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Hierarchically porous nickel oxide nanoflake arrays grown on carbon cloth by chemical bath deposition as superior flexible electrode for supercapacitors

Ruiping Zhang [a,*], Jun Liu [b], Hongge Guo [a], Xili Tong [c]

[a] Institute of Electronic Information technology, Taiyuan University of Science and Technology, Taiyuan 030024, China
[b] North University of China, Key Lab on Instrumentation Science & Dynamic Measurement of the Ministry, Taiyuan 030051, China
[c] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, CAS, Taiyuan 030001, China

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ABSTRACT

Hierarchical porous NiO nanoflake arrays on carbon cloth are fabricated by a simple chemical bath deposition (CBD) method. Free-standing NiO nanoflakes with thicknesses of ~10 nm grow quasi-vertically to the carbon cloth forming an integrated flexible electrode. When evaluated as electrode materials for supercapacitors, such nanoflake array electrode exhibits electrochemical performances with high capacitance and desirable high-rate cycle life. The porous NiO nanoflake arrays on carbon cloth deliver a high specific capacitance of 660 F g^{-1} at 2 A g^{-1}. In addition, the integrated flexible electrode exhibits excellent mechanical behavior and long-term cyclic stability (82% retention after 4000 cycles).

1. Introduction

Flexible energy storage devices are highly desirable for portable electronics and wearable gadgets. Among various energy storage devices, flexible supercapacitors (FSCs) have attracted great attention due to their fascinating properties in terms of high power density, excellent reversibility, flexibility and long cycle life [1]. In order to attain high-performance FSCs, particular attention has been paid to design and fabricate advanced flexible electrodes. Generally, the flexible electrodes are required to be highly conductive and possess high surface area as well as flexibility. Recently, various strategies have been developed for the fabrication of flexible electrodes for supercapacitors. These strategies could be classified into two categories: (i) fabricating free-standing flexible film materials and (ii) assembling active materials on flexible substrates [2]. For the first strategy, high specific capacitances have been obtained in these flexible film materials, but the mechanical strength of the as-prepared FSCs is not strong enough and severely restricts their applications. Meanwhile, attention is increasingly turning towards the second strategy, which adopts flexible substrates to support active materials to construct high-performance flexible electrodes [3].

Carbon cloth, an excellent flexible substrate and current collector, has been widely studied because of its unique chemical/physical properties such as light-weight, high electrical conductivity, strong mechanical property, and high flexibility [4]. Previously, Shen's group synthesized Co_9S_8 arrays and Co_3O_4@RuO_2 nanosheet arrays on carbon cloth as positive and anode materials for FSCs [5]. Their FSCs exhibited a stable rate capability and noticeable flexible property. In addition, H–TiO_2 nanorod arrays on carbon cloth were also reported with good supercapacitor performance [6]. Inspired by these results, it would be interesting to rationally design and fabricate flexible electrodes based on carbon cloth.

Nickel oxide is a promising candidate for supercapacitors due to its easy availability, cost effectiveness, and good pseudocapacitive behavior [7]. To date, although many NiO nanostructures (nanowall [8], nanoparticle [9], and nanosheet [10]) have been reported, there are few reports about NiO/carbon cloth flexible electrodes for supercapacitor application. In the present work, we demonstrate a facile chemical bath deposition (CBD) method to prepare porous NiO nanoflake arrays on carbon cloth serving as flexible electrode materials for FSCs. The carbon cloth supported NiO nanoflake arrays deliver high specific capacitance (765 F g^{-1}) and good cycling stability (82% capacitance retention rate). The proposed synthetic strategy can be extended to synthesis of other metal oxides/carbon cloth flexible electrodes for supercapacitors.

2. Experimental

The carbon cloth supported NiO nanoflake arrays were fabricated as follows. Before CBD of NiO on carbon cloth, the carbon

* Corresponding author. Tel.: +86 351 4605282.
E-mail address: ruipingty@126.com (R. Zhang).

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cloth was treated in a mixed acid solution of H_2SO_4 and HNO_3 (volume ratio: 3:1) at 80 °C for 12 h. Then, the carbon cloth was cleaned in acetone, deionized water, and ethanol for 30 min, correspondingly. The CBD solution was obtained by mixing 80 ml of 1 M nickel sulfate, 60 ml of 0.25 M potassium dichromate, and 20 ml of aqueous ammonia (28%). The above cleaned carbon cloth was used as substrates and fixed on the slide glass. The carbon cloth was placed vertically in the fresh CBD solution and kept at 25 °C for 1 h to deposit the precursor film. After that, the precursor film was washed and then annealed at 300 °C for 1 h in argon. The load weight of NiO was about 2 mg cm^{-2}. The involved CBD reactions were illustrated as follows:

$$Ni[(H_2O)_{6-x}(NH_3)_x]^{2+} + 2OH^- \leftrightarrow Ni(OH)_2 + (6-x)H_2O + xNH_3 \quad (1)$$

$$2Ni(OH)_2 + Cr_2O_7^{2-} + 2OH^- + H_2O \rightarrow 2NiOOH \cdot H_2O + 2CrO_4^{2-} + 2H_2O \quad (2)$$

During the annealing process:

$$NiOOH \cdot H_2O - e^- \rightarrow Ni(OH)_2 + OH^- \quad (3)$$

$$Ni(OH)_2 \rightarrow NiO + H_2O \quad (4)$$

The morphology and structure of the as-synthesized samples were characterized by field emission scanning electron microscopy (FESEM, FEI SIRION), transmission electron microscopy (TEM, JEOL JEM200CX) and Brunauer–Emmett–Teller (NOVA-1000e). The electrochemical measurements were carried out in a

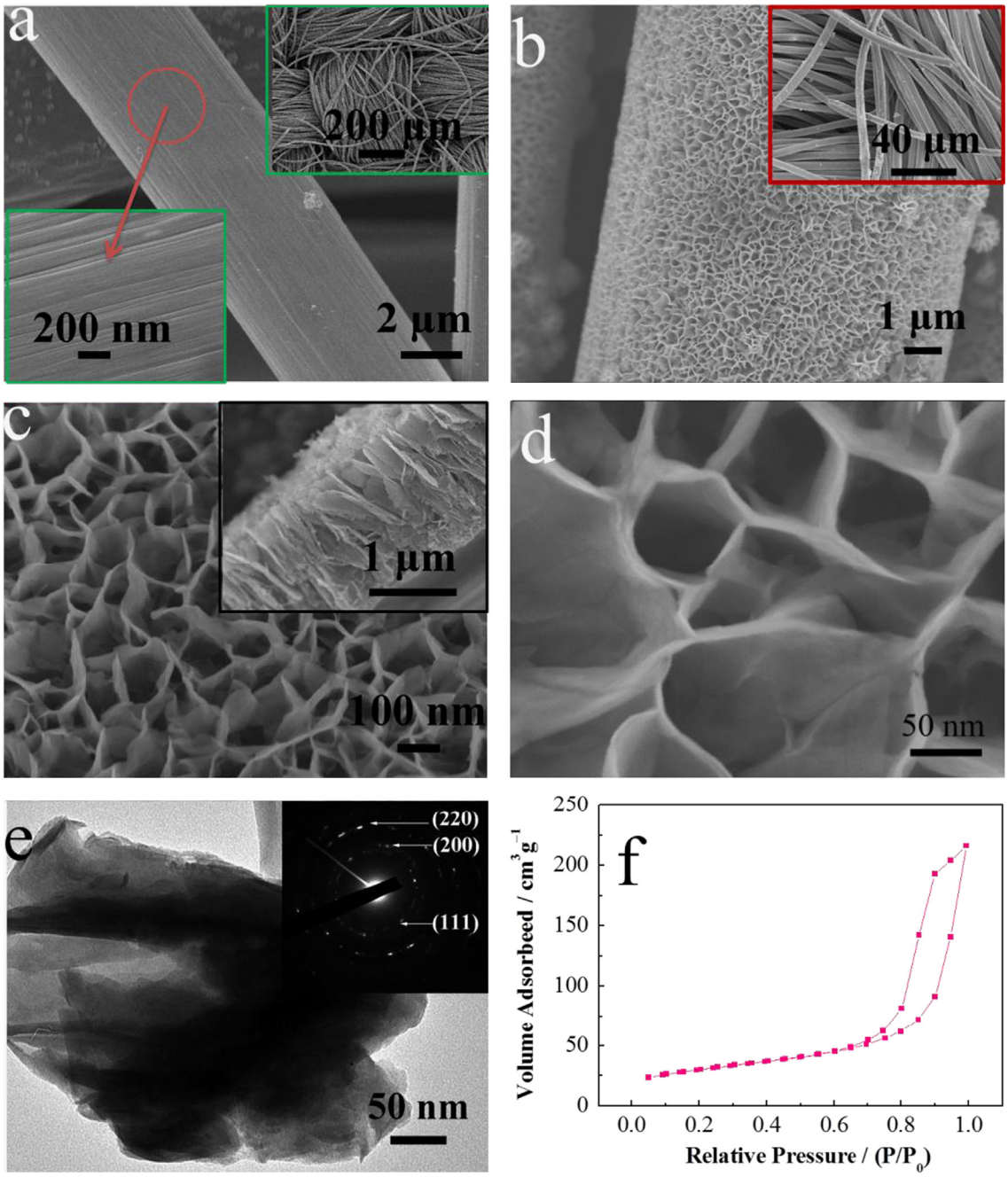

Fig. 1. Morphological and structure characterizations of carbon cloth and hierarchical porous NiO nanoflake arrays/carbon cloth electrode: (a) carbon cloth (fine structure in inset); (b and c) SEM images of NiO nanoflake arrays on carbon cloth (side view and large-scale image in inset); (d) fine structure of NiO nanoflake; (e) TEM image (SAED pattern in inset); and (f) BET measurement of NiO nanoflakes.