

Controlled-synthesis of NiS hierarchical hollow microspheres with different building blocks and their application in lithium batteries

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Supplementary Information

S1. XRD pattern of products obtained under different reaction conditions

With the aim of obtaining a pure phase of NiS, we varied the sulfur source (thioacetamide, TAA), the reaction temperature (100 °C and 210 °C), the amount of Na₂S (10.0 g) and the reaction time (96 h). However, no pure phase of NiS was obtained (See Table S1 and Fig. S1).

Table S1 Summary of the products obtained under different reaction conditions

Reaction type	Sample	Reaction Conditions						Phase
		Ni(OH) ₂ /g	Na ₂ S /g	TAA ^a /g	NaOH/ g	Temp ^b / °C	Time / h	
1D-hollow ^c	A	0.35	5.0	-	5.0	180	48	β-NiS, α-NiS
0D-hollow ^d	B	0.35	5.0	-	-	180	48	β-NiS, α-NiS
Temp-1	C	0.35	5.0	-	5.0	100	48	Ni(OH) ₂ , β-NiS, α-NiS
Temp-2	D	0.35	5.0	-	5.0	210	48	β-NiS, α-NiS
Time	E	0.35	5.0	-	5.0	180	96	β-NiS, α-NiS
TAA	F	0.35	-	1.56 ^e	5.0	180	48	Ni(OH) ₂ , β-NiS, α-NiS
Na ₂ S	G	0.35	10.0	-	5.0	180	48	β-NiS, α-NiS

^a TAA means thioacetamide;

^b Temp means temperature;

^c 1D-hollow means nanorod-based hierarchical hollow microspheres;

^d 0D-hollow means nanoparticle-based hierarchical hollow microspheres;

^e 1.56 g ≈ 20.8 mmol (thioacetamide), 5.0 g ≈ 20.8 mmol (Na₂S).

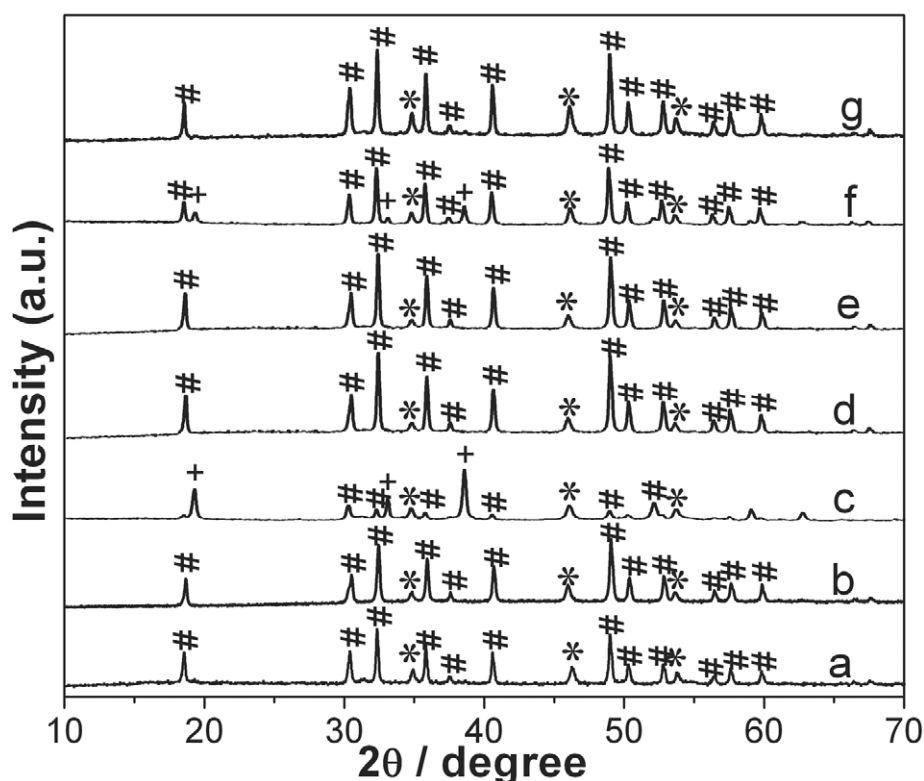


Fig. S1 XRD patterns of the products obtained under different reaction conditions: (a) sample A (nanorod-based hierarchical hollow microspheres); (b) sample B (nanoparticle-based hierarchical hollow microspheres); (c) sample C (100°C); (d) sample D (210°C); (e) sample E (96 h); (f) sample F (TAA); (g) sample G (10.0 g Na₂S). β-NiS (#), α-NiS (*) and Ni(OH)₂(+).

S2. SEM images of Ni(OH)₂ precursor spheres

In addition to the description in the main text, this supplementary material provides the information about Ni(OH)₂ hollow microspheres which were fabricated via a hydrothermal approach in strong alkaline solution of glycine. A typical experiment can be summarized: 5.0 mmol of Ni(NO₃)₂·6H₂O and 2.0 g of glycine as well as 2.0 g of Na₂SO₄ salt were dissolved in 25 mL of deionized water, then 10 mL of NaOH solution (5 M) was added dropwise into the above solution under magnetic stirring to form a clear blue solution. The solution was then sealed into a Teflon-lined autoclave, followed by hydrothermal treatment at 100-180 °C for 24 h in an electric oven. After the treatment, green Ni(OH)₂ products were collected by filtration, successively washed three times with deionized water, and dried at room temperature for 24 h. Fig. S2 shows the typical SEM images of the Ni(OH)₂ precursor microspheres.

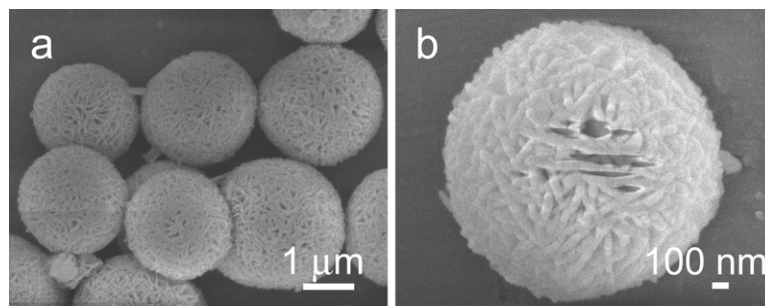


Fig. S2 (a)-(b) SEM images of $\text{Ni}(\text{OH})_2$ precursors observed under different magnifications.

S3. Experimental section of the first controlled experiment

In a typical experiment, 5.0 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 5.0 g of Na_2S as well as 5.0 g of NaOH were dissolved in 35 mL of deionized water to form a mixture. The resulting suspension was then sealed into a 50 mL Teflon-lined autoclave, followed by hydrothermal treatment at 180 °C for 48 h in an electric oven. After the treatment, black products were collected by filtration, washed three times with deionized water, and dried at room temperature for 24 h.

S4. XRD patterns of $\text{Ni}(\text{OH})_2$ precursor and NiS products with different reaction time (the third controlled experiments)

The formation process of nanorod-based NiS hierarchical hollow microspheres is indicated in the following series of time-dependent experiments (5.0 g of Na_2S and 5.0 g of NaOH were dissolved in 35 mL of deionized water to form a solution, then 0.35 g of $\text{Ni}(\text{OH})_2$ precursor was added into the solution. The resulting suspension was then sealed into a 50 mL Teflon-lined autoclave. After that, the autoclave was transferred to an electric oven at 180 °C and kept for 2h, 10h, and 48 h respectively). The XRD patterns clearly show the phase transformation from $\text{Ni}(\text{OH})_2$ to NiS (Fig. S3). All four systems give the same transformation trend, which means that the pure $\text{Ni}(\text{OH})_2$ is the only template in forming nanorod-based NiS hierarchical hollow microspheres. In Fig. S3a, the as-prepared $\text{Ni}(\text{OH})_2$ precursor is identified as the single phase $\beta\text{-Ni}(\text{OH})_2$ with a suitably crystalline hexagonal structure ($a = 0.3126$ nm, $c = 0.4605$ nm, JCPDS file No. 14-0117, signal +). No peaks from other phases are found, suggesting high purity of the as-synthesized $\beta\text{-Ni}(\text{OH})_2$. In Fig. S3b, XRD analyses indicate that the sample prepared at 180°C with reaction time of 2h is a mixture of NiS ($\beta\text{-NiS}$, JCPDS Card No. 12-0041, signal #; $\alpha\text{-NiS}$, JCPDS Card No. 02-1280, signal *) and $\beta\text{-Ni}(\text{OH})_2$ (signal +). As shown in Fig. S3c-d, however, no peaks from $\text{Ni}(\text{OH})_2$ are found, indicating that the $\text{Ni}(\text{OH})_2$ precursors are completely converted to NiS.

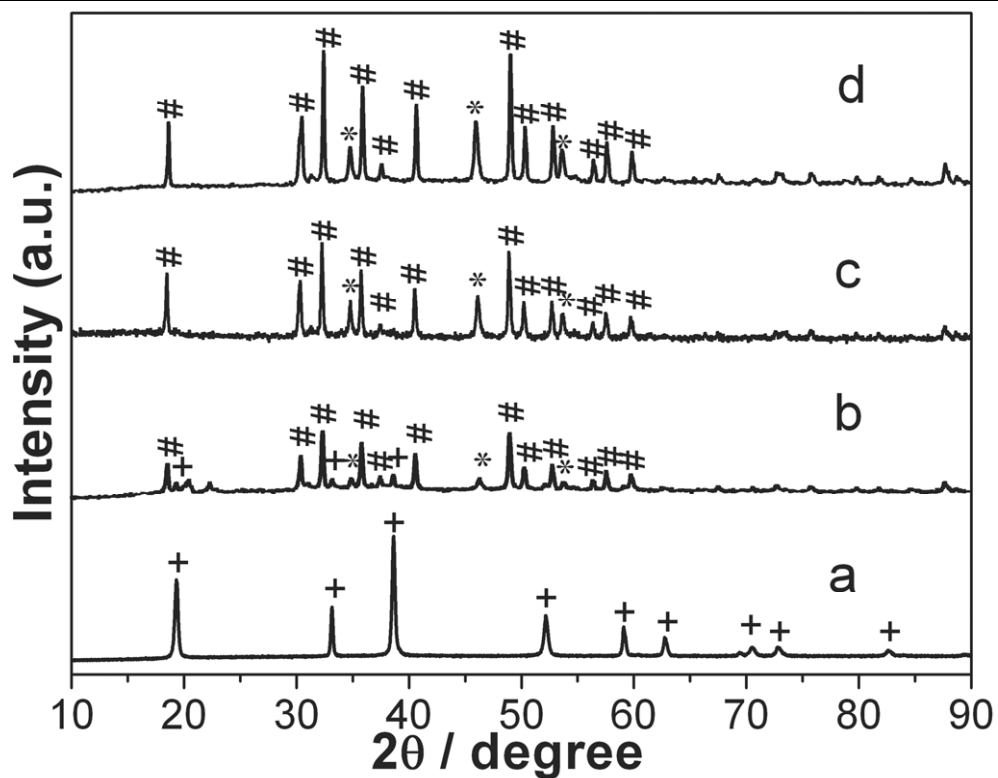


Fig. S3 X-ray diffraction pattern of (a) Ni(OH)_2 precursor and NiS hollow spheres prepared at 180°C with different experimental time: (b) 2 h; (c) 10 h; (d) 48 h. $\beta\text{-NiS}$ (#), $\alpha\text{-NiS}$ (*) and Ni(OH)_2 (+).