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Large-scale synthesis of cobalt sulfide/carbon nanotube hybrid and its excellent electrochemical capacitance performance

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ABSTRACT

In this paper, cobalt sulfide (CoS) in-situ hybridized with carbon nanotube (CNT) is achieved through a hydrothermal process with the presence of polyvinylpyrrolidone (PVP). The morphology and structure of CoS/CNT hybrids are investigated by using field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). The results show that the product consists of CoS nanoparticles with the diameter of 30–50 nm that well dispersed on the outer surface of CNTs. Furthermore, CoS/CNT hybrid has shown excellent electrochemical capacitance and exhibited favorable electrochemical cycling stability with 93.4% capacitance retention over 1000 cycles. Therefore, the CoS/CNT hybrids can be considered as promising electrode materials for supercapacitor.

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1. Introduction

Climate change and reducing fossil energy consumption are the most urgent issues that human faces in this century. Renewable energy production and electrical energy storage have received worldwide attention to meet higher requirements of future systems from portable electronics to electric automobiles and large electrical grid [1,2]. Supercapacitors (SCs), also called electrochemical capacitors, ultracapacitors and power capacitors, will conquer the market of energy storage applications that especially require high power, long cyclic life, fast charge and discharge rates and low cost [3,4]. Sulfur has been found to have reversible valence variation and investigated as promising new Li-sulfur battery electrode with large energy storage capacity. Recently, nanostructured metal sulfides, such as SnS [5], β -NiS [6], Bi₂S₃ [7], MoS₂ [8], Sb₂S₃ [9], have been sequentially synthesized and shown largely improved electrochemical energy storage performance as SC electrode materials. Among them, CoS has been studied for its high theoretical specific capacitances, low-cost, and long-term stability [10,11]. Nevertheless, CoS nanoparticles practically do not supply ideal specific capacitance and show poor cycling stability [12,13]. Accordingly, improving electrochemical capacitance substantially to meet the requirements of future practical applications

and advancing our understanding of the electrochemical interfaces by developing new materials at the nanoscale are urgently desirable.

Carbon nanotube (CNT) has been widely known to have network like aggregate state which endow the bulk materials of CNTs with high electrical conductivity, excellent mechanical flexibility, high thermal and chemical stability and easy functionalization make it ideal materials to construct conductive nano porous network based high power density SCs [14–16]. The well dispersion of sulfion in CNT network will prevent it from solubilizing into electrolyte and allow full transition of sulfion back into sulfur nanoparticles. The largely reinforced reversibility of structure variation has thus largely enhanced cyclic stability of electrode.

In this work, we report a facile one-step hydrothermal route to synthesize CoS/CNT hybrid. The electrochemical tests showed that CoS/CNT hybrid exhibits significantly improved electrochemical properties compared with pure CoS because of enhanced interfacial faradaic process and charge accession.

2. Experimental

2.1. Treatment of CNTs

CNTs were refluxed in 68 wt% HNO₃ at 180 °C for 16 h. The mixture was then washed several times with deionized water on a sintered glass filter. Finally, the CNTs were dried in an oven at

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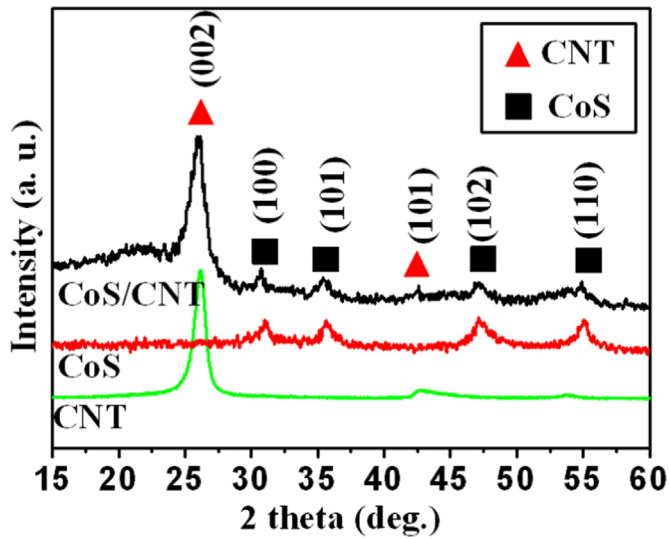


Fig. 1. XRD patterns of CNT, CoS and CoS/CNT hybrids.

80 °C for 6 h.

2.2. Synthesis of CoS/CNT hybrid

0.34 g thioacetamide, 1.2 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1.0 g polyvinylpyrrolidone, 40 μl HCl and 0.05 g CNT were initially dissolved in 20 mL water and 20 mL ethylene glycol and vigorously stirred.

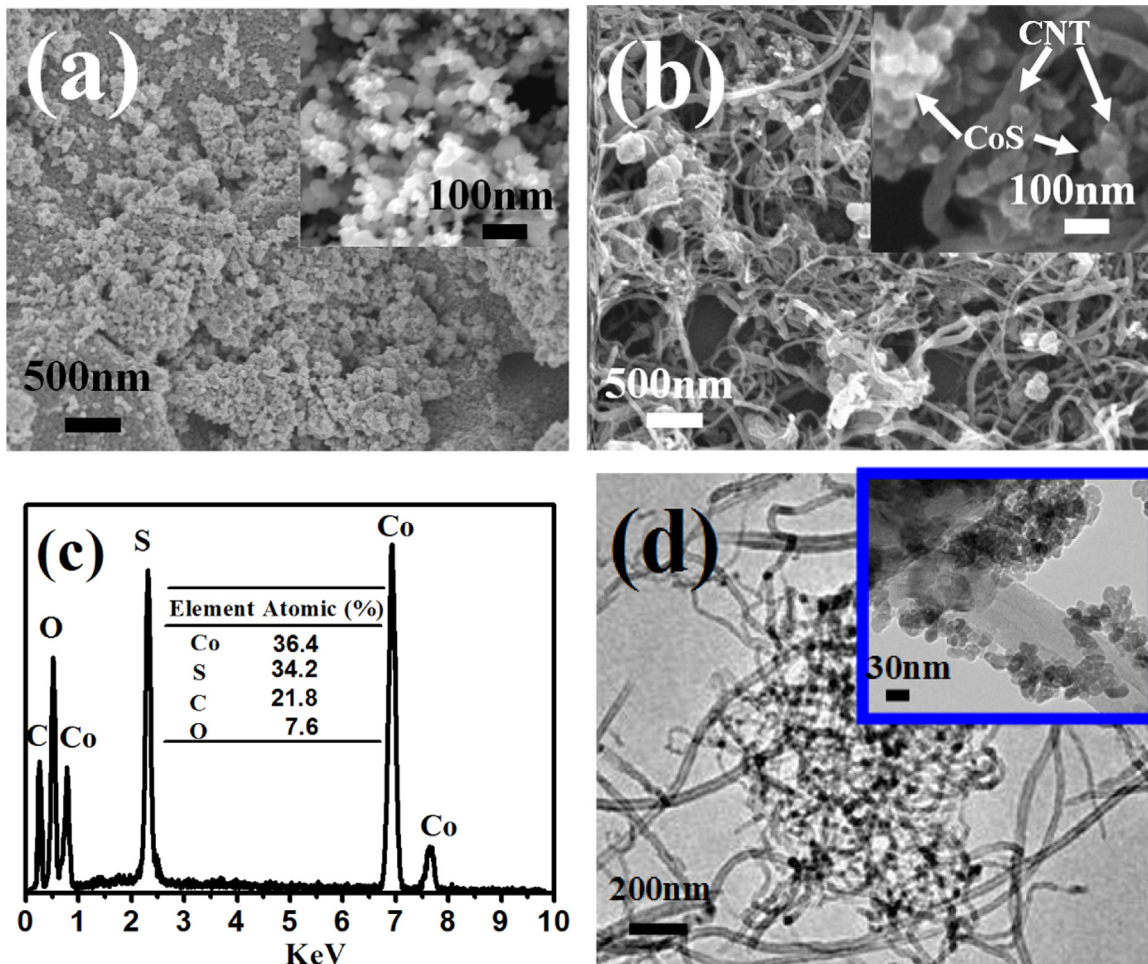


Fig. 2. FESEM images of (a) CoS and (b) CoS/CNT hybrids, (c) EDS spectrum of CoS/CNT hybrids and (d) TEM image of CoS/CNT hybrids.

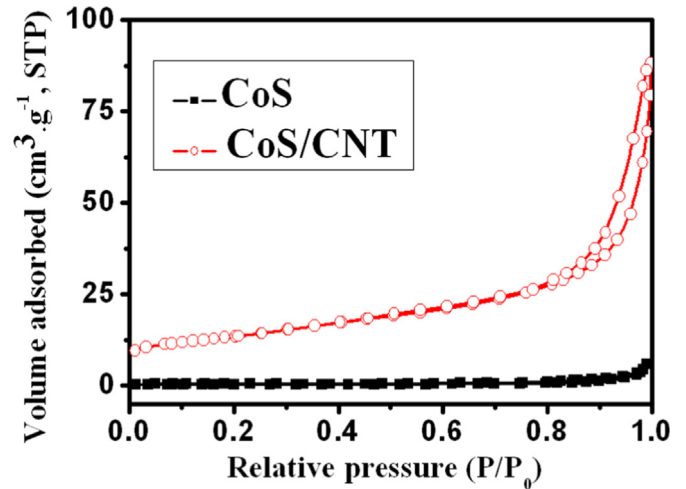


Fig. 3. Isotherms for N_2 adsorption-desorption of CoS and CoS/CNT.

And then, the mixture was further transferred into a 50 mL Teflon-lined autoclave and subsequently heated at 180 °C for 12 h. When it cooled down to room temperature naturally, the products were washed with water on a sintered glass filter and were finally dried at 80 °C for 6 h. And more than 0.4 g sample can be obtained in one time.

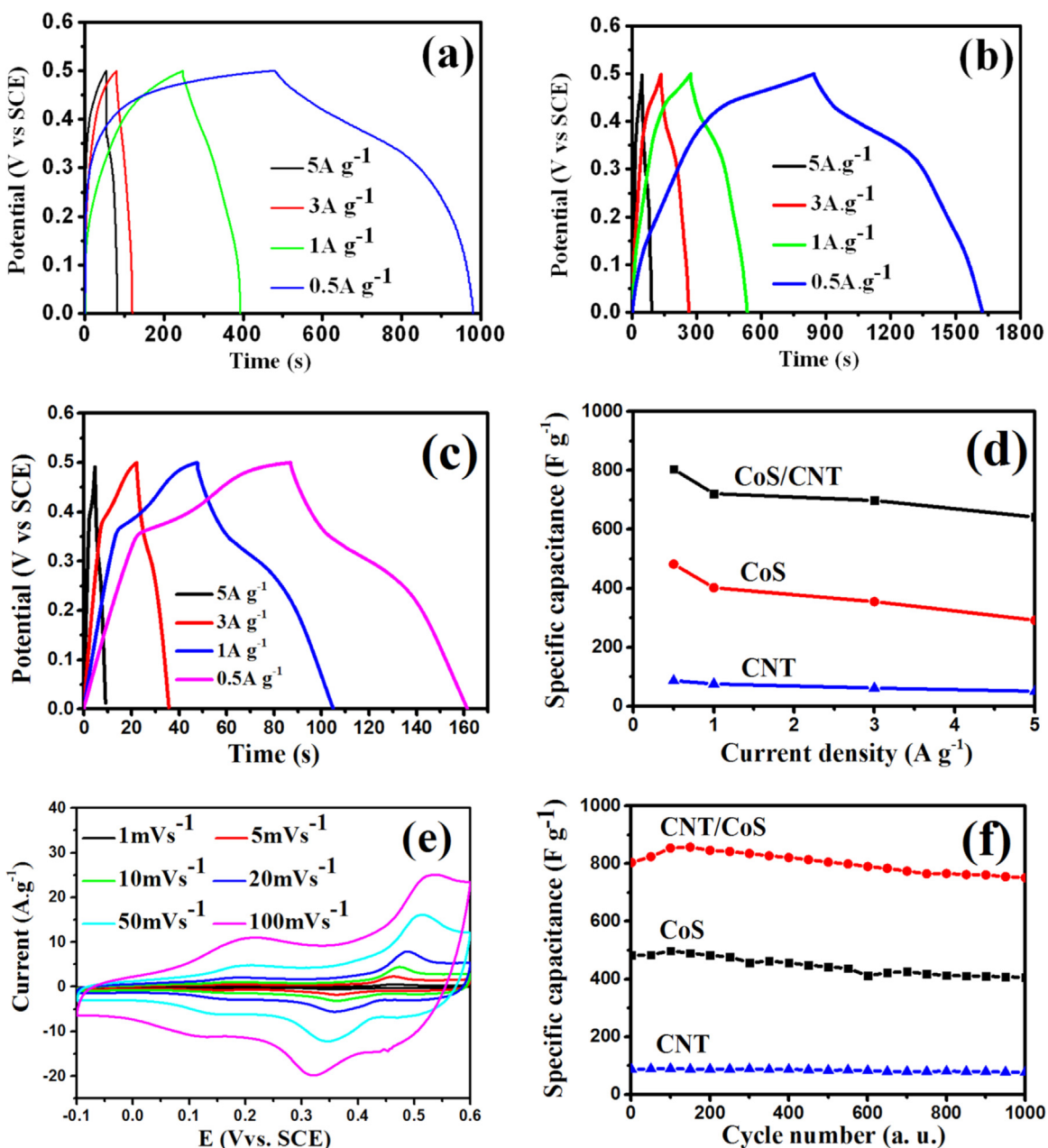


Fig. 4. Galvanostatic charge–discharge of (a) CoS, (b) CoS/CNT and (c) CNT, (d) Variation of specific capacitance against current densities for CoS, CoS/CNT and CNT, (e) CV curves of CoS/CNT hybrids at different scan rate, and (f) cycle performance measured at 0.5 A g^{-1} .

2.3. Characterization

X-ray diffraction (XRD) analysis of phases was carried out using a Rigaku D/MAX 24000 diffractometer. The morphologies of samples were recorded using a field emission scanning electron microscopy (FESEM, JSM-6700F) equipped with an Inca energy dispersive spectrometer (EDS) and JEOL 2010 transmission electron microscopy (TEM).

2.4. Electrochemical measurements

Fabricating the working electrodes required mixing 80 wt% active materials with 15 wt% acetylene black and 5 wt% PTFE binder. Electrochemical measurements were carried out using 6 M KOH aqueous solution as electrolyte. A platinum foil and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. All cyclic voltammetry (CV) and

galvanostatic charge–discharge processes were performed on a Shanghai Chenhua CHI 660D workstation. The specific capacitance (C [F g^{-1}]) of the electrode materials was calculated from the discharge curve according to the following equations:

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

where I is the discharge current (A); Δt is the discharge time (s); ΔV is the voltage change (V), excluding the IR drop in the discharge process; and m is the mass of the working electrode material (g), excluding the binder and conductive carbon black.

3. Results and discussion

Fig. 1 shows the XRD patterns of CNT, CoS and CoS/CNT hybrids, respectively. All the diffraction peaks of pure CoS match well with the hexagonal CoS (JCPDS 75-0605). The broad peak at 26.26° is

attributed to the characteristic peak of CNTs.

Fig. 2a and b show the FESEM images of CoS nanoparticles and CoS/CNT hybrids, respectively. As indicated in Fig. 2a, the size of as-synthesized CoS nanoparticles was 30–50 nm. The FESEM image depicted in Fig. 2b clearly displays that there are some CoS nanostructures attached to the outer surface of CNTs. The EDS spectrum of CoS/CNT hybrids in Fig. 2d indicated that the hybrid only contains elements of C, Co, S and O. Fig. 2d shows the TEM image of CoS/CNT hybrids, CoS nanoparticles are strongly attracted to the outer surface of CNT.

Fig. 3 shows the N₂ adsorption-desorption isotherms for CoS and CoS/CNT hybrids at 77 K. CoS/CNT hybrid has much larger specific surface area (47.2 m²/g) than that of pure CoS (1.2 m²/g).

Fig. 4a, b and c show the charge-discharge curves for CoS, CoS/CNT and CNT, respectively. According to Eq. (1), Fig. 4d shows the corresponding specific capacitances of CoS, CNT and CoS/CNT. CoS/CNT presented the maximum specific capacitance of 804 F g⁻¹ at 0.5 A g⁻¹, which is 1.7 times and 9.2 times than that of pure CoS nanoparticles (473 F g⁻¹) and CNT (87 F g⁻¹), respectively. Thus, CoS effectively attached to the surfaces of conductive CNT networks can effectively make its intrinsic electrochemical capacitance well embodied. Moreover, CNT supplied sufficient electrochemically active sites for effective redox reactions on the CoS surfaces and provided effective conductive channels for the deep intercalation or de-intercalation of ions, which is beneficial to the fast transfer of ions throughout the whole electrode, consequently improving electrochemical performance. Fig. 4e presents the CV curve of CoS/CNT hybrids within the electrochemical window from -0.1 to 0.6 V at different potential scan rates. The two anodic peaks at the voltages of 0.1–0.2 and 0.3–0.4 are likely due to the oxidations of CoS to CoSOH and CoSOH to CoSO, separately [17]. Fig. 4f shows electrochemical stability of CoS/CNT, CNT and CoS electrodes by galvanostatic charging-discharging at a current density of 0.5 A g⁻¹ for 1000 cycles. 93.4% of the initial capacitance of CoS/CNT is preserved after 1000 charge-discharge cycles, but CoS nanoparticles only retains 81.2% of initial capacitance after 1000 cycles. The improvement in cycling stability is attributed to the delivered CNT which not only improves electrical accessions within bulk materials but also offers porous network that on one hand enhances the ionic diffusion within the bulk materials and on the other hand prevents CoS nanoparticles from aggregating into large aggregate during the cyclic charge-discharge process.

4. Conclusions

A promising route for easy and large-scale synthesis of CoS/CNT hybrid was developed. The CoS nanoparticles with the size of 30–50 nm are well dispersed on the outer surface of CNTs. The as-synthesized CoS/CNT hybrid exhibited attractive specific capacitance and long life time, which will supply a new insight for various energy applications in the future.

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