**Preparation and lithium ion batteries properties of SnS₂
nanoparticle/reduced graphene oxide nanosheet nanocomposites
using supercritical carbon dioxide**

Keyu Li^a, Shancheng Yan^{a*}, Zixia Lin^b, Xiubin Dai^a, Peng Qu^{c*}

^aSchool of Geography and Biological Information, Nanjing University of Posts and
Telecommunications, Nanjing 210023, P. R. China

^bNational Laboratory of Solid State Microstructures, School of Electronic Science and
Engineering, Nanjing University, Nanjing 210093, P. R. China

^cHenan Key Laboratory of Biomolecular Recognition and Sensing, College of Chemistry
and Chemical Engineering, Shangqiu Normal University, Shangqiu 476000, P. R. China

Tel: (86) 25-85866635

Fax: (86) 25-85866634

E-mail: yanse@njupt.edu.cn; qupeng0212@163.com

Abstract: Graphene-based nanocomposites have been widely investigated as promising anode materials because of the high specific capacity and good rate capability. However, effective distributing the nanomaterials into graphene conductive network still remains some challenges. In this study, the supercritical carbon dioxide (SC CO₂) route as a good strategy is developed to prepare SnS₂/reduced graphene oxide (RGO) nanocomposites, which integrates the complementary effect of ultrasmall SnS₂ nanoparticle and RGO nanosheet in the nanocompositions. The SnS₂/RGO nanocomposite exhibits high initial discharge capacity of 1466.1 mAhg⁻¹ (100 mA g⁻¹), good capacity retention of about 492 mAhg⁻¹ (100 mA g⁻¹) after 70 cycles and good rate capacity as an anode material for lithium ion batteries. These results demonstrate that supercritical CO₂ (SC CO₂) possess significant technological value to enhance the energy storage properties of other two-dimensional (2D) nanocomposites.

Keywords: Supercritical CO₂, SnS₂ nanoparticle, Nanocomposites, Anode Materials, Lithium-ion batteries

1. Introduction

Rechargeable lithium ion batteries (LIBs) with high energy density, stability and environmentally friendly is playing a critical role in portable electronic devices, electric vehicles and hybrid electric vehicles, which have been widely studied for power source [1-6]. Graphene has been used for the application of lithium ion battery due to its unique two dimensional (2D) single layer structures, high thermal conductivity and high surface area [2, 7, 8]. However, the relatively low theoretical capacity (372mAhg^{-1}) of graphite can not fully meet the requirements for high-power rechargeable LIBs application, which cause the rise of alternative higher capacity materials, such as SnO_2 , MoS_2 , SnS_2 , WS_2 , etc. [1-3, 9] Among them, SnS_2 has attracted much attention as anode material of LIBs battery via hydrothermal, solvothermal and reflux synthesis techniques [1, 4, 8-12]. Nevertheless, the electrical conductivity and rate capability of SnS_2 are restricted from the volume expansion and capacity fading in the process of ion insertion and extraction [8, 12-15]. Thus, the graphene with unique properties can be used as a conductive matrix to enhance electron transport and buffer the volume expansion, resulting in the rapid development of graphene-based nanocomposites [8, 14-20]. The typological nanocomposites are supposed to maximize structure compatibility and obtain greater capacity than the individual components [14]. In addition, the simple, fast, cost-effective and environmentally friendly synthetic method still is a challenge [8].

Herein, the supercritical carbon dioxide (SC CO_2) route as a good strategy has been developed to synthesis SnS_2/RGO nanocomposites, owing to its advantages,

such as low viscosity, low interfacial tension, outstanding wetting of surfaces and high diffusion coefficients. Meanwhile, the SC CO₂ also possesses near-zero surface tension and excellent penetration ability, which can help to prevent the restacking of RGO nanosheets and to reinforce the contact between the SnS₂ nanoparticles and RGO nanosheets [7, 21, 22]. These characteristic can be fully utilized to control of the solubility of a solute in SC-CO₂ by changing the pressure and temperature [21]. The formation of SnS₂/RGO nanocomposites using these reactants of SnCl₄·5H₂O, RGO and thiourea via SC CO₂ process can be seen in scheme 1. The SnS₂/RGO nanocomposites exhibit high irreversible initial discharge capacity and a higher reversible capacity as anode materials for lithium ion batteries. The superior performance and good rate capacity demonstrate that the SC CO₂ synthesis techniques for the formation of SnS₂/RGO nanocomposites are believed to function synergistically energy storage of the anode material.

2. Experimental details

2.1. Preparation of SnS₂ and SnS₂/RGO nanocomposites

All chemical reagents were analytical grade and used without further purification. SnCl₄·5H₂O and thiourea were all purchased from Aladdin Industrial Corporation. GO was made by the modified Hummers method, and exfoliated using a high pressure homogenizer, then annealed at 300°C for 3h under Ar atmosphere. The final product is called reduced graphene oxide (RGO).

In a typical reaction, the solution used to prepare SnS₂/RGO nanocomposites was first composed of 0.1753 g SnCl₄·5H₂O, 0.0952 g thiourea, 0.0292 g of RGO. The

solvent was 30 mL ethylene glycol. The mixture was transported to a preheated (100 °C) stainless steel reactor (50 mL), and CO₂ was charged into the reactor to the desired pressure (15 MPa). The mixture was reacted in the SC CO₂ for 120 min. Subsequently, the products were cooled at room temperature, separated by centrifugation, washed several times with distilled water, and then dried in a vacuum at 60 °C for 4 h.

2.2. Materials characterizations

Field emission scanning electron microscopy (JSM-7000F) was used to determine the morphology of the samples. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained using a JEOL model JEM2100 instrument at an accelerating voltage of 200 kV. The crystal phase properties of the samples were analyzed with a Bruker D8 Advance X-ray diffractometer (XRD) using Ni-filtered Cu K α radiation at 40 kV and 40 mA at 2 θ ranging from 10° to 90° with a scan rate of 0.02 ° per second. Raman spectra were obtained on a Raman spectrometer (JY T64000) excited by the 514.5 nm line of an Ar⁺ laser under 100 μ W. X-ray photoelectron spectroscopy (XPS) analysis (PHI5000 Versaprobe) was used to determine the chemical composition of the products. The TG experiments were conducted on a simultaneous thermal analyzer (DTA-TG, NEFZSCH STA 499F3) in an Ar and 8% O₂ atmosphere from 30 °C to 850 °C at the heating rate of 10 °C min⁻¹.

2.3. Electrochemical measurements

For lithium ion battery measurements, slurry of active material was prepared with carbon black and polyvinylidene fluoride (PVDF) in a weight ratio of 80:10:10,

to form homogeneous slurry in N-methyl-pyrrolidone (NMP). This was then filmed for about thickness of 50 μm on a copper foil and dried in vacuum at 80 $^{\circ}\text{C}$ for 12 h. The electrodes were pressed to enhance the contact between the active materials and the conductive carbon. Coin cell assembly was done at room temperature in a glove box under argon. The cyclic voltammograms and galvanostatic charge/discharge cycling were performed at current rates (0.1 A/g) in the voltage range of 0.01 and 3V (versus Li^+/Li). The tenth-cycle discharge capacity of SnS_2/RGO nanocomposites electrode were performed at current density of 0.1, 0.2, 0.4, and 0.8 Ag^{-1} , respectively. The first five cyclic voltammograms (CV) over a voltage rang of 0.01-3 V at a scanning rate of 0.1 mV/s. Electrochemical impedance spectroscopy (EIS) of the fresh cell and after cycling electrodes obtained by applying a sine wave with an amplitude of 5.0 mV over the frequency range of 1000 kHz-0.01 Hz.

3. Results and discussion

Here Fig. 1

The microstructure morphologies of SnS_2/RGO nanocomposites can be observed from field emission scanning electron microscopy (FESEM) images in Fig. 1a (low-magmification) and Fig. 1b (high-magmification). The image with high-magmification further conform that SnS_2 nanoparticles are closely anchored and distributed uniformly on the RGO nanosheets surface. The agglomeration of small SnS_2 nanoparticles may be prevented effectively by the restacking of RGO nanosheets to further facilitate Li^+ diffusion. The result of TEM characterization exhibits that some homogeneous ultrasmall SnS_2 nanoparticles with size in the range of 2-4 nm are

loaded in RGO network and the diameter distribution is shown in the inset of Fig. 1c, which indicates a closely connection between the SnS₂ nanoparticles and RGO nanosheets. More details are observed in the HRTEM image of part of the SnS₂/RGO nanocomposites (Fig. 1d). SnS₂ has a parallel lattice frings with interplanar distance of 0.32 nm, which can be ascribed the *d* value of (100) plane (amplified (100) lattice figure in the inset of Fig. 1d). Furthermore, a series of experiments to explore the optimum experimental condition are shown in Fig. S1 and Table S1 (See the supporting information). The result is in good accordance with the below XRD analysis (Fig. S2). The crystal structure and composition of the as-prepared samples are investigated by X-ray powder diffraction (XRD) in the Fig. S2. The five peaks of (001), (100), (101), (110) and (111) can be well indexed to the peaks of standard hexagonal SnS₂ (JCPDS 23-0667) with lattice parameters *a*=0.365nm and *c*=0.590nm. The peak at $2\theta \approx 22.69^\circ$ corresponding to RGO is the major differences from the SnS₂/RGO, while other peaks are similar to that of pristine SnS₂, which demonstrates the formantion of SnS₂/RGO nanocomposites during the SC CO₂ synthesis techniques [23, 24].

Here Fig. 2

The chemical compositions of as-prepared SnS₂/RGO nanocomposite are further investigated by the X-ray photoelectron spectroscopy (XPS) measurements (Fig. 2). The detected elements by XPS survey spectrum are O, Sn, C and S components in Fig.2a. The C1s spectrum can be fitted and splitted with three different peaks of 284.4 eV, 285.0 eV and 287.4 eV corresponding to the C-C, C-O, and C=O bonds,

respectively (Fig. 2b) [23-26]. Fig. 2c shows the two peaks separated by ~ 8.500 eV at 496.100 eV and 487.600 eV, which indicates the presence of Sn $3d_{3/2}$ and Sn $3d_{5/2}$, respectively [27]. The high-resolution spectrum for the S 2p region can be splitted into two peaks of S2p $_{3/2}$ at 164.0 eV and S2p $_{1/2}$ at 165.2 eV (Fig.2d) [25].

Here Fig. 3

The content of RGO in the SnS₂/RGO nanocomposites plays an important role in their lithium storage performance, so the TG-DTA are conducted in an Ar and 8% O₂ atmosphere from 30 °C to 850 °C at the heating rate of 10 °C min⁻¹. As shown in Fig. 3a, two-stage weight loss regions accompanied with two exothermic processes can be observed. The initial weight loss (86.64 wt%, up to 200 °C) can be attributed to the evaporation of physically absorbed plenty of water and the residual oxygen-containing groups [28, 29]. The second weight loss (10.87 wt%, between 450°C and 650°C) is related to decomposition of RGO and the phase transformation from SnS₂ to SnO₂, and the amount of SnS₂ can be calculated from the residual SnO₂ [28, 30]. Accordingly, the composite contains about 96.98 wt% RGO and 3.02 wt% SnS₂, wherein the high concentration of RGO provides a highly conductive network to act a good buffering matrix as LIB anode materials [26-29]. The Raman spectroscopy (Fig. 3b) of RGO shows two sharp peaks of 1342 cm⁻¹ (D band) and 1581 cm⁻¹ (G band), while two sharp peaks from SnS₂/RGO Raman spectroscopy are 1357 cm⁻¹ (D band) and 1597 cm⁻¹ (G band). The D band is related to the defects and disorder in the hexagonal graphitic layers, while the G band is related to the vibration of the sp²-bonded carbon atoms in a two dimensional hexagonal lattice [31]. Besides,

a very weak peak appears at about 311 cm^{-1} (see figure of amplification in Fig. 3b), which is attributed to the A_{1g} mode of SnS_2 , indicating the formation of SnS_2/RGO nanocomposite [31, 32]. The disorder degree and average size of the sp^2 domains can be indicated by the I_D/I_G intensity ratio. The two peaks of 1357 cm^{-1} (D band) and 1597 cm^{-1} (G band) relative to 1342 cm^{-1} (D band) and 1581 cm^{-1} (G band) move about 15 cm^{-1} to high frequency, which is partially due to the decrease of hole doping or electron concentration in the system [33]. In addition, the intensity ratio D band and to the G band (I_D/I_G) are calculated to be 1.45 for RGO and 1.18 for SnS_2/RGO , respectively, indicating that less defects in the SnS_2/RGO nanocomposites [26, 34-36]. The results of Raman spectroscopy confirm the very harmonious integration of small SnS_2 nanoparticles and RGO nanosheets in the synthesis process.

Here Fig. 4

The first five cyclic voltammetry (CV) are performed over a voltage rang of 0.01-3 V at a scanning rate of 0.1 mV/s to learn the storage mechanism as anodes in LIBs (Fig. 4a). The lithiation mechanism of SnS_2 can be expressed by a two-step reaction as follows [9, 11, 27]:

Remarkably, two reduction peaks at 0.64 V and 1.49 V during the first scan can be attributed to the decomposition of SnS_2 into Sn and Li_2S and the formation of irreversible solid electrolyte interface (SEI) film by Eq.(1) [24, 25, 28]. The CV curves of SnS_2/RGO are almost overlapped after the first cycling, suggesting the

stable reversible electrochemical reactions. The characteristic pair of reduction and oxidation peaks (0.0-0.2 V, 0.2-0.5 V) can be ascribed to the intercalation /de-intercalation of lithium ions by Eq. (2) [29, 32]. In addition, a weaker reduction peak at 1.8 V is assigned to the intercalation of lithium ions into the SnS₂ layers without phase decomposition and the three oxidation peaks at 1.21 V, 1.88 V, and 2.33 V can be attributed to the deintercalation of lithium ions into the SnS₂ layers without phase decomposition [34, 37]. The CV curve well corresponds to the charge/discharge platforms in the picture below (Fig. 4b).

The small SnS₂ nanoparticles decorated RGO nanosheets electrodes are tested as an anode for LIBs at a current of 0.1 A/g (Fig. 4b). The initial high discharge of 1466.1 mAhg⁻¹ during the first cycle is related to the first-step irreversible reaction and the formation of solid electrolyte interface (SEI) film. Subsequently, the reversible capacities during the second and third discharge cycles are 585.7 mAhg⁻¹ and 524.2 mAhg⁻¹, respectively. The 524.2 mAhg⁻¹ in the third cycle is 89.5% of 585.7 mAhg⁻¹ in the second cycle, indicating the slowly capacity decay from the buffer function in the composite. Even after 30 cycles, the discharge capacity achieves 459.4 mAhg⁻¹, which is much higher than theoretical capacity of graphite (372 mAhg⁻¹). The discharge and charge capacities of 459.4 mAhg⁻¹ and 441.8 mAhg⁻¹ after 30 cycles, corresponding to a high coulombic efficiency of about 96%. The corresponding cycling performance of SnS₂/RGO electrodes at a current density of 100 mA g⁻¹ is shown in the Supporting Information Fig. S3. These results may be partly attributed to the coexistence of ultrathin SnS₂ nanoparticles and RGO

nanosheets resulting in more high reversible capacity [37]. Moreover, the SnS₂ nanoparticles are sandwiched between RGO nanosheets, which are beneficial for buffering the volume changes during cycling reaction.

To further investigated the effect of SnS₂ decorated RGO for lithium ion storage capacity, the rate performance of the as-prepared SnS₂/RGO nanocomposites are examined at various current densities of 0.1 A/g, 0.2 A/g, 0.4 A/g and 0.8 A/g (Fig. 4c), which delivered averaged rate capacity of ~478 mAhg⁻¹, ~450 mAhg⁻¹, ~376 mAhg⁻¹ and ~323 mAhg⁻¹, respectively [37]. When the current density backs to 0.1 A/g again, the rate capacity is ~492 mAhg⁻¹. The corresponding voltage profiles of SnS₂/RGO electrodes in 30th, 40th, 50th, 60th and 70th at different current density can be seen in the Supporting Information Fig. S4. The specific capacities at these current densities are still deceasing step by step on increasing the current density from 0.1A/g to 0.8A/g. The telectrochemical impedance spectroscopy (EIS) measurements are obtained from the fresh cell and after cycling electrodes. Nyquist plots are shown in Fig.4d, which contains one depressed semicircle at high/medium frequency and inclined line at low frequency [28, 29]. The compressed semicircle can be assigned to the internal resistance of the battery, the solid electrolyte interphase resistance and the charge transfer resistance, and an approximately 45 ° inclined line representing the warbury impedance is related to the solid-state diffusion of Li⁺ [29, 35]. The size of semicircle after cycling is slightly than the fresh cell, which may be associated with the irreversible reaction during first cycle [35, 37]. These results manifest RGO can effectively prevent the aggregation of SnS₂ and enhance contact surface areas of

active component with electrolyte to improve its Li ions storage performance [2].

4. Conclusions

In summary, small SnS₂ nanoparticles are successfully anchored and dispersed on RGO nanosheets with conductive networks via supercritical CO₂ method. The synthetic conditions such as pressure, temperature and reaction time have critical influence on the morphologies and sizes of the produce. The cycle voltammetry, charge/discharge and electrochemical impedance spectroscopy are be used to investigate the electrochemical storage performance. The SnS₂/RGO nanocomposites exhibit high irreversible initial discharge capacity and a higher reversible capacity compared with the theoretical value of graphite as anode materials for lithium ion batteries. The superior performance and good rate capacity demonstrate that the SC CO₂ synthesis techniques for the formation of ultrathin SnS₂/RGO nanocomposites are believed to function synergistically energy storage of the anode material.

Acknowledgments: This work was financially supported by the National Basic Research Program of China (973 Program: 2013CB932903, No. 21475085), the National Science Foundations of China (No. 61205057, No. 11574136), Qing Lan Project, the ‘1311 Talent Plan’ Foundation of Nanjing University of Posts and Telecommunications, Six talent peaks project in Jiangsu Province (JY-014), the Open Research Fund of State Key Laboratory of Bioelectronics, Southeast University, and Jiangsu Provincial Key R & D Program (Grant No. BE2015700).

References

- [1] D. Xie, W.J. Tang, X.H. Xia, D.H. Wang, D. Zhou, F. Shi, X.L. Wang, C.D. Gu, J.P. Tu, *Journal of Power Sources*, 296 (2015) 392-399.
- [2] H. Tang, X. Qi, W. Han, L. Ren, Y. Liu, X. Wang, J. Zhong, *Applied Surface Science*, 355 (2015) 7-13.
- [3] A.Y. Kim, J.S. Kim, C. Hudaya, D. Xiao, D. Byun, L. Gu, X. Wei, Y. Yao, R. Yu, J.K. Lee, *Carbon*, 94 (2015) 539-547.
- [4] S. Liu, X. Yin, L. Chen, Q. Li, T. Wang, *Solid State Sciences*, 12 (2010) 712-718.
- [5] Y. Xiao, *Ieee Transactions on Industrial Electronics*, 62 (2015) 3112-3122.
- [6] M. Gruetzke, V. Kraft, W. Weber, C. Wendt, A. Friesen, S. Klamor, M. Winter, S. Nowak, *Journal of Supercritical Fluids*, 94 (2014) 216-222.
- [7] W. Wang, Y. Wang, Y. Gao, Y. Zhao, *Journal of Supercritical Fluids*, 85 (2014) 95-101.
- [8] L. Ji, H.L. Xin, T.R. Kuykendall, S.-L. Wu, H. Zheng, M. Rao, E.J. Cairns, V. Battaglia, Y. Zhang, *Physical Chemistry Chemical Physics*, 14 (2012) 6981-6986.
- [9] T.-J. Kim, C. Kim, D. Son, M. Choi, B. Park, *Journal of Power Sources*, 167 (2007) 529-535.
- [10] D. Kong, H. He, Q. Song, B. Wang, Q.-H. Yang, L. Zhi, *Rsc Advances*, 4 (2014) 23372-23376.
- [11] Y. Zou, Y. Wang, *Chemical Engineering Journal*, 229 (2013) 183-189.
- [12] W.D. Shi, L.H. Huo, H.S. Wang, H.J. Zhang, J.H. Yang, P.H. Wei,

- Nanotechnology, 17 (2006) 2918-2924.
- [13] S.-C. Zhu, H.-C. Tao, X.-L. Yang, L.-L. Zhang, S.-B. Ni, Ionics, 21 (2015) 2735-2742.
- [14] D. Chen, W. Chen, L. Ma, G. Ji, K. Chang, J.Y. Lee, Materials Today, 17 (2014) 184-193.
- [15] X. Jiang, X. Yang, Y. Zhu, J. Shen, K. Fan, C. Li, Journal of Power Sources, 237 (2013) 178-186.
- [16] K. Siwinska-Stefanska, B. Kurc, Journal of Power Sources, 299 (2015) 286-292.
- [17] Y. Wang, J. Ding, Y. Liu, Y. Liu, Q. Cai, J. Zhang, Ceramics International, 41 (2015) 15145-15152.
- [18] S.K. Park, H.J. Lee, M.H. Lee, H.S. Park, Chemical Engineering Journal, 281 (2015) 724-729.
- [19] H. Li, K. Yu, H. Fu, B. Guo, X. Lei, Z. Zhu, Physical chemistry chemical physics : PCCP, 17 (2015) 29824-29833.
- [20] M. Zhang, D. Lei, X. Yu, L. Chen, Q. Li, Y. Wang, T. Wang, G. Cao, Journal of Materials Chemistry, 22 (2012) 23091-23097.
- [21] A. Ohashi, K. Shiratori, H.-B. Kim, Talanta, 146 (2016) 789-794.
- [22] M. Gruetzke, X. Moennighoff, F. Horsthemke, V. Kraft, M. Winter, S. Nowak, Rsc Advances, 5 (2015) 43209-43217.
- [23] D. Wan, C. Yang, T. Lin, Y. Tang, M. Zhou, Y. Zhong, F. Huang, J. Lin, Acs Nano, 6 (2012) 9068-9078.
- [24] S. Liu, X. Lu, J. Xie, G. Cao, T. Zhu, X. Zhao, Acs Applied Materials &

- Interfaces, 5 (2013) 1588-1595.
- [25] P.V. Prikhodchenko, D.Y.W. Yu, S.K. Batabyal, V. Uvarov, J. Gun, S. Sladkevich, A.A. Mikhaylov, A.G. Medvedev, O. Lev, Journal of Materials Chemistry A, 2 (2014) 8431-8437.
- [26] X. Bian, X. Lu, Y. Xue, C. Zhang, L. Kong, C. Wang, Journal of Colloid and Interface Science, 406 (2013) 37-43.
- [27] C. Zhai, N. Du, H. Zhang, J. Yu, D. Yang, Acs Applied Materials & Interfaces, 3 (2011) 4067-4074.
- [28] J. Li, P. Wu, F. Lou, P. Zhang, Y. Tang, Y. Zhou, T. Lu, Electrochimica Acta, 111 (2013) 862-868.
- [29] Q. Zhang, R. Li, M. Zhang, B. Zhang, X. Gou, Electrochimica Acta, 115 (2014) 425-433.
- [30] N. Du, X. Wu, C. Zhai, H. Zhang, D. Yang, Journal of Alloys and Compounds, 580 (2013) 457-464.
- [31] L. Mei, C. Xu, T. Yang, J. Ma, L. Chen, Q. Li, T. Wang, Journal of Materials Chemistry A, 1 (2013) 8658-8664.
- [32] H. Zhong, G. Yang, H. Song, Q. Liao, H. Cui, P. Shen, C.-X. Wang, Journal of Physical Chemistry C, 116 (2012) 9319-9326.
- [33] J. Yin, H. Cao, Z. Zhou, J. Zhang, M. Qu, Journal of Materials Chemistry, 22 (2012) 23963-23970.
- [34] B. Qu, C. Ma, G. Ji, C. Xu, J. Xu, Y.S. Meng, T. Wang, J.Y. Lee, Advanced Materials, 26 (2014) 3854-3859.

- [35] B. Luo, Y. Fang, B. Wang, J. Zhou, H. Song, L. Zhi, *Energy & Environmental Science*, 5 (2012) 5226-5230.
- [36] Z. Jiang, C. Wang, G. Du, Y.J. Zhong, J.Z. Jiang, *Journal of Materials Chemistry*, 22 (2012) 9494-9496.
- [37] R. Chen, T. Zhao, W. Wu, F. Wu, L. Li, J. Qian, R. Xu, H. Wu, H.M. Albishri, A.S. Al-Bogami, D. Abd El-Hady, J. Lu, K. Amine, *Nano Letters*, 14 (2014) 5899-5904.

Figure captions

Scheme1. The formation of SnS₂/RGO nanocomposites using SC CO₂ route.

Fig. 1 (a) and (b) SEM images of SnS₂/RGO nanocomposites, (c) TEM image of SnS₂/RGO nanocomposites and (d) Its HRTEM image.

Fig. 2 (a) Full XPS spectrum of the SnS₂/RGO nanocomposites, (b) XPS spectrum of curve fitting and splitting peaks from C1s, (c) high-resolution XPS spectra of the SnS₂/RGO nanocomposites in the Sn 3d, (d) XPS spectrum of curve fitting and splitting peaks from S 2p.

Fig.3 (a) TG-DTA curves of SnS₂/RGO nanocomposites, (b) Raman spectra of RGO and SnS₂/RGO nanocomposites.

Fig.4 (a) The first five cyclic voltammograms over a voltage range of 0.01-3 V at a scanning rate of 0.1 mV/s, (b) Discharge/charge voltage profiles of ultrathin SnS₂/RGO anode at a current of 0.1 A/g, (c) Rate capabilities of ultrathin SnS₂/RGO anode; inset: discharge/charge voltage profiles of ultrathin SnS₂/RGO anode at current density of 0.1, 0.2, 0.4, and 0.8 A/g, (d) Nyquist plots of the fresh cell and after cycling electrodes obtained by applying a sine wave with an amplitude of 5.0 mV over the frequency range of 1000 kHz-0.01 Hz.

Scheme1. The formation of SnS_2/RGO nanocomposites using SC CO_2 route

Fig. 1 (a) and (b) SEM images of SnS₂/RGO nanocomposites, (c) TEM image of SnS₂/RGO nanocomposites and (d) Its HRTEM image.

Fig. 2 (a) Full XPS spectrum of the SnS₂/RGO nanocomposites, (b) XPS spectrum of curve fitting and splitting peaks from C1s, (c) high-resolution XPS spectra of the SnS₂/RGO nanocomposites in the Sn 3d, (d) XPS spectrum of curve fitting and splitting peaks from S 2p.

Fig.3 (a) TG-DTA curves of SnS₂/RGO nanocomposites, (b) Raman spectra of RGO and SnS₂/RGO nanocomposites.

Fig.4 (a) The first five cyclic voltammograms over a voltage range of 0.01-3 V at a scanning rate of 0.1 mV/s, (b) Discharge/charge voltage profiles of ultrathin SnS_2/RGO anode at a current of 0.1 A/g, (c) Rate capabilities of ultrathin SnS_2/RGO anode; inset: discharge/charge voltage profiles of ultrathin SnS_2/RGO anode at current density of 0.1, 0.2, 0.4, and 0.8 A/g, (d) Nyquist plots of the fresh cell and after cycling electrodes obtained by applying a sine wave with an amplitude of 5.0 mV over the frequency range of 1000 kHz-0.01 Hz.