

Building Ni₃S₂ nanotubes array and application as an electrode in lithium ion battery

Experiments details

Fabrication procedure: All the reagents are of analytical grade and were used directly without any purification. A typical synthesis of the Ni₃S₂ nanotubes array is as follows. Na₂S₂O₃ (0.2 mmol, 48 mg), Na₂SO₄ (1 mmol, 142 mg), and 35 mL DI water were mixed step-by-step under stirring. After the mixture becomes a homogeneous and transparent solution, it was transferred into a Teflon-lined stainless steel autoclave with a capacity of 50 mL. A piece of cleaned Ni foam (100 PPI pore size, 380 g m⁻² areal density, and 1.5 mm thick) with an area of 3 × 2.5 cm² was put into the autoclave as both reactant and substrate. The autoclave was maintained in an oven at 130 °C for 2 h. After the autoclave was cooled naturally to room temperature, the Ni foam piece with the synthesized Ni₃S₂ nanotubes array on it was fetched out and rinsed with deionized water and absolute ethanol several times, and then dried at 60 °C in vacuum. On average, the mass loading of the Ni₃S₂ nanotubes is about 2 mg cm⁻² on Ni foam. By carefully weighting the mass of Ni foam before and after reaction, the active mass of Ni₃S₂ (m_{NiS}) was derived from $m_{\text{NiS}} = 3m \times 240.2 / 64.13$, where $3m$ is the mass difference of the Ni foam before and after the hydrothermal synthesis. The mass was weighed by a microbalance (Mettler, XS105DU) with an accuracy of 0.01 mg.

Structural characterization: The crystal structures of the resultant materials and the used Ni foam were characterized by X-ray powder diffraction (XRD, Rigaku D/Max-2400, Cu K radiation, $\lambda = 0.15418$ nm) with 2θ range from 10° to 90° and X-ray photoelectron spectroscopy (XPS, ESCALAB 250) analysis using a monochromic Al-K X-ray source ($E = 1486.6$ eV). The morphologies of the samples were observed using field-emission scanning electron microscopy (SEM, HitachiS-4800) and transmission electron microscopy (TEM, FEI Tecnai G2 F30).

Electrochemical characterization: The electrochemical measurements were performed using CR-2032 coin cells. The cells were assembled in a high-purity argon filled glove box ($\text{H}_2\text{O} < 0.5$ ppm, $\text{O}_2 < 0.5$ ppm, MBraun, Unilab) by using the Ni₃S₂ nanotubes array grown on Ni foam as the working electrodes and lithium foil as the counter and reference electrode. Celgard 2320 was used as the separator membrane. The electrolyte was 1 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC) in a 1:1:1 volume ratio. The galvanostatic discharge/charge cycling and cyclic voltammetry measurements were carried out at room temperature by using a multichannel battery tester (Neware BTS-610) and an electrochemical workstation (CHI 660C), respectively.

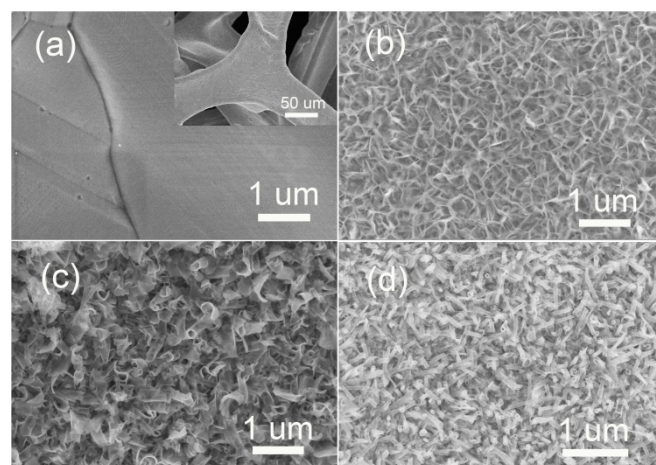


Fig. S1 SEM images of the used Ni foam substrate (a) and the Ni₃S₂ nanostructures synthesized for 0.5 h (b), 1 h (c) and 1.5 h (d).

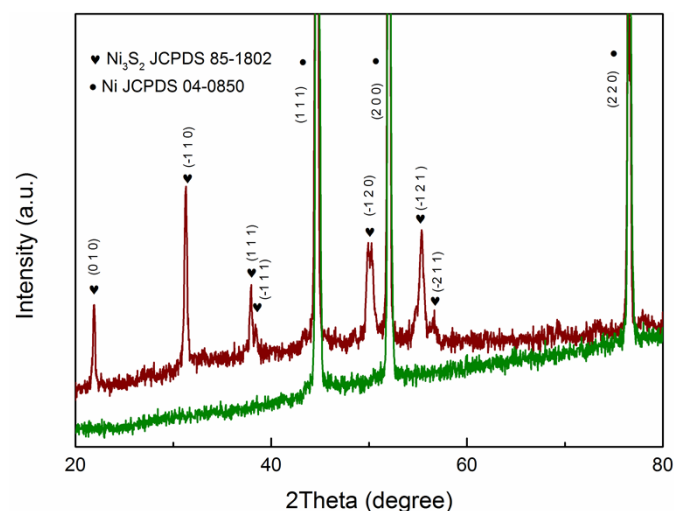


Fig. S2 XRD patterns of the synthesized Ni₃S₂ nanotubes array and the used nickel foam.

Fig. S3 shows the XPS spectra of the Ni₃S₂ nanotubes array electrode. The elemental composition is shown in Fig. S3 (a) in a wide-scan XPS spectrum. The high-resolution XPS spectra for Ni 2p and S 2p are shown in Fig. S3 (b) and (c). The Ni 2p spectrum shows peaks at 855.9 and 873.7 eV, which correspond to Ni 2p_{3/2} and Ni 2p_{1/2}, respectively. The S 2p spectrum indicates the existence of the S 2p_{3/2} and S 2p_{1/2}, with binding energies of 161.8 and 162.5 eV, respectively.¹

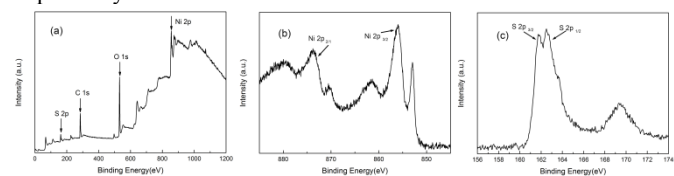


Fig. S3 XPS spectra of the Ni₃S₂ nanotubes array on the nickel foam.

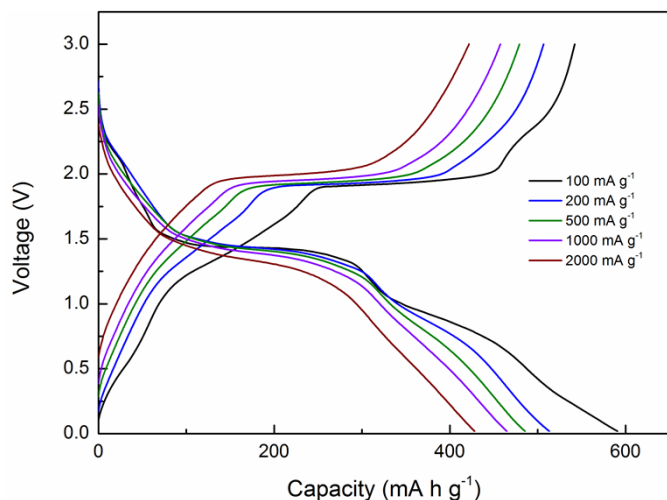


Fig. S4 Discharge/charge voltage profiles of the Ni_3S_2 nanotubes array electrode at different current densities.

Fig. S5 shows the morphologies of the Ni_3S_2 nanotubes array electrode after 50 cycles at a current density of 500 mA g^{-1} . As shown in Fig. S5 (a), the structure of the nanotubes is still preserved and stucked on the current collector in a large area (Fig. S5 (b)). It indicates that the synthesized Ni_3S_2 nanotubes array on Ni foam as an electrode for LIBs is very stable during cycling.

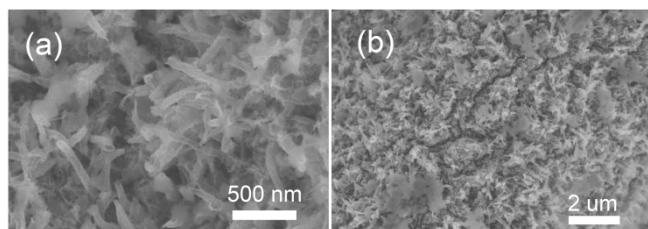


Fig. S5 (a) High- and (b) low-magnification SEM images of the Ni_3S_2 nanotubes array electrode after 50 discharge/charge cycles at a current density of 500 mA g^{-1} .

References

1 Q. Wang, R. Gao and J. Li, *Appl. Phys. Lett.*, 2007, **90**, 143107.