Taizhou University, Taizhou, Zhejiang 318000, China

HIGHLIGHTS

- Construct a self-supported porous Co_3O_4/NiO/C core/shell nanowire array.
- Core/shell nanowire array shows high Li ion battery properties.
- Core/shell nanowire array structure is favorable for fast ion and electron transfer.

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ABSTRACT

Self-supported core/shell nanowire arrays are highly desirable for designing high-performance electrochemical energy storage devices. Herein, we report self-supported ternary core/shell nanowire arrays of Co_3O_4/NiO/C on the nickel foam with the help of hydrothermal synthesis, chemical bath deposition and annealing carbonation methods. As an anode material for lithium ion batteries, the Co_3O_4/NiO/C core/shell nanowire arrays exhibit excellent electrochemical performances with lower polarization, higher capacity, improved cycle life and better high-rate capability than the pure Co_3O_4 nanowire arrays and single NiO nanoflake arrays. The enhanced electrochemical properties are mainly ascribed to the core/shell nanowire architecture with potential synergistic contribution such as improved mechanical stability and enhanced conductivity as well as faster ion/electron transfer.

1. Introduction

Lithium ion batteries (LIBs) are one of the most popular power sources for consumer electronics and electric vehicles [1–3]. To date, various materials have been exploited as the anode materials for LIBs, such as graphitic/non-graphitic carbon [4,5], graphene [6], transition metal oxides (Co_3O_4 [7], NiO [8], Fe_2O_3 [9], MnO_2 [10], SnO_2 [11], TiO_2 [12], WO_3 [13], etc.), Li alloys with Si and Sn [14,15], polymers [16], nitrides [17], and transition metal phosphide (M–P, M = Fe, Co, Ni, Cu, etc.) [17,18]. Among them, transition metal oxides have attracted extensive interest for LIBs due to their high theoretical capacity (several times larger than that of graphite, for example, the theoretical capacity of Co_3O_4 and NiO is 890 and 718 mA h g^{-1}, respectively), low cost, environmental friendliness, and natural abundance. However, they suffer from large volume expansion/contraction and severe aggregation associated with the Li^+ insertion and extraction process. These problems lead to electrode pulverization and loss of active materials, and cause a large irreversible capacity loss and poor cycling stability. Furthermore, the low conductivity of transition metal oxides aggravates the fading process especially at high current densities. It is highly desirable to design and fabricate high-performance transition metal oxides electrode by modifying or ameliorating their kinetics issue. To meet the requirement of high capacity and structural stability, one promising route is to scrupulously design nanoporous electrode materials and smart hybridization of bespoke materials [19–24].

Recently, a novel kind of electrode design, core/shell nanoarray structure, has been attracted great attention [20,21,25,26]. It has been proposed that integration of active materials into the core/shell hetero-structured nanoarrays can lead to further enhancement of the capacity and stability due to potential synergistic effects, for example, much more efficient utilization of the remaining free space, more efficient electrolyte penetration and structural stability [27,28]. This is especially important for the core/shell structures whose core and shell are both active metal oxides.

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* Corresponding authors. Tel.: +86 576 88661937.
E-mail addresses: wujb@tzc.edu.cn (J.B. Wu), guorqtz@126.com (R.Q. Guo).

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Previously, Liu et al. [20] reported Co_3O_4 nanowire @MnO_2 ultrathin nanosheet core/shell arrays and their high-performance electrochemical properties as pseudo-capacitor electrode due to the unique core/shell structure and compositions. Besides, branched Co_3O_4/Fe_2O_3 nanowires reported by Zheng group showed higher specific capacity and cyclical stability than the single component as anode of LIBs [26]. Tu group synthesized hierarchical Fe_2O_3@Co_3O_4 nanowire array for LIBs and exhibited superior rate capability and cycling stability [29].

On the other hand, electrochemical performances of these core/shell nanomaterials are still unsatisfactory due to the lower conductivity of metal oxides compared with that of metal and carbon. A possible and facile method is to coat a thin layer of carbon on transition metal oxides to further improve the electrochemical performance. Previously, Tu group synthesized a nanosized $LiFePO_4$/C composite with a homogeneous and thin carbon-shell, and exhibited noticeable high rate capability and good cycling performance [30]. Recently, Chen et al. reported Co_3O_4 nanowire arrays coated by a thin layer of sputtered carbon and their improved electrochemical performances as compared to the bare Co_3O_4 [7]. The carbon shell not only provides a flexible buffer to accommodate the volume change during lithium insertion/extraction, but also increases the conductivity of the electrode. Even so, there is still much space for progress to fabricate high-performance Co_3O_4 based anode materials with enhanced cycle performance and high rate capability. Inspired by the results above, herein, we report a ternary Co_3O_4/NiO/C core/shell nanowire arrays synthesized via a three-step solution method with the aid of hydrothermal synthesis, chemical bath deposition and facile annealing carbonation. Free-standing Co_3O_4 nanowire arrays act as the backbone for the growth of NiO nanoflake shell and carbon layer. The electrochemical performances of the Co_3O_4/NiO/C core/shell nanowire arrays as the anode material for LIBs are fully characterized and show superior properties to the single Co_3O_4 nanowire and NiO nanoflake arrays.

2. Experimental

First, self-supported Co_3O_4 nanowire arrays were prepared by a facile hydrothermal synthesis method. The solution was prepared by dissolving 2 mmol of $Co(NO_3)_2$, 4 mmol NH_4F, and 10 mmol of $CO(NH_2)_2$ in 70 mL of distilled water. Then this resulting solution was transferred into Teflon-lined stainless steel autoclave linear. Nickel foams were immersed into the reaction solution. Top sides of the substrates were uniformly coated with a polytetrafluoroethylene tape to prevent the solution contamination. The linear was sealed in a stainless steel autoclave and maintained at 110 °C for 5 h and then cooled to room temperature. The samples were collected and rinsed with distilled water several times. Finally, the samples were annealed at 350 °C in normal purity argon for 2 h to obtain Co_3O_4 nanowire arrays. The porous Co_3O_4 nanowire arrays come from the thermal decomposition of precursor–basic cobalt carbonate hydroxide $Co_2(OH)_2CO_3$ nanowire arrays after heat-treatment. The reactions involved may be illustrated as follows [21].

$$Co^{2+} + xF^- \rightarrow [CoF_x]^{(x-2)-} \tag{1}$$

$$H_2NCoNH_2 + H_2O \rightarrow 2NH_3 + CO_2 \tag{2}$$

$$CO_2 + H_2O \rightarrow CO_3^{2-} + 2H^+ \tag{3}$$

$$NH_3 \cdot H_2O \rightarrow NH_4^+ + OH^- \tag{4}$$

$$2[CoF_x]^{(x-2)-} + CO_3^{2-} + 2OH^- + nH_2O \rightarrow Co_2(OH)_2CO_3 \cdot nH_2O + 2xF^- \tag{5}$$

During annealing process:

$$3Co_2(OH)_2CO_3 \cdot nH_2O + O_2 \rightarrow 2Co_3O_4 + (3n+3)H_2O + 3CO_2 \tag{6}$$

Then, the self-supported Co_3O_4 nanowire arrays were used as the scaffold for the growth of NiO nanoflake shell in a simple chemical bath. The Co_3O_4 nanowire arrays grown on nickel foam (masked with polyimide tape to prevent deposition on the back sides) were placed vertically in a 250 mL Pyrex beaker. Solution for chemical bath deposition (CBD) was prepared by adding 20 mL of aqueous ammonia (25–28%) to the mixture of 100 mL of 1 M nickel sulfate and 80 mL of 0.25 M potassium persulfate. Immersing into the CBD solution for 8 min at 20 °C, the substrates were taken off and rinsed with distilled water. The samples were annealed at 350 °C in argon for 1.5 h. Then samples immersed into 0.05 M aqueous glucose solution for 12 h. Finally, the free-standing Co_3O_4/NiO/C core/shell nanowire arrays were formed by carbonization at 450 °C for 2 h in argon. The carbon comes from the decomposition of glucose. The precursor reactions for the growth of NiO nanoflake via CBD are represented as follows [31]:

$$\left[Ni(H_2O)_{6-x}(NH_3)_x\right]^{2+} + 2OH^- \rightarrow Ni(OH)_2 + (6-x)H_2O + xNH_3 \tag{7}$$

$$2Ni(OH)_2 + S_2O_8^{2-} + 2OH^- + H_2O \rightarrow 2NiOOH \cdot H_2O + 2SO_4^{2-} + 2H_2O \tag{8}$$

During annealing process:

$$NiOOH \cdot H_2O - e^- \rightarrow Ni(OH)_2 + OH^- \tag{9}$$

$$Ni(OH)_2 \rightarrow NiO + H_2O \tag{10}$$

For the sake of comparison, individual Co_3O_4 nanowire arrays and NiO nanoflake arrays were also prepared as the same preparation parameters on nickel foam substrates, respectively. The Co_3O_4 nanowire arrays were fabricated by the hydrothermal synthesis method in a 70 mL solution containing 2 mmol of $Co(NO_3)_2$, 4 mmol NH_4F, and 10 mmol of $CO(NH_2)_2$ and kept at 110 °C for 5 h. Then, the samples were annealed at 350 °C in normal purity argon for 2 h to obtain Co_3O_4 nanowire arrays. Meanwhile, the single NiO nanoflake arrays were prepared via the CBD method by adding 20 mL of aqueous ammonia (25–28%) to the mixture of 100 mL of 1 M nickel sulfate and 80 mL of 0.25 M potassium persulfate. Immersing into the CBD solution for 8 min at 20 °C, the nickel foam substrates were taken out and rinsed with distilled water. Finally, the samples were annealed at 350 °C in argon for 1.5 h to form NiO nanoflake arrays.

The morphologies and structures of the as-synthesized samples were characterized by field emission scanning electron microscopy (FESEM, FEI SIRION), X-ray diffraction (XRD, RIGAKU D/Max-2550 with Cu Kα radiation), transmission electron microscopy (TEM, JEOL JEM200CX), high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010F) and Raman spectroscopy (LABRAM HR-800).

For the electrochemical tests, CR2025 coin-type cells were directly fabricated from the core/shell nanowire arrays (Co_3O_4 mass ≈ 1.5 mg cm^{-2}, NiO mass ≈ 0.8 mg cm^{-2}, C