

Fabrication of 1D Nickel Sulfide Nanocrystals with High Capacitances and Remarkable Durability

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Experimental Section:

Material synthesis: Experimental Details. All chemical reagents used in this work were analytical grade without further purification. Synthesis of NiS nanorods: NiCl₂ (0.1 g) was added in 1-dodecanethiol (10 mL) under stirring. The reactant mixture was then transferred into a 15 mL Teflon-lined autoclave and heated at 200 °C for 20 h, named as NiS-NR (sample 1). The synthesis of NiS nanowires, named as NiS-NW (sample 2) were similar with NiS nanorods, excepted that NiCl₂ was replaced by Ni(acac)₂, however, while using Ni(NO₃)₃ as the precursor, mixture of NiS and Ni₉S₈ were obtained (sample 3).

Synthesis of Nickel sulfides nanoparticles: Ni₃S₂ nanoparticles were prepared by a typical solvothermal method with 1-octadecene (ODE, 5 mL) and oleylamine (OAm, 5 mL) as solvent in a three-neck flask, 0.1 g Ni(acac)₂ and 0.05 g sulfur powder were added at 80 °C, then heating to 200 °C and kept for 20 minutes (sample 4). NiS₂ nanoparticles were obtained by at the same process as sample 1 except with Na₂S as sulfur source (sample 5). The using of thiourea resulted in a mixture of NiS and Ni₃S₄ (sample 6).

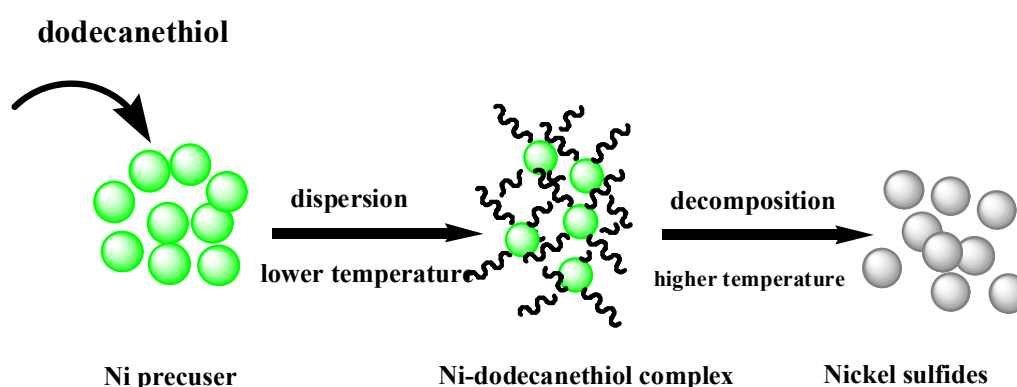
Besides, NiS nanorods can be obtained by an alternative method: 0.1 g Ni(acac)₂ was added into three-neck flask at 80 °C, then the reaction mixture were heated to 200

°C for 20 minutes, Ni-dodecanethiol complex was obtained (sample 7), while raising the temperature to 240 °C, NiS nanorods were obtained (sample 8).

Material Characterizations: The X-ray Diffraction (XRD) patterns of samples were collected on a Rigaku D/max-2400 diffractometer operated at 40 kV voltage and a 200 mA current with Cu Ka radiation ($\lambda = 1.5418 \text{ \AA}$). The morphologies were analyzed on a Hitachi H-800 transmission electron microscope (TEM) and scanning electron microscopy (SEM, HitachiS-3000N) techniques. High-resolution scanning electron microscopy (HRTEM) images were recorded by a FEI Tecnai G2 F20 S-Twin high-resolution transmission electron microscope working at 200 kV and a FEI Titan 80–300 transmission electron microscope equipped with a spherical aberration (Cs) corrector for the objective lens working at 300 kV.

Electrochemical measurement: All the electrochemical measurements were carried out in a conventional three-electrode system in 6 M KOH aqueous electrolyte at room temperature. The as-synthesized electrode materials, a platinum wire electrode and a silver chloride electrode (Ag/AgCl) were used as working electrode, counter electrode and reference electrode, respectively. The working electrode was prepared by mixing sample (90 wt%) as an active material with poly(tetrafluoroethene) (PTFE, 10 wt%) in ethanol to produce a homogeneous paste. Then the resulting mixture was coated onto the Ni foam substrate. The foam was dried at 80 °C in air for 12 h to remove the solvent. The electrochemical performances of the as-prepared material electrodes were tested using a cyclic voltammetry (CV) method, galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) on an electrochemical workstation

(CHI 660D, Shanghai CH Instrument Company, China). The measurements were carried out in 6 M KOH aqueous electrolyte at room temperature. CV tests were done between 0 V and 0.5 V (vs SCE) at scan rates of 2, 10, 20, 40, 50 mV•s⁻¹. Galvanostatic charge/discharge curves were measured in the potential range of 0 – 0.4 V at different current densities, and the EIS measurements were carried out in the frequency range from 100 kHz to 0.1 Hz at open circuit potential with an ac perturbation of 5 mV.



Scheme 1. The scheme of the mechanism of synthetic procedure.

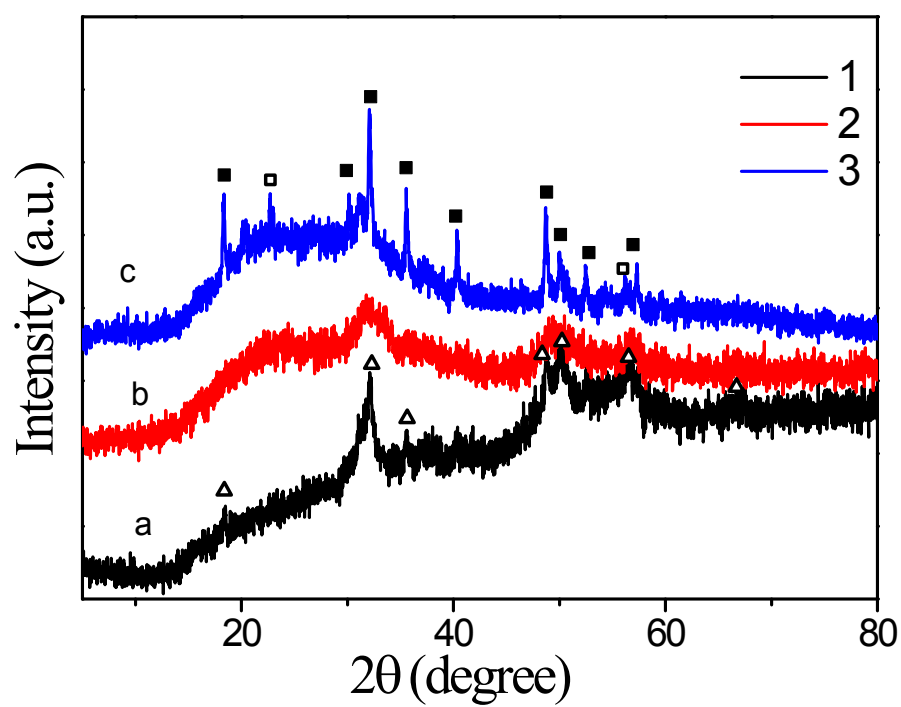


Figure S1 XRD patterns of as-synthesized nickel sulfides (Sample **1-3**, 1 for NiS NR, 2 for NiS NW and 3 for NiS and Ni₃S₂)

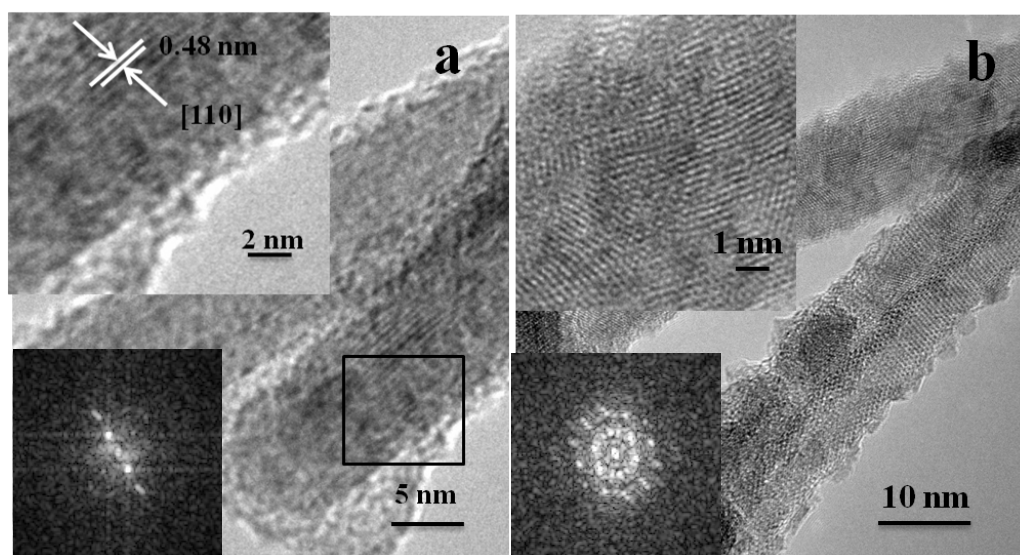


Figure S2 HRTEM images of NiS-NR (a) and NiS-NW (b)

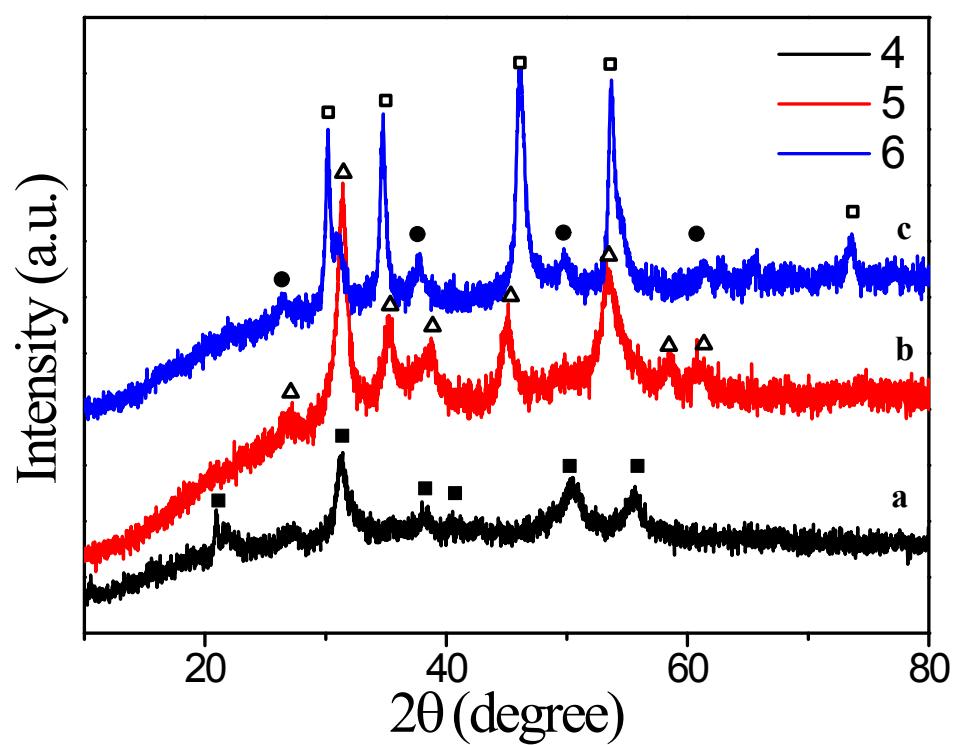


Figure S3 XRD patterns of as synthesized sample 4-6 (4 for Ni_3S_2 , 5 for NiS_2 , 6 for NiS and Ni_3S_4)

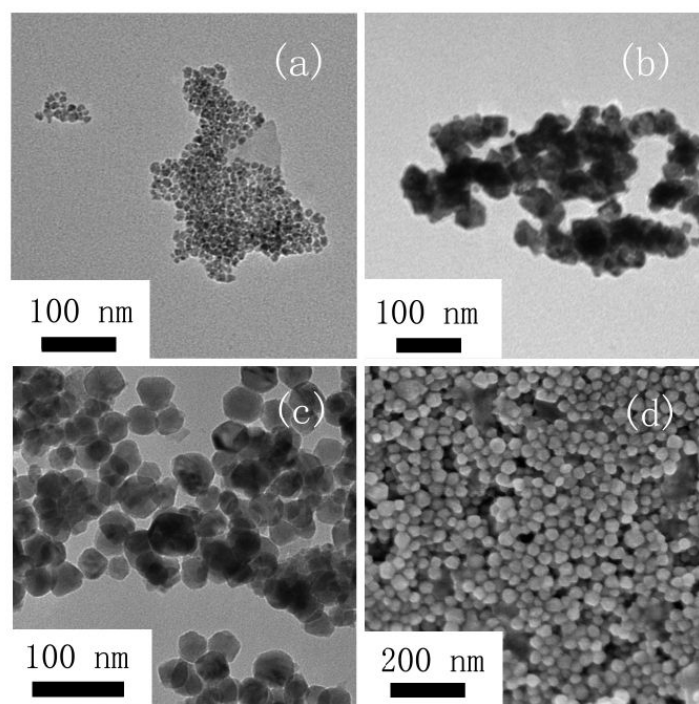


Figure S4 Typical TEM images of nickel sulfides (a)-(c) (sample 4-6), (d) SEM image of sample 6

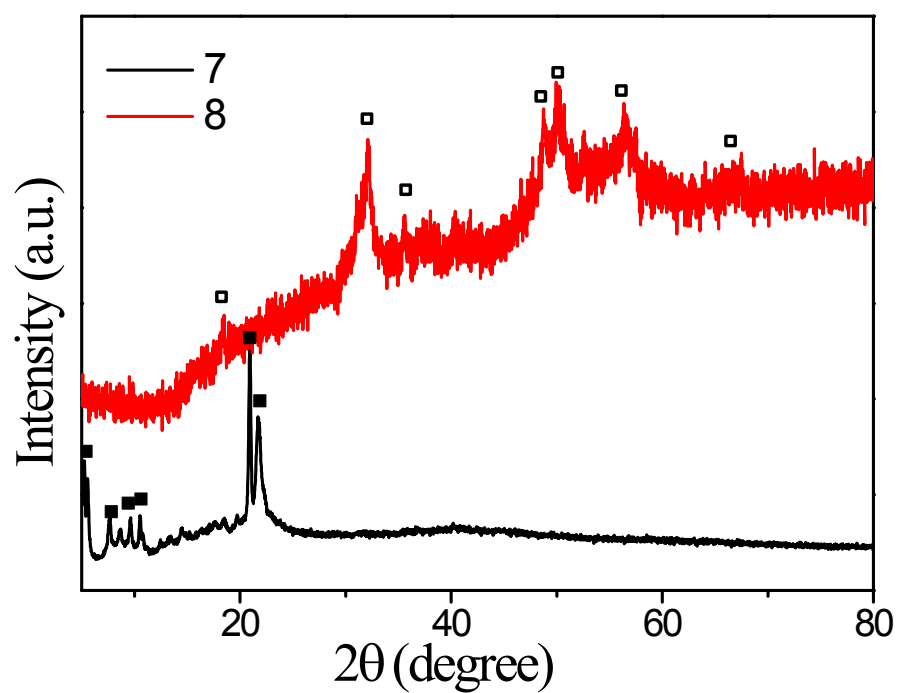


Figure S5 XRD patterns of as synthesized sample 7-8 (7 for nickel-dodecanethiol complex, 8 for NiS)

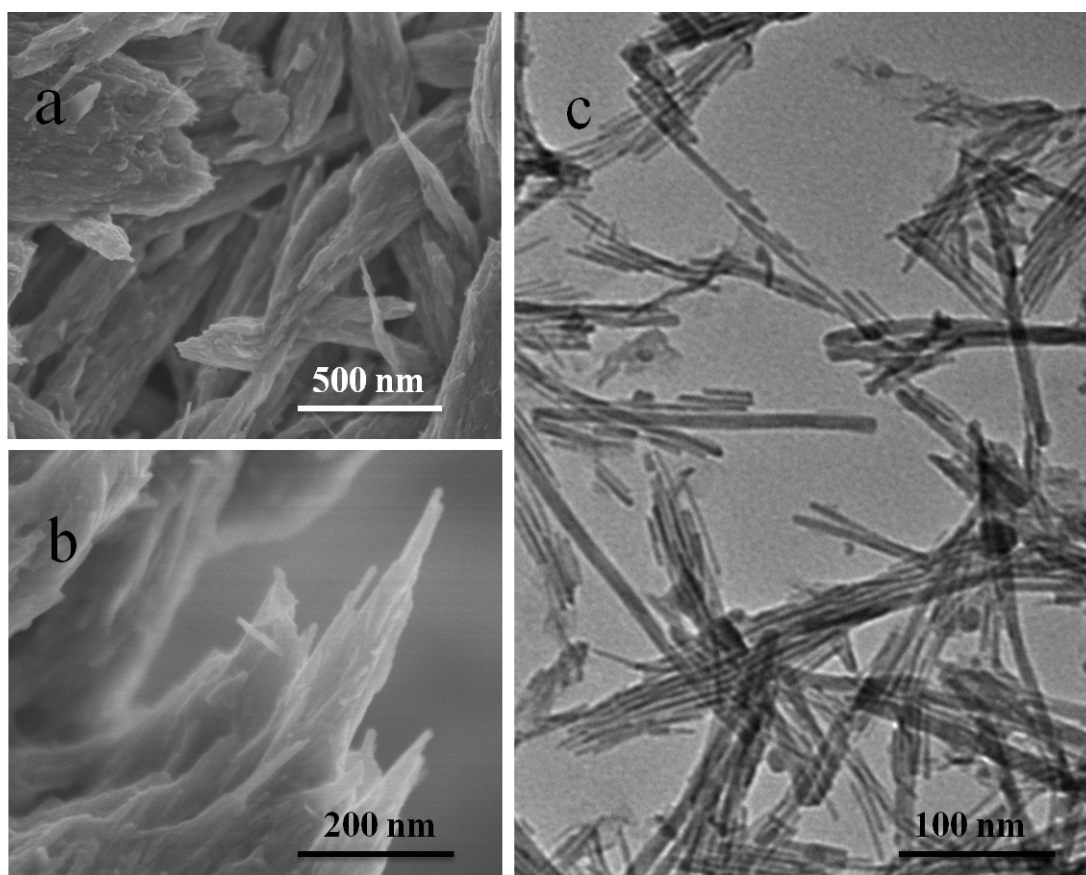


Figure S6 SEM and TEM images of NiS nanorods (Sample 8)

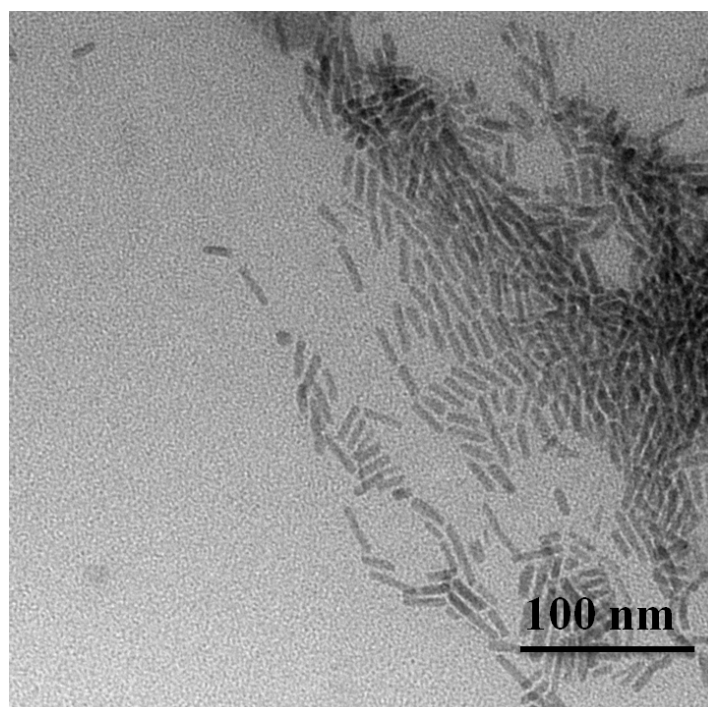


Figure S7 Typical TEM image of nickel- Dodecanethiol complexes (sample 7)

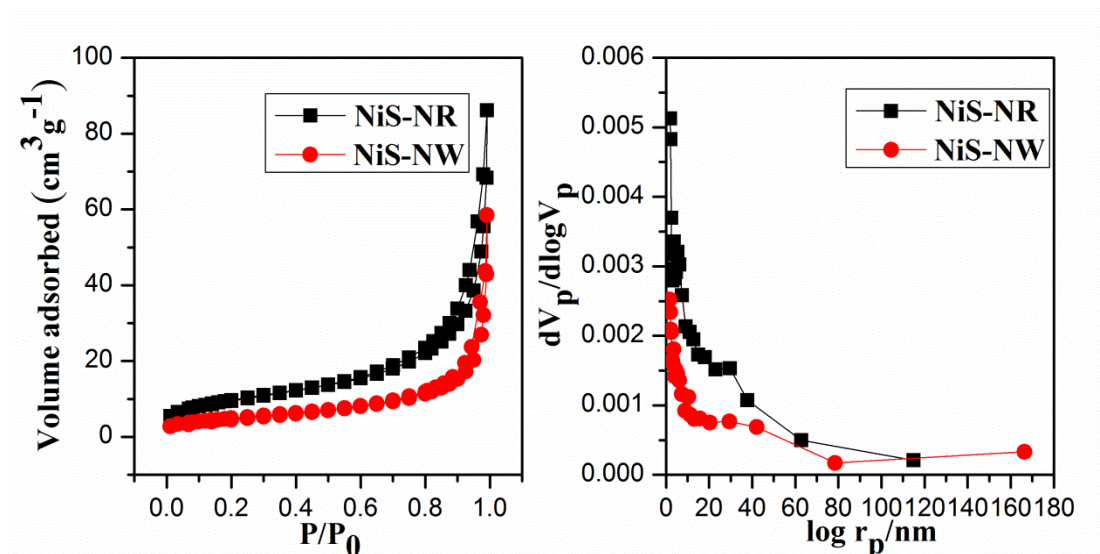


Figure S8 Nitrogen adsorption/desorption isotherms (a) and BJH pore size distributions (b) for NiS-NR and NiS-NW nanomaterials.

Table S1. The synthesis parameters of different nickel sulfids products

Samples	Metal sources	Sulfides sources	solvents	Temperatue (°C)	products	Time
1	NiCl ₂	dodecanethiol	-	200	NiS-NW	20 h
2	Ni(acac) ₂	dodecanethiol	-	200	NiS-NR	20 h
3	Ni(NO ₃) ₃	dodecanethiol	-	200	NiS, Ni ₃ S ₂	20 h
4	Ni(acac) ₂	sulfur powder	ODE, OAM	200	Ni ₃ S ₂	20 min
5	Ni(acac) ₂	Na ₂ S	ODE, OAM	200	NiS ₂	20 min
6	Ni(acac) ₂	thiourea	ODE, OAM	200	NiS, Ni ₃ S ₄	20 min
7	Ni(acac) ₂	dodecanethiol	-	200	Ni-dodecanethiol	20 min
8	Ni(acac) ₂	dodecanethiol	-	240	NiS	20 min

Table S2 The capacitances of NiS-NR and NiS-NW at different current densities

Current Density Sample	1 A/g	2 A/g	3 A/g	4 A/g	5 A/g
NiS nanorods	1403.8 F/g	1077.5 F/g	948.0 F/g	875.5 F/g	870.8 F/g
NiS nanowires	859.8 F/g	696.5 F/g	654.8 F/g	624.0 F/g	494.0 F/g