Electrochimica Acta 286 (2018) 14–21

Contents lists available at ScienceDirect

Electrochimica Acta

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

Low crystalline 2D CoS_x derived from cobalt carbonate hydroxide by sulfidation at room temperature for supercapacitor

J.P. Cheng [a, *], W.Q. Chen [a], S.Q. Gao [a], S.H. Guo [a, b], F. Liu [a]

[a] State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Key Laboratory of Advanced Materials and Applications for Batteries of Zhejiang Province, Zhejiang University, Hangzhou, 310027, China
[b] Center for High Pressure Science and Technology Advanced Research (HPSTAR), Shanghai, 201203, China

ARTICLE INFO

Article history:
Received 18 June 2018
Received in revised form
30 July 2018
Accepted 8 August 2018
Available online 9 August 2018

Keywords:
Cobalt sulfide
Phase transition
Electrode materials
Supercapacitor

ABSTRACT

Low crystalline CoS_x was fabricated by anion-exchange of 2-dimensional (2D) cobalt carbonate hydroxide (CoCH) using aqueous sodium sulfide solution at room temperature. It was proved that single crystalline CoCH nanoplates would transform into porous 2D CoS_x with low crystallinity after the anion-exchange. When they were used as electrode materials for supercapacitor, the 2D CoS_x material had a much higher specific capacitance than its precursor due to their different compositions and electroconductivities. CoS_x had a high specific capacitance of 863 F g^{-1} at 1 A g^{-1} and a good stability during long time charge-discharge processes, about 64.7% of initial capacitance retention after 10000 cycles. Asymmetric hybrid devices using 2D CoS_x as positive electrode and activated carbon as negative electrode were assembled, and the capacitor devices were able to achieve a high energy density of 33.56 Wh kg^{-1} at the power density of 400 W kg^{-1}. The high performances of the porous CoS_x make it a promising electrode material for energy storage.

1. Introduction

With the high-speed development of the society, renewable energy resources and energy storage devices have received much research attention in the world. The electrochemical storage devices including Li-ion batteries and supercapacitors (SC) are applied widely in many fields, such as portable devices, electric vehicles, *etc* [1]. The electrode materials are the most important factor for the performance of these energy storage devices [2,3]. Compared with Li-ion batteries, SCs are of higher power density, longer lifespan and faster charge/discharge process. However, the energy density of SCs is still limited. Thus, there were many previous reports which focused on the improvement of electrode materials for SCs [4–6]. In addition to carbon materials, battery-like electrode materials including transition metal oxides/hydroxides [3,7,8], sulfides [9,10] and their composites [11,12] have been deeply researched as novel electrode materials.

It is demonstrated by previous reports that transition metal sulfides have emerged as one of prominent candidates for SCs due to their high electroconductivity and rich redox chemistry [9,13–15]. $NiCo_2S_4$ and its composites have drawn much attention from researchers so far [16–19]. In general, the electrochemical performances of metal sulfides are strongly dependent on their composition and microstructure/morphology [20]. Among them, cobalt sulfides (CoS_x) have been also researched as electrode materials for SCs by Faradaic reaction due to its multiple phases and convenient synthesis. Recently, different morphologies of CoS_x materials such as hierarchical structures [21–23], nanowires [24–26], nanotubes [27], hollow structures [28,29], 2-dimensional (2D) nanosheets [30,31] and composites [32–35] have been reported as electrode materials for SCs. Until now, the research of 2D CoS_x for SCs still has many limitations. Rakhi et al. reported that Co_9S_8 nanoflakes nucleated over carbon fibers showed a high specific capacitance of 1056 F g^{-1} at 5 mV s^{-1} [32]. Han and co-workers prepared Co_9S_8 nanosheet arrays on Ni foam which exhibited a high specific capacitance of 1098.8 F g^{-1} at 0.5 A g^{-1} [31]. Above reports are related to 2D Co_9S_8 films grown on current collectors for SCs. However, the research on powder 2D CoS_x is still very limited.

In this work, 2D CoS_x powder with low crystallinity was fabricated by simple anion exchange of cobalt carbonate hydroxide using Na_2S solution at room temperature. The microstructure and electrochemical performance of 2D CoS_x were investigated. The 2D

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

https://doi.org/10.1016/j.electacta.2018.08.035
0013-4686/

CoS_x material had the similar morphology to its precursor and showed a high specific capacitance of 863 F g^{-1} at 1 A g^{-1} as well as a good cycling stability. When it was used as a positive electrode and combined with activated carbon as a negative electrode to assemble a hybrid capacitor, the capacitor could deliver a high energy density of 33.56 Wh Kg^{-1} at 400 W kg^{-1} in a voltage window of 1.6 V, showing its great potential for energy storage.

2. Experimental

2.1. Materials

Cobalt acetate, hexamethylene tetramine (HMT), sodium sulfide, and KOH were used as received without further purification. Deionized water was used in all of the experiments.

2.2. Preparation of 2D CoS_x

In a typical procedure for the synthesis of 2D cobalt carbonate hydroxide, 2.5 mmol cobalt acetate and 7.5 mmol HMT were dissolved in 16 mL water. The obtained solution was transferred into a Teflon-lined stainless-steel autoclave with a total volume of 20 mL. The autoclave was sealed and maintained at 210 °C for 2 h reaction. Thereafter, the solution was cooled down to room temperature and filtered, and the obtained cobalt carbonate hydroxide (CoCH) with pink color was rinsed by water several times to remove the residual reactant. To prepare 2D CoS_x, the CoCH powder was anion exchanged by Na_2S solution. The method was similar to our previous report [9]. 20 mL saturated Na_2S solution was dropwise added into the suspension of 0.2 g CoCH in 50 mL water at room temperature under a nitrogen atmosphere in 1 h. After the suspension was stirred for 3 more hours at room temperature, black CoS_x product was filtered and washed by adequate water, and then dried at 80 °C.

2.3. Structure and electrochemical measurements

The phase of cobalt compounds was characterized by a powder X-ray diffractometer (XRD, PANalytical, Empyrean) using Cu-Kα irradiation (λ = 1.5406 Å) from 10° to 80°. A scanning electron microscope (SEM, Hitachi S-4800) and a transmission electron microscope (TEM, Philips-CM200) were used to characterize their morphologies and microstructures. The chemical analysis of materials was carried out by X-ray photoelectron spectroscopy (XPS, Shimadzu, AXIS Supra). Fourier transformed infrared (FTIR) spectrum was measured by a Bruker spectrometer (TENSOR 27).

The electrochemical performance of the materials was measured under a three-electrode system in 2 M KOH aqueous solution as electrolyte. The electrode was prepared by painting 80 wt% active material onto the surface of Ni foam using 10 wt% acetylene black and 10 wt% PVDF as conductive addition and polymer binder, respectively, and the mass loading of active material on each electrode was about 5 mg. The specific capacitance (C_s, in F g^{-1}) is calculated by the following equation,

$$C_s = I \times t/(m \times \Delta V) \quad (1)$$

wherein I (A), t (s), m (g), ΔV (V) represent the discharge current, discharge time, mass of active material and potential window, respectively.

Hybrid capacitors with 2D CoS_x as positive electrode and activated carbon (AC) as negative electrode, a piece of cellulose paper as the separator were assembled to evaluate their potential application. The electrochemical properties of the hybrid capacitors were measured in a two-electrode system in 2 M KOH. The energy density (E, Wh Kg^{-1}) and power density (P, W Kg^{-1}) of the hybrid capacitors can be calculated according to the following two equations,

$$E = \frac{1}{7.2} C \times \Delta V^2 \quad (2)$$

$$P = E/\Delta t \quad (3)$$

where C (F g^{-1}), ΔV (V), Δt (s) represent the specific capacitance of hybrid capacitor, potential window and discharge time, respectively.

3. Results and discussions

3.1. Structure and morphology characterization

The XRD patterns of CoCH precursor and CoS_x are shown in Fig. 1. In Fig. 1a, the high intensity of XRD peaks implies the crystalline nature of CoCH. The peaks at 14.65°, 17.44° and 24.03° are corresponding to the (020), (120) and (220) planes of cobalt carbonate hydroxide (PDF No. 29-1416). In addition to the peaks from CoCH, some diffraction peaks from cobalt carbonate (PDF No. 11-0692) can be also observed. We found that the reaction temperature was a rather important factor for the phase of the final product. Below 120 °C, the main product was alpha cobalt hydroxide [36,37].

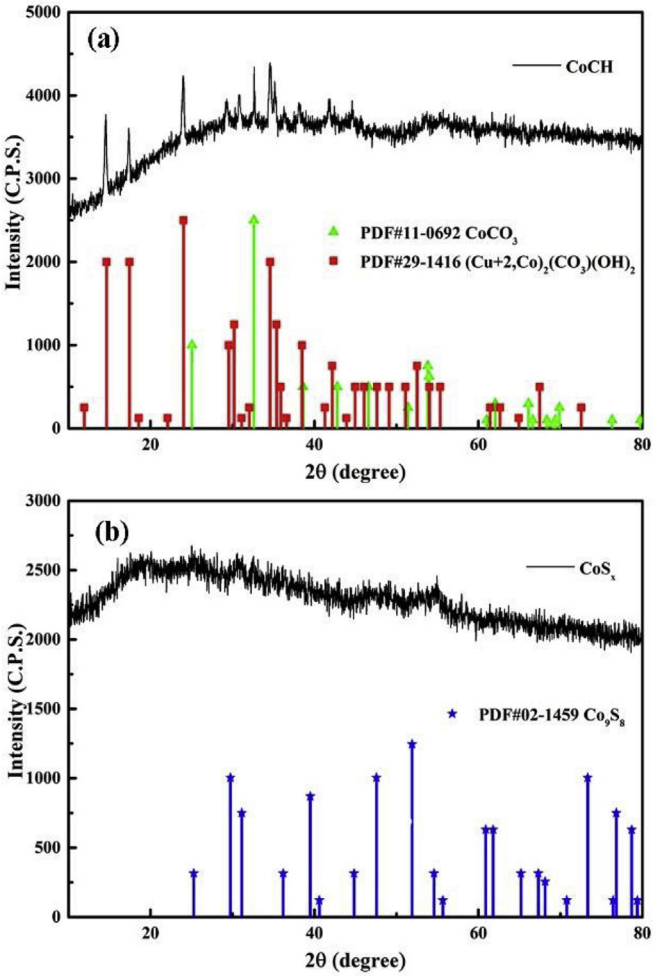

Fig. 1. XRD patterns of CoCH (a) and CoS_x (b).