Supplementary Information (SI) for Inorganic Chemistry Frontiers.

Supplementary Information

Hierarchical assembly of SnS micro flowers and Ni_3S_2 nanofibers in situ grown on nickel foam for highly efficient capture of iodine vapor

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1. Materials

Nickel foam (NF, Shenzhen Tianchenghe Technology Co., Ltd., thickness is 1.6 mm, density is 0.45 g·cm^{-3}), tin (IV) chloride pentahydrate ($SnCl_4 \cdot 5H_2O$, Shanghai Macklin Biochemical Co., Ltd., 99.0%), thioacetamide (CH_3CSNH_2, Shanghai Macklin Biochemical Co., Ltd., 99.0%), iodine (I_2, Shanghai Macklin Biochemical Co., Ltd., 99.99%), acetone (CH_3COCH_3, Beijing Tongguang Fine Chemicals Company, AR), muriatic acid (HCl, Beijing Tongguang Fine Chemicals Company, GR), ethanol (C_2H_5OH, Tianjin Dingshengxin Chemical Reagent Co., Ltd., AR).

All of the reagents and materials were purchased commercially and used without any further purification.

2. Treatment of nickel foam (NF)

First, a large piece of NF (size: 50×6 cm^2) was cut into many small pieces with the size of 1×2 cm^2. These NF pieces were put into 1 M HCl (about 200 mL) with ultrasonic treatment for 30 min to remove the surface oxide layer and acid-soluble impurities. At this point, the solution turned slightly green (with Ni^{2+} being partially released into the acidic solution), and then NF pieces were repeatedly washed with deionized water until pH = 7. It was then ultrasonically cleaned 30 min in acetone and ethanol in sequence, and vacuum-dried for later use.

3. Characterization techniques

X-ray diffraction (XRD) was used to characterize the crystal structures of the as-prepared products and I-loaded samples (X'pert pro MPD diffractometer, Cu Kα radiation, λ = 0.15406 nm, operation at 40 kV and 40 mA). Field emission scanning electron microscope (FESEM) was used to observe morphologies and microstructures of samples (SU-8010, Hitachi, 10 kV). High-resolution transmission electron microscope (HRTEM) was used to observe the microstructures (JEM-2010, JEOL and FEI Technai G2 F20, 200 kV). X-ray photoelectron spectroscopy (XPS) was used to investigate the elemental valence and chemical environment of the products (ESCALAB 250Xi spectrometer, Thermo Fisher, Al Kα radiation). Microscopic confocal Raman spectrometer (Raman) was used to analyze chemical bonds of the samples (LabRAM Aramis, Horiba Jobin Yvon, He-Ne laser, λ = 633 nm). Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was used to quantitatively analyze the chemical compositions of products (Jarrel-ASH, ICAP-9000). Thermogravimetric (TG) analysis was performed to study the thermal stability of samples (HITACHI STA200, N_2 atmosphere, 10 °C/min).

4. Calculations of chemical composition of 0.6-SnS/Ni_3S_2/NF

We used an indirect calculation method to determine the specific chemical composition of the 0.6-SnS/Ni_3S_2/NF sample. Initially, the mass of bare NF was measured to be 72.3 mg (0.0723 g). After the solvothermal reaction, the mass of the sample increased to 77.3 mg (0.0773 g), indicating a mass increase of 5 mg (= 77.3-72.3), which is attributed to the introduction of Sn (of SnS) and S (of SnS and Ni_3S_2). In order to quantify the components in the sample, 2.7 mg (0.0027g) of the 0.6-SnS/Ni_3S_2/NF sample was dissolved completely in aqua regia and diluted to 50 mL, and 5 mL solution was taken for ICP tests. Based on the measured mass concentrations of Sn (0.63 mg/L) and Ni (40.1 mg/L), the mass percentages of Sn and Ni are determined to 1.17% (=0.63×0.05/2.7×100%) and 74.26% (= 40.1×0.05/2.7×100%).

For the 0.6-SnS/Ni_3S_2/NF sample with a mass of 77.3 mg, the contents of Sn and Ni would be 0.90 mg (= 77.3×1.17%) and 57.4 mg (= 77.3×74.26%), respectively. Combined with the total mass increase of 50 mg of Sn+S, the S content would be 5-0.90 = 4.1 mg.

If the chemical formula of 0.6-SnS/Ni_3S_2/NF is written as $(SnS)_x(Ni_3S_2)_y(Ni)_z$, then there will be the following equations:

S: $(x + 2y) \times 32 = 4.1$

Sn: $x \times 118.71 = 0.90$

Ni: $(3y+z) \times 58.69 = 57.4$

Thus:

$x = 0.0076, y = 0.0600, z = 0.7980$

If fix the molar number of Ni to 1, the molar numbers of SnS and Ni_3S_2 would be 0.0095 and 0.075, thus, the chemical composition of 0.6-SnS/Ni_3S_2/NF could be quantitatively expressed as $(SnS)_{0.0095}(Ni_3S_2)_{0.075}(NF)$ with a molecular weight of 78.1.

Table S1 Parameters for DFT calculations.

Functional	*k*-point sampling	Cutoff energy	whether vdW corrections were used
Perdew-Burke-Ernzerh of (PBE) functional	2×2×1 for structural optimization 3×3×3 for density of state 2×2×1 for charge density difference	450 eV	No

Table S2 Binding energies of Ni_3S_2/NF, 0.6-SnS/Ni_3S_2/NF and 0.6-SnS/Ni_3S_2/NF-I.

Samples	Binding energies (eV)	Corresponding ions and orbitals
Ni_3S_2/NF	873.5/855.6	2p of Ni^{2+}
	870.4/853.0	2p of Ni^0
	163.7/162.7	2p of S^{2-}
0.6-SnS/Ni_3S_2/NF	873.8/855.9	2p of Ni^{2+}
	870.4/853.0	2p of Ni^0
	163.0/162.0	2p of S^{2-}
	168.2	2p of S^{6+} (SO_4^{2-})
	494.8/486.4	3d of Sn^{2+}
0.6-SnS/Ni_3S_2/NF-I	874.0/856.0	2p of Ni^{2+}
	164.7/162.5	2p of S^0
	169.5	2p of S^{6+} (SO_4^{2-})
	495.6/487.2	3d of Sn^{4+}
	630.5/619.0	3d of I^-
	632.0/620.7	3d of I^0 (I_2)

Table S3 The adsorption energy E_{ad} (eV), adsorption bond length (*B,* Å) and the I-I bond length (*L,* Å) of I_2 adsorbed on the composites.

	SnS	Ni_3S_2	SnS/Ni_3S_2	Ni_3S_2/SnS
E_{ad} (Metal site)	-2.94	-4.67	-2.83	-3.23
$B_{M\text{-}I}$	2.955	2.532, 2.539, 2.630	2.996	2.540, 2.743, 2.769
L	2.858	3.057	2.832	2.962
E_{ad} (S site)	-2.86	-4.26	-2.78	-2.65
$B_{S\text{-}I}$	2.875	2.959	2.932	2.841
L	2.795	2.760	2.783	2.780

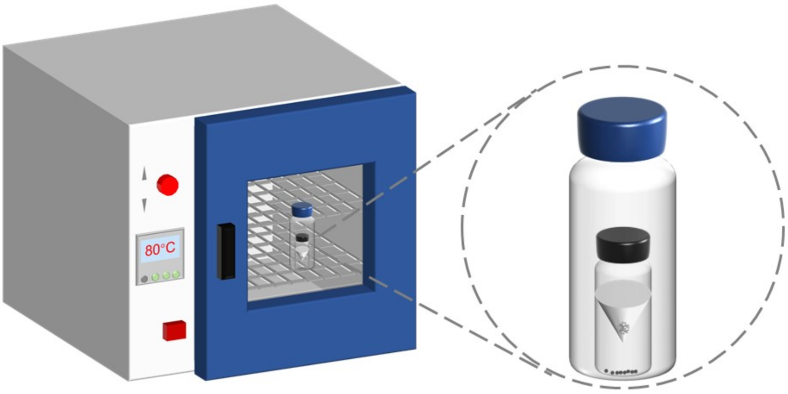

Fig. S1 Schematic diagram of iodine adsorption experiment.

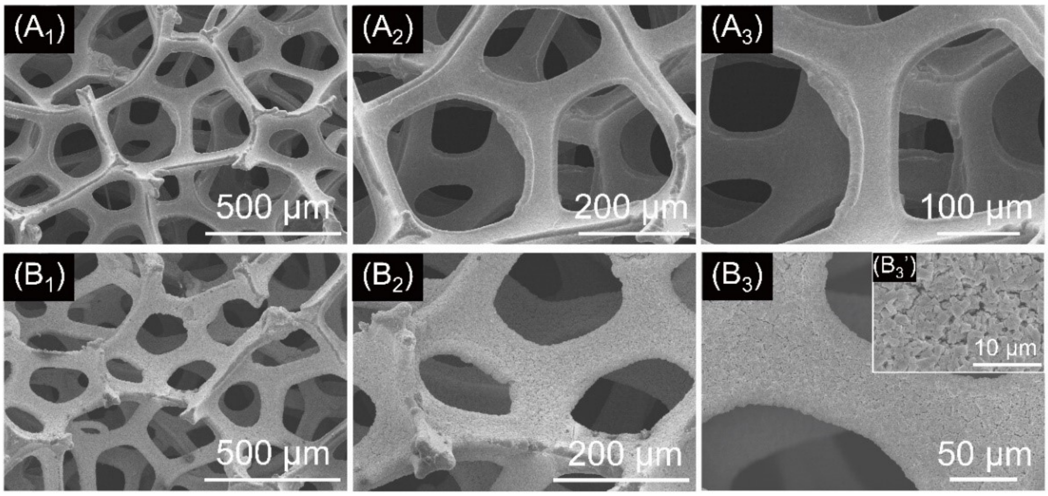

Fig. S2 SEM images of (A_1-A_3) NF and (B_1-B_3) NF-I.

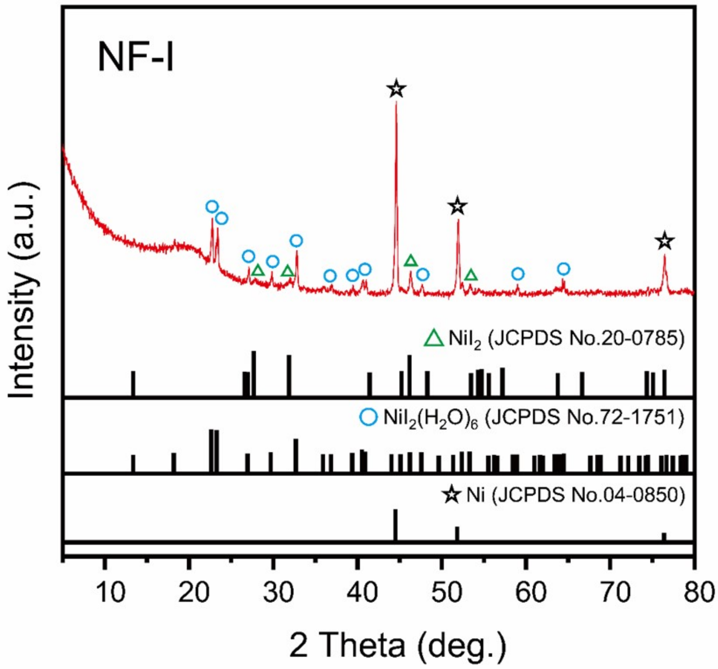

Fig. S3 XRD pattern of the sample of NF-I.

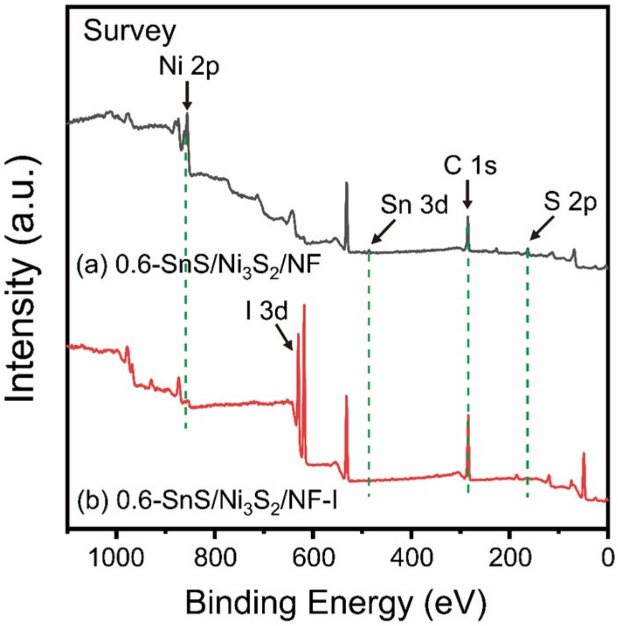

Fig. S4 XPS survey spectra of (a) 0.6-SnS/Ni_3S_2/NF and (b) 0.6-SnS/Ni_3S_2/NF-I.

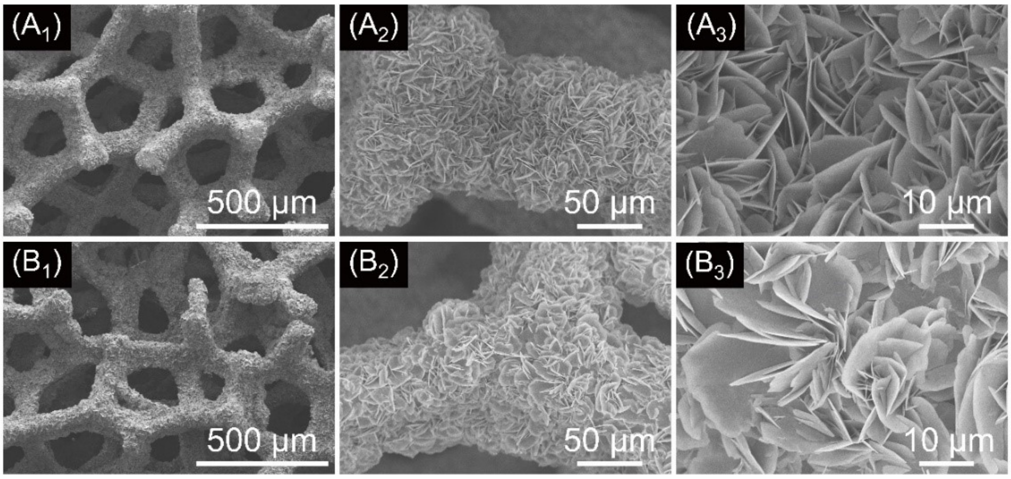

Fig. S5 SEM images of I-loaded samples after (A_1-A_3) desorption (first-cycle) and (B_1-B_3) resorption (that is, second-cycle adsorption).

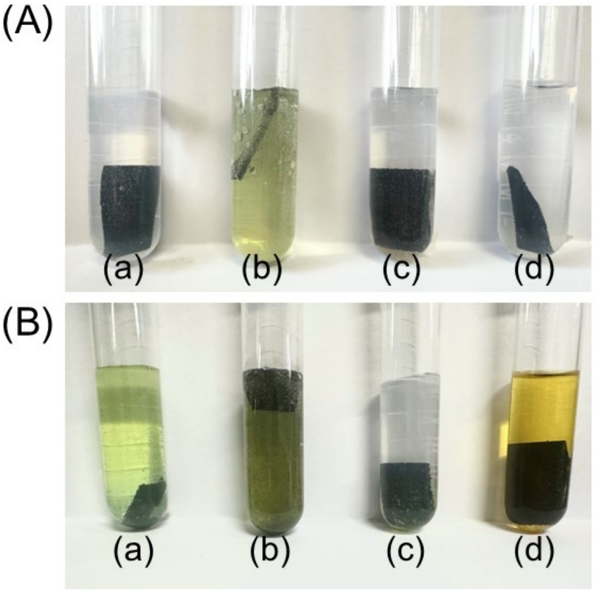

Fig. S6 (A) Photographs of 0.6-SnS/Ni_3S_2/NF in (a) deionized water, (b) 12 M HCl, (c) saturated NaOH solution and (d) ethyl acetate; (B) Photographs of 0.6-SnS/Ni_3S_2/NF-I in (a) deionized water, (b) 12 M HCl, (c) saturated NaOH solution and (d) ethyl acetate.

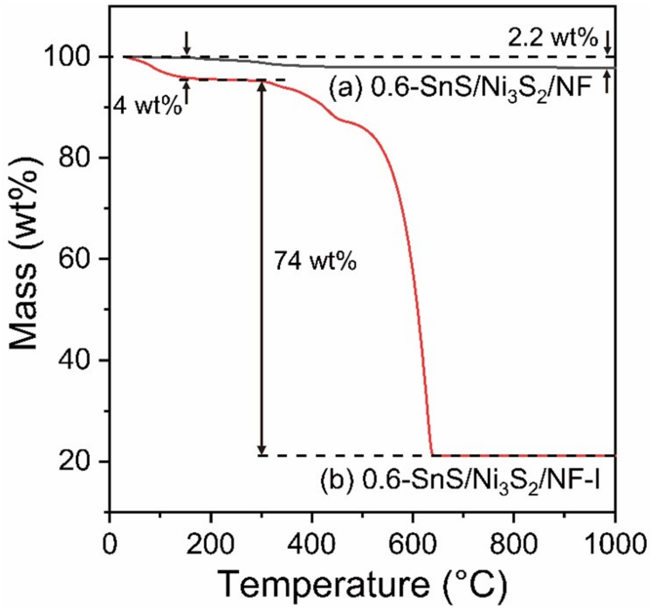

Fig. S7 Thermogravimetric (TG) curves of (a) 0.6-SnS/Ni_3S_2/NF and (b) 0.6-SnS/Ni_3S_2/NF-I.

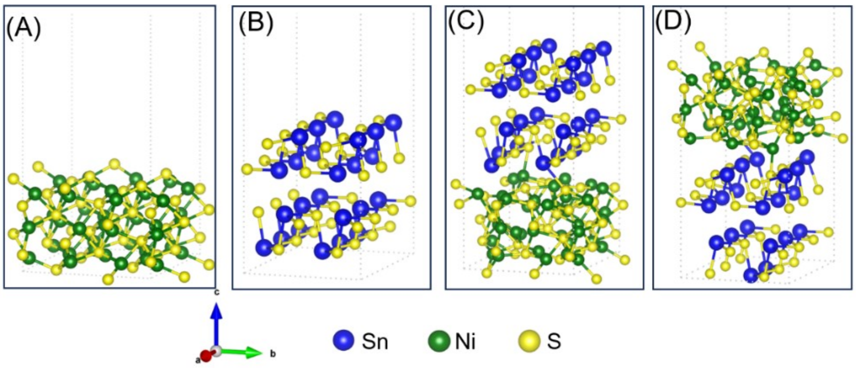

Fig. S8 The optimized structural models of (A) Ni_3S_2, (B) SnS, (C) SnS/Ni_3S_2 heterojunction (with SnS as sorption surface) and (D) Ni_3S_2/SnS heterojunction (with Ni_3S_2 as sorption surface).

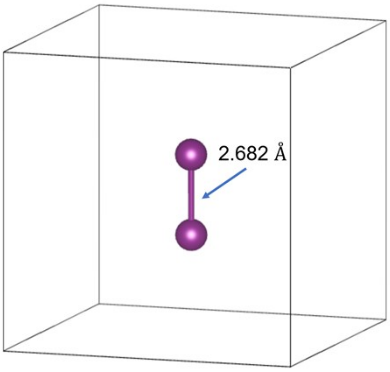

Fig. S9 The optimized structural model of I_2 molecule.