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Construction of desirable $NiCo_2S_4$ nanotube arrays on nickel foam substrate for pseudocapacitors with enhanced performance

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ABSTRACT

Ternary $NiCo_2O_4$ synthesized via annealing NiCo-precursor has been extensively studied as an advanced electrode material for high-performance supercapacitors. In this work, we demonstrate a facile hydrothermal synthesis of $NiCo_2S_4$ nanotube arrays (NTAs) by simply treating the NiCo-precursor with Na_2S solution based on the Kirkendall effect. The $NiCo_2S_4$ NTAs grown on nickel foam substrate are directly evaluated as binder-free electrode for supercapacitors. Impressively, the $NiCo_2S_4$ NTA electrode delivers an ultrahigh capacitance of 15.58 F cm^{-2} at a current density of 10 mA cm^{-2}, which is much higher than 3.63 F cm^{-2} of the mesoporous $NiCo_2O_4$ nanowire array (NWA) electrode. In addition, the $NiCo_2S_4$ NTA electrode also exhibits good cycling stability with 79.3% capacitance retention at high current density of 60 mA cm^{-2} after 2000 cycles. In view of the excellent electrochemical performance and the facile and cost-effective synthesis, such $NiCo_2S_4$ NTA electrode would hold great promise for high-performance supercapacitor applications in future.

1. Introduction

Supercapacitors, also called electrochemical capacitors, have attracted great attention from both industry and academia since they are assigned to be as important as batteries for future energy storage systems by the US Department of Energy [1,2]. Compared with batteries, supercapacitors are superior in the areas of high power density, fast charge/discharge process, long lifespan, environmental friendliness, and safety [3–5]. In general, supercapacitors are classified into electrical double layer capacitors (EDLCs) and pseudocapacitors based on their different charge storage mechanism. Compared with the electrical double-layer capacitors (EDLCs), pseudocapacitors can achieve much higher specific capacitance and energy density as they can provide a variety of oxidation states for efficient redox reactions [6,7]. In recent years, significant progress has been achieved in developing various electrode materials for supercapacitor applications [8–12]. Despite of the present progress, it is still important and challenging to explore advanced electrode materials with high capacitance, as well as environmental friendliness and low cost.

Recently, extensive research efforts have been devoted to the development of transition metal sulfides, which have been conceived as new type electrode materials for pseudocapacitors with good performance [13–15]. In particular, ternary $NiCo_2S_4$ possess an electric conductivity ~100 times than that of $NiCo_2O_4$ due to the lower band gap [16–19], although $NiCo_2O_4$ has been reported to possess a much better electric conductivity than those of NiO and Co_3O_4 [20–22]. Taken in this sense, ternary $NiCo_2S_4$ are expected to hold great promise as an advanced electrode material for high-performance supercapacitors. Recently, Lou and co-workers synthesized $NiCo_2S_4$ hollow prisms, which delivered a high capacitance of 834.4 F g^{-1} at 2 A g^{-1} [16]. Jiang and co-workers reported the highly conductive $NiCo_2S_4$ urchin-like nanostructures, which exhibited a high capacitance of 1062 F g^{-1} at 4 A g^{-1} [18].

Undoubtedly, the great development of supercapacitor technologies are benefited from nanostructured materials [4,23,24]. Because pseudocapacitors store charge only in the first few nanometers from the surface, thus decreasing the particle size increases active material usage. Accordingly, the morphology and size of the active materials play a vital role in determining their electrochemical performance [1,12,25]. In this regard, construction of nanostructures with desirable morphology and size is of great significant for improving the supercapacitor performance. Among various nanostructures, the hollow tubular nanostructures have attracted extensive research interests [26–30]. For examples, Lu

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and co-works synthesized the ordered MnO_2 nanotube arrays using porous alumina templates, which exhibited superior capacitive behavior than that of the MnO_2 nanowire arrays. Compared to the solid-core nanowires, nanotubes possess a larger surface area by exposing both inner and outer walls for electrochemical reactions, resulting in a better utilization of the active material. Furthermore, the hollow interiors with good permeability could enable the active surface area to be fully accessible to electrolyte ions [27]. Recently, Wan and coworkers have reported the $NiCo_2S_4$ porous nanotubes for supercapacitors, which showed a low specific capacitance of 933 F g^{-1} at 1 A g^{-1} and only 63% of the initial specific capacitance remained after 1000 cycles [28]. Pu and coworkers have reported the growth of $NiCo_2S_4$ nanotube arrays on nickel foam for supercapacitors, which displayed a low specific capacitance of 783 F g^{-1} at a current density of 4 A g^{-1} [29]. However, the electrochemical results are still unsatisfactory, which can not fulfill the demands for high-performance supercapacitor applications. In this work, we successfully synthesize the desirable $NiCo_2S_4$ NTAs grown on nickel foam substrate through a facile two-step hydrothermal method. For comparison, the mesoporous $NiCo_2O_4$ NWAs are also synthesized via annealing the corresponding NiCo-precursor NWAs at 400 °C for 3 h in air. Herein, the active materials are directly grown on current collector, which can ensure good mechanical adhesion and electrical contact with the conductive substrate. Moreover, this electrode design can avoid the use of polymer binder and conducting additives, improving the utilization of the electrode materials even at a high mass loading [31,32]. In addition, the $NiCo_2S_4$ NTAs grown on nickel foam are synthesized with the help of surfactant, which can avoid forming dense structure and ensure larger surface areas for Faradaic reactions [33]. Impressively, the $NiCo_2S_4$ NTA electrode exhibits much enhanced electrochemical performance than the mesoporous $NiCo_2O_4$ NWA electrode, which would hold great promise for high-performance supercapacitor applications.

2. Experimental Section

2.1. Materials synthesis

Synthesis of $NiCo_2S_4$ NTAs and $NiCo_2O_4$ NWAs: Prior to the synthesis, the Ni foam ($4 \times 1 \times 0.1$ cm) was cleaned by sonication in acetone, ethanol, and deionized (DI) water in sequence for 10 min each to clean the surface. In a typical synthesis, 5 mmol Co$(NO_3)_2 \cdot 6H_2O$, 2.5 mmol of $NiCl_2 \cdot 6H_2O$, 2 mmol hexadecyl trimethyl ammonium bromide, 9 mmol of urea are dissolved into 35 mL of DI water to form a transparent pink solution. The solution was transferred to a 50 mL Teflon–lined stainless steel autoclave with a piece of pretreated Ni foam immersed into the reaction solution. The autoclave was sealed and maintained at 120 °C for 6 h, and then cooled down to room temperature. After hydrothermal growth, the Ni foam loaded with NiCo-precursor NWAs was carefully rinsed several times with de-ionized water and absolute ethanol with the assistance of ultrasonication, and finally dried in air. The $NiCo_2O_4$ NWAs were obtained via annealing the precursor on Ni foam at 400 °C in air for 3 h. The $NiCo_2S_4$ NTAs were obtained through a simple and facile hydrothermal method based on the Kirkendall effect. Typically, the Ni foam loaded with NiCo-precursor was placed in a 50 mL Teflon–lined stainless steel autoclave with a solution containing 30 mL sodium sulfide (0.1 M) at 120 °C for 6 h.

2.2. Materials Characterization

The powder X–ray diffraction (XRD) patterns were recorded on a Panalytical X–pert diffractometer with Cu Kα irradiation. The morphology and size of the samples were observed by scanning electron microscopy (SEM, Zeiss SUPRA 55) and high–resolution transmission electron microscopy (HRTEM, JEOL JEM 2100) with an acceleration voltage of 200 kV.

2.3. Electrochemical Measurements

The electrochemical measurements were carried out in a three–electrode electrochemical cell containing 2 M KOH aqueous solution as the electrolyte. The $NiCo_2S_4$ NTAs and $NiCo_2O_4$ NWAs on Ni foam were directly used as the working electrodes. The area of the working electrode immersed into the electrolyte was cut into about 1 cm^2. The mass loading of $NiCo_2S_4$ nanotubes and $NiCo_2O_4$ nanowires on nickel foam is around 7.5 and 2.5 mg cm^{-2}, respectively. The electrochemical measurements were conducted with a CHI660E electrochemical workstation. A standard calomel electrode (SCE) was used as the reference electrode and a Pt foil as the counter electrode, and all the experiments were done at ambient temperature. The areal and specific capacitance (C) were calculated according to the following equations [20,21]:

$$C = \frac{It}{SV} \text{and} C = \frac{It}{mV} \quad (1)$$

where I was the constant discharge current (A), t was discharge time (s), V was the potential window (V), m was the mass (g) of the active material on the electrode, and S was the geometrical area (cm^2) of the electrode.

3. Result and discussion

The schematic illustration of the typical synthetic strategy is displayed in Fig. 1. It clearly shows that the whole process involves two steps: (1) surfactant-assisted hydrothermal growth of NiCo-precursor NWAs on nickel foam as previously reported by zhang et al. [33] (2) using Na_2S as the sulfur source, the NiCo-precursor NWAs are transformed into $NiCo_2S_4$ NTAs on the basis of the Kirkendall effect. The morphology and structure of the as-prepared $NiCo_2S_4$ sample were examined by SEM and TEM observations. Fig. 2A–E shows low and high-magnification SEM images of the $NiCo_2S_4$ nanotubes on nickel foam. It is observed that the high density $NiCo_2S_4$ nanotubes are uniformly grown on nickel foam. It is mentioning that the presence of the surfactant can avoid forming dense structure, ensuring larger surface areas for Faradaic reactions [33]. The high magnification SEM images (Fig. 2D and E) show that nanotube arrays instead of nanowire arrays are aligned on the nickel foam substrate. The opening ends can be clearly seen for some of the nanotubes. This unique feature not only increases the contact area between the active material and the electrolyte but also benefits the penetration of the electrolyte, resulting in a full utilization of the electrode materials [27]. The formation of the $NiCo_2S_4$ nanotubes can be explained by the Kirkendall effect, which has been used to guide the growth of various hollow nanoparticles and nanotubes [26]. Firstly, S^{2-} ions react with the NiCo-precursor forming a thin layer of $NiCo_2S_4$ nanoparticles, which acts as a physical barrier to prevent the direct chemical reaction between outside S^{2-} ions and inner NiCo-precursor. Therefore, further reaction depends on the relative diffusion of metal or sulfide ions through this newly formed $NiCo_2S_4$ shell. Because the outward diffusion rate of the cobalt and nickel source is faster than the inward transport rate of S^{2-} ions, this unequal diffusion of reacting species would produce voids at the center of the nanowire. With the reaction going on, the $NiCo_2S_4$ shell will be increased and the NiCo-precursor core is gradually decreased, thus finally forming $NiCo_2S_4$ nanotubes [13,16,29]. The $NiCo_2S_4$ nanotubes are grown vertically on nickel substrate and