Electronic supplementary information

Nanostructured SnS-N-doped graphene as an advanced

electrocatalyst for the hydrogen evolution reaction

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Experimental section

Materials and Methods

Chemicals and materials: Tin(II) chloride [98%, SnCl₂], sodium sulfide [99%, Na₂S], (Sigma-Aldrich), N,N-dimethylformamide (N,N-DMF) [99%, $C_3H_7NO_7$, ethylene glycol (EG) [99%, $C_2H_6O_2$, Daejung], hydrazine hydrate (N₂H₄, 50-60%), dicyanamide (DCDA), graphite powder, CNTs, potassium permanganate (ACS, 99%), sulfuric acid [99%, Samchun Chemicals], and Nafion-117 solution [5% in a mixture of lower aliphatic alcohols and water] (Sigma-Aldrich) were used in the present study. All chemicals were used as received without further purification. The water used throughout all experiments was purified with a Millipore system.

Synthesis of the N-graphene (N-Gr): Briefly, graphite powder (3.0 g) was added to concentrated H₂SO₄ (70 mL) while stirring in an ice bath. Under vigorous agitation, KMnO₄ (9.0 g) was added slowly to maintain a suspension temperature lower than 20 °C. Successively, the reaction system was transferred to 40 °C in an oil bath and vigorously stirred for about 30 min. Then, 150 mL water was added, and the solution was stirred for 15 min at 95 °C. Additional 500 mL water was added and followed by a slow addition of 15 mL H₂O₂ (30%). The mixture was filtered and washed with 1:10 HCl aqueous solution to remove metal ions. The mixture was subjected to centrifugation at 12,000 rpm, and the supernatant solution was decanted. The remaining material was subjected to multiple washes with water, ethanol, acetone, and polyether in sequence and conserved for further use. The obtained GO was thermally reduced at 900 °C for 3 h to achieve pure graphene (Gr). N doping was carried out through direct thermal exfoliation of lyophilized Gr powder with DCDA powder at 1:5 mass ratios. Briefly, Gr and the DCDA were ultrasonically dispersed in ethanol for about 30 min, concentrated by rotary evaporation and lyophilized. The respective mixture was then exfoliated at 900 °C for 3 h under N₂ in a quartz glass ampoule and then allowed to cool to room temperature. These samples were used for further testing. Similarly N-CNTs also prepared inserting CNT instead of Gr.

Synthesis of SnS/N–rGr hybrid: In typical synthesis of the SnS/N–rGr hybrid, 11.5 mg of SnCl₂ and 11.7 mg of Na₂S were added to 15 mg of N–Gr dispersed in 15 ml of DMF, followed by addition of 15 ml ethylene glycol with vigorous stirring for 30 min. The mixture was sonicated at room temperature for approximately 10 min until a clear, homogeneous solution was achieved. After that, 0.2 mL of hydrazine hydrate was added. The reaction

solution was further sonicated for 30 min before being transferred to a 40 mL Teflon–lined autoclave. It was then heated in an oven at 180 °C for 12 h with no intentional control of the ramping or cooling rate. The product was collected by centrifugation at 8000 rpm for 5 min, washed with DI water and recollected by centrifugation. The washing step was repeated at least 5 times to ensure that most of the DMF and EG were removed. Finally, the product was lyophilized overnight to obtain solid SnS/N-rGr hybrid catalyst.

Preparation of SnS nanoparticles (NPs): In a typical synthesis of SnS NPs, 11.5 mg tin chloride and 11.7 mg sodium sulfide were mixed in 15 mL of anhydrous N,N-dimethylformamide (DMF) for 10 min, followed by addition of 15 mL EG. The mixture was vigorously stirred for 10 min and sonicated for 30 min. The suspension was maintained at 180 °C for 12 hours in an autoclave. After cooling to room temperature, the sample was collected by centrifugation, washed several times with water and finally lyophilized to obtain solid SnS NPs.

Electrochemical measurements: To form a homogeneous ink, 4 mg of catalyst and 100 μ L of 5 wt% Nafion solutions were dispersed in 1 ml of ethanol over at least 30 min of sonication. Then 5 μ L of the catalyst ink (containing 20 μ g of catalyst) was loaded onto a 3-mm-diameter glassy carbon electrode. Linear sweep voltammetry (using the Pontentiostat from CH Instruments) with a scan rate of 5 mVs⁻¹ was conducted in 0.5 M H₂SO₄ using Ag/AgCl as the reference electrode, a Pt wire as the counter electrode and a glassy carbon electrode as the working electrode. Electrochemical impedance spectroscopy (EIS) was performed in a frequency range of 20 Hz – 2 MHz with a 5 mV amplitude at a bias potential of 0.1 V. All potentials were referenced to that of a reversible hydrogen electrode (RHE) by adding a value of (0.205 + 0.059 × pH) V. The electrolytes were degassed by bubbling N₂ for at least 30 min before the electrochemical measurements.

Characterizations: The scanning electron microscope (FE-SEM) images and EDS mapping were obtained using a TESCAN (MIRA3). Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2010 operated at 200 kV. The X-ray diffraction patterns were measured using a Rigaku instrument (D/MAX-2500/PC) with a Cu target. The X-ray photoelectron spectra (XPS) were collected by a high-resolution and high-sensitivity hemispherical electron analyzer with nine-channel electron multipliers (VG SCIENTA (R

3000)). The incident radiation was monochromatic Al Ka X–rays (1,486.6 eV) at 225W (15 kV, 15 mA). Raman spectra were produced on RM 1000 (Ranishaw, UK) spectrometer.



Results and discussion

Figure S1 (a) Detailed growth mechanism of SnS nanostructures with N-graphene; (b) Unit cell, and different plane orientations



Figure S2 Element mapping images of C, Sn, S and N in the SnS/N–rGr hybrid catalyst.



Figure S3 XPS analysis of the SnS/N–rGr hybrid. (a) Survey scan, (b) High-resolution C 1s, (c) Sn 3d, (d) S 2p and (e) N 1s spectra. The atomic percentage was determined to be 63.26% C, 17.28% Sn, 17.31% S, and 2.15% N.



Figure S4 HER polarization curves of SnS/Se–rGr, SnS/P–rGr, SnS/CNT and SnS/N-CNT hybrid electrocatalysts in 0.5 M H₂SO₄.

Catalyst	Current density (mA cm ⁻²)	Overpotential (mV, vs RHE)	Tafel value (mV/dec)	Electrolyte	I ₀ (mA cm ⁻²)	Ref.
Ni ₂ P	20	-130	30	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	2.7	1
(1 mg/cm^2)						
MoS ₂ /RGO	10	-150	41	$0.5 \ M \ H_2 SO_4$	_	2
(0.28 mg/cm^2)						
Bulk Mo ₂ C	20	-240	_	$0.5 \text{ M} \text{ H}_2\text{SO}_4$	_	3
Bulk MoB	20	-240	_	$0.5 \ M \ H_2 SO_4$	_	3
Mo ₂ C/CNT	10	-150	150	0.5 M	_	4
(2 mg/cm^2)				HClO ₄		
Ni-Mo-N	3.5	-200	_	0.5 M	_	5
nanosheets (0.25				HClO ₄		
mg/cm ²)						
Ni-Mo	10	-80	80	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	_	6
(3 mg/cm^2)						
Fe _{0.9} Co _{0.1} S ₂ /CNT	20	-120	46	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	_	7
(7 mg/cm^2)						
Ni_xS_y	10	-253	88	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	_	8
CoP	10	-297	82	$0.5 \text{ M} \text{ H}_2\text{SO}_4$	0.003	9
CoP/CNT	10	-122	54	$0.5 \text{ M} \text{ H}_2\text{SO}_4$	0.13	10
MoP	30	-180	54	$0.5 \ M \ H_2 SO_4$	0.034	11
MoP	20	-140	48	1 M KOH	0.046	11
SnS/N-rGr	10	-125	38	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	6.23	This work
$(20 \ \mu g/cm^2)$						
SnS/N-rGr	10	-196	59	0.5 M	4.59	This work
$(20 \ \mu g/cm^2)$				Na_2SO_4		
SnS/N-rGr	10	-279	98	0.5 M KOH	4.61	This work
$(20 \ \mu g/cm^2)$						
SnS/N-rGr	10	-405	163	$0.5 \text{ M} \text{ H}_2\text{SO}_4$	0.43	This work
$(20 \ \mu g/cm^2)$						

 Table S1 Summary of representative HER catalysts (as mentioned in the main text).

Active sites calculation: The number of active sites (n) was examined using CVs with H_2SO_4 at a scan rate of 50 mV s⁻¹. When the number of voltammetric charges (Q) was obtained after a deduction of the blank value, n (mol) was calculated with the following equation:

$$n = \frac{Q}{2F}$$

where *F* is Faraday's constant (96480 C.mol⁻¹). For the sample of SnS/N-rGr, Q was 8.64×10^{-3} C (Fig. S4), n (mol) = $8.64 \times 10^{-3}/(2 \times 96480)$ mol= 4.48×10^{-8} mol. Similarly the active sites in SnS/rGr also calculated and it is found to be 2.94×10^{-9} mol.

Turnover frequency (TOF) calculation: The TOF (s⁻¹) was calculated with the following equation: $TOF = \frac{I}{2Fn}$

where *I* is the current of the polarization curve obtained from the LSVs measurements. Two electrons are required to form one hydrogen molecule; thus, the TOF value was divided by two.



Figure S5 CV of SnS/N-rGr hybrid catalysts in H₂SO₄ vs. RHE at a scan rate of 50 mV/s.



Figure S6 Polarization curve and amount of hydrogen gas were measured on glassy carbon with loading of 20 μ g/cm². The hydrogen gas generated on the hybrid catalyst on glassy carbon was collected in a sealed glass container under different applying voltages. The gas sample (1mL) was collected using a micro syringe and measured using gas chromatography with a TCD detector. Also, the calculated Faraday yield of hydrogen production was greater than 99 % during 10 min of electrolysis.



Figure S7 Current versus time during the long term (500 min) with a constant potential (-0.13 V) electrolysis of SnS/N-rGr hybrid catalyst in 0.5 M H₂SO₄.



Figure S8 X-ray diffraction patterns of SnS/N-rGr hybrid after stability test. Original crystal structure of SnS/N-rGr hybrid has been retained identically before and after the stability test. However, a slight decrement in crystallinity has been observed upon stability test in basic electrolyte.



Figure S9 XPS analysis of the SnS/N–rGr hybrid after stability test. (a) C 1s, (b) N 1s, (c) Sn 3d and (d) S 2p spectra. Note that there is slight elemental degradation for a basic electrolyte, and the corresponding atomic percentages are 63.71% C, 17.26% Sn, 16.89% S, and 2.14% N.

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