

Facile one-step synthesis of SnS₂ nanoscale hollow spheres for enhanced lithium-ion storage performance as anode

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The SnS₂ hollow nanospheres are successfully fabricated using SnCl₄·5H₂O, thiourea and urea as raw materials via a mild one-step hydrothermal process. The size of SnS₂ hollow nanosphere is about 400 nm, and the shell thickness of it is about 50 nm, consisting of nanoparticles with the size of 3 nm. The formation of such hollow structure could be mainly ascribed to the soft template effect of carbon-dioxide and ammonia bubbles decomposed from urea. The obtained hollow nanospheres possess a higher specific surface area of 142 m² g⁻¹ compared with that of the SnS₂ granular aggregate sample (34 m² g⁻¹), presenting better cycling stability and rate capability.

1. Introduction: Nanostructures have drawn much attention because of their unique optical, electrical, catalytic, electrochemical and other functional properties. Especially used as electrode materials of lithium-ion battery, nanomaterials exhibit good electrochemical properties because the nanostructure shortens the diffusion path of Li⁺ ions, increase the contact area between the electrodes and the electrolyte and accelerate the intercalation and deintercalation of Li⁺ ions [1–3]. Among the reported anode materials [4–7], SnS₂ has a high theoretical capacity (645 mAh g⁻¹) and is considered to be an excellent alternative to traditional graphite (372 mAh g⁻¹) [8]. The flower-like SnS₂ prepared by Ren *et al.* [9] had an initial discharge capacity of 776.1 mAh g⁻¹ at a current density of 20 mA g⁻¹. The hierarchical SnS₂/SnO₂/C heterostructures fabricated by Chen *et al.* [10] have a superior rate capability of 550.8 mAh g⁻¹ at the 1C rate. The SnS₂ nanoflakes prepared by Ren *et al.* [11] exhibit a high capacity of 818.4 mAh g⁻¹ after 500 cycles at 1 A g⁻¹. Flexible free-standing SnS₂@graphene nanosheets show excellent cycling performance with a capacity of 378 mAh g⁻¹ after 200 cycles at a specific current density of 1200 mA g⁻¹ [12]. The SnS₂ hollow microsphere reported by Chen *et al.* has the capacity of about 430 mAh g⁻¹ at a current density of 100 mA g⁻¹ after 60 times cycling [13].

The preparation of SnS₂ hollow microsphere reported by Chen *et al.* [13] requires reagents including SnCl₂·2H₂O, Na₂S₂O₃·5H₂O, sulphur powders, hexadecyl trimethyl ammonium bromide, tartaric acid, sodium hydroxide and ethanol. In this Letter, nevertheless, we use only SnCl₄·5H₂O, thiourea and urea as raw materials to synthesise the SnS₂ nanoscale hollow spheres via a facile one-step hydrothermal process.

2. Materials and methods: In a typical synthesis process, 0.36 g SnCl₄·5H₂O, 2 g thiourea, 3 g urea and 30 ml of deionised water were added into a 100 ml teflon stainless autoclave. The hydrothermal synthesis was conducted at 180°C for 12 h, the final products were centrifuged, washed with deionised water and anhydrous ethanol for several times, and dried at a vacuum freeze drier for 12 h. For comparison, an experiment without urea was also carried out under the same hydrothermal condition.

The phase-structural composition of the product was characterised using powder X-ray diffraction [XRD, Rigaku, D/max-2200PC, copper (Cu) Kα₁ radiation, λ = 1.5406 Å]. The morphology of as-prepared samples were characterised via transmission electron microscopy (TEM, FEI Tecnai, G2 F20 S-TWIN) and

field-emission scanning electron microscopy (FE-SEM, Hitachi, S-4800). Specific surface areas were calculated based on the Brunauer–Emmett–Teller (BET) method together with the nitrogen adsorption/desorption isotherms acquired at 77 K using a surface area and pore size analyser (NOVA 2200e). The electrochemical properties of the electrode material were evaluated using the CR2032 coin cell. The synthesised SnS₂, acetylene carbon black and the polyacrylic acid binder were at a mass ratio of 8:1:1 in a volume ratio of 1–1.5 ml deionised water to form the uniform slurry. The flowing slurry was then coated on Cu foil and dried under vacuum at 70°C for 12 h. The foil was cut into round pieces (diameter: 16 mm). The loading density of the active materials is calculated as 2.0 mg cm⁻² and the thickness of which is 0.15 mm. The coil-type half cells was assembled under an argon atmosphere in a glove box (Braun Insert gas-System GmbH) and lithium plates were used as the counter and reference electrodes. 1 M lithium hexafluorophosphate (ethylene carbonate (EC):dimethyl carbonate (DMC):ethyl methyl carbonate (EMC)=1:1:1, vol.%) was used as an electrolyte and a porous polypropylene film (Celgard 2400) was used as a separator. The galvanostatic charge–discharge measurements were conducted at different current densities in the voltage range of 0.005–3.0 V versus Li⁺/Li via a computer-controlled Neware battery testing system. The frequency range of the electrochemical impedance spectroscopy (EIS) is 100 k–0.01 Hz.

3. Results and discussion: The XRD patterns of the samples synthesised at conditions with/without urea are shown in Fig. 1. It is found that all diffraction peaks of these samples can be indexed well to an SnS₂ hexagonal structure (PDF No. 23-0677) and the diffraction peaks intensity of the samples synthesised at conditions with urea is weaker than that without urea. It is indicated that the addition of urea influences not the formation of SnS₂ phase but the crystallinity of SnS₂ samples. However, it is worth noting that the morphology of the samples obtained at conditions with/without urea is completely different.

Fig. 2a is the SEM image of the SnS₂ sample obtained at conditions without urea. It is observed that the SnS₂ sample obtained at conditions without urea is a granular aggregate consisting of nanoparticles with the size of about 30 nm. It is interesting that the SnS₂ sample obtained at conditions with urea presents the nanosphere morphology with sizes of 500 nm (Fig. 2b). Moreover, it is found that such nanosphere is the hollow opening structure from the broken sphere. In TEM image of the SnS₂ nanospheres,

there is the strong contrast between the dark edge and the pale centre of nanospheres (Fig. 2c), the thickness of dark edge (the shell thickness) is about 50 nm and the shell consists of nanoparticles with the size of 3 nm (Fig. 2d). Above results clearly testify that the SnS₂ sample obtained at conditions with urea has the hollow nanosphere structure. The hollow structure SnS₂ reported by Chen *et al.* is a micron-sized hollow sphere (2–5 μm) [12] and shell thickness of the hollow nanospheres is about 150 nm. Moreover, the BET analysis results suggest that such SnS₂ hollow nanospheres obtained at condition with urea possess a higher specific surface area of 142 m² g⁻¹ compared with that of the SnS₂ nanoparticles sample obtained at condition without urea (34 m² g⁻¹). The formation of such hollow structure could be mainly ascribed to the addition of urea. The urea decomposes into carbon-dioxide (CO₂) and ammonia (NH₃) bubbles under hydrothermal conditions. These CO₂ and NH₃ bubbles are used as soft template, the crystallised SnS₂ nanoparticles aggregate around these bubbles, growing and forming the hollow nanospheres. The similar formation mechanism of hollow spheres materials based on bubble template was also reported by a lot of literatures [14–17].

Fig. 3a displays the electrochemical performance of samples tested at the current density of 100 mA g⁻¹. The initial capacities of the hollow nanospheres sample and granular aggregate sample are 1001 and 1107 mAh g⁻¹, respectively. After ten cycles, they exhibit the reversible capacity of 580 mAh g⁻¹ (hollow nanospheres) and 500 mAh g⁻¹ (granular aggregate), respectively. After 100 cycles, the hollow nanospheres remain 476 mAh g⁻¹, and has a capacity loss of 0.20% per cycle from 11th to 100th.

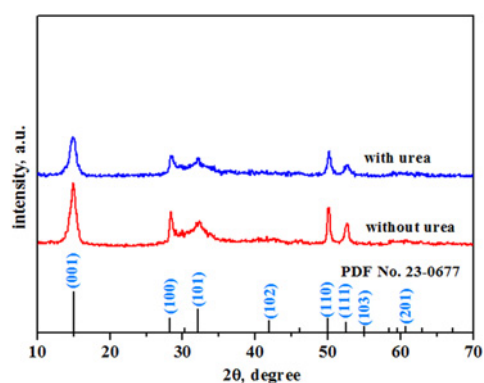


Fig. 1 XRD patterns of the samples obtained at conditions with/without urea

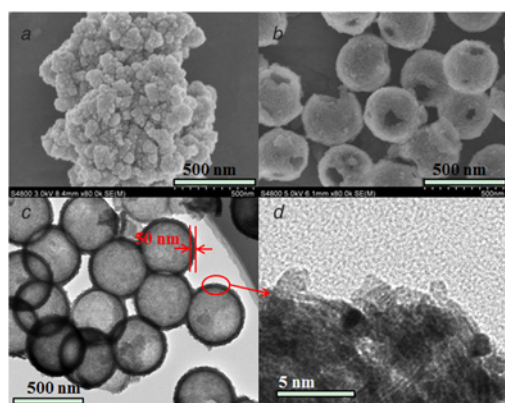


Fig. 2 SEM images of the samples obtained at conditions
a With urea
b Without urea
TEM images of the samples obtained at conditions
c, d With urea

Nevertheless, the capacity of granular aggregate sample decreases to 205 mAh g⁻¹ after 100 cycles, and per cycle its capacity loss is 0.66% from 11th to 100th. Chen *et al.* reported that the SnS₂ hollow microsphere has the reversible capacity of about 430 mAh g⁻¹ under the current density of 100 mA g⁻¹ after 60 times cycling [13]. Besides, as the current densities range from 50 to 800 mA g⁻¹, the SnS₂ hollow nanospheres still display a better discharge capacity than that of the SnS₂ nanoparticles sample (Fig. 3b). The EIS analysis indicates the hollow

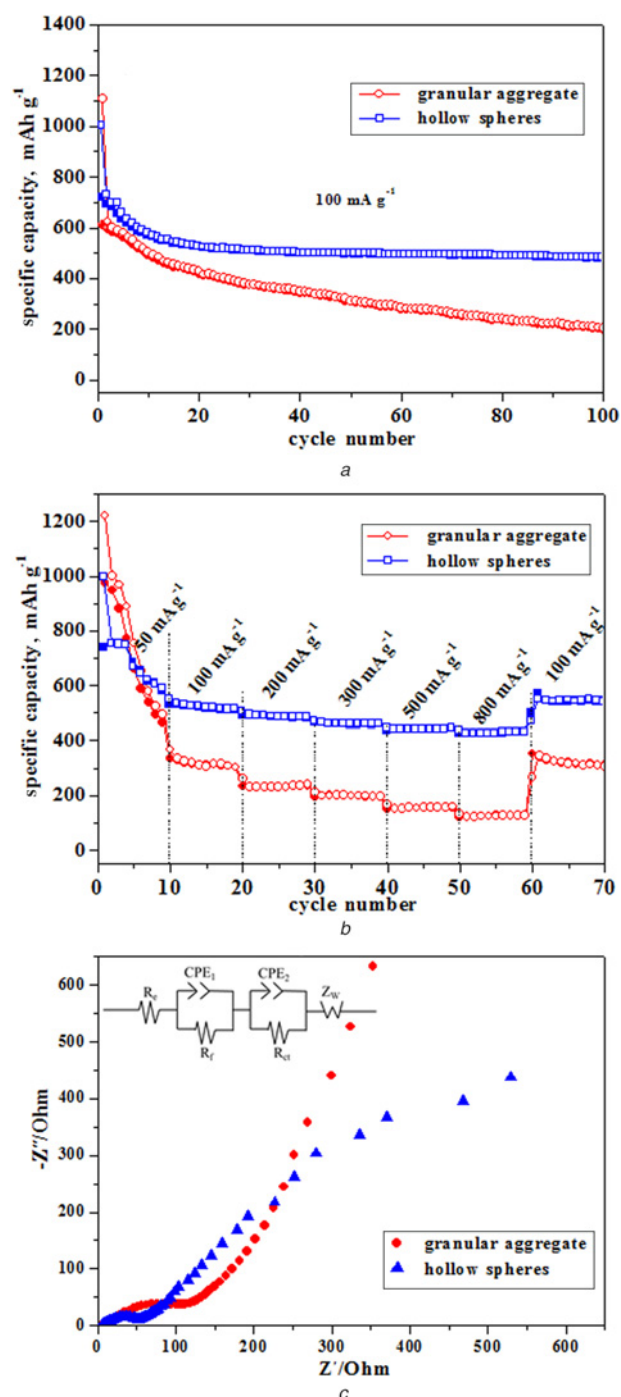


Fig. 3 Electrochemical performance of samples
a Charge-discharge cycling performances
b Rate performance
c Nyquist plots for the selected cycles of SnS₂ hollow nanospheres and SnS₂ granular aggregate electrodes in the frequency range of 100 k–0.01 Hz, the insert diagrams in Fig. 3c is the equivalent circuit model of the two electrodes

nanospheres possess a smaller charge transfer impedance than that of granular aggregate sample (Fig. 3c). The significantly improved electrochemical properties of the SnS₂ hollow nanospheres' electrodes may result from its higher specific surface area and smaller size [18–21].

4. Conclusion: The SnS₂ hollow nanospheres are successfully fabricated using the bubble as soft template via a facile one-step hydrothermal process. The obtained SnS₂ hollow nanosphere has a size of about 400 nm, and the shell thickness of it is about 50 nm, consisting of nanoparticles with the size of 3 nm. It possesses a higher specific surface area of 142 m² g⁻¹. The researches of electrochemical properties indicate that such hollow nanospheres possess better cycling stability and rate capability. Therefore, the SnS₂ hollow nanospheres exhibit significant potential for achieving stable anode performance at high current densities for Lithium ion batteries (LIBs).

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6 References

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