Nano Energy 26 (2016) 313–323

Contents lists available at ScienceDirect

Nano Energy

journal homepage: www.elsevier.com/locate/nanoen

Engineering sulfur vacancies and impurities in $NiCo_2S_4$ nanostructures toward optimal supercapacitive performance

Fei Lu [a], Min Zhou [a,b,*], Wanrong Li [a], Qunhong Weng [b], Cuiling Li [b], Yanming Xue [b], Xiangfen Jiang [b], Xianghua Zeng [a,**], Yoshio Bando [b], Dmitri Golberg [b,**]

[a] College of Physical Science and Technology, and Institute of Optoelectronic Technology, Yangzhou University, Yangzhou 225002, China
[b] World Premier International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba 305-0044, Japan

ARTICLE INFO

Article history:
Received 2 April 2016
Received in revised form
18 May 2016
Accepted 26 May 2016
Available online 27 May 2016

Keywords:
Pseudocapacitor
Transition metal sulfide
Sulfur vacancy
Controlled sulfurization
Solid-state supercapacitor

ABSTRACT

High efficiency supercapacitors require the electrode materials which integrate high specific capacitance, favorable rate capability and long-term cyclic stability. These features are often associated with vacancies and impurities in the electrodes. Understanding the mechanism behind the related process provides a deep insight into improved supercapacitive performance. Here we present the synthesis of spinel structured nickel cobalt sulfide ($NiCo_2S_4$) nanomaterials with tunable sulfur vacancy concentrations and impurities by controlling the sulfurization process. The effects of these defects on the nanomaterial supercapacitive properties were then clearly identified. Interestingly, on one hand, the sulfur vacancies were found to increase the specific capacitance by improving electrical conductivity, while, on the other hand, they hindered the rate capability and cyclic stability due to the increased crystal structure disordering. An optimal supercapacitive performance was achieved, namely, high specific capacitance, favorable rate capability and long-term cyclic stability were documented for both three-electrode system and solid-state asymmetric supercapacitor device. These results have significant implications for the design and optimization of pseudocapacitive properties of transition metal compounds.

1. Introduction

Electrochemical supercapacitors are attractive candidates for the next-generation energy storage devices because of their high power density during a discharging process [1–6]. Pseudocapacitors, in which energy is stored through reversible Faradaic reactions on the electrode materials, possess larger specific capacitance than electrical double-layer capacitors [7–9]. However, the poor charge transfer ability in pseudocapacitive materials, such as transition metal oxides and hydroxides, prevents these systems from applications that require high rate charging and discharging [10,11].

Shortening the charge transfer distance and improving the intrinsic conductivity of electrode materials are two strategies commonly employed to facilitate the charge transfer in pseudocapacitors [12]. The former refers to, for example, in-situ growth of pseudocapacitive materials onto conductive substrates, such as graphene, carbon fibers and nickel foam [11,13–15]. Despite remarkable improvements which have been evidenced with respect to those hybrid electrodes, the promotion of intrinsic conductivity of pseudocapacitive materials is still a challenge. Recently, defect engineering on transition metal oxides has been reported as an effective route to improve their intrinsic conductivity. For instance, Lu and co-workers found that oxygen-deficient α-Fe_2O_3 nanorods had shown an enhanced electrochemical performance compared to that of pristine α-Fe_2O_3, which was due to the increased donor density and number of active sites resulted from the oxygen vacancies [16]. Another example was demonstrated by Li and co-workers, who obtained an improved supercapacitive performance from $NiCo_2O_4$ hollow spheres combining large surface area and high conductivity. A hydrogenation process was employed to increase oxygen vacancies in the electrode material, and therefore to lower the internal resistance as well as the Warburg impedance [12]. Other reports suggested that the introduction of defects, nevertheless, is usually associated with the crystalline structure disordering, which is adverse to the rate capability and cyclic performance [17,18]. In this regard, a synthetic assessment on the defect-related pseudocapacitive performance, including specific capacitance, rate capability and cyclic stability, is desired and of prime significance.

* Corresponding author at: College of Physical Science and Technology, and Institute of Optoelectronic Technology, Yangzhou University, Yangzhou 225002, China.
** Corresponding authors.
E-mail addresses: minzhou@yzu.edu.cn (M. Zhou), xhzeng@yzu.edu.cn (X. Zeng), GOLBERG.Dmitri@nims.go.jp (D. Golberg).

http://dx.doi.org/10.1016/j.nanoen.2016.05.042
2211-2855/

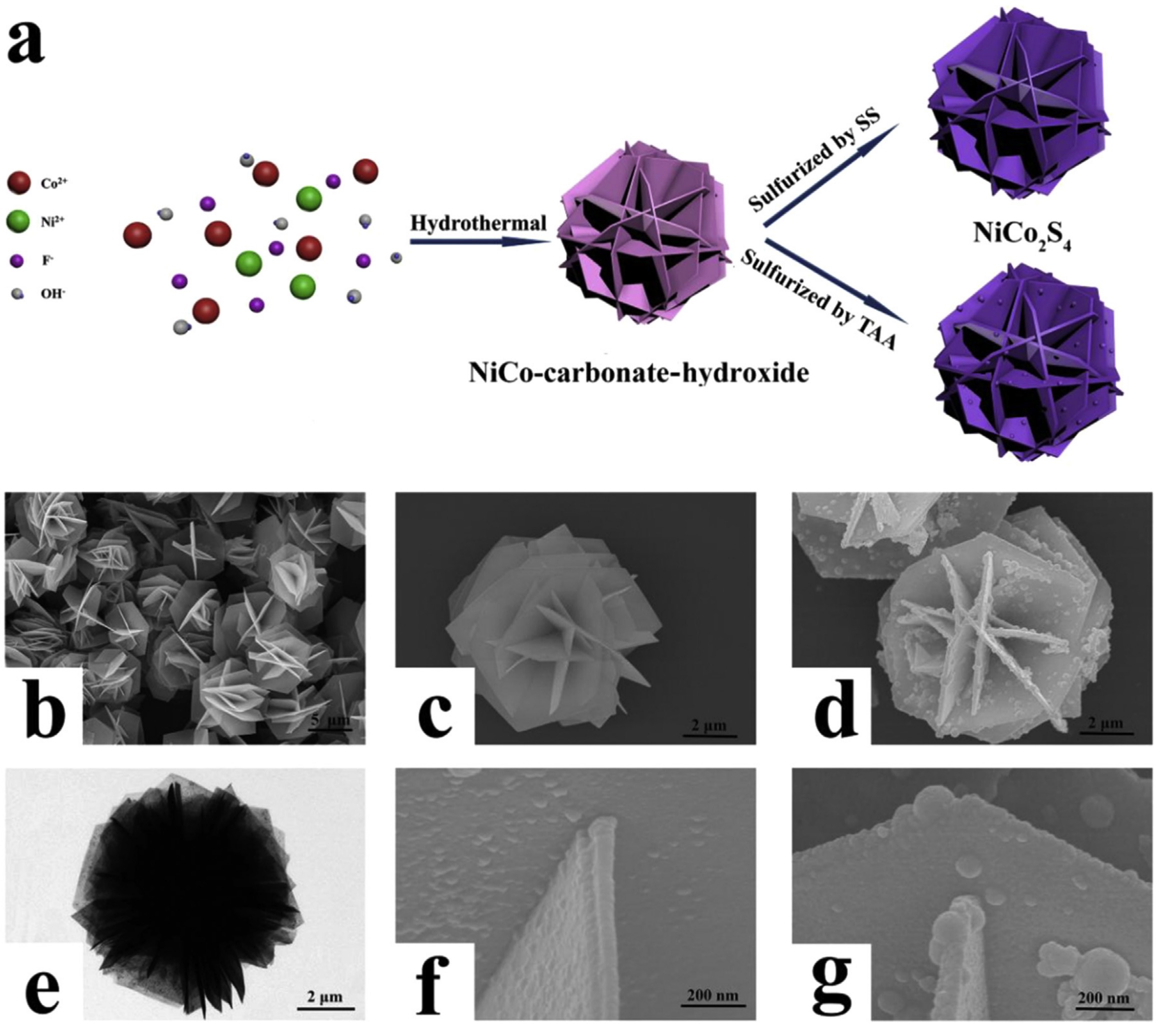

Fig. 1. (a) Schematic illustration of the formation process of $NiCo_2S_4$ nanostructure assembled as nanoflakes, (b) SEM and (e) TEM images of NiCo-precursors, SEM images with varied magnification of (c, f) SS-6 and (d, g) TAA-6 samples.

Mixed valence transition metal oxides and sulfides have been extensively studied as electrode materials in supercapacitors [19]. Specifically, spinel structured nickel-cobalt sulfide ($NiCo_2S_4$) displayed a distinguished electrochemical performance because of its intriguing features of multiple Faradaic reactions and, more importantly, superior conductivity compared with other pseudocapacitive materials [4,8,20–23]. Recent reports have revealed that oxygen vacancies in spinel structured $NiCo_2O_4$ are critical for electrochemical processes in it [12,24]. Considering the similar crystalline structure between $NiCo_2S_4$ and $NiCo_2O_4$ phases [25], it is reasonable to anticipate that sulfur vacancies in nickel cobalt sulfides could play the key roles in tuning their pseudocapacitive properties, which up to now have not been properly considered. Furthermore, various synthetic methods employed in the synthesis of $NiCo_2S_4$ led to the crystallization difference, e.g. defects and impurities [22,25]. Due to the lack of consistency among the various experimental results, the optimal synthetic conditions for nickel cobalt sulfides fabrication towards superior supercapacitive performance have not been identified yet.

In this study, we present the controlled sulfurization of three dimensional (3D) $NiCo_2S_4$ nanostructures, in which the sulfur vacancy concentration and impurities were engineered by varying the sulfur source and sulfurization duration. The effects of sulfur vacancy concentration and impurities on the material supercapacitive performance were clearly identified. Interestingly, we found that the sulfur vacancies improved the specific capacitance of the electrode, yet decreased the rate capability as well as cyclic stability at the same time. The resulted supercapacitive performance was tuned based on the competitive mechanisms of charge transfer ability and disordering of the crystal structure. An optimal supercapacitive performance integrating high specific capacitance, favorable rate capability and long-term cyclic stability was finally realized. This research not only uncovers the optimal sulfurization conditions for the spinel nickel cobalt sulfides, but also shows effective routes to tune the supercapacitive performance, such as specific capacitance, rate capability and cyclic stability of the electrode.

2. Experimental section

2.1. Synthesis of 3D-structured NiCo-carbonate-hydroxide

All chemicals were of analytical grade and were used without further purification. In a typical synthesis of a NiCo-carbonate-hydroxide precursor, 2 mmol $Co(NO_3)_2$, 1 mmol $Ni(NO_3)_2$, 15 mmol urea and 6 mmol NH_4F were dissolved into 35 ml distilled water to form a transparent pink solution. This aqueous solution was then transferred into a 46 ml Teflon-lined stainless steel autoclave and kept at 100 °C for 3.5 h. After cooling to room temperature naturally, the purple precipitate was separated under centrifugation in distilled water and ethanol several times, and vacuum dried at 80 °C for 6 h.