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Synthesis of shish-kebab-like NiO@Co_3O_4 nanowire arrays and their application for electrochemical energy storage

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ABSTRACT

Multicomponent hetero-structured metal oxide arrays are playing important roles in the development of advanced optical and electrochemical devices. Herein, we report shish-kebab-like NiO@Co_3O_4 nanowire arrays by a simple two-step hydrothermal method. Interestingly, lots of hexagonal NiO nanoflakes are randomly assembled on the preformed Co_3O_4 nanowire arrays forming a shish-kebab-like architecture. As cathode of alkaline battery, the as-prepared NiO@Co_3O_4 nanowire arrays exhibit a specific capacity of 89 mAh g^{-1} at 1.25 A g^{-1} and 75 mAh g^{-1} at 20 A g^{-1}, respectively. The unique architecture provides higher reaction surface area resulting in higher capacity.

1. Introduction

Electrochemical energy storage devices with high power/energy density and fast recharge capability have captured great research efforts [1,2]. Among the explored power sources, high-rate alkaline batteries based on metal oxides are one of the representative devices because of their high power density, long cycling life and fast recharge capability [3,4]. The performance of alkaline batteries is mainly determined by the electrochemical reactivity of electrode materials and reaction kinetics. Transition metal oxides (Co_3O_4 [5], NiO [6], MnO_2 [7], etc.) have been widely studied due to their high capacities arising from faradic redox reactions as well excellent redox reactivity. However, these oxide materials often result in compromises of rate capability and reversibility because they rely on faradic redox reactions and the active materials are typically too insulating to support fast electron transport required by high rates.

In the past decades, researchers have reached a consensus that nanoporous design of metal oxides can effectively improve the electrochemical performances by introducing more reaction active sites and shorter ion diffusion path [8]. Until now, many nanostructured metal oxides electrodes, including nanowires [9], nanoflakes [10], nanotubes [7] and core/shell structures [11], have been prepared and demonstrated with enhanced electrochemical performance. Particularly, freestanding one-dimensional (1D) core/shell arrays of metal hydroxides/oxides have sparked great interest due to their interesting physical and chemical properties as compared to the single components. Various metal hydroxides/oxides ($Co(OH)_2/Co_3O_4$) and oxides/oxides (Co_3O_4/MnO_2) core/shell arrays have been synthesized and show superior electrochemical performances [12].

As a new structure, in this work, we report shish-kebab-like NiO@Co_3O_4 nanowire arrays via a simple two-step hydrothermal method. NiO nanoflakes are decorated on the preformed Co_3O_4 nanowire to form a unique shish-kebab-like structure. The electrochemical performances of the as-prepared NiO@Co_3O_4 nanowire arrays as cathode of alkaline batteries are investigated. Compared with the pristine Co_3O_4 nanowire, the as-prepared core/shell arrays exhibit enhanced electrochemical performance with higher capacity and better cycling life.

2. Experimental

The NiO@Co_3O_4 nanowire arrays were prepared by a facile two-step hydrothermal method. First, self-supported Co_3O_4 nanowire arrays were prepared according to the reference [10]. Then, the Co_3O_4 nanowire arrays were used as the backbone for the growth

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of NiO flakes. 70 mL 1 M $Ni(NO_3)_2$ solution was transferred into the liner as the reaction solution. The liner was sealed in a stainless steel autoclave and maintained at 110 °C for 3 h. Finally, the samples were annealed at 350 °C in normal purity argon for 2 h to obtain NiO@Co_3O_4 arrays.

The samples were characterized by X-ray diffraction (XRD, RIGAKU D/Max-2550 with Cu Kα radiation), field emission scanning electron microscopy (FESEM, FEISIRION) and high-resolution transmission electron microscopy (HRTEM, JEOLJEM-2010F). The electrochemical measurements were carried out in a three-electrode electrochemical cell containing 2 M KOH aqueous solution as the electrolyte. Cyclic voltammetry (CV) measurements were performed on a CHI660e electrochemical work station (Chenhua, Shanghai), with Hg/HgO as the reference electrode and a Pt foil as the counter-electrode. The galvanostatic charge/discharge test was conducted on a LAND battery program-control test system.

3. Results and discussion

SEM–TEM images of the Co_3O_4 and NiO@Co_3O_4 nanowire arrays are presented in Fig. 1. Observe that the Ni foam is covered by the quasi-vertical Co_3O_4 nanowires with sharp tips and average diameter of ca. ~90 nm (Fig. 1a). The magnified SEM image reveals that the surface of nanowire is uneven, which is also confirmed by the TEM image (Fig. 1b). As shown in the TEM image, the needle-like nanowire is highly porous and composed of nanoparticles of ca. ~4 nm. In addition, all the diffraction rings in the SAED pattern of the nanowire can be indexed with the spinel Co_3O_4 phase (JCPDS 42-1467) [10]. After growth of the NiO nanoflakes, the Co_3O_4 nanowires are decorated by NiO nanoflake forming binary NiO@Co_3O_4 shish-kebab-like nanowires (Fig. 1c). The NiO nanoflakes show a regular hexagonal morphology. Obviously, no NiO is packed in the interspace among the nanowires, indicating that the NiO nanoflakes are preferentially grown on the Co_3O_4 nanowire. As shown in the TEM (Fig. 1d), the NiO nanoflake is tightly bonded on the Co_3O_4 surface. The diffraction rings in the SAED pattern of the nanoflake are indexed to the cubic NiO phase (JCPDS 4-0835). Moreover, the high-resolution SEM image further indicate that the NiO nanoflakes are strung by the Co_3O_4 nanowires forming shish-kebab-like structure (Fig. 1e). Fig. 2a shows the XRD patterns of both samples. In order to reduce the strong impact of the Ni foam substrate, both samples are scratched from the substrate for XRD analysis. The XRD confirms that before growth of NiO, all the peaks belong to the spinel Co_3O_4 phase (JCPDS 42-1467). After growth of the NiO nanoflakes, two extra peaks characteristic of NiO phase

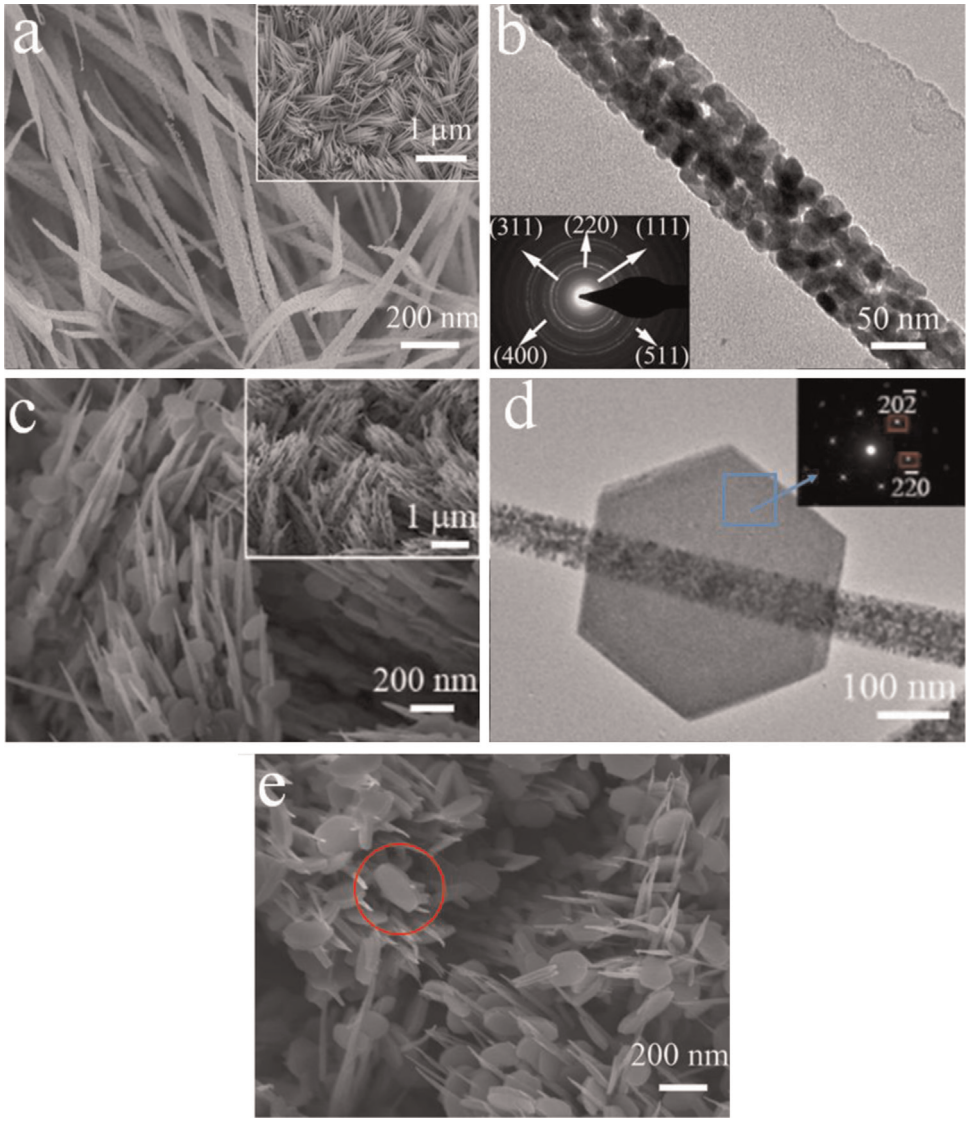

Fig. 1. SEM–TEM images of (a,b) Co_3O_4 nanowire arrays and (c–e) shish-kebab-like NiO@Co_3O_4 nanowire arrays.