

Fabrication of CoSe₂/carbonized foam with stable durability for supercapacitor

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In this work, CoSe₂/carbonized foam hybrids are fabricated. The effects of selenization temperature on the composition and morphology of CoSe₂/carbonized foam hybrids are investigated. Results show that the selenization temperature affects the particle size of CoSe₂ and the resulting electrochemical performance. And the sample obtained at 900 °C shows good properties as supercapacitor electrode material. Even after 5000 cycles, 132.8 % of the initial specific capacitance can be remained. The outstanding stability may be ascribed to its unique morphology and carbon skeleton.

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1. Introduction

Supercapacitor has received wide attention in recent years, due to the relative high power density, reliable service safety and excellent cycling durability [1-3]. Electrode materials affect the electrochemical performance of supercapacitor. Therefore, it is very urgent to develop high-performance, low cost and environmentally friendly electrode materials. Transitional-metal compounds have received particular attention as energy storage electrode materials, owing to the good electrochemical performance and abundant reserves in nature. Among them, Co-based selenides have been extensively studied for the rich valences and redox reactions [4, 5]. Co-based selenides show outstanding electronic conductivity, compared to other Co-based chalcogenides [6, 7]. According to the reports, carbon materials have been introduced to synthesize Co-based hybrids, in order to improve the electrical conductivity and provide skeletal support [8, 9]. However, developing Co-based selenides with long stability still remain a challenge.

Herein, we propose a facile strategy for fabrication of CoSe₂/carbonized foam. The fabrication procedure is easy-manipulated in a tubular furnace. At high temperature, cobalt is selenized with selenium powder while the melamine foam is carbonized. The obtained carbonized foam plays the role of dispersing cobalt selenide and skeleton support. At optimized selenized temperature, the obtained CoSe₂/carbonized foam exhibits moderate specific capacitance and outstanding cycling performance with 132.8 % of the initial specific capacitance even after 5000 cycles. So the obtained CoSe₂/carbonized foam delivers promising application prospects in supercapacitor.

2. Experimental

The main reagents used are Co(NO₃)₂·6H₂O,

2-methylimidazole, anhydrous ethanol, selenium powder and potassium hydroxide. The above materials are purchased from Sinopsin Chemical Reagent Co., LTD.. Melamine foam is purchased from Puyang Green New Material Technology Co., LTD. All chemical reagents are analytical grade and can be used without further purification. The water is self-made distilled water.

2.1. Synthesis of precursor

Firstly, the melamine foam (MF) was cut into 3 cm×2 cm×1 cm and then washed with self-made distilled water and anhydrous ethanol for 15 minutes, respectively. Secondly, 0.546 g Co(NO₃)₂·6H₂O was added to 15 mL methanol and then stirred to dissolve to form solution. 0.616 g 2-methylimidazole was added to 15 mL methanol and then stirred to dissolve to form solution. The obtained 2-methylimidazole solution was evenly injected into the above solution containing cobalt using a peristaltic pump. Finally, the melamine foam was immersed into the aforesaid solution for 15 minutes and then vacuum-dried. The obtained cobalt-loaded melamine foam through above process acted as precursor.

2.2. Synthesis of CoSe₂/carbonized foam

The above precursor was selenized using selenium powder in a tubular furnace under Ar/H₂ atmosphere for 4 hours at certain temperature. And the heating rate was set at 5° C min⁻¹. The selenization temperature was set at 700 °C, 800 °C, 900 °C and 1000 °C, respectively. And then the resulting samples were cooled naturally. The obtained CoSe₂/carbonized foam hybrids at above temperature are named as CoSe₂/C-700°C, CoSe₂/C-800°C, CoSe₂/C-900°C and CoSe₂/C-1000°C, respectively.

2.3. Materials characterization

XRD patterns were obtained by analytical X'pert PROX-ray diffractometer with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). SEM images were studied through S-4800 SEM. Thermogravimetric analysis (TGA) of the samples was tested by SDTQ600 TG-DSC apparatus between 25–800 °C under air flow.

2.4. Electrochemical performance test

The working electrode was prepared by fixing the CoSe₂/carbonized foam on nickel foam. And the mass load of CoSe₂/carbonized foam on nickel foam is about 3 mg cm⁻². Electrochemical measurements (CV test and GCD test) were performed on CHI760E electrochemical workstation with a standard three-electrode cell, where Pt foil and saturated calomel electrode worked as the counter electrode and the reference electrode, respectively. 2 mol L⁻¹ KOH solution acted as the electrolyte solution.

Specific capacitance of the obtained samples was calculated using the equation (1), according to the GCD curves.

$$C = I\Delta T/m\Delta U \quad (1)$$

where I (A) represents the current density, ΔT (s) is the discharging time, ΔU (v) represents the voltage change, and m (g) is the mass of CoSe₂/carbonized foam. Cycling performance was carried out on CT2001A Land (Wuhan) electrochemical test system.

3. Results and discussion

The crystallographic structure of the CoSe₂/carbonized foam hybrids obtained at different temperature was tested by XRD. As shown in the Fig. 1, XRD patterns of the samples are similar and the diffraction peaks are indexed to CoSe₂ (PDF#00-053-0449). In details, the major diffraction located peaks at 28.9°, 30.8°, 34.5°, 35.9°, 47.7°, 50.2°, 53.5° and 63.3° match well with the (011), (101), (111), (120), (211), (002), (031) and (122) facets of CoSe₂ (PDF#00-053-0449). Furthermore, no impurity peaks are detected, showing high purity and crystallinity of CoSe₂.

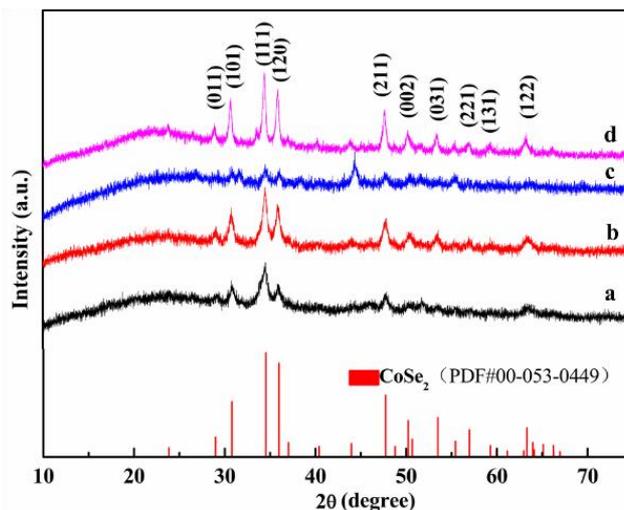


Fig. 1. XRD patterns of the CoSe₂/carbonized foam composites obtained at different temperature. A, b, c and d represent the CoSe₂/C-700 °C, CoSe₂/C-800 °C, CoSe₂/C-900 °C and CoSe₂/C-1000 °C, respectively (color online)

The morphology of the obtained hybrids has been investigated by the SEM technique, as shown in Fig. 2. At high temperature, melamine foam is carbonized into carbonized foam under Ar/H₂ atmosphere. The obtained carbonized foam presents broken structure after selenification process, which can be seen in the Fig. 2a, Fig. 2c, Fig. 2e and Fig. 2g. And it is clearly, there is CoSe₂ on the surface of the carbonized foam. In details, when the selenification temperature is 700 °C, the obtained CoSe₂ is impact and distributed on surface of the carbonized foam, as shown in the SEM image of CoSe₂/C-700 °C (Fig. 2b). As the selenification temperature increases to 800 °C, the granular CoSe₂ appears in the obtained sample CoSe₂/C-800 °C. And the CoSe₂ particles of CoSe₂/C-800 °C hybrid are evenly distributed on the surface of the carbonized foam and closely adjacent to each other (Fig. 2d). Further increasing temperature to 900 °C, the size of CoSe₂ particles in the obtained CoSe₂/C-900 °C hybrid increases and the gap between particles appears, as shown in the Fig. 2e. When the selenization temperature continues to increase to 1000 °C, the size of selenide particles in CoSe₂/C-1000°C increases and the particle size becomes uneven. At high temperatures (1000 °C), larger particles appear.

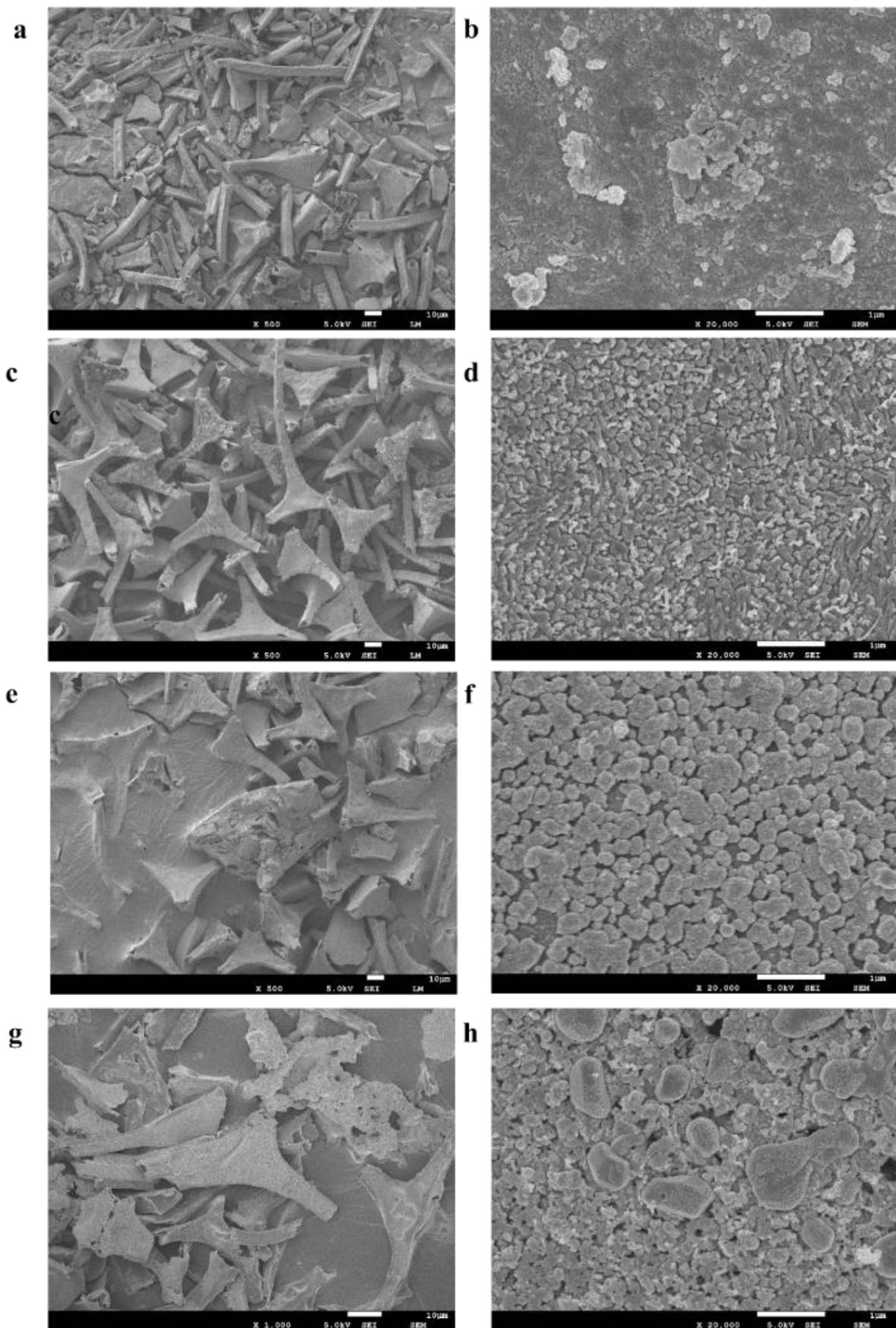


Fig. 2. SEM images of samples: (a-b) CoSe_2/C -700 °C, (c-d) CoSe_2/C -800 °C, (e-f) CoSe_2/C -900 °C and (g-h) CoSe_2/C -1000 °C

To quantify the content of CoSe_2 in the obtained CoSe_2/C -900 °C hybrid, TGA test was performed in air atmosphere from 25 to 800 °C. It can be seen from the Fig. 3 that there is an obvious weight loss during 450-600 °C, which can be attributed to the loss of carbonized foam, the oxidation of CoSe_2 and the formation of Co_3O_4 [10]. And the content of CoSe_2 in CoSe_2/C -900 °C hybrid is approximate 60.7 wt%.

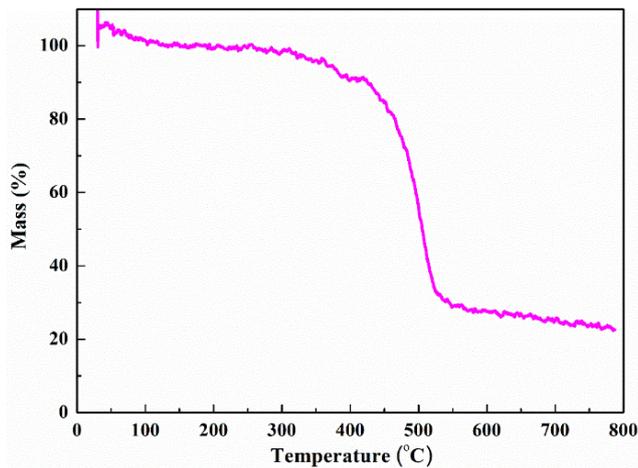


Fig. 3. TGA curve of the sample CoSe_2/C -900 °C (color online)

Electrochemical properties of the CoSe_2 /carbonized foam hybrids obtained at different temperature were characterized by CV and GCD test in 2 mol L^{-1} KOH solution. The CV curves of the obtained CoSe_2 /carbonized foam hybrids at 30 mV s^{-1} can be seen in the Fig. 4a. Every sample shows a pair of redox peaks in the corresponding CV curve. So the obtained CoSe_2 /carbonized foam hybrids are battery-like electrode materials [11, 12]. As for the sample CoSe_2/C -900 °C, the enclosed area of CV curve is the largest, showing the highest specific capacitance. And the CV curves of CoSe_2/C -900 °C obtained during 5-60 mV s^{-1} are shown in the Fig. 4b. Even if the scan rate increases to 60 mV s^{-1} , the redox peaks are still symmetrical, showing its redox reaction is reversible. Voltage platform appears in the GCD curves of CoSe_2/C -900 °C (Fig. 4c), which further confirms its battery-like behavior [13, 14]. The above phenomenon is consistent with the CV test results. The specific capacitance of samples is shown in the Fig. 4d. Specific capacitance of CoSe_2/C -900 °C is the highest. In details, it shows 530.4, 480.1, 465.7, 438.1, 414.3, 393.4 and 328.9 F g^{-1} at 1, 2, 3, 4, 8, 10 and 20 A g^{-1} , respectively. The relative high capacitance may be attributed to its unique structure. As for the sample CoSe_2/C -900 °C, its particles are uniform and particle size is proper, compared to other samples. During charge and discharge process, the electrolyte ion can diffuse into the space between the particles.

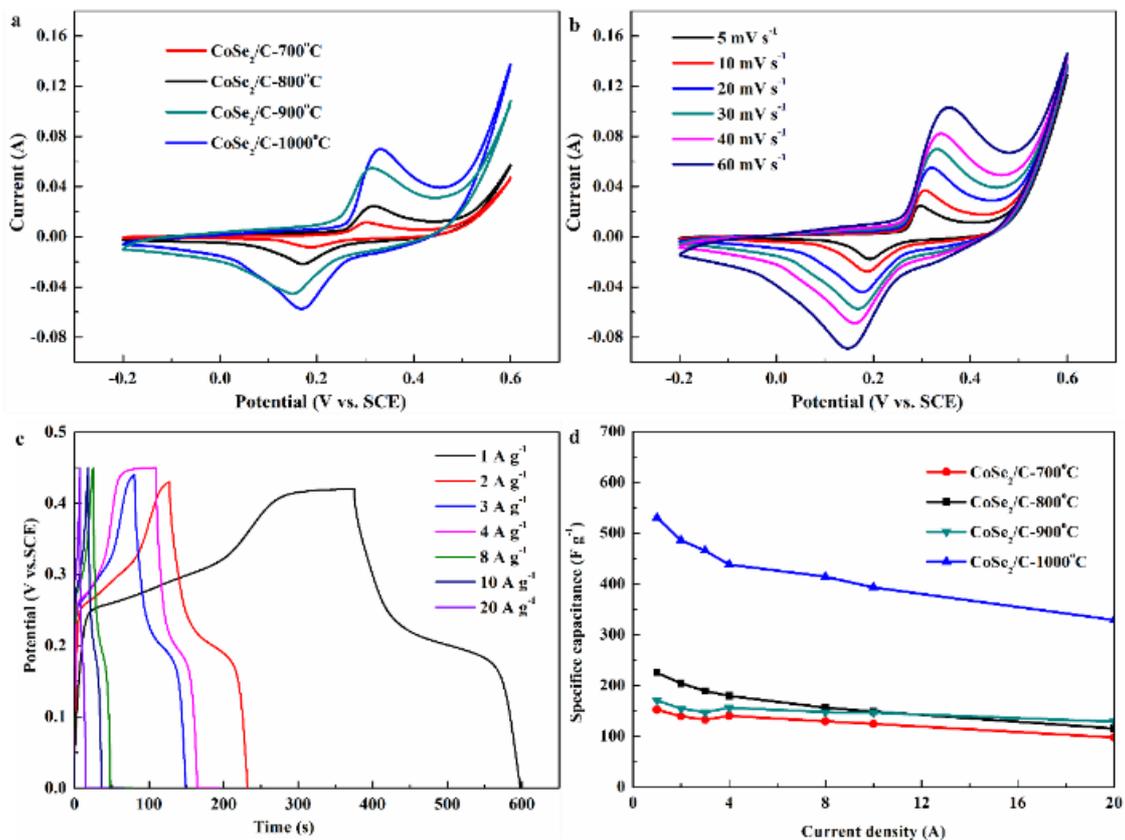


Fig. 4. (a) CV curves of the CoSe_2 /carbonized foam composites obtained at different temperature at 30 mV s^{-1} , (b) CV curves of the sample CoSe_2/C -900 °C, (c) GCD curves of the sample CoSe_2/C -900 °C, (d) Specific capacitance of the CoSe_2 /carbonized foam composites obtained at different temperature (color online)

The cycling performance of the sample CoSe₂/C-900 °C is evaluated at 10 A g⁻¹, as shown in the Fig. 5. It can be seen that the specific capacitance increases sharply in the initial charging/discharging process and remains basically stable with a slow growth rate after 100 cycles. Impressively, 132.8 % of the initial capacitance retention is observed even after 5000 cycles. The increase of specific capacitance in the initial charging/discharging process may be due to the activation of electrode material and selenides may be converted to hydroxides with higher theoretical capacity in alkaline electrolyte [15]. More importantly, during the charging/discharging process, the carbonized foam in the hybrid plays a role of skeleton support, which is conducive to the improvement of stability.

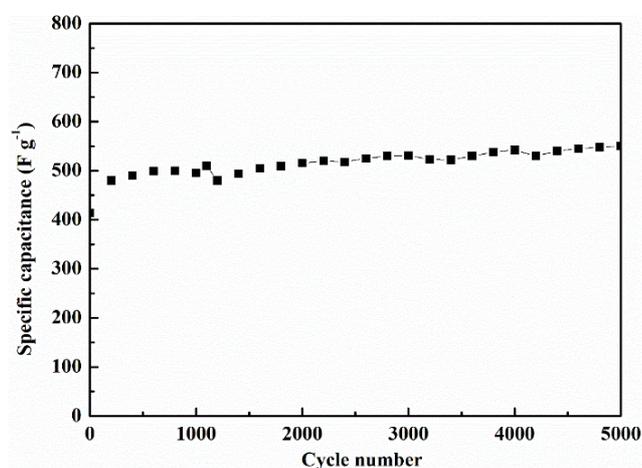


Fig. 5. Capacitance retention of the sample CoSe₂/C-900°C at 10 A g⁻¹

4. Conclusion

In this work, CoSe₂/carbonized foam hybrids were in suit fabricated. Selenization temperature affects the morphology and the resulting electrochemical properties. At optimized condition, the obtained CoSe₂/C-900 °C shows moderate specific capacitance and long stability. During charging/discharging process, the obtained carbonized foam may act as carbon skeleton, which is conducive to the improvement of stability.

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