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Improved hydrogen evolution with SnS_2 quantum dots incorporated black Si photocathode

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Experiential Section

Synthesis of black Si

Firstly, the p-type (100) Si wafers (resistivity 1–10 Ω cm, thickness 500 μm, single-sided polished) were cut into small pieces (1cm*1cm), then suffered an ultrasonically clean process with acetone, ethanol, and deionized (DI) water for 15 min sequentially. Secondly, the surface oxide layer coated on Si was removed by immersing in a mixture solution of H_2O_2 and H_2SO_4 (1:3, v:v) at 80 ℃ for 20 min. Thirdly, the cleaned Si samples were immersed in a mixture etching solution (2 M NH_4F, 1.89M HNO_3 and 0.02 M $AgNO_3$) for 10 minutes to fabricate nanowires. Finally, the Si samples were immersed in a clearing solution (HCl: HNO_3: H_2O (1:1:1, v:v:v)) overnight to thoroughly remove residual silver dendrites followed by rinsed with copious of DI water.

Synthesis of SnS_2 QDs

0.7012 g of $SnCl_4 \cdot 5H_2O$ and 0.3005 g of CH_3CSNH_2 were dissolved in 40 mL of DI water at room temperature. After stirring the mixture for 60 min, the solution was transferred into a 50 mL autoclave and maintained at 180 °C for 12 h. Then the mixture solution was cooled down naturally. SnS_2 powder was collected and washed with DI water and ethanol several times before being centrifuged for 10 min at the speed of 10000 rpm. After drying, 120 mg of the SnS_2 powder was dissolved in 30 ml of 1-Methyl-2- pyrrolidone (NMP). and then a sonication-assisted liquid exfoliation process was employed for 6 hours. After that, the dispersion was centrifuged at 10000 rpm for 60 min, and the brown supernatant which contained SnS_2 QDs was separated from the centrifugate. Finally, the SnS_2 QDs solution was diluted with NMP to 0.5 $mg \cdot mL^{-1}$.

Synthesis of SnS_2/bSi

SnS_2 QDs were deposited on bSi by the spin-coating technique. 50 μL of the SnS_2

QDs solution was spin-coated over the sample (1 cm^2) using a micropipette at the speed of 2000 rpm for 60 s, and the samples were subsequently annealed in a tube furnace under nitrogen atmosphere at 180℃ for 3 h.

Characterization

X-ray diffraction (XRD) measurements were investigated on a diffractometer with Cu Ka radiation (D/MAX2500V). Scanning electron microscopy (FE-SEM, SU8020), dimension icon (AFM, Bruker) and transmission electron microscopy were employed to reveal the morphologies of the samples (TEM, JEM-2100F). Elemental maps were carried out using an energy-dispersive X-ray spectroscopy (EDS) system. Diffuse reflectance spectroscopy measurements of planar Si, black Si, and SnS_2/bSi were conducted on a UV-vis spectrophotometer (CARY 5000) with $BaSO_4$ as reference. X-ray photoelectron spectroscopy (XPS) was carried out with a photoelectron spectrometer (ESCALAB 250).

Photoelectrochemical measurements

All photoelectrochemical (PEC) measurements were carried out in 0.5 M H_2SO_4 (pH=0.3) with a CHI660D electrochemical workstation. The SnS_2/bSi photocathode was used as the working electrode, a Pt foil (1.5*1.5 cm^2) was used as the counter electrode, and an Ag/AgCl electrode as the reference electrode. To enable the conductive connection between the Si electrode and conducting Cu plate, the In/Ga eutectic alloy was firstly applied to the back side of silicon sample, then the silver gel was used to stick the silicon to the Cu plate, finally, the electrode was sealed with epoxy resin except for the frontside of Si sample. A 300 W Xe lamp with an AM 1.5 G filter was used as a light source to obtain the light intensity of 100 mW/cm^2 (1 sun). All potentials in the test were converted to the reversible hydrogen electrode (RHE) with: $E_{RHE} = E_{Ag/AgCl} + 0.197\ V + 0.059 * pH$. Photocurrent density–potential (*J*–*E*) was recorded from 0.2 to -1 V vs. Ag/AgCl, with a scan rate of 10 $mV \cdot s^{-1}$. PEC electrical impedance spectra were performed at 0 V vs. RHE under 1 sun illumination, with a 12 mV sinusoidal perturbation in the range of 0.1–100 kHz. Mott-Schottky measurement

was carried out in the dark at 1 kHz, when preparing SnS_2 sample for Mott-Schottky test, a 5μL homogerous solution (470μL isopropanol， 30μL nafion solution and 5mg SnS_2 powders) was coated on the Glassy Carbon Electrode. The photocurrent-time measurement was evaluated in a sealed electrochemical cell with an applied bias of 0 V vs. RHE under 1 sun illumination and the corresponding generated hydrogen was measured by a gas chromatograph (FULI-9790II) with a TCD detector. The H_2 standard fitting curve ($y = 594918x + 17057$, $R^2 = 0.9994$) shows a good linear relationship of intensity with H_2 amount (Fig. S7).

The Faradaic efficiency (FE) could be calculated according to the following formula:

$$FE(\%) = \frac{2 \times F \times n}{Q} \times 100\%$$

where F is the Faraday constant, n represents the number of H_2 moles and Q is the quantity of total charge during HER.

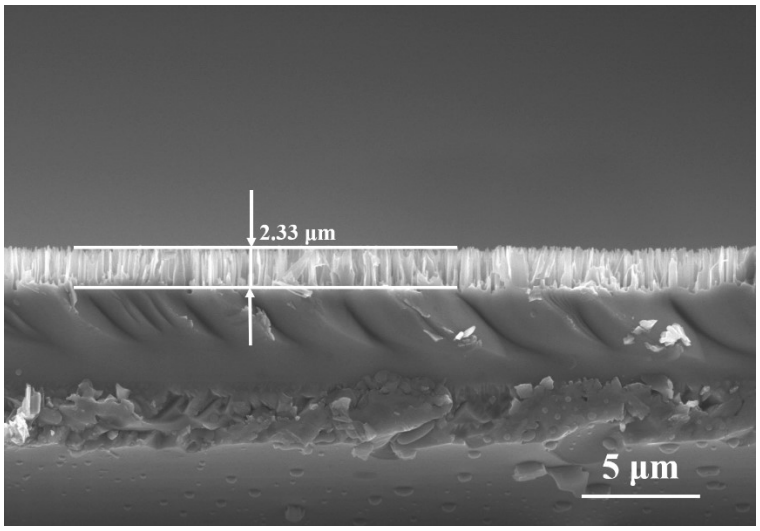

Figure S1. SEM image of black Si.

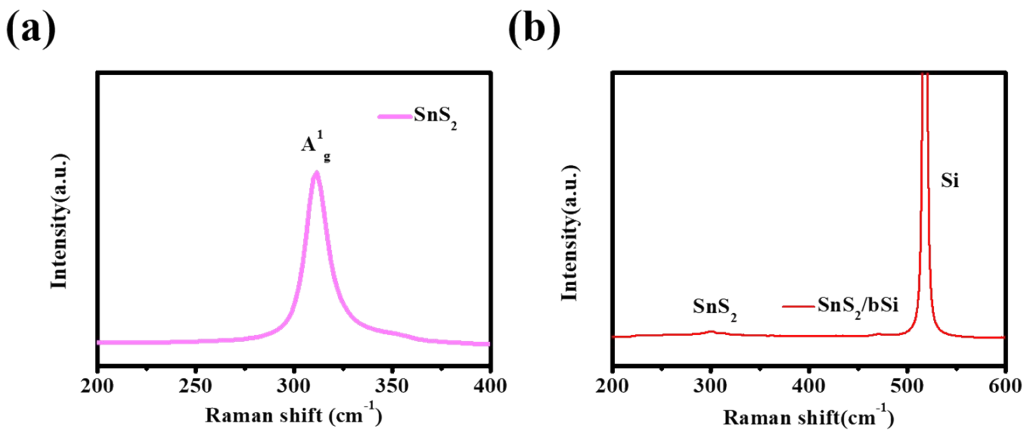

Figure S2. Raman spectrum of black Si and SnS_2/bSi sample. (a) SnS_2, (b) SnS_2/bSi.

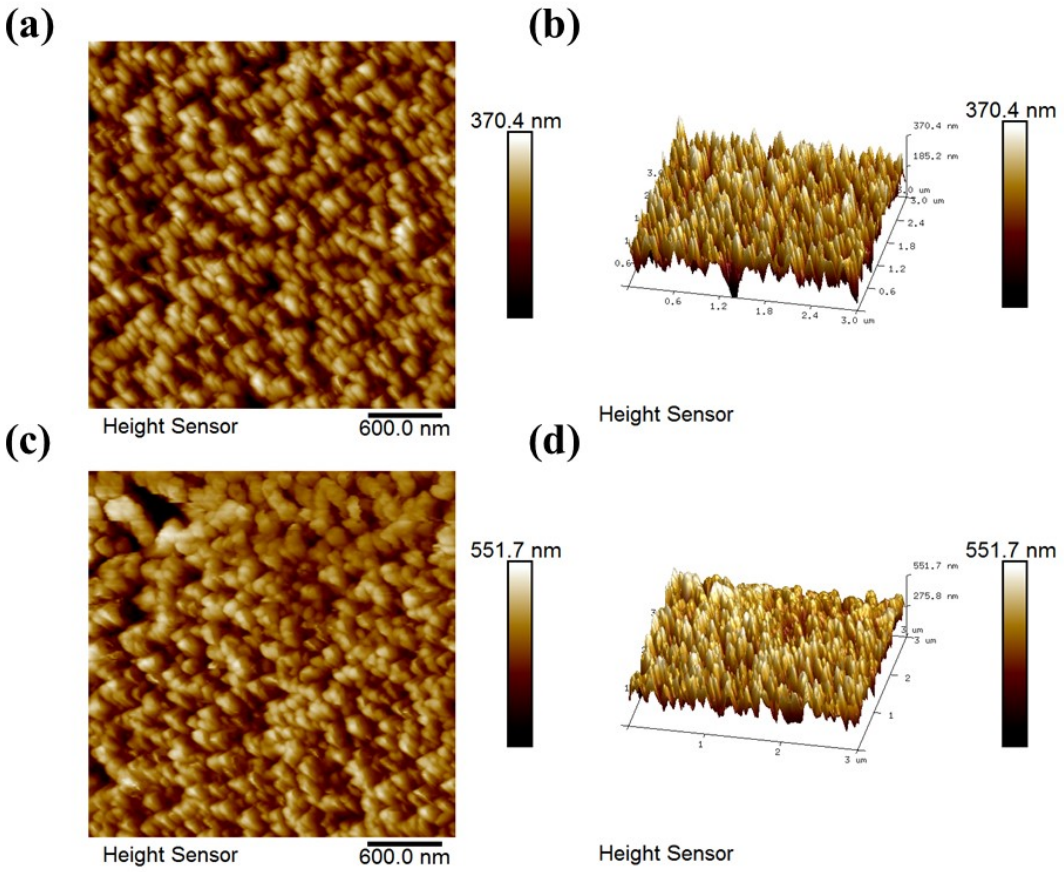

Figure S3. Top view AFM images obtained on (a, b) pristine black Si, and (c, d) SnS_2/bSi, respectively.

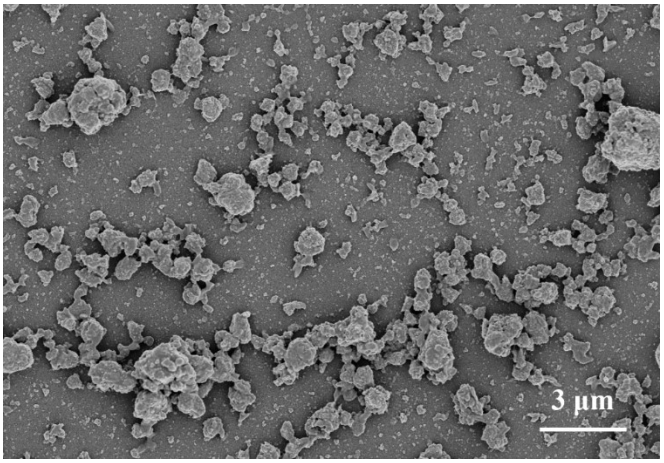

Figure S4. SEM image of SnS_2 without ultrasonic peeling treatment.

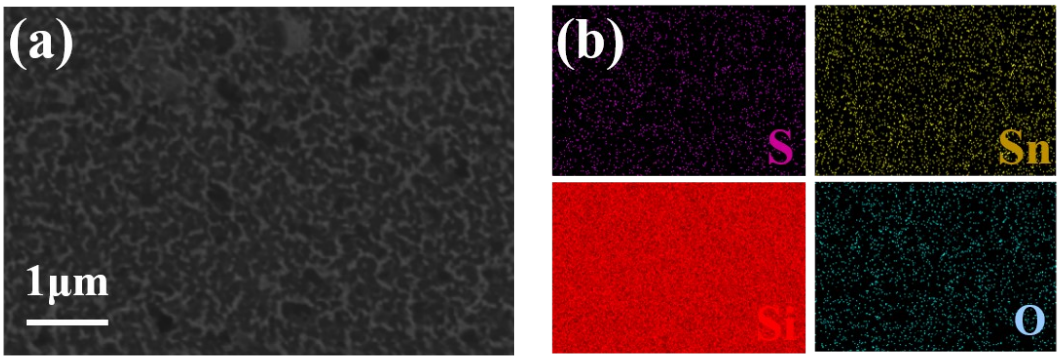

Figure S5. (a) SEM image of SnS_2 /bSi, and the corresponding element maps (b).

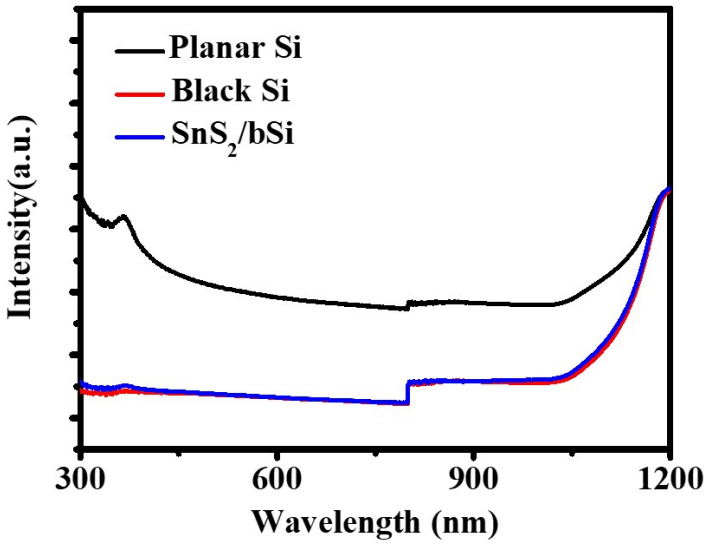

Figure S6. UV-vis reflectance spectra of planar Si, black Si, and SnS_2/bSi sample.

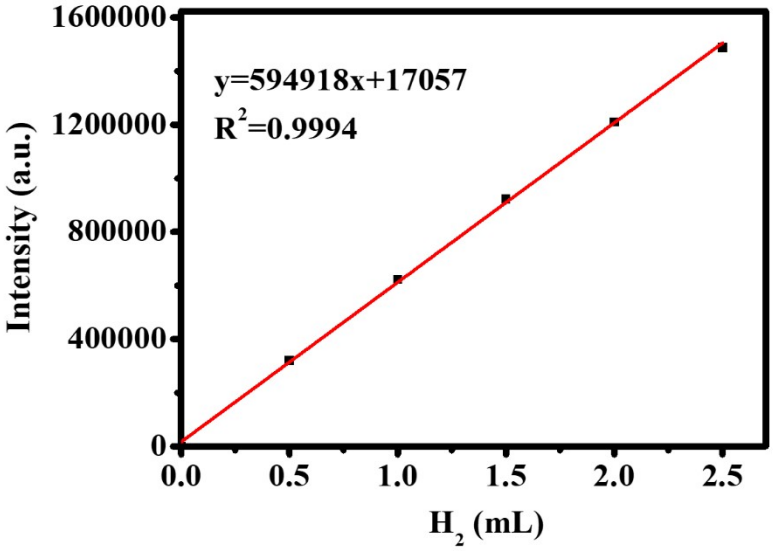

Figure S7. The calibration curve of the H_2 amount with a series of H_2 volume.

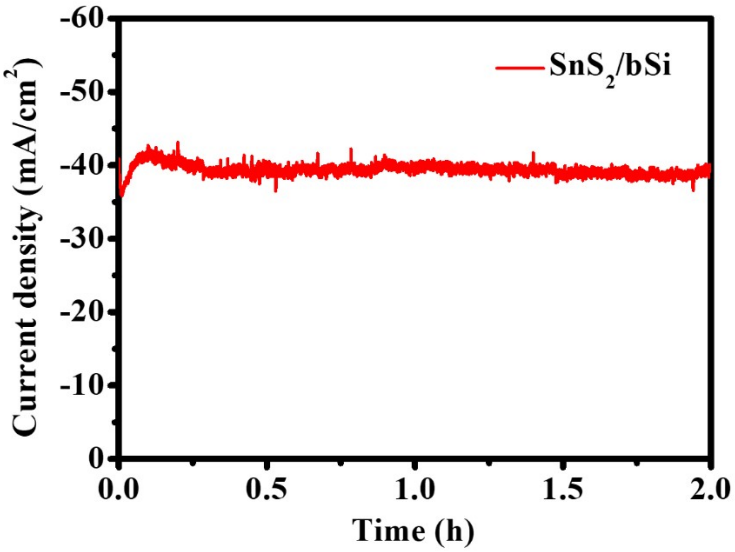

Figure S8. The stability test of SnS_2/bSi photocathode at -1 V vs. Ag/AgCl under 1 sun illumination.

Table S1. The fitted data table of EISs tests.

	R_s	R_{ct}	CPE-T	CPE-P
Black Si	4.928	1187	8.798E-6	0.95322
SnS_2/bSi	6.66	79.53	2.024E-5	0.94314