Supporting Information

Non-Planar Vertical Photodetectors Based on Free-Standing Two-Dimensional SnS_2 Nanosheets

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Experimental Section

Synthesis of Free-standing 2D SnS_2 Nanosheets. Free-standing 2D SnS_2 nanosheets were vertically grown onto FTO substrate by CVD method in a two-temperature zone tube furnace. In a typical growth procedure, 100 mg $SnCl_4·5H_2O$ powder was loaded in an alumina boat, was placed at the center of the downstream heating zone. A FTO substrate was placed downstream to the $SnCl_4·5H_2O$ powder. The distance of the $SnCl_4•5H_2O$ alumina boat and the substrate is ~3 cm. 200 mg S powder was placed in another alumina boat at the upstream heating zone. Before the start of the growth, the furnace chamber was flushed with 1200 sccm high purity Ar gas for ~20 min to remove oxygen in the chamber. Next, the center of the downstream heating zone was heated to 450°C from room temperature at a ramp rate of 10°C. At the same time, the temperature of the S powder at the upstream heating zone was set to 250°C. The temperature in the downstream heating zone was kept at 450°C for 5 min for the SnS_2 growth under a mixture carrier gas of H_2 (15 sccm) and Ar (45 sccm). After the growth, the furnace was naturally cooled down to room temperature and free-standing vertical 2D SnS_2 nanosheets on FTO substrate were obtained.

Device Fabrication. To fabricate the vertically structured optoelectronic device, free-standing vertical SnS_2 nanosheets were firstly prepared on conductive FTO substrate. Then, a PMMA layer was spin-coated onto the substrate to wrap the SnS_2 nanosheets. After that, the top part of the PMMA was etched away by using oxygen plasma, exposing fresh and clean tips of the nanosheets. Then, Au film with a thickness of 20 nm was deposited on the top of the exposed nanosheets by thermal evaporation. For fabricating the parallel SnS_2 nanosheet photodetector, the as-grown vertical SnS_2 nanosheets were firstly transferred from FTO to SiO_2/Si substrates. Au electrodes with thickness of 30 nm were then deposited via thermal evaporation using a copper grid shadow mask. The device was annealed at 200 °C to reduce resistance before measurements.

Materials and Device Characterizations. The crystallographic characterization of the samples was performed using a Philips Panalytical X'Pert Pro multipurpose diffractometer with Cu-Kα X-ray radiation (λ=1.5418 Å). The morphologies of the samples were examined using a Hitachi SU8000 field-emission scanning electron microscope (FE-SEM) with a 20 kV accelerating voltage. Atomic force microscopy (AFM) characterizations were performed using a Bruker Dimension Icon AFM. The detailed microstructure, growth orientations and composition of the SnS_2 nanosheets were carried out by a Tecnai-G2 F30 transmission electron microscopy (TEM) attached with an energy dispersive X-ray spectroscopy (EDS) system, operating at

300 kV. The temperature gradient in the furnace was detected by using a TES-1310 digital thermometer equipped with a WRNK-81530 thermocouple (TES Electrical Electronic Corp., Taipei). Raman and photoluminscence (PL) spectra for the vertically oriented 2D SnS_2 nanosheets were collected from a LabRAM XploRA laser Raman spectrometer (HORIBA Jobin Yvon CO. Ltd) wtih excitation wavelength of 442 nm and 532 nm, intensity of 82 μW and 150 μW, respectively. Oxygen plasma treatment was performed on a PDC-32G-2 Plasma Cleaner (Harrick Plasma). The device was characterized using a semiconductor analyzer (Keithley 4200 SCS) combined with a Lakeshore probe station. Photoelectric data are obtained by using a 500 W xenon lamp as the light source. Mono-chromatic lights of 254-850 nm are obtained using optical filters. The intensities of incident light source are measured by a power and energy meter (Model 372, Scienteck).

Supplementary Figures

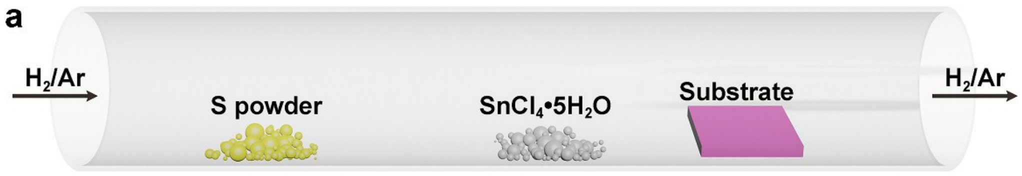

Figure S1. Schematic for CVD synthesis setup of vertical SnS_2 nanosheets.

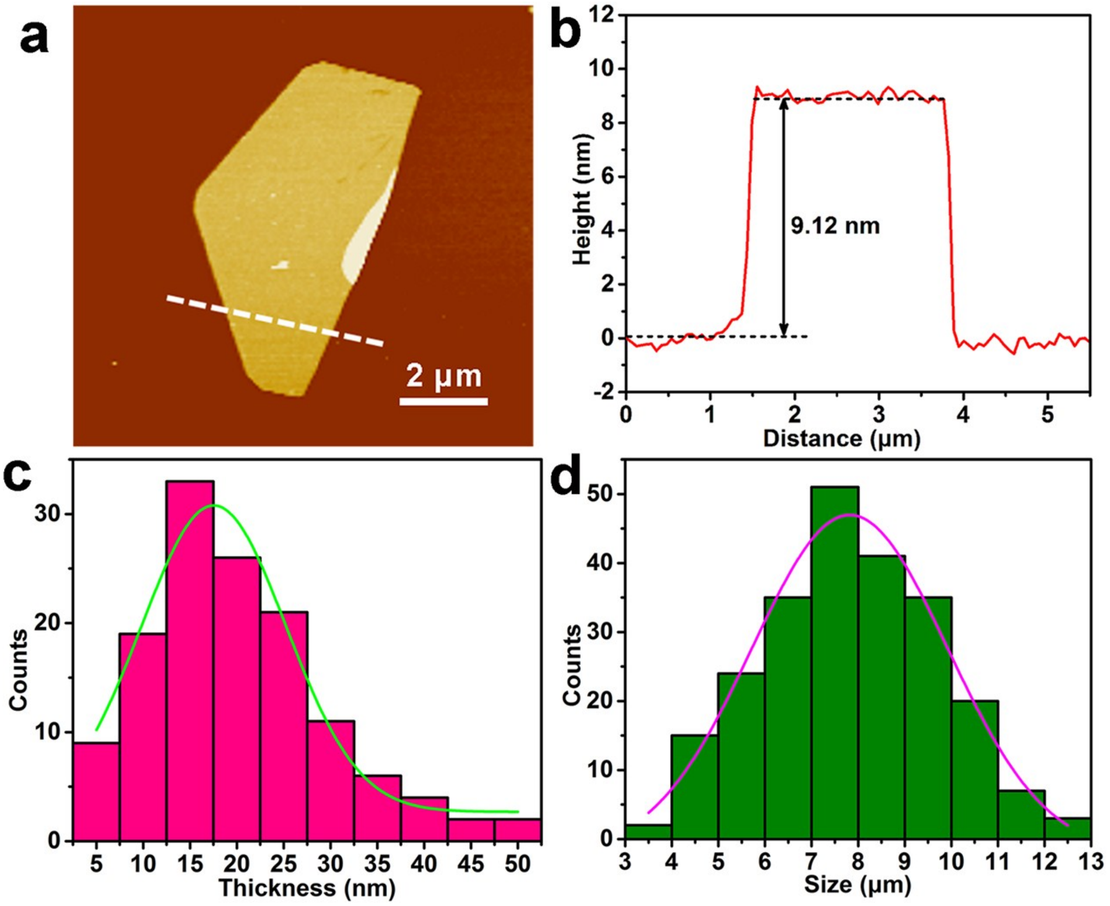

Figure S2. Statistical distribution of thickness and size of the as-grown vertical SnS_2 nanosheets: (a) Typical AFM image and (b) height profile of a 2D SnS_2 nanosheet. (c) Statistical distribution of the SnS_2 crystal thickness, smooth curve is the Gaussian fit of the thickness distribution. (d) Statistical distribution of the SnS_2 crystal domain size, smooth curve is the Gaussian fit of the size distribution.

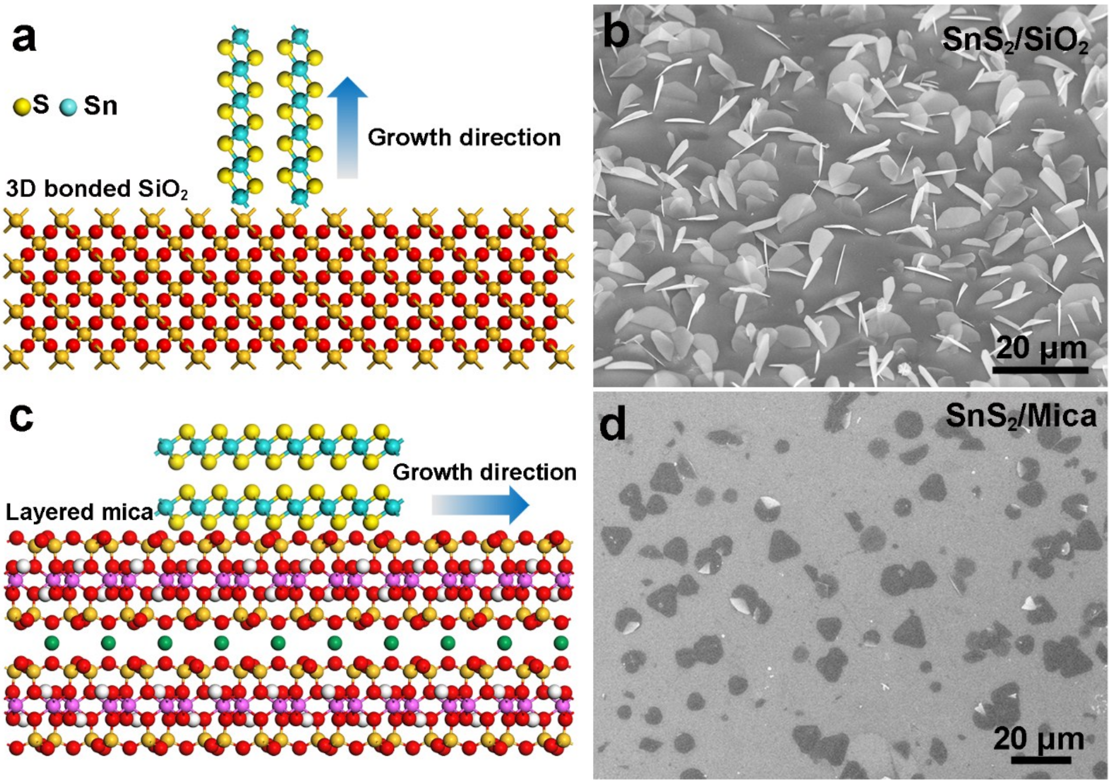

Figure S3. Schematic illustrations of SnS_2 grown on (a) SiO_2 and (c) mica substrates. SEM image of as-grown SnS_2 nanosheets on (b) SiO_2 and (d) mica substrates.

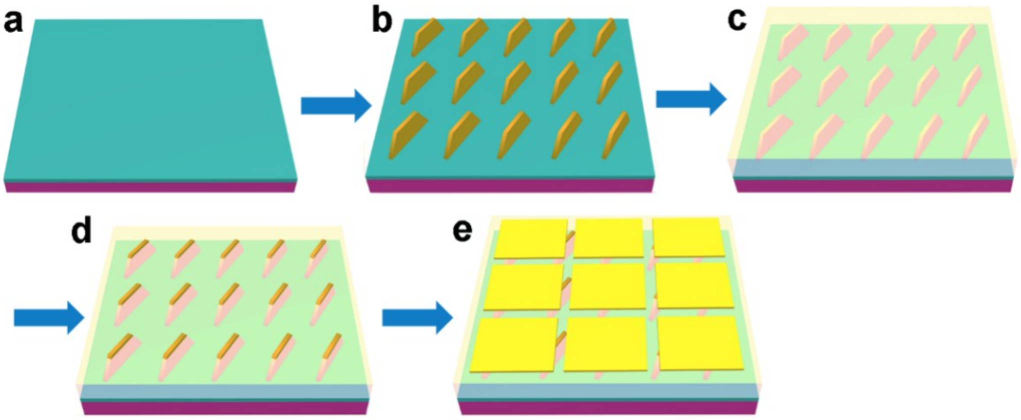

Figure S4. Steps for fabrication of vertical SnS_2 nanosheets optoelectronic device. (a) Bare FTO substrate, (b) vertical SnS_2 nanosheets grown by CVD, (c) spin-coating polymethyl-methacrylate (PMMA) that covers both the bottom and top of the nanosheets, (d) after oxygen plasma etching, the tips of the nanosheets are exposed, (e) deposition of Au electrode with thickness of 20 nm on the top of the nanosheets.

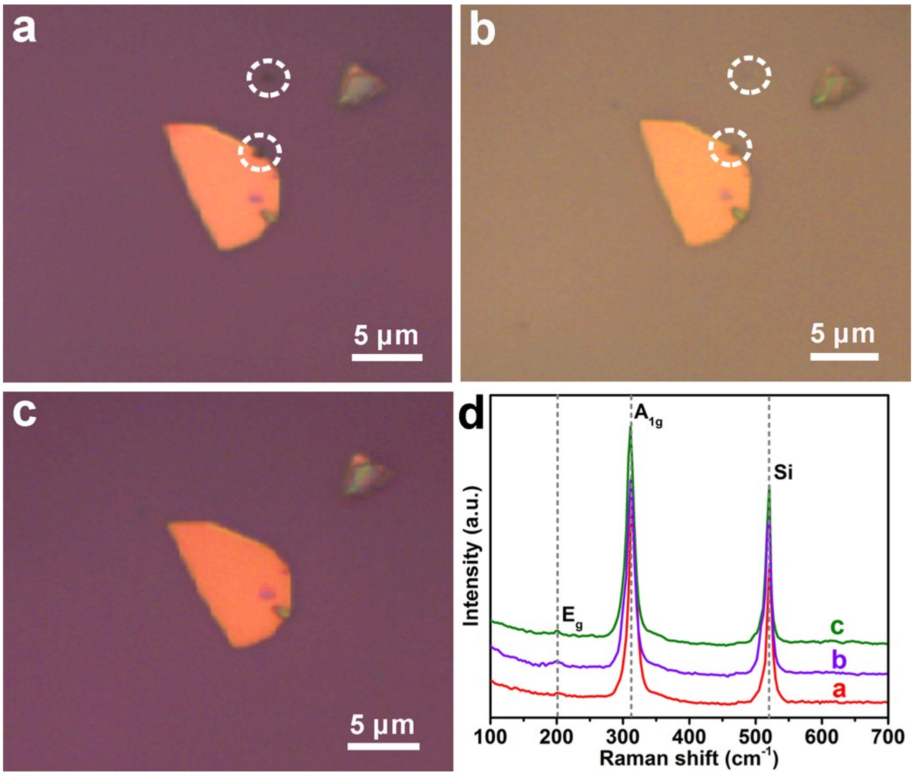

Figure S5. Oxygen plasma etching of SnS_2 nanosheet. (a) Primitive SnS_2 nanosheet, (b) after spin coating PMMA, (c) after O_2 plasma treatment for 30 min, (d) Raman characterizations.

According to a previous report,[1] the oxygen plasma has no affect on the SnS_2 nanosheets. To further confirm this, we performed a supplemtary study on the oxygen plasma etching of our grown 2D SnS_2 nanosheets. As shown in Figure S5, we firstly transfered a SnS_2 nanosheet onto SiO_2/Si substrates (Figure S5a, the white circles denote organic residues on substrates). Then a PMMA layer was spincoated onto the substrate to wrap the SnS_2 nanosheet (Figure S5b). As seen that after spin coating the colors of the substrate is changed, indicating the successful coverage of PMMA layer. After oxygen plasma treatment for 30 min, as seen in Figure S5c, the substrate color restored, implying the PMMA layer was completely removed. In addition, the residues on substrates were also removed, however, the SnS_2 nanosheet did not show any change. The above results prove that oxygen plasma etching has no effect on the SnS_2 nanosheets, but may be used to selectively remove organic residues on the substrates, which is consistent with the findings reported by P. Sutter and coauthors.[1] Meanwhile, the SnS_2 nanosheet also showed no change in Raman peaks before and after oxygen plasma treatment (Figure S5d), further confirming there was no SnS_2 etching occurred.

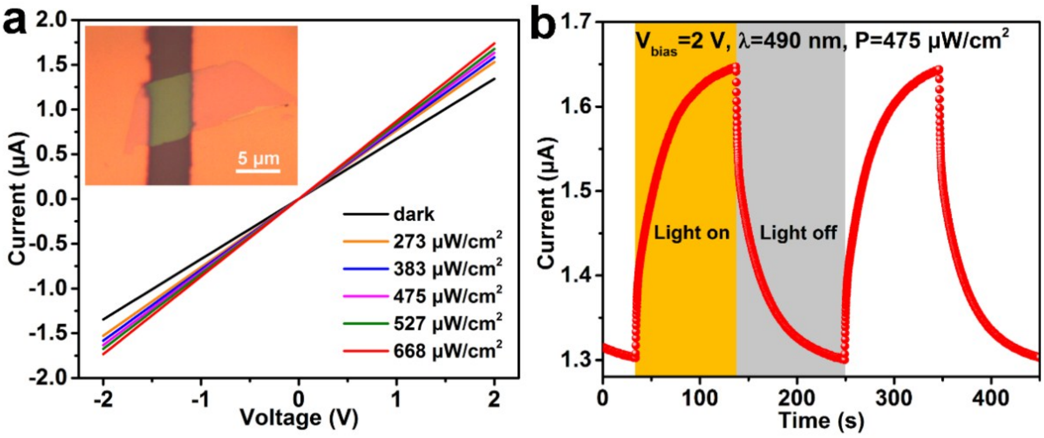

Figure S6. Optoelectronic properties of the parallel SnS_2 nanosheet photodetector with Au electrodes only. (a) *I*-*V* characteristics of the device in the dark and under light illumination with various power intensities. (b) *I*-t curve of the device at $V_{bias} = 2$ V, $\lambda = 490$ nm, and $P_{light} = 475$ μW/cm^2.

Table S1 Performance comparison of SnS_2 and other 2D-LMDs based photodetectors.

Device	Bias (V)	Responsivity (A/W)	EQE (%)	Detectivity (Jones)	Rise time (ms)	Decay time (ms)	References
FL SnS_2	-	100	-	-	44	44	1
FL SnS_2	2	8×10^{-3}	2.4	2×10^{9}	5×10^{-3}	7×10^{-3}	2
FL SnS_2	10	2	-	-	42	42	3
FL SnS_2	3	100	-	-	330	130	4
FL SnS_2	1	0.31	71	-	42	40	5
FL SnS_2	1	261	9.3×10^{4}	1.9×10^{10}	20	16	6
FL SnS_2	5	0.65	0.15	1.13×10^{8}	360	360	7
SnS_2 film	5	6.12×10^{-6}	-	-	460	880	8
SnS_2 flake	1	1.19	-	2.35×10^{11}	1	1	9
FL $SnSe_2$	3	1.1×10^{3}	2.6×10^{5}	1.01×10^{10}	14.5	8.1	10
1L MoS_2	1	7.5×10^{-3}	-	-	50	50	11
Vertical SnS_2	2	1.85	469	4.91×10^{9}	43.4	64.4	This work

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