Journal of Alloys and Compounds 772 (2019) 25–32

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

All-solid-state asymmetric supercapacitor based on porous cobalt selenide thin films

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ARTICLE INFO

Article history:
Received 17 February 2018
Received in revised form
24 August 2018
Accepted 2 September 2018
Available online 8 September 2018

Keywords:
Cobalt selenide
Electrochemical properties
Asymmetric
All-solid-state supercapacitors

ABSTRACT

As a significant semiconductor material, cobalt selenide has enormous potential and extensive application prospects in the field of solar cells, photocatalysis and supercapacitor. In this paper, porous CoSe thin films were successfully fabricated on stainless-steel sheet using a facile, effective electrodeposition technique. Electrochemical tests reveal that the specific capacitance reaches as high as 510 F g^{-1} at the current density of 1 A g^{-1} with the capacitance retention of 91% over 5000 cycles. An asymmetric all-solid-state supercapacitor is fabricated using CoSe thin film as the positive electrode and activate carbon as the negative electrode. The combined solid device displays a high area specific capacitance of 18.1 mF cm^{-2} accompanied with good cycling stability, outstanding flexibility and satisfactory mechanical stability. Furthermore, the solid devices connected in series can power the red light-emitting diodes. The results show great potential for preparing large scale high energy density storage systems.

1. Introduction

Supercapacitor (SC) is a new type energy storage component, which plays a vital role in the field of high-performance power sources. Compared with secondary batteries and traditional capacitors, SCs have the advantages of high power density, fast dynamic response, excellent charge-discharge efficiency and superior cycling stability [1–4]. In recent years, flexible all-solid-state asymmetric supercapacitors (ASCs) made significant progress that they could further improve capacitance and energy density, widen the operation voltage window and reduce manufacturing costs to meet the actual requirements in portable and wearable electronics [5,6].

Two types of capacitor active materials are widely studied in the past decades. Among them, carbonaceous materials, such as carbon nanotubes (CNT) [7–9], graphene [10–13] and active carbon (AC) [4,14–16], show good conductivity and outstanding stability, while the capacitance is less than 250 F g^{-1}. Such low capacitance is possibly attributed to the limitation of electronic double-layer (EDL) energy storage mechanism. The others are metal oxides/sulfides, such as NiO [17–21], CoO [22–25], MnO_2 [26–29], CoNiS [30–33] et al. These active materials are famous for high energy density due to their interfacial reversible redox reactions, whereas they are short of electrical conductivity and mechanical properties. Therefore, discovering neoteric electro-active materials or material combinations which strengthen the specific capacitance and energy density without sacrificing their conductivity and stability remains a great challenge in the field of materials science.

Compared with transition metal oxides, metal selenides possess higher electrochemical activity since the electronegativity of selenium is lower than that of oxygen. Thus, the substitution of selenium for oxygen could create a more flexible microstructure. Furthermore, transition metal selenides exhibit much enhanced electrical conductivity compared with metal oxides/sulfides [34]. Therefore, it can be expected that transition metal selenides would show good electrochemical properties as electrode active materials. In the past few years, some metal selenides, such as hierarchical GeSe nanostructures [35], SnSe and $SnSe_2$ nanosheets [36], CuSe nanosheet arrays [37] have been developed to construct all-solid-state SCs and achieved great success. As a significant p-type multifunctional semiconductor, cobalt selenide has been extensively studied in the field of solar cells, superconductor and photocatalysis. The cobalt selenides are composed of two stable forms

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https://doi.org/10.1016/j.jallcom.2018.09.023
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(CoSe, $CoSe_2$) and two possible compounds (Co_3Se_4, Co_2Se_3) at room temperature. Although a variety of methods have been adopted to prepare CoSe nano-materials [38–40], the synthesis of porous CoSe thin films and their application in supercapacitor has not been explored yet.

In this paper, porous CoSe thin films were successfully deposited on a stainless-steel substrate by traditional electrodeposition method. The CoSe thin films are used as the electrode materials for supercapacitors. Electrochemical tests revealed that the specific capacitance reached as high as 510 F g^{-1} at the current density of 1 A g^{-1}, which is much higher than that of carbonous materials and comparable to that of transition metal oxides/sulfides. The capacitance retention reaches 91% over 5000 cycles indicating the excellent cycling stability. Owing to its high specific capacitance and excellent cycling stability, CoSe thin films are used as positive electrode to fabricate all-solid-state ASCs. The combined solid device displays a high area specific capacitance of 18.1 mF cm^{-2} accompanied with good cycling stability, outstanding flexibility and satisfactory mechanical stability. Furthermore, the solid devices connected in series can power the red light-emitting diodes (LED). The results show great potential for preparing large scale high energy density storage systems.

2. Experimental section

2.1. Synthesis of CoSe thin films on stainless-steel sheet

Before the electrodeposition, the stainless-steel sheets ($1.25 \times 4\ cm^2$) were subjected to ultrasonic cleaning in acetone for 30 min and soaked in acetone for more than 24 h in order to eliminate the influence of oil and grease on the surface. Then, the stainless-steel sheets were dried in a vacuum oven at 50 °C for 2 h. CoSe thin films were deposited in a standard three-electrode configuration using a stainless-steel sheet, a Pt sheet, and a saturated calomel electrode (SCE) as the working electrode, counter electrode, and reference electrode, respectively. A series of experiments were conducted to optimize the deposition parameters. The deposition potentials varied from −0.5 to −0.8 V, the deposition temperatures were tuned from 20 to 80 °C and the deposition time was adjusted from 5 to 30 min. The electrolyte was prepared as follows: $Co(CH_3COOH)_2$ (2 mM), SeO_2 (2 mM), and KCl (0.1 M) were dissolved in 1000 mL of distilled water and the pH of the solution was adjusted to 3.5 with 0.2 M hydrochloric acid. In order to get high loading of CoSe, the concentration of $Co(CH_3COOH)_2$ and SeO_2 were increased to (5, 10, 20, 50 mM) for comparison while the other parameters were fixed.

2.2. Materials characterization

Scanning electron microscopy (SEM, FEI quanta 200) was used to study the morphology evolution of the as-prepared samples under different electrodeposition parameters. X-ray diffractometer (XRD, Bruker D8 ADVANCE) was employed to analyze the phase composition of the deposited films. Transmission electron microscope (TEM, FEI, Tecnai F20) and high resolution TEM images were taken to confirm the size as well as the crystalline structure of CoSe nanosheets. Integrated elemental composition over an area were collected using energy dispersive X-ray spectroscopy (EDS, EDAX Co.) equipped with TEM. X-ray photoelectron spectroscopy (XPS, ESCALAB 250 Xi, Thermo Fisher Scientific) measurements were performed by using a scanning X-ray microprobe.

2.3. Fabrication of CoSe//AC all-solid-state ASCs

Flexible all-solid-state ASCs were assembled by using CoSe/stainless-steel as positive electrode and AC/stainless-steel as negative electrode. PVA-KOH gel and cellulose septum were used as electrolyte and separator respectively. Briefly, CoSe/stainless-steel and AC/stainless-steel were immersed in the PVA-KOH gel solution for 3 min to adsorb a layer of the solid electrolyte. After the excess water was vaporized, the cellulose septum was adhered in the middle of two electrodes to forming sandwich structure. Finally, the device was dried in a vacuum oven at 50 °C for 24 h. The preparation of PVA-KOH gel electrolyte was performed as follows: 3 g KOH was added to 10 mL deionized water. 6 g PVA was added into 50 mL of deionized water and stirred at 85 °C until the solution became limpid, then the solution was cooled to room temperature. After that, the KOH solution was dropped in PVA solution to form gel electrolyte.

2.4. Electrochemical measurement

Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) were used to evaluate the electrochemical performance of CoSe thin films and ASC devices. All experiments were carried out on an electrochemical workstation (CHI 660D) at room temperature. Electrochemical performance of CoSe thin films were conducted using a three-electrode configuration, a CoSe thin film, a Pt sheet, and an SCE were used as the working electrode, counter electrode, and reference electrode, respectively. The electrolyte was 1 M KOH aqueous solution. The all-solid-state ASC devices were examined in the two-electrode mode.

3. Results and discussion

3.1. Characterization of the CoSe thin films

CoSe thin films were formed by the potentiostatic electrodeposition method. In order to obtain high-quality CoSe thin films with splendid electrochemical performance, various electrodeposition parameters were adjusted to optimize the growth conditions. Fig. 1 shows the SEM images of the as-synthesized CoSe thin films under different deposition potentials with the temperature of the electrolyte at 60 °C. It is clearly seen that a compact thin film decorated with some nanoparticles was obtained at −0.5 V (*vs*. SCE) as shown in Fig. 1a. When decreasing the deposition potential to −0.6 V (*vs*. SCE), the nanoparticles became even bigger and formed some wide clearances (Fig. 1b). When the deposition potential was further decreased to −0.7 V (*vs*. SCE), the nanoparticles were connected by some thin nanosheets (Fig. 1c, more detailed information seen in TEM images). Because the nanosheets supported each other, the films would keep stable structure when constructing the all-solid-state device. Additionally, the porous structures are suitable for the proton exchange during the charge/discharge delivery process and were expected to have an enhanced electrochemical property. With continued decreasing the deposition potential to −0.8 V (*vs*. SCE), some cracks appeared on the surface of CoSe thin films, which made them peel off from the substrate easily. Thus, we choose −0.7 V (*vs*. SCE) to fabricate large area porous CoSe thin films. Other deposition parameters were also studied systematically as shown in supporting information (SI). The crystallinity of the sample will be reduced accompanied with the generation of some Se nanoparticles on the surface of the sample when the deposition temperature is lower than 60 °C. (Fig. S1). The loading amount and the thickness of the obtained CoSe thin film is greatly influenced by the deposition time (Fig. S2). In addition, Fig. S3 shows the morphology of CoSe thin films prepared at different pH values of the electrolyte. By integrating the above experiments, the porous CoSe thin films were synthesized under