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3D interconnected ultrathin cobalt selenide nanosheets as cathode materials for hybrid supercapacitors

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ABSTRACT

3D interconnected ultrathin CoSe nanosheets are prepared via a hydrothermal synthesis method and utilized as superior battery-like electrode material for the first time. Due to the features of the unique 3D interconnected ultrathin nanosheets with a large BET specific surface area, superior mesoporous structure and good electrical conductivity, the as-resulted 3D interconnected ultrathin CoSe nanosheets manifests a high specific capacity of 70.6 mAh g^{-1} at 1 A g^{-1} and remarkable rate performance with 52.8% of capacity retention rate at 100 A g^{-1} compared with 1 A g^{-1}. Furthermore, a novel aqueous hybrid supercapacitor is assembled by employing 3D interconnected ultrathin CoSe nanosheets and activated carbon as the cathode and anode, respectively. The assembled hybrid device displays a specific energy of 18.6 Wh kg^{-1} at a specific power of 750 W kg^{-1} and outstanding cycling life with 95.4% of the initial capacity retention for 20000 cycles at 5 A g^{-1}. These results imply that the unique 3D interconnected ultrathin CoSe nanosheets can be considered as highly potential candidate electrode materials for hybrid supercapacitors.

1. Introduction

Electrochemical energy conversion and storage are playing important roles in modern society for solving the shortage of fossil fuels and the global warming issues [1,2]. Batteries and supercapacitors are regarded as the best two technologies for electrochemical energy storage systems. Since supercapacitors possess the advantages of high power density, ultrafast charge-discharge rate and remarkable cycling stability, they have stimulated extensive attention in recent years [3–5]. Nowadays they have shown tremendous prospect in many fields such as consumer electronics, hybrid electric vehicles, breaking systems, new energy and industrial power equipment [6–8].

Recently, battery-like electrode materials have attracted researcher's attention because of their high specific capacity [9–13]. Among them, metal sulfides as a new type of battery-like electrode materials have received increasing interests as promising hybrid supercapacitor electrode materials [14,15]. They not only own rich redox chemistry, but also possess better electronic conductivity, thermal and mechanical stability than those of their corresponding metal oxides, leading to the enhancement of the specific capacity and capacity retention rate. Some metal sulfides such as NiS, CoS, MnS, MoS_2, CuS and so forth [16–21], have been developed as potential candidate cathode materials for supercapacitors in view of their superior electrochemical performances. It is noteworthy that another new class of metal selenides is far less reported than that of metal sulfides. Some reported literature [22,23] have revealed that metal selenides even own a narrower band gap than the corresponding metal sulfides, which give rise to a higher electronic conductivity, leading to the enhancement of the electrochemical properties. Li et al. [23] explored the influence of S and Se to the electrochemical performances of nickel-cobalt oxides by the electrochemical tests, revealing the higher specific capacity of nickel-cobalt selenides than nickel-cobalt sulfides. Thus, metal selenides show great potential as superior supercapacitor electrode materials. Besides, metal selenides have also been reported to show good performance in such areas as lithium/sodium ion batteries [24–29], electrocatalysts for oxygen evolution reaction [30–34], dye-sensitized solar cells [35–37], magnetic devices [38], and so on. Nevertheless, metal selenides have not attracted extensive attention for the use as hybrid supercapacitor electrode materials so far

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although several reports have demonstrated that metal selenides appear quite promising materials used in supercapacitors. For instance, Wang et al. [39] successfully fabricated 3D hierarchical $GeSe_2$ nanostructures utilising a facile thermal evaporation way, which manifested a specific capacitance of 300 F g^{-1} at 1 A g^{-1}. Guo et al. [40] developed a simple one-step solvothermal way of synthesizing hierarchical NiSe microspheres by using Ni foam as substrate, which demonstrated good capacitive property with a specific capacitance of 492 F g^{-1} at 0.5 A g^{-1}. Banerjee et al. [41] synthesized $Co_{0.85}Se$ hollow nanowires array on conductive carbon fiber paper through a secondary hydrothermal method and it exhibited superior pesudocapacitive performance with a specific capacity of 674 F g^{-1} at 1.48 A g^{-1}, good rate capability with 65.9% of capacity retention rate at 11 A g^{-1} and superior cycling life with 89% of initial capacity retention for 2000 cycles. However, as far as we know, it is still few study about CoSe as electrode material for application in supercapacitor, although there is the report of CoSe employed as electrocatalysts for oxygen evolution reaction [34]. Therefore, it is very significant to conduct a research.

Herein, we firstly report the synthesis of 3D interconnected ultrathin CoSe nanosheets through a facile hydrothermal synthetic route for the use as supercapacitor electrode materials. The resulting 3D interconnected ultrathin CoSe nanosheets are characterized in detail by XRD, FESEM, EDS, TEM, HRTEM, SAED, XPS and BET. When estimated in three-electrode configuration, the as-obtained 3D interconnected ultrathin CoSe nanosheets manifest superior electrochemical properties with a specific capacity of 70.6 mAh g^{-1} at 1 A g^{-1} and remarkable rate capability with 52.8% of capacity retention rate at 100 A g^{-1}. Moreover, the assembled CoSe//AC hybrid device displays a high specific energy (18.6 Wh kg^{-1}) or specific power (18.75 kW kg^{-1}). In addition, the hybrid device displays a very high long-term cycling life with 95.4% of initial capacity retention for 20000 cycles at 5 A g^{-1} and exceptional coulombic efficiency (~100%) in the charge/discharge cycling process.

2. Experimental section

2.1. Materials preparation

In the synthesis of CoSe, 0.48 mmol of $CoCl_2 \cdot 6H_2O$ was added to a Teflon-lined stainless steel autoclave (100 mL), which was dissolved in 50 mL of distilled water. Subsequently, 0.48 mmol of selenium powder was added into the autoclave under strong stirring. Afterward, 10 mL of $N_2H_4 \cdot H_2O$ (85 wt%) was further added to the above mixture under vigorous stirring. After continually stirring for 30 min, the Teflon-lined stainless steel autoclave was kept at 100 °C for 24 h in an oven. After naturally cooling to ambient temperature, the product was centrifuged and rinsed with distilled water five times and absolute ethanol one time, and lastly dried at 60 °C for 12 h.

2.2. Materials characterization

The X-ray diffractometer (XRD, Rigaku D/max 2550 VB^+) was utilized to determine the structure and phase purity of the as-synthesized sample. Field emission scanning electron microscopy (FESEM, MIRA3) and the corresponding energy dispersive spectroscopy (EDS) were employed to characterize the morphology and elemental data of the as-obtained sample. Transmission electron microscopy (TEM, JEM-2100F), High resolution transmission electron microscopy (HRTEM, JEM-2100F) and the corresponding selected area electron diffraction (SAED) were utilized to investigate the morphology and microstructure of the as-resulted sample. X-ray photoelectron spectrometer (XPS, K-Alpha) was employed to analyze the chemical composition of the resulting sample. Nitrogen adsorption/desorption measurement (BET, BELSORP-MINIII) was conducted to evaluate the specific surface area and pore structure of the resulting sample.

2.3. Electrochemical test

The electrochemical performances of the CoSe electrode were firstly investigated utilising a conventional three-electrode configuration with 2 M KOH as electrolyte. The working electrode was prepared by mixing active material (3D interconnected ultrathin CoSe nanosheets), conductive agent (carbon black, super P) and binder (polyvinylidene difluoride, PVDF) in a mass ratio of 7:2:1 with a small amount of N-methy-*l*-2-pyrrolidine (NMP). The mixture was then coated on the Ni-foam current collector, which was pretreated referring to our previous research work [42,43]. Ni-foam was first immersed in HCl solution (0.1 M) for 24 h, and then rinsed in an ultrasonic bath with acetone and absolute ethanol for three times, respectively. Finally, the rinsed Ni-foam was vacuum-dried at 70 °C for 10 h. The as-fabricated electrode was dried in a vacuum oven at 100 °C for 10 h and then pressed at 10 MPa for several seconds. The electrode area of Ni-foam is about 1.32 cm^2, and the mass loading of active materials on Ni-foam is controlled at about 2.8 mg. The electrochemical properties of the resulting CoSe electrode were studied on a Modulab electrochemical workstation by employing cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) tests with a three-electrode system where CoSe electrode, Pt foil and Hg/HgO utilized as the working electrode, counter electrode and reference electrode, respectively.

The electrochemical performances of the CoSe electrode were further estimated by fabricating the coin cell utilising CoSe as the cathode electrode, activated carbon (AC) as the anode electrode, glassy fibrous material as the separator and 2 M KOH as electrolyte, respectively. The coin cell (CR 2016) was assembled in air and composed of cathode electrode, separator and anode electrode in sequence, where a certain amount of electrolyte was added to guarantee the adequate wetting of the two electrodes. Subsequently, the assembled coin cell was further sealed to avoid the leakage of electrolyte. The preparation of AC was reported in our previous research [42,43]. The AC electrode was fabricated by employing the same way as the CoSe electrode. The mass ratio of the CoSe electrode to the AC electrode was controlled at about 1:1, and the mass loading of active materials of the two electrode is about 2 mg cm^{-2}. The CV, GCD and EIS of the hybrid device were conducted on a CHI 660D electrochemical workstation, and the cycling life of the hybrid device was measured by utilising the CT2001A battery test system.

3. Results and discussion

3.1. Structure and morphology of the 3D interconnected ultrathin CoSe nanosheets

The structure and phase purity of the resulting CoSe sample was characterized by XRD, as demonstrated in Fig. 1. The main peaks of the XRD pattern of the as-obtained sample coincide with the freboldite phase of CoSe (JCPDS No. 89–2004). The characteristic diffraction peaks appeared at 33.2°, 44.8°, 50.5°, 60.1°, 61.8° and 69.7° could be indexed to the (101), (102), (110), (103), (201) and (202) planes of CoSe, respectively. No peaks owing to the presence of impurities can be observed when compared to the standard diffraction patterns, which is indicative of the formation of pure CoSe product.

The morphology and microstructure of the CoSe sample were studied by FESEM, TEM, HRTEM, SAED and EDS, as displayed in