Supplementary material

Template-free synthesis of β-NiS ball-in-ball microspheres for highperformance asymmetrical supercapacitor

Qin Hu ^a, Wenpo Li ^a, Shengtao Zhang ^{a*}, Jiangyu Hao ^a, Lulu Zhang ^a, Lijin Yan ^a,

Xuefeng Zou b*

^a Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China.

^b Guizhou Provincial Key Laboratory of Computational Nano-Material Science,
Guizhou Education University, Guiyang 550018, China.

* Corresponding author, E-mail: shengtaozhangcqu@163.com, njzouxf@gznc.edu.cn.

1. Experimental section

1.1 Materials

2-mercaptopropionic acid (2-MPA, 96⁺%, Aladdin), Thiourea (TU, 96⁺%, Adamas), Thioacetamide (TAA, 96⁺%, Adamas), nickel (II) chloride hexahydrate (NiCl₂·6H₂O, AR), ethanol (AR), n-propanol (AR), n-butanol (AR), isopropanol (AR), and isobutyl alcohol (AR) were purchased from Guangdong Guanghua company.

1.2 Synthesis of nickel sulfides

Typically, 3 mmol of $C_3H_6O_2S$ and 1 mmol of NiCl₂·6H₂O were dissolved into 30 mL of distilled water (DI). After mixing uniformly, the solution was sealed in a Teflon-lined autoclave (50 mL) and healed at 200 °C for 24 h. After cooled down to room temperature, the product was carefully washed for several times and dried at 60 °C in a vacuum oven for 12 h, and being labeled as NS-1.

Keeping the other synthetic conditions constant, the NSs synthesized with different solvents (ethanol, n-propanol, n-butanol, isopropanol, and isobutyl alcohol) were labeled as NS-2, NS-3, NS-4, NS-5, and NS-6, successively. To investigate the growth process of NS-2, we prepared samples under different reaction time, and the corresponding samples were named as NS-2-1h, NS-2-2h, NS-2-4h, NS-2-12h, and NS-2-18h. Under similar synthetic condition, the NSs obtained using TU and TAA as sulfur sources were designated as NS-7 and NS-8, respectively. The abbreviations of different products and their corresponding synthetic conditions are listed in Table 1.

Abbreviations	nickel	sulfur source	solvent	Reaction	reaction
for different	source			temperature	time
products					
NS-1	NiCl ₂ ·6H ₂ O	2-MPA	H ₂ O	200 °C	24 h
NS-2	NiCl ₂ ·6H ₂ O	2-MPA	ethanol	200 °C	24 h
NS-3	NiCl ₂ ·6H ₂ O	2-MPA	n-propanol	200 °C	24 h
NS-4	NiCl ₂ ·6H ₂ O	2-MPA	n-butanol	200 °C	24 h
NS-5	NiCl ₂ ·6H ₂ O	2-MPA	isopropanol	200 °C	24 h
NS-6	NiCl ₂ ·6H ₂ O	2-MPA	isobutyl alcohol	200 °C	24 h
NS-7	NiCl ₂ ·6H ₂ O	TU	ethanol	200 °C	24 h
NS-8	NiCl ₂ ·6H ₂ O	ТАА	ethanol	200 ℃	24 h

Table 1 The abbreviations of different products and their corresponding synthetic condition.

1.3 Synthesis of reduced graphene oxide (rGO)

Graphene oxide (GO) was synthesized by modified Hummer's method. The rGO was synthesized by a flame-induced method [1].

1.4 Characterization

The crystal structure and composition of samples were detected by X-ray diffractometer (XRD). The valence state of elements was investigated by X-ray photoelectron spectroscopy (XPS, ESCALAB 250 Xi). Morphology of product was observed by field emission scanning electron microscope (FESEM, JSM-7800F) and transmission electron microscopy (TEM, FEI Talos F200S G2).

1.5 Electrochemical measurements

Electrochemical experiments including galvanostatic charge/discharge (GCD), cyclic voltammetry (CV), and electrochemical impedance (EIS) were performed on a CHI760E (Shanghai Chenghua, China) electrochemical workstation. Among which, the EIS plots were measured in a frequency from 100 kHz to 0.01 Hz at an open circuit potential with 5 mV AC amplitude. The working electrode was prepared by firstly mixing the NSs, acetylene black, and polyvinylidene fluoride at a weight ratio of 8:1:1 in N-methyl pyrrolidone to form a slurry. After that, the slurry was uniformly coated on a clean nickel foam and dried at 60 °C under vacuum, and the mass loading of electrode was controlled at about 2.4 mg. In a three-electrode system, the Pt electrode (2×2 cm²) and saturated calomel electrode (SCE) were employed as counter and reference electrode, respectively. A 2 M KOH aqueous solution was used as electrolyte. The specific capacity is calculated by the following equations.

$$C_m = I \times \Delta t / (m \times 3.6) \tag{1}$$

The NS-2//rGO ASC was assembled using NS-2 as the cathode material, rGO as the anode material, 2 M KOH solution as electrolyte, and a fresh filter paper membrane as separator, respectively. The energy density (E, W h kg⁻¹) and power density (P, W kg⁻¹) were calculated by the following equations:

$$E = 1/2 \times C_m \times \Delta \nu \tag{2}$$

$$P = E \times 3600 \,/\,\Delta t \tag{3}$$

Where *I* is the current (A g⁻¹), Δt is the discharge time (s), *m* is the mass loading of active material, Δv is the voltage window (V), and C_m is the specific capacity (mAh g⁻¹), respectively.



Fig. S1 XRD patterns of NS-5 and NS-6.



Fig. S2 SEM images of NS-3 (a, b), NS-4 (c, d), NS-5(e, f), and NS-6 (g, h).



Fig. S3 SEM images of NS-7 (a, b) and NS-8 (c, d).



Fig. S4 TEM images and elemental mapping images of NSs synthesized by different branch chain alcohols: (a- c) NS-3 and (d-f) NS-4.



Fig. S5 (a, b) CV and GCD curves of NS-1.



Fig. S6 Separation of diffusion and capacitive-controlled charges at 4 mV s⁻¹ for NS-1 (a) and NS-2 (b).

Reference

[1] X. Zou, Y. Zhou, Z. Wang, S. Chen, W. Li, B. Xiang, L. Xu, S. Zhu, J. Hou, Free-standing,

layered graphene monoliths for long-life supercapacitor, Chem. Eng. J. 350 (2018) 386-394.