

Short communication

Biomolecule-assisted synthesis of cobalt sulfide nanowires for application in supercapacitors

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Abstract

A biomolecule-assisted hydrothermal process is developed to synthesize cobalt sulfide (CoS), in which L-cysteine is used as the sulfide source and directing molecule. By controlling the synthesis conditions, CoS nanospheres and nanowires can be assembled. The as-synthesized samples are characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) are used to study the effects of microstructure and morphology of the samples on their capacitance and conductivity. A specific capacitance, as high as 508 F g^{-1} , is achieved for CoS nanowires. This is very competitive with the best supercapacitor material, RuO_2 ($720\text{--}760 \text{ F g}^{-1}$), but its cost is remarkably lower than RuO_2 . Thus the nanowires are a promising material for low-cost, high-performance supercapacitors. This method could provide a universal green chemistry approach to synthesize other metal sulfides.

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1. Introduction

Due to concerns over environmental pollution and the depletion of fossil fuels, the development of alternative energy conversion/storage systems with high specific power and energy is of great importance. Among the different technologies, electrochemical capacitors (ECs) or supercapacitors (SCs) that have higher specific power and longer cycle-life than secondary batteries and higher specific energy than conventional electrical double-layer capacitors are attracting much attention [1]. The supercapacitors are being developed for a variety of applications such as mobile electronic devices, back-up power supplies, and hybrid electric vehicles [1–3]. Prototypes made with hydrous ruthenium oxide (RuO_2) exhibit the highest specific capacitance, i.e., $720\text{--}760 \text{ F g}^{-1}$, and such performance has enhanced the research and development of ECs [4,5]. Unfortunately, the high cost of RuO_2 greatly limits its commercialization. Hence,

extensive studies have been conducted to explore alternative, economic supercapacitor materials.

In the last few years, nanostructured metal sulfides have been investigated as a new type of energy storage materials and have achieved good performance, of which sponge-like Ni_3S_2 [6] and ‘flower-like’ Bi_2S_3 [7] demonstrate their hydrogen storage capability, while ZnS [8] and CoS nanoparticles [9,10] are used in ECs or rechargeable lithium batteries. Nevertheless, the synthesis of one-dimensional metal sulfide nanomaterials requires expensive and toxic organic agents, as well as high reaction temperatures, and produces pungent H_2S from the sulfur sources used (thioacetamide, thiourea, sodium thiosulfate, Na_2S or H_2S) [6,7]. A new, environment-friendly, biomolecule-assisted synthesis method, a green chemistry approach, has recently been developed to produce different sulfur-based nanomaterials, such as ZnS and Bi_2S_3 [7,11–14].

In the work reported here, a simple and efficient biomolecule-assisted hydrothermal process is developed to produce cobalt sulfide (CoS) for the first time. This method is used not only to fabricate nano-CoS, but also to tailor its nanostructure for superior physical and chemical properties. Different nanostruc-

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tured CoS can be produced simply by altering the polarity of the precursor solution through addition of ethanol. The possible formation mechanisms of CoS under different conditions are proposed. The electrochemical properties of different nanostructured CoS materials are studied systematically for their use as EC electrodes. It is discovered that the morphology has a remarkable effect on the capacitive behaviour of the samples, among which CoS nanowires provide good conductivity and large capacitance.

2. Experimental

2.1. Material preparation

All chemical reagents were analytical grade and used as-received. The synthesis was performed via a simple hydrothermal process, in which 3 mmol L-cysteine was dissolved in 45 mL de-ionized water and 3 mmol $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 45 mL de-ionized water or ethanol, respectively. Then the CoCl_2 solution was added to the L-cysteine solution with constant and vigorous stirring. After 15 min, the resulting mixture was transferred into a Teflon-lined stainless-steel autoclave, that was then sealed and maintained at 190°C for 6 h followed by cooling down to room temperature. The prepared products were washed three-times with de-ionized water and ethanol, respectively, followed by drying in a vacuum oven at 50°C for overnight.

2.2. Material characterization

The crystal structure of the product was characterized by X-ray diffraction (XRD, Bruker AXS X-ray diffractometer). The morphology and microstructure of the synthesized materials were examined by field-emission scanning electron microscopy (FESEM, JSM-6700F, Japan) and transmission electron microscopy (TEM, Hitachi 600, Japan).

2.3. Electrochemical measurements

The working electrodes of the ECs were fabricated by mixing the prepared powder with 15 wt.% acetylene black and 5 wt.% polytetrafluorene-ethylene (PTFE) binder. A small amount of distilled water was added to the mixture to produce a more homogeneous paste. The mixture was pressed on to nickel foam current-collectors ($1.0\text{ cm} \times 1.0\text{ cm}$) to make electrodes. Before the electrochemical test, the prepared electrode was soaked overnight in 3 M KOH solution. Electrochemical characterization was carried out in a conventional three-electrode cell with 3 M KOH as the electrolyte. Platinum foil and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. All electrochemical measurements were conducted with a CHI 660 electrochemical workstation (CH Instruments Inc., Texas, USA).

3. Results and discussion

3.1. Characterization of materials

The synthesized new materials were first examined by XRD. As shown in Fig. 1, all of the diffraction peaks for both samples synthesized from different solutions can be indexed to a hexagonal phase of CoS, which is well-matched with its standard XRD pattern (ICSD No. 029305). No impurity peaks are observed, which indicates that pure CoS is produced by the biomolecule-assisted hydrothermal method in different solutions.

The prepared products were examined further by FESEM. As shown in Fig. 2, the microstructure and morphology of the products synthesized with different conditions is very distinctive, of which the CoS obtained from aqueous solution is uniform spheres (Fig. 2a) constructed by interleaving rice-like rods (Fig. 2b). Interesting morphology and microstructures are illustrated in Fig. 2c and d, in which the low-magnification FESEM images (Fig. 2c) show that the material formed in the ethanol aqueous solution is produced as nanowires. The higher magnification FESEM image in Fig. 2d reveals its detailed nanostructure, in which the CoS nanowires are shown to consist of many interconnected, small, flower-like particles formed by interleaving nanoflakes.

TEM was employed to study the synthesized products, which were dispersed completely using sonication for 1 h in ethanol prior to examination. CoS made from the aqueous solution (Fig. 3a) is seen to be composed of small particles, while CoS synthesized from ethanol aqueous solution (Fig. 3b) has a nanowire structure even after sonication. The results are in agreement with the SEM images.

3.2. Formation mechanism of different structured CoS

On the basis of the FESEM and TEM analyses, a possible mechanism is proposed to explain the formation of different nanostructured CoS. Functional groups, such as $-\text{NH}_2$, $-\text{COOH}$ and $-\text{SH}$ of the L-cysteine molecule, have a strong tendency to coordinate with inorganic cations and metals, as demon-

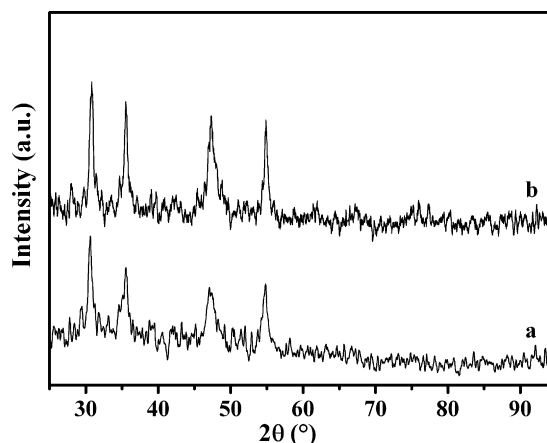


Fig. 1. XRD patterns for (a) sample obtained in aqueous solution and (b) sample obtained by ethanol aqueous solution.

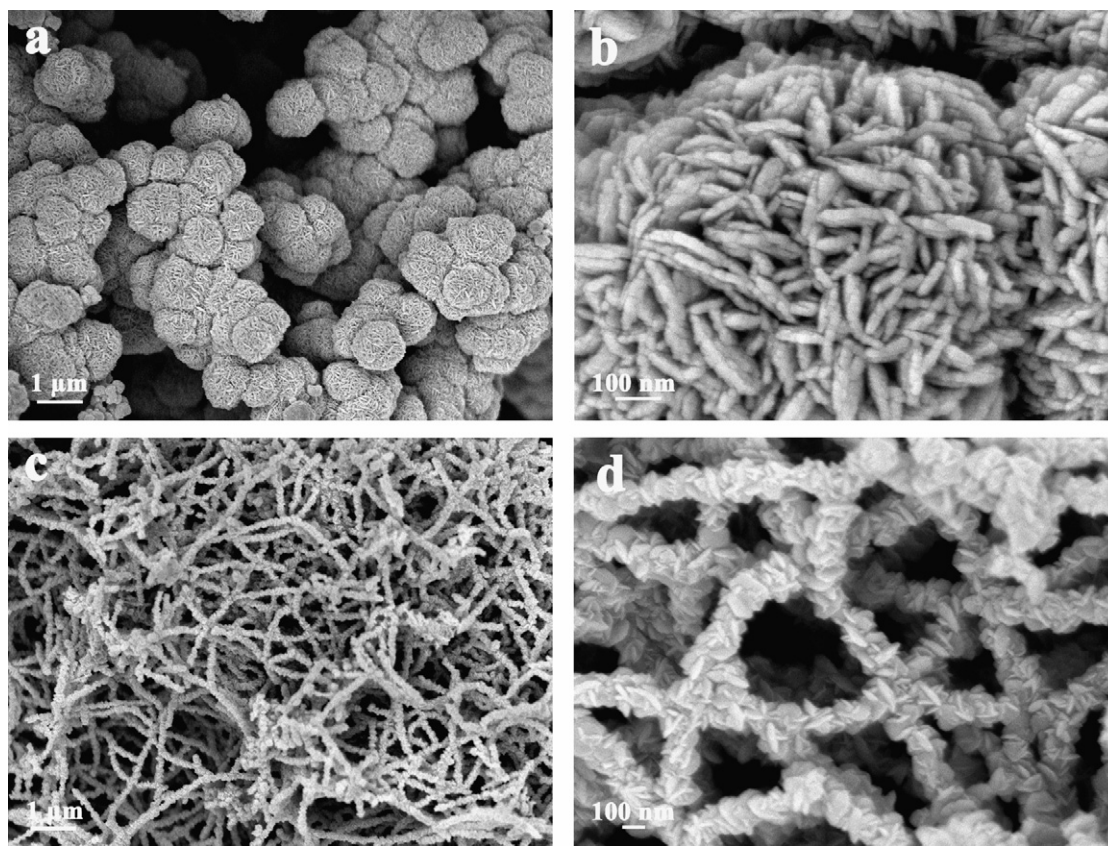


Fig. 2. FESEM images of samples: (a) low-magnification FESEM and (b) high-magnification FESEM of CoS obtained in aqueous solution; (c) low-magnification FESEM and (d) high-magnification FESEM images of CoS obtained in ethanol aqueous solution.

strated by Burford and co-workers [7,15]. In a homogenous system composed of L-cysteine and CoCl_2 solution, Co^{2+} can coordinate with cysteine molecule to form a complex. With increased reaction time, the strong coordination bonds between the hydrosulfide group and Co^{2+} could weaken the S–H bond and further break it due to the high reaction temperature. In aqueous solution, due to the interaction of hydrogen bonds, small CoS nanoparticles could aggregate together to produce flower-like CoS bundles. On the surface of these bundles, many nanorods are formed because of the oriented growth of cysteine-based molecules and the Ostwald ripening process [16–18], further resulting in a flower-like CoS sphere structure with intercrossing rods. Metal sulfides with similar structure are also observed in the synthesis of ZnS [12] and Bi_2S_3 [7], using L-cysteine as the sulfide source. This confirms that L-cysteine plays a critical role in the synthesis of the flower-like metal sulfide. In the ethanol aqueous solution, the surface energy of the CoS nanoparticles and the interaction of hydrogen bonds between small CoS nanoparticles decrease significantly, hence, flower-like CoS nanowires are formed. The proposed mechanism is illustrated in Scheme 1.

3.3. Electrochemical characterization

Different nanostructured CoS were used to make supercapacitor electrodes and their electrochemical properties were compared by means of CV and EIS measurements. Representa-

tive CV curves of the CoS electrodes in 3 M KOH are presented in Fig. 4. The shapes of the curves show that the capacitive characteristic is clearly distinguishable from that of electric double-layer capacitance, for which the CV curve is close to the ideal rectangular shape. Two pairs of redox peaks are visible in the CV curves. This implies that the measured capacitance mainly arises from a pseudocapacitive capacitance caused by reversible electrochemical reactions. The mechanism of electrochemical reactions of CoS in alkaline electrolyte is still not fully understood, but, since their redox peak potentials are very close to those of $\text{Co}(\text{OH})_2$ [19] and sulfur is in the same family as oxygen, Li and co-workers [9] suggest that the redox transitions of CoS in alkaline system should take place between different valence states of cobalt.

From a comparison of Fig. 4a with b, the area under the CV curve for CoS nanowires is apparently larger than that of CoS spheres. This indicates that the CoS nanowires have a higher capacitance than that of CoS spheres, possibly due to a more slack structure and larger specific surface area.

EIS measurements were carried out to compare the characteristics of charge and ion transfer in different structured CoS materials. The Nyquist plots (Fig. 5a) show a well-defined semicircle over the high-frequency range, followed by a straight sloped line in the low-frequency region for both samples. Such an EIS pattern can be fitted by an equivalent circuit, as shown in the inset of Fig. 5a. The diameter of the semicircle corresponds to the interfacial charge-transfer resistance (R_{ct}), which

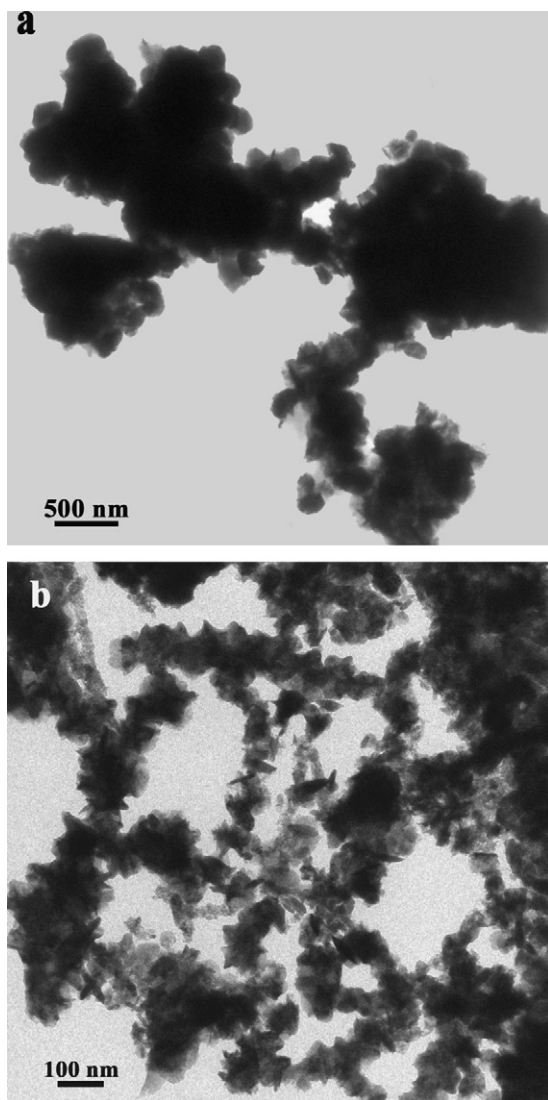


Fig. 3. TEM images of CoS (a) obtained in aqueous solution and (b) obtained in ethanol aqueous solution.

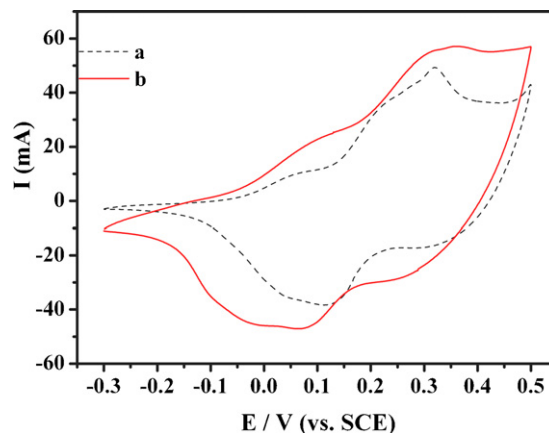
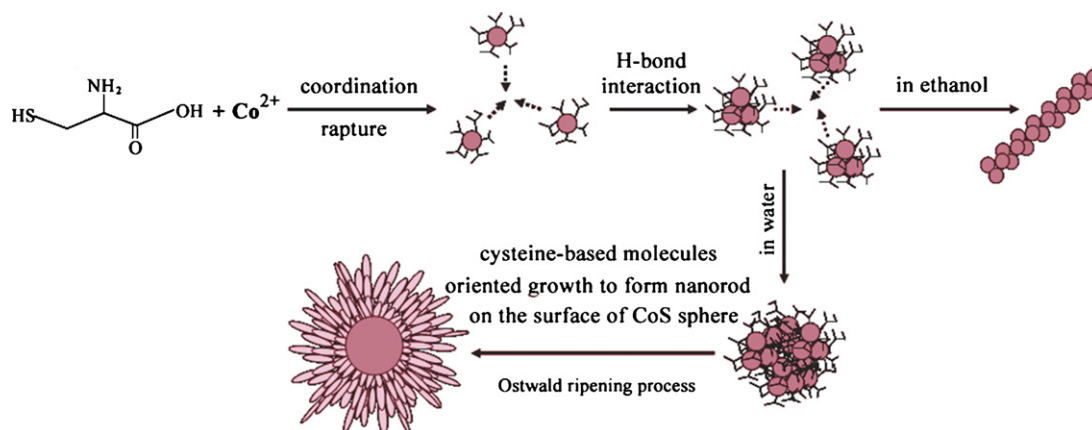


Fig. 4. Cyclic voltammograms of CoS-based electrodes in 3 M KOH electrolyte at a scan rate of 5 mV s^{-1} . (a) CoS spheres obtained in aqueous solution; (b) CoS nanowires obtained in ethanol aqueous solution.

usually represents the resistance of the electrochemical reactions on the electrode and is called the Faraday resistance [20,21]. The straight line is ascribed to the diffusive resistance (Warburg impedance, W) of the electrolyte in the electrode pores and proton diffusion in the host materials [22]. The diameter of the semicircle in Fig. 5a (II) is found to be much smaller than that in Fig. 5a (I) although the impedance spectra have similar shapes, and the straight line part at lower frequencies for CoS nanowires is straighter than that for CoS spheres, which indicates that the CoS nanowires electrode has much lower reaction and diffusion resistances. Bode plots of the capacitance (normalized to electrode mass) are shown in Fig. 5b. For frequencies from 0.01 to ~ 2 Hz, the capacitance of the CoS nanowires electrode is significantly higher than that of the CoS spheres electrode. The result is in agreement with the CV analysis and confirms that the microstructure and morphology of the material have a significant effect on electrochemical capacitance and conductivity.

Based on the above results, further charge–discharge performance measurements were focused on the CoS nanowires. As shown in Fig. 6, during the charge and the discharge steps, the curves display two variation ranges. A perfect variation of potential vs. time dependence (below about 0 V) parallel to the potential axis indicates pure double-layer capacitance behaviour



Scheme 1. Proposed growth process for formation of CoS with different structures.

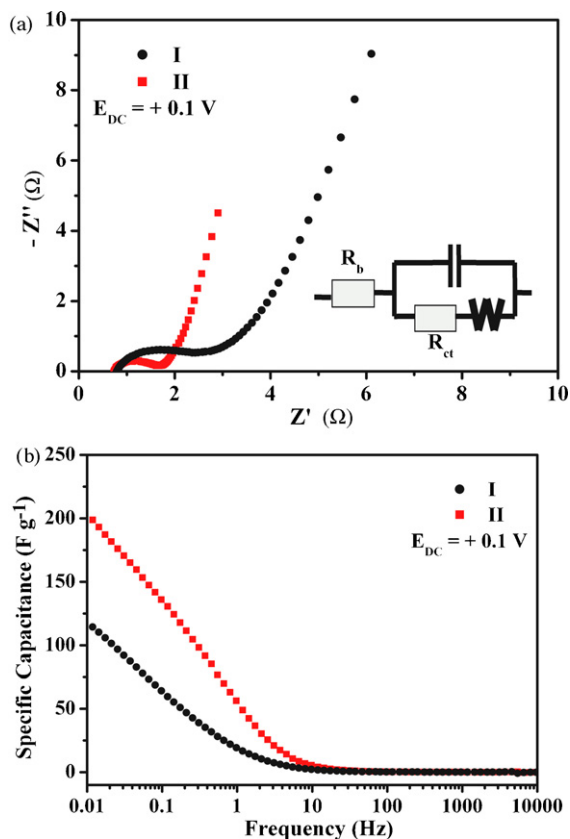


Fig. 5. (a) Nyquist plots of different CoS electrodes at ac voltage amplitude of 5 mV. Inset of (a) is the equivalent circuit; (b) bode plots from impedance spectroscopic analysis of different CoS electrodes. (I, CoS spheres obtained in aqueous solution; II, CoS nanowires obtained in ethanol aqueous solution.)

from the charge separation at the electrode|electrolyte interface. By contrast, a sloped variation of potential vs. time (0–0.4 V) indicates typical pseudocapacitance behaviour, caused by electrochemical adsorption/desorption or a redox reaction at the electrode|electrolyte interface [4,23]. The specific capacitance of the electrode at different current densities is calculated by $C = I \times \Delta t / \Delta V \times m$ from the discharge curves, where I is the constant discharge current, Δt is the discharge time, ΔV is the potential drop during discharge, and m is the mass of CoS.

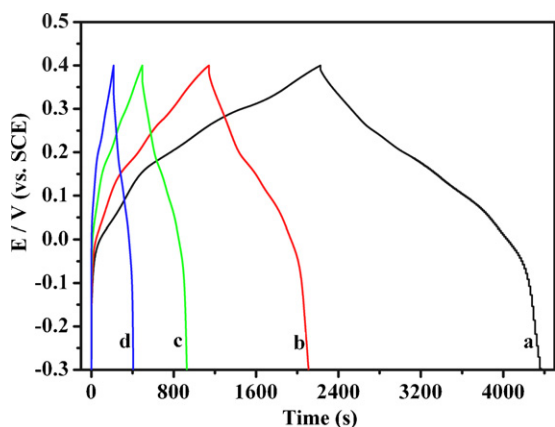


Fig. 6. Charge–discharge curves of CoS nanowires electrode at different current densities: (a) 2.5; (b) 5; (c) 10; (d) 20 mA cm⁻².

The specific capacitance value is 508, 462, 424 and 377 F g⁻¹ for CoS nanowires electrode at 2.5, 5, 10 and 20 mA cm⁻², respectively. That is, when the discharge current density is 5, 10 and 20 mA cm⁻², their capacitance is 91, 83.4, and 74.2% of that obtained at 2.5 mA cm⁻², which is competitive with the best supercapacitor material, RuO₂ (720–760 F g⁻¹ for single electrode) [4,5]. It is noted that the cost of CoS is remarkably lower than that of RuO₂. Further, the specific energy of the CoS nanowires supercapacitor is 34 Wh kg⁻¹, which is significantly larger than that of carbon-based, double-layer capacitors (about 5 Wh kg⁻¹) [24].

The electrochemical stability of the CoS nanowires electrode in 3 M KOH electrolyte was examined by chronopotentiometry at 20 mA cm⁻². It is found that the CoS nanowires supercapacitor retains 81.2% of initial capacitance after 500 cycles, which reveals that cycling does not induce noticeable degradation of the microstructure, and therefore this material is a promising candidate for ECs.

4. Conclusions

In summary, an environment-friendly, biomolecule-assisted, hydrothermal process has been modified to fabricate nanostructured CoS. The method is easy, efficient and economic. It is found that the microstructure and surface morphology can be simply tailored by adjustment of the polarity of the precursor solutions, and results in nanospheres and nanowires of CoS. The microstructure of CoS has a significant effect on their electrochemical performance when they are used as electrode materials for ECs. CoS nanowire assembled by nanoflowers provides a very high specific capacitance (508 F g⁻¹) with high specific energy, excellent discharge rate, and good stability. Thus, it is very competitive with the best supercapacitor material, RuO₂ (720–760 F g⁻¹), and has a markedly lower cost. By virtue of these attributes, it is a promising material for the development of high-performance supercapacitors. The preparative method could be a universal green chemistry approach to the synthesis of other metal sulfides.

Acknowledgement

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References

- [1] V. Subramanian, H. Zhu, R. Vajtai, P.M. Ajayan, B. Wei, J. Phys. Chem. B 109 (2005) 20207–20214.
- [2] B.E. Conway, Electrochemical Supercapacitors, Kluwer Academic/Plenum Publishers, New York, 1999.
- [3] S. Sarangapani, B.V. Tilak, C.P. Chen, J. Electrochem. Soc. 143 (1996) 3791–3799.
- [4] W. Sugimoto, H. Iwata, Y. Yasunaga, Y. Murakami, Y. Takasu, Angew. Chem. Int. Ed. 42 (2003) 4092–4096.
- [5] A.E. Fischer, K.A. Pettigrew, D.R. Rolison, R.M. Stroud, J.W. Long, Nano Lett. 7 (2007) 281–286.
- [6] B. Zhang, X.C. Ye, W. Dai, W.Y. Hou, Y. Xie, Chem. Eur. J. 12 (2006) 2337–2342.

- [7] B. Zhang, X.C. Ye, W.Y. Hou, Y. Zhao, Y. Xie, *J. Phys. Chem. B* 110 (2006) 8978–8985.
- [8] M. Jayalakshmi, M.M. Rao, *J. Power Sources* 157 (2006) 624–629.
- [9] F. Tao, Y.Q. Zhao, G.Q. Zhang, H.L. Li, *Electrochem. Commun.* 9 (2007) 1282–1287.
- [10] J. Wang, S.H. Ng, G.X. Wang, J. Chen, L. Zhao, Y. Chen, H.K. Liu, *J. Power Sources* 159 (2006) 287–293.
- [11] Q.Y. Lu, F. Gao, S. Komarneni, *J. Am. Chem. Soc.* 126 (2004) 54–55.
- [12] H. Tong, Y.J. Zhu, L.X. Yang, L. Li, L. Zhang, J. Chang, L.Q. An, S.W. Wang, *J. Phys. Chem. C* 111 (2007) 3893–3896.
- [13] C.B. Mao, D.J. Solis, B.D. Reiss, S.T. Kottmann, R.Y. Sweeney, A. Hayhurst, G.B. GeorgiouIverson, A.M. Belcher, *Science* 290 (2000) 1744–1747.
- [14] H. Xin, A.T. Woolley, *J. Am. Chem. Soc.* 125 (2003) 8710–8711.
- [15] N. Burford, M.D. Eelman, D.E. Mahony, M. Morash, *Chem. Commun.* 1 (2003) 146–147.
- [16] B. Li, G. Rong, Y. Xie, L. Huang, C. Feng, *Inorg. Chem.* 45 (2006) 6404–6410.
- [17] W.Z. Ostwald, *Phys. Chem.* 34 (1900) 495–503.
- [18] S.J. Bao, Q.L. Bao, C.M. Li, T.P. Chen, C.Q. Sun, Z.L. Dong, Y. Gan, J. Zhang, *Small* 3 (2007) 1174–1177.
- [19] L. Cao, F. Xu, Y.Y. Liang, H.L. Li, *Adv. Mater.* 16 (2004) 1853–1856.
- [20] S.S. Zhang, K. Xu, T.R. Jow, *Electrochim. Acta* 49 (2004) 1057–1061.
- [21] A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd ed., Wiley, New York, 2001.
- [22] C. Lin, J.A. Ritter, B.N. Popov, *J. Electrochem. Soc.* 145 (1998) 4097–4103.
- [23] G.Q. Zhang, Y.Q. Zhao, F. Tao, H.L. Li, *J. Power Sources* 161 (2006) 723–729.
- [24] A. Burke, *Electrochim. Acta* 53 (2007) 1083–1091.