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Nickel–Cobalt hydroxide microspheres electrodepositioned on nickel cobaltite nanowires grown on Ni foam for high-performance pseudocapacitors

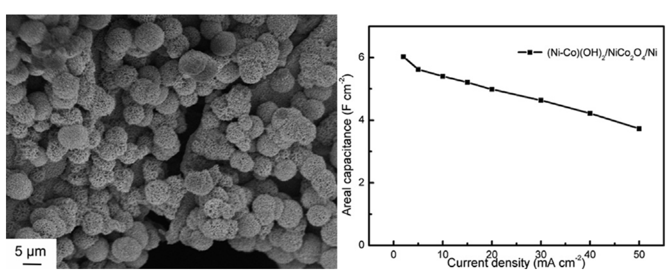
Xuefei Gong [a], J.P. Cheng [a,*], Fu Liu [a], Li Zhang [b,c], Xiaobin Zhang [a]

[a] Department of Materials Science and Engineering, State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, PR China
[b] Department of Mechanical and Automation Engineering, The Chinese University of Hong Kong, Hong Kong, PR China
[c] Shun Hing Institute of Advanced Engineering, The Chinese University of Hong Kong, Hong Kong, China

HIGHLIGHTS

- Nickel–Cobalt hydroxide microspheres were electrodeposited on $NiCo_2O_4$ nanowire arrays.
- The electrode of 10 min electrodeposition delivered a high areal capacitance of 6 F cm^{-2}.
- The synergic effect of conductive $NiCo_2O_4$ nanowires and porous hydroxides is important.

GRAPHICAL ABSTRACT



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ABSTRACT

Nickel–Cobalt hydroxide microspheres are electrodepositioned on the films of $NiCo_2O_4$ nanowires grown on the current collector through a facile approach and the hierarchical structures are then investigated as an electrode material for high-performance supercapacitors. Owing to the superior electrical conductivity of $NiCo_2O_4$ nanowires, the porous structure of the $(Ni–Co)(OH)_2$ microspheres and the synergic effect of the multi-components, the electrode can deliver a high areal capacitance of 6 F cm^{-2} and a corresponding specific capacitance of 1132 F g^{-1} at a current density of 2 mA cm^{-2}, as well as a good rate capability (61.8% capacitance retention from 2 mA cm^{-2} to 50 mA cm^{-2}), and excellent cycling stability (90% capacitance retention after 2000 cycles). The results suggest that our research opens up the possibility for the fabrication of high-performance energy-storage devices of binder-free electrodes.

1. Introduction

Supercapacitors, also known as electrochemical capacitors, have attracted more and more attention due to their many advantages, such as high power capacity, fast charge/discharge rate and long lifespan, which can be applied in many fields including electric vehicles [1–4]. There are two types of supercapacitors based on the underlying energy storage mechanism: electrical double-layer capacitors and pseudocapacitors. In general, a pseudocapacitor electrode, usually made of transition metal oxides/hydroxides materials with multiple valence states, has excellent theoretical capacitance because of reversible Faradaic redox reactions [5–10]. For example, RuO_2 can exhibit noteworthy specific capacitance and remarkable electrochemical reversibility, while its high cost and

* Corresponding author.
E-mail address: chengjp@zju.edu.cn (J.P. Cheng).

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scarcity impede the commercial and practical applications [11]. Thus, tremendous efforts have been devoted to the synthesis of alternative electrode materials with a high-performance.

Among various metal oxides, ternary nickel cobaltite has recently aroused great interest because of some advantages such as low cost, rich sources and environmental friendliness. Moreover, it possesses much higher electrical conductivity which can facilitate a faster electron transport, and more excellent electrochemical activity resulting from simultaneous effects of nickel and cobalt ions in the Faradaic redox reactions than other metal oxides [12–15], thus it can display a wonderful electrochemical performance. For example, Xiao and co-workers successfully obtained porous $NiCo_2O_4$ of flower-like nanostructures with largely enhanced electrochemical performance (658 F g^{-1} at 1 A g^{-1} and 93.5% of specific capacitance could be retained after 1000 cycles) through a simple hydrothermal and subsequent annealing process [16]. Though $NiCo_2O_4$ shows a remarkable electrochemical performance, the experimental values of specific capacitance are still much lower than its theoretical values and not satisfactory for practical application. It is partially caused by the introduction of conductive agent and a polymer binder leading to an extra contact resistance and dead surface, thus hindering the diffusion of electrolyte. Therefore, it is desirable to grow electrode materials on current collector directly and be used as a binder-free electrode [17–19]. Thus, mesoporous $NiCo_2O_4$ nanosheets on Ni foam have been prepared, and the areal capacitance can be 3.51 F cm^{-2} at the current density of 1.8 mA cm^{-2} [14].

Meanwhile, it is necessary to seek for other materials with a high capacitance. According to results of previous literature, specific capacitances of transition metal hydroxides are usually higher than the oxides. However, metal hydroxides usually exhibit a worse cycling stability than oxides due to its low conductivity [20–28]. Therefore, to get a better electrochemical performance for a pseudocapacitor, it is highly desirable to engineer electrodes with the combination of multi-component materials, which can make use of synergistic effects from the individual constituents [29–33]. The structure of electrodes should possess large highly-accessible specific surface area to guarantee a large amount of electroactive materials to simultaneously take part in the Faradaic reactions and fast ion diffusion for supercapacitors [34]. Regarding to above considerations, it is of great significance to directly grow hierarchically multi-component materials on the current collector with highly-accessible structure as binder-free electrodes.

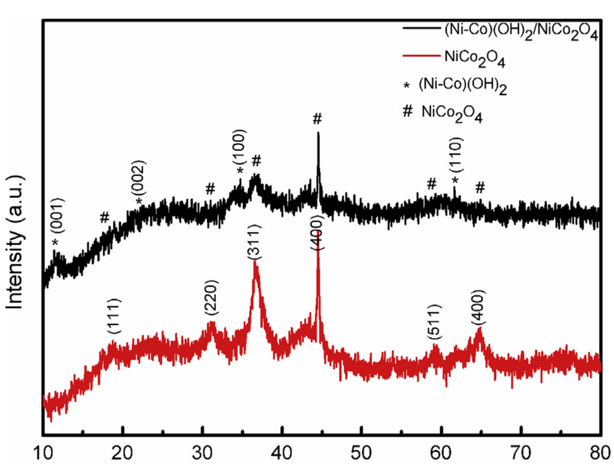

Fig. 1. XRD patterns of $NiCo_2O_4$ nanowire arrays and $(Ni–Co)(OH)_2/NiCo_2O_4$ hybrid arrays.

In this work, we developed a facile and scalable strategy to synthesize Nickel–Cobalt hydroxide microspheres electrodepositioned on $NiCo_2O_4$ nanowire arrays which were grown on Ni foam as a binder-free electrode directly. The areal capacitance of the electrode can reach 6 F cm^{-2} at a current density of 2 mA cm^{-2} and the corresponding specific capacitance is 1132 F g^{-1}. Moreover, 61.8% of its initial capacitance is maintained when the current density increases from 2 mA cm^{-2} to 50 mA cm^{-2}. The capacitance decay is only about 10% after 2000 charge–discharge cycles. The above excellent electrochemical performances indicate that the electrode can be potentially applied in practical use.

2. Experimental

2.1. Materials

All the chemicals were purchased from Aladdin, which were of analytical purity and used without any further purification.

2.2. Synthesis of $NiCo_2O_4$ nanowire arrays on Ni foam

$NiCo_2O_4$ nanowire arrays were prepared by a hydrothermal and subsequent annealing process. In a typical procedure, 1.8 mmol $Co(NO_3)_2 \cdot 6H_2O$, 0.9 mmol $Ni(NO_3)_2 \cdot 6H_2O$, and 18 mmol $CO(NH_2)_2$

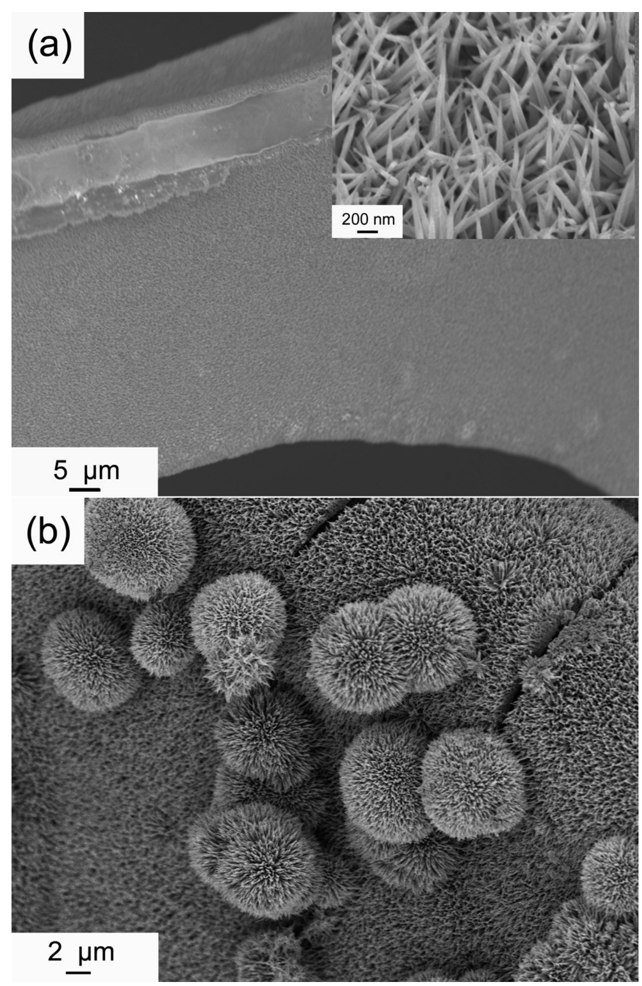

Fig. 2. (a) SEM images of the $NiCo_2O_4$ nanowire arrays grown on Ni foam. (b) SEM images of the $(Ni–Co)(OH)_2$ microspheres electrodepositioned on $NiCo_2O_4$ nanowire arrays grown on Ni foam.