

# Preparation and electrochemical performances of carbon-coated nanoscale SnS for supercapacitors

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**Abstract** Carbon-coated SnS as electrode materials for supercapacitor were synthesized by high-energy ball milling and following co-heating with polyvinyl alcohol. The morphology and structure of prepared carbon-coated SnS were studied by high-resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD). Electrochemical investigation indicated that carbon-coated SnS presented preferable electrochemical performances than pristine SnS. In comparison to pristine SnS, carbon-coated SnS had better capacitive response in cyclic voltammetry and could deliver larger specific capacitance of 28.47 F/g in galvanostatical charge–discharge process. Enhanced conductivity of carbon-coated SnS revealed by Nyquist plots was considered to be responsible for its enhanced electrochemical performances.

**Keywords** SnS · Carbon coated · Supercapacitors · Electrochemical capacitors

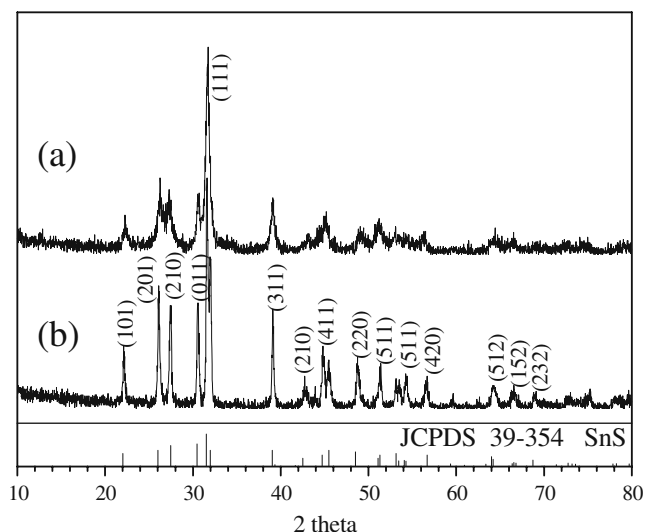
## Introduction

As a new kind of energy storage device, supercapacitor has attracted much attention in recent years by its long cycle life, high efficiency, high power density, and environmentally friendly characters. Besides well-known carbon series materials, some transition metal oxides have been proved to be outstanding electrode materials for supercapacitor due to their pseudo-capacitance charge storage mechanism, including RuO<sub>2</sub> and MnO<sub>2</sub>, etc. RuO<sub>2</sub> has been revealed to have large

capacitance and excellent electrochemical performances [1, 2], but the cost of RuO<sub>2</sub> material is too expensive to be practically applied in commercial usage. MnO<sub>2</sub>, with its low cost and toxicity, is believed to be a very promising electrode material for supercapacitor. The electrochemical properties of MnO<sub>2</sub> strongly lie on its morphology, dimensionality, crystalline structure and bulk density. MnO<sub>2</sub> with specific morphologies, such as MnO<sub>2</sub> nanowire [3], and MnO<sub>2</sub> nanorod [4], presented attractive supercapacitor properties in comparison with common MnO<sub>2</sub>. But the preparation of specific MnO<sub>2</sub> tends to be experimentally fussy and hard to be produced in large scale. Furthermore, electrochemical improvements can be achieved by combining MnO<sub>2</sub> with carbon materials, including carbon nanotube [5], carbon aerogel [6], activated carbon [7], etc. MnO<sub>2</sub> is a semi-conductor with poor electron conductivity, leading to low efficiency of electron exchange upon proton intercalation/de-intercalation and small capacitance. When MnO<sub>2</sub> and carbon materials are combined to form a MnO<sub>2</sub>/Carbon compound electrode, the electrochemical performances could be predominantly improved due to excellent electron conductivity of carbon materials.

SnS is an orthogonal IV-VI group semi-conductor material and generally has lamellar structure. It has been proved that SnS has potentially excellent properties for application in various areas, such as photovoltaic material [8] and anode of lithium ion batteries [9]. Jayalakshmi. M. et al. [10] investigated hydrothermal prepared nano SnS as an electrode active material for supercapacitor. Their results indicate that nano SnS has good stability and the capacitance is impressively higher in both alkali and neutral solutions. Up to now, there have few reports about SnS on its supercapacitor application. As a potential alternative for traditional carbon series materials used in supercapacitor, SnS needs more exploration.

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**Fig. 1** X-ray diffraction patterns of as-synthesized (a) pristine SnS; (b) carbon-coated SnS

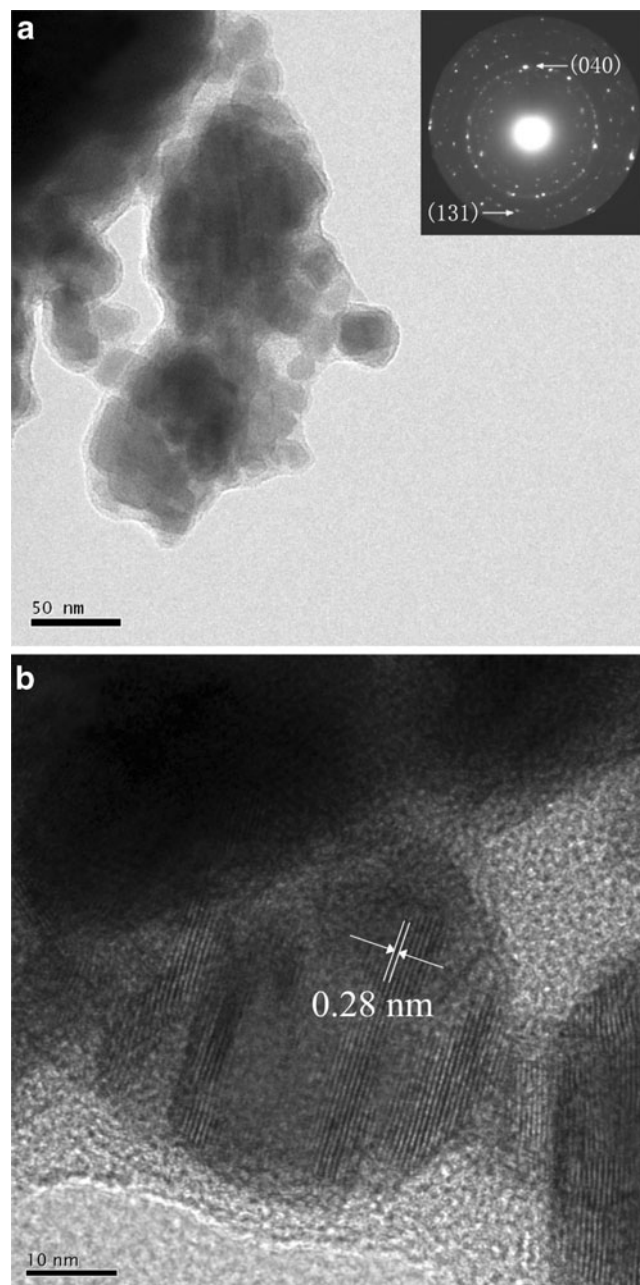
In present work, we attempt to make use of good electron conductivity of carbon to alleviate poor electron exchange due to semi-conductor property of SnS. Carbon-coated nanoscale SnS are prepared and its supercapacitor behaviors are investigated and discussed.

## Experimental

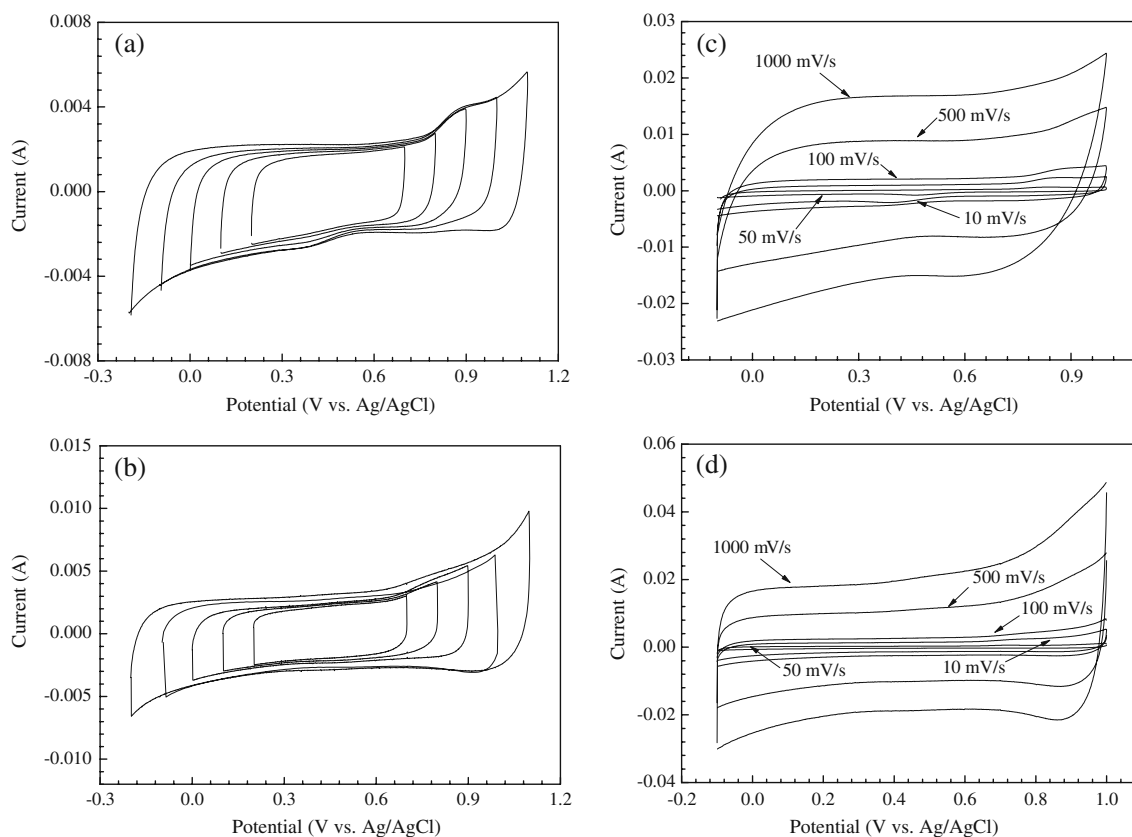
Nanoscale SnS powder was synthesized by high-energy ball-milling method and then coated with amorphous carbon by co-heating with polyvinyl alcohol (PVA) at 700 °C. The detailed procedure for preparing carbon-coated nanoscale SnS is described elsewhere [11]. Briefly, equal mole Sn (74  $\mu\text{m}$ ) and S (50  $\mu\text{m}$ ) powders were mixed and put into a stainless steel container with a ball-to-powder ratio of 20:1. The container was fixed on a planetary high energy ball mill for milling 100 h at 300 rpm. Obtained powders were adequately mixed up with PVA at weight ratio of 1:1 in an agate mortar. The mixture was heated at 10 °C/min heating rate in the quartz boat at 700 °C under a flow rate of 80 mL/min argon. The obtained products were grinded in an agate mortar after furnace cooling. The pristine and co-heated SnS powders were examined by X-ray diffraction (XRD; D8-ADVANCE, Cu  $K\alpha$ ) and high resolution transmission electron microscopy (HRTEM; FEI, TECNAI G<sup>2</sup>-F20)

The electrodes for evaluating the electrochemical properties of as-prepared powders were fabricated by mixing synthesized SnS with 20 wt.% conducting agent (acetylene black) and 5 wt.% polytetrafluoroethylene latex as binder. A slurry consisting of above mixture was smeared into a 1 cm<sup>2</sup> area foam nickel mesh. Subsequently, the mesh was dried in air at 120 °C for 2 h to remove solvent and finally was pressed

under 10 MPa pressure to keep good adherence between electrode material and the nickel mesh current collector. Electrochemical investigations were carried out in three-electrode cell using carbon as counter electrode and Ag/AgCl as reference electrode. The electrolytes contained 0.1 M KOH, used to study the capacitive behavior of as-prepared electrodes. Cyclic voltammetry (CV) studies were performed at a potential range of  $-0.1\sim 1.0$  V versus Ag/AgCl at a scan rate of 10 mV/s, 50 mV/s, 100 mV/s, 500 mV/s and 1,000 mV/s on CHI660C electrochemical workstation (Chenghua, Shanghai China). Galvanostatical charge–discharge test were conducted



**Fig. 2** HRTEM images of as-prepared carbon-coated SnS



**Fig. 3** Cyclic voltammograms of different potential ranges for **a** pristine SnS; **b** carbon-coated SnS; and under different scan rates for **c** pristine SnS; **d** carbon-coated SnS in 0.1 M KOH solution

at a current density of 200 mA/g between  $-0.1$  V to  $1.0$  V versus Ag/AgCl using computer controlled cycling equipment (LAND, Wuhan China). Electrochemical impedance spectra were measured over the frequency range  $100$  kHz~ $10$  mHz at a potentiostatic signal amplitude of  $5$  mV on same workstation as CV test.

**Results and discussion**

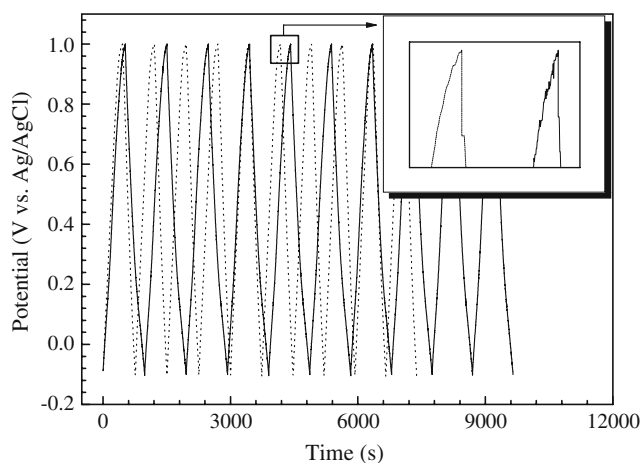
Figure 1 shows the XRD patterns of as synthesized pristine SnS and carbon-coated SnS powders. Diffraction peaks could be clearly observed, which are corresponding to the characteristic peaks of orthorhombic SnS phase (JCPDS 39-354). No diffraction peaks of Sn, S, and other impurities, etc. appear. But in XPS investigation (data is not showed here), trace amount of Sn-related impurities are found out, which would not

has great impact on performance of SnS. The diffraction peaks of carbon-coated SnS powders are sharper than that of pristine SnS powders, because the crystallization of SnS becomes more completed after the heat treatment under  $700$  °C.

HRTEM morphologies of carbon-coated SnS particles are demonstrated in Fig. 2. SnS particles distribute homogeneously with sizes of about  $20\sim 30$  nm (Fig. 2a). The selected area diffraction rings in Fig. 2a inset confirm the crystalline characteristics of as-prepared SnS. Evidently, SnS particles are uniformly covered with a thin carbon coating. Coated SnS in Fig. 2b provide further insight into SnS particles and carbon coating. The carbon coating of several nanometers in thickness on SnS particle surface can be distinguished clearly. It is indicated in Fig. 2b that the lattice-fringe distance is about  $0.28$  nm, corresponding to the (040) d-space of orthorhombic SnS (JCPDS files No. 39-354), which is consistent with the XRD results.

**Table 1** Specific capacitances of pristine and carbon-coated SnS electrodes under various scan rates

Scan rate (mV/s)		10	50	100	500	1000
Specific capacitance (F/g)	Pristine SnS	21.55	17.84	12.17	8.29	6.51
	Carbon-coated SnS	30.12	22.65	16.91	10.28	8.04



**Fig. 4** X-ray diffraction patterns of as-synthesized **a** pristine SnS; **b** carbon-coated SnS. Galvanostatical charge–discharge test conducted at a current density of 200 mA/g between  $-0.1$  V~ $1.0$  V versus Ag/AgCl (solid line for carbon-coated SnS and dot line for pristine SnS)

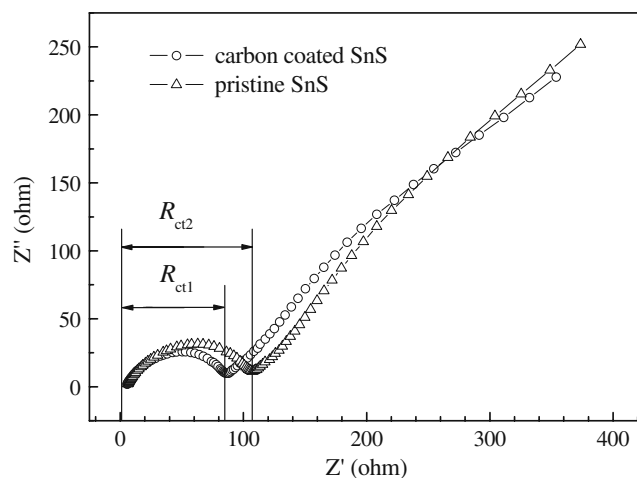
Figure 3 shows typical CV curves of pristine SnS and carbon-coated SnS electrodes in 0.1 M KOH solution at room temperature. In Fig. 3a, b, CV profiles within different potential range are presented. The shapes of all CV curves show roughly rectangular mirror images, which are characteristics of capacitive behaviors. For pristine SnS sample, a small anodic peak, which is probably caused by some redox processes, appears at about 0.9 V vs. Ag/AgCl when the upper potential cut-off window is great than 0.8 V in Fig. 3a. Because no such anodic reaction takes place under all potential cut-off windows for carbon-coated SnS sample in Fig. 3b, we think that carbon coating has effects on the profile of CV curves at about 0.9 V vs. Ag/AgCl. With the range of potential cut-off windows increasing gradually, the cathodic and anodic current all augment progressively due to enhanced polarization effects. When the potential cut-off window is set between  $-0.2$ ~ $1.1$  V, the cathodic and anodic currents are nearly twice than that of potential cut-off window  $0.2$ ~ $0.7$  V. Furthermore, we observe that three electrodes testing system keeps stable but gas bubbles separate out from electrodes at potential cut-off window  $-0.2$ ~ $1.1$  V. So the maximum appropriate scan potential cut-off window can be determined as  $-0.1$ ~ $1.0$  V. To study the capacitive behaviors of pristine SnS and carbon-coated SnS electrodes, scan rates of 10, 50, 100, 500, and 1,000 mV/s are applied in CV investigation, demonstrated in Fig. 3c, d. We can see that all CVs curves present roughly rectangular mirror shapes due to capacitive properties of pristine SnS and carbon-coated SnS electrodes, which mean that prepared electrodes exhibit highly electrochemical reversibility between  $-0.1$  and 1.0 V. And, the profiles of carbon-coated SnS electrode in Fig. 3d are more close to rectangle, which indicates that carbon-coated SnS has better capacitive response and is more suitable for

application as electrode of supercapacitor. With increasing scan rates, the shapes of CVs show no apparent change and the areas of CVs enlarge gradually. Similar to oxides like  $\text{MnO}_2$  and  $\text{RuO}_2$ , etc., the capacitance of SnS is believed to be predominantly arisen from pseudo-capacitance, which is attributed to reversible redox reaction happened between electrode and electrolyte. In this work, Specific capacitance (SC) of working electrodes is estimated based on following equation [12]:

$$C = \frac{q}{\Delta V \times w} \quad (1)$$

where  $C$ ,  $q$ ,  $\Delta V$ , and  $w$  are the specific capacitance, voltammetric charge, potential cut-off window, and mass of electro-active material, respectively. SC of pristine and carbon-coated SnS electrodes, calculated with Eq. (1) under various scan rates, are listed in Table 1. Obviously, SC of electro-active materials is in inverse proportion to scan rates for both electrodes. With increasing scan rates, the potential on electrodes changes more and more, leading to inadequate redox reactions on interfaces between electrode and electrolyte. So the pseudo-capacitance mainly originated from redox reactions decreases gradually. The maximum capacitance value of pristine SnS and carbon-coated SnS reach 21.55 and 30.12 F/g under 10 mV/s, respectively. It is nearly 39.8% of the enhancement of SC after carbon coated for SnS. Similarly, evident increases of SC are obtained for both electrodes under 50, 100, 500 mV/s, and 1,000 mV/s.

The charge–discharge curves of pristine SnS and carbon-coated SnS electrodes are shown in Fig. 4. Usually, when the charge state converts to discharge state under galvanostatic measurement, the discharge curves have a vertical linear portion parallel to  $y$ -axis, which could be assigned as the sudden  $iR$  drop due to the internal resistance, presenting



**Fig. 5** X-ray diffraction patterns of as-synthesized **a** pristine SnS; **b** carbon-coated SnS. Impedance spectra of pristine SnS and carbon-coated SnS electrodes

a conductive characteristic of semi-conductor material [13]. There all have only small voltage drop at the beginning of the discharge processes in Fig. 4, indicating that our prepared electrochemical test system have relatively small internal resistances. The magnification of the state transition from charge to discharge is presented in inset. It can be seen that the  $iR$  drop of pristine SnS electrode is larger than that of carbon-coated SnS electrode. We believe that enhanced electron conductivity of carbon coating on carbon-coated SnS surface is responsible for its smaller  $iR$  drop. Moreover, the potential- $t$  relationships on charge–discharge profiles are all approximately linear, which means that both electrodes have regular capacitive behaviors and good cycling stability. With charge–discharge curves in Fig. 4, the SC could be calculated from:

$$C = \frac{I \cdot \Delta t}{\Delta V \times w} \quad (2)$$

where  $C$ ,  $I$ ,  $\Delta t$ ,  $\Delta V$ , and  $w$  are indicating of the specific capacitance, galvanostatic current, charge–discharge time, potential cut-off window and mass of electro-active material. Electrochemical performances of carbon-coated SnS electrodes, calculated from equation (2), have been obviously improved. The SC of carbon-coated SnS reaches 28.47 F/g, while pristine SnS delivers less SC of 19.25 F/g. Such results are similar to that of CV curves and superior to the performances of nano SnS prepared by Jayalakshmi. M. et al. [10]. It is believed that carbon coating on SnS surface helps to obtain electrochemical enhancement. Excellent electron conductivity of carbon coating is beneficial to electron exchange between electrode and electrolyte, leading to more pseudo-capacitance faradic reactions and generating larger capacitances. As shown in Fig. 5, the impedance spectra of pristine and carbon-coated SnS electrodes are typical Nyquist plots. The plots present a semicircle at high frequencies, which implies a typical charge transfer process of electrode interface, and nearly 45° inclined line at low frequencies. The corresponding values of intersection of semicircle and x-coordinate represent the charge transfer impedances  $R_{ct1}$  and  $R_{ct2}$  of carbon-coated SnS and pristine SnS electrodes, indicating the properties with respect to redox reactions at the interface between electrode and electrolyte. Apparently, the impedance value  $R_{ct1}$  is smaller than  $R_{ct2}$ , which proves that the charge transfer process is more facile to be carried out on the interface for carbon-coated SnS electrode than for pristine SnS electrode. Enhanced electron conductivity of carbon coating on SnS surface is believed to result in lower impedance value and preferable electrochemical performances. We have examined the amount of carbon in carbon-coated SnS by weight loss before and after co-heating at 700 °C. The percent of carbon in carbon-coated SnS is about 6.2%. We think that such small amount of carbon could not evidently increase the capacitance of carbon-coated SnS, although it is

well known that carbon materials have considerable high capacitance as a supercapacitor electrode material. Furthermore, as-prepared carbon coating on SnS maybe is not a high capacitance carbon material and has little effects on total capacitance of carbon-coated SnS. The elevated performance of carbon-coated SnS is attributed to increased electron conductivity with carbon coating, which can be proved by low resistance of carbon-coated SnS in Fig. 5.

## Conclusions

By high-energy ball milling and following co-heating with polyvinyl alcohol, carbon-coated SnS as electrode materials for supercapacitor were synthesized successfully. It was revealed that carbon coating on surface of SnS was several nanometers in thickness by HRTEM. In comparison with pristine SnS, carbon-coated SnS had superior capacitive response in CV curves and could obtain larger specific capacitance in galvanostatical discharge-charge process, indicating that carbon-coated SnS was more attractive to be an electrode material of supercapacitor than pristine SnS. It was believed that enhanced conductivity of carbon-coated SnS due to its surface carbon coating could account for increased electrochemical performances of carbon-coated SnS.

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