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Synergetic Effect of Three-Dimensional Co_3O_4@$Co(OH)_2$ Hybrid Nanostructure for Electrochemical Energy Storage

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ABSTRACT

A novel three-dimensional (3D) Co_3O_4@$Co(OH)_2$ hybrid nanostructure is synthesized by using two-step hydrothermal and electrodeposition methods. The composite can be employed as an efficient electrode of a high-performance supercapacitor. Scanning electron microscopy and high-resolution transmission electron microscopy images show that $Co(OH)_2$ nanosheets can grow both in the space and on the tops of Co_3O_4 nanotubes. In comparison with the sole Co_3O_4 nanotubes and $Co(OH)_2$ nanosheets, the hybrid Co_3O_4@$Co(OH)_2$ electrode with a naturally formed nanostructure exhibits much improved battery-type performances in a 3 mol L^{-1} KOH electrolyte solution, as evidenced by the high specific capacity of 1876 C g^{-1} at a current density of 5 mA cm^{-2}. A good retention capability is also demonstrated, 83.1% of initial capacity value is maintained after 1000 cycles at a current density of 25 mA cm^{-2}. The observed high performances of Co_3O_4@$Co(OH)_2$ hybrid electrode with the 3D nanostructure make it attractive for the development of high-efficiency electrochemical energy storage devices.

1. Introduction

Recently, high-energy-density supercapacitors have been the focus of extensive research and development for more than two decades, due to their unique advantages such as high power density, long cycle life, safe operation, and low maintenance costs [1–5]. Based on these advantages, supercapacitors find applications in various areas, including portable electronics, memory backup systems, transportations and even stationary power banks. However, the relative low energy density storage and instability are the two key issues that must be overcome in order to make supercapacitors viable for commercial applications. The utilization of nanostructure electrodes based on new materials has been an effective way to increase the energy density storage and improve the stability of supercapacitors. In addition to the widely used carbonaceous materials, many other materials, such as MnO_2 [6,7], Co_3O_4 [8,9], NiO [10,11], $Co(OH)_2$ [9,12], $Ni(OH)_2$ [13,14], and $NiCo_2O_4$ [15,16], have been extensively investigated as the electrode materials candidate for supercapacitors. Among them, cobalt-containing electrodes, such as Co_3O_4 and $Co(OH)_2$, have received special attentions due to their predominant advantages of high electroactivity, natural abundance, environmental friendliness and easy fabrication [9].

It is well acknowledged that the charge-storage capability of a supercapacitor mainly depends on both the material and the structure of electrode. An ideal structure of an electrode typically has a large surface-to-volume ratio and a balance between the material bulk property and the ionic diffusing distance. Such electrode enables fast kinetics and large-area contacts with the electrolytes. Additionally, the electrode can provide more electroactive sites for Faradaic energy storage, resulting in a high specific capacity at high current density [17]. Currently, designing an electrode with a special nanostructure, which increases the surface-to-volume ratio, is attracting great interest. To improve the electrochemical performances of electrode, much efforts have been devoted to the synthesis of advanced composite based on three-dimensional (3D) hybrid nanostrutures combining two different materials, such as Co_3O_4@$CoMoO_4$ nanopine forest [8], hierarchical $ZnCo_2O_4$@$Ni_xCo_{2x}(OH)_{6x}$ core/shell nanowire arrays [18], hierarchical Fe_3O_4@Fe_2O_3 core-shell nanorod arrays [19], cobalt oxide nanobrush-graphene@$Ni_xCo_{2x}(OH)_{6x}$ [20],

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hierarchical $NiCo_2O_4$@nickel-sulfide nanoplate arrays [15], and multilayer MnO_2/graphene oxide nanoflakes [6]. Particularly, cobalt oxide/hydroxide with multiple oxidative states has the ability to facilitate redox reactions with a maximum theoretical "pseudocapacitance" of $\sim$3500 F g^{-1} [9]. However, so far, quite few reports have systematically investigated the synergetic effect of cobalt oxide/hydroxide electrode on the electrochemical performances, which deserves further researching yet.

In this work, we introduce a simple method for the preparation of 3D Co_3O_4@$Co(OH)_2$ hybrid nanostructure on Ni foam substrates. The approach to construct the hybrid nanostructure combines the hydrothermal synthesis and electrodeposition method. In comparison with single Co_3O_4 nanotubes and $Co(OH)_2$ nanosheets, the developed Co_3O_4@$Co(OH)_2$ nanostructure contains a large number of active sites, which facilitate the ionic diffusion and charge transfer processes. Consequently, the synthesized Co_3O_4@$Co(OH)_2$ electrode exhibits the significant enhancement of specific capacity as well as cycle life for supercapacitors application.

2. Experimental

Synthesis of 3D Co_3O_4@$Co(OH)_2$ hybrid nanostructure

Firstly, Co_3O_4 nanotubes were developed using hydrothermal synthesis inside a Teflon-lined stainless steel autoclave. A piece of pretreated nickel foam (area is approximately $1 \times 4\,cm^2$) was prepared in advance by immersing it in an aqueous solution of a mixture of 62.45 mg L^{-1} $Co(NO_3)_2 \cdot 6H_2O$ and 291.38 mg L^{-1} urea.

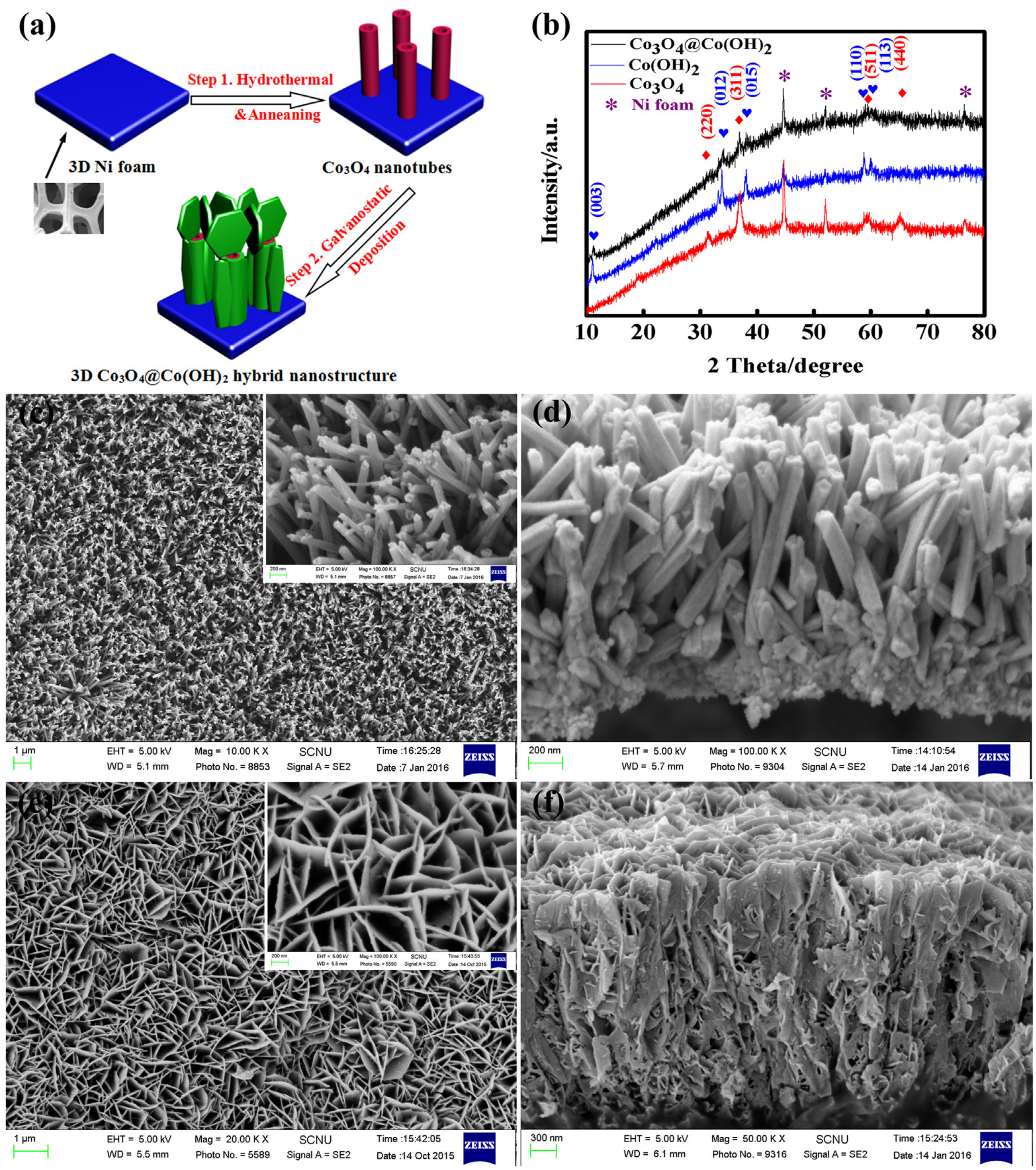

Fig. 1. (a) Schematic diagram showing the growth process for the developed 3D Co_3O_4@$Co(OH)_2$ hybrid nanostructure. (b) XRD patterns of Co_3O_4, $Co(OH)_2$, and 3D Co_3O_4@$Co(OH)_2$ hybrid nanostructure. (c) Plan view and (d) cross-sectional SEM images of the Co_3O_4 nanotubes. (e) Plan view and (f) cross-sectional SEM images of the 3D Co_3O_4@$Co(OH)_2$ hybrid nanostructure on Ni foam.