# **Supporting Information**

# Macroporous SnO<sub>2</sub>/MoS<sub>2</sub> Inverse Opal Hierarchitecture for Highly

## Efficient Trace NO<sub>2</sub> Gas Sensing

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#### Note S1. Materials and Methods

Synthesis of hierarchical  $MoS_2/SnO_2$  macroporous inverse opal films. All reagents of analytical grade were used without further purification. Firstly, a self-assembled polystyrene (PS) colloidal monolayer was prepared on glass slides by our previously reported method<sup>1</sup>. Then, the glass slide with PS monolayer was slowly dipped into a solution of 0.2 mol/L SnCl<sub>4</sub>·5H<sub>2</sub>O. Subsequently, the solution-dipped PS monolayer was picked up using alumina sensor substrate with Au interdigital electrodes (8 pairs, 150 µm spacing). The dipped substrate was then annealed in air at 500 °C for 2 h to burn away the PS template and generate SnO<sub>2</sub> MIO film. Next, the SnO<sub>2</sub>covered substrate was immersed in a solution comprised of 36 mL DMF (dimethylformamide) and 0.04 g (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub>, and then transferred into a 50 ml Teflon autoclave at 210 °C for 15 h. After natural cooling, the substrate was picked up and rinsed with ethanol for three times, obtaining the hierarchical MoS<sub>2</sub>/SnO<sub>2</sub> MIO thin film. For reference, the pure MoS<sub>2</sub> nanosheets was also prepared just with the only procedure of the hydrothermal step.

*Characterizations.* The sample morphologies and nanostructures were characterized by a fieldemission scanning electron microscopy (SEM, FEI Verios 460), equipped with an accelerating voltage of 5 kV and a high-resolution transmission electron microscopy (TEM, JEOL, JEM-2100 F). The crystal structure and the phase analysis of the samples were investigated using X-ray powder diffraction (XRD, SHIMADZU XRD-7000S diffractometer) with a Cu K $\alpha$ 1 radiation source ( $\lambda = 1.5406$  Å) for 2 $\theta$  (10 – 80°). X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB Xi+) was performed to investigate the chemical states of sample surfaces.

*Gas sensing measurements.* To fabricate the  $SnO_2$  and  $MoS_2/SnO_2$ -based gas sensors, the honeycomb-like  $SnO_2$  and  $MoS_2/SnO_2$  porous arrays were *in situ* synthesized on the Au sensing electrode (interdigital, 8 pairs with microheater underneath, 150 µm spacing). For the synthesis of

the MoS<sub>2</sub>-based gas sensor, the MoS<sub>2</sub> powder in ethanol (0.02 g/mL) was dip coated onto the Au sensing electrode using a pipette. The sensing property evaluation was performed with a homemade system reported in our previous work<sup>2</sup>. The devices were connected to this test system by two Au wires with conductive silver paint. Two mass-flow controllers were used to accurately control the flows of the analyte gases and dry air, respectively, in order to obtain controlled concentrations of the target gases. The constant flow rate was 0.6 L/min, the bias voltage applied on the sensor was 5 V, and the electrical signal was recorded by Keithley 2602B acquisition system. The sensor response is calculated as  $R_g/R_a$  (for oxidizing gases) or  $R_a/R_g$  (for reducing gases), where  $R_g$  and  $R_a$  indicate the resistance of the gas sensor exposed to NO<sub>2</sub> and dry compressed air, respectively. The response time and recovery time are defined as the time required for reaching 90% of the full response and recovery values, respectively. The humidity-NO<sub>2</sub> cross sensing properties were tested by mixing the NO<sub>2</sub>, dry air and wet air (from saturated K<sub>2</sub>SO<sub>4</sub> solution).

*Density functional theory calculations.* Device Studio program provides a number of functions for performing visualization and modeling<sup>4</sup>. Using (001) tangent plane of  $MoS_2$  (2×3×1 supercell), (001) tangent plane of  $SnO_2$  (2×2×1 supercell) and  $MoS_2/SnO_2$  heterostructure (splicing of (001) and (002) crystal planes) as calculation models. DFT calculation was performed by using the projector augmented-wave (PAW) method in the Vienna Ab Initio Simulation Package (VASP) code<sup>5</sup>. Electronic exchange-correlation function was examined by the generalized gradient approximation (GGA) and Perdew-Burke-Ernzerhof (PBE)<sup>6</sup>. For all cases, the cutoff energy was set to 500 eV; 2×3×1, 2×3×1, 2×1×1 k-meshes were used to sample the Brillouin zone for geometry optimization of  $MoS_2$ ,  $SnO_2$ , and  $MoS_2/SnO_2$  heterostructure; 1×10<sup>-5</sup> eV and 0.02 eV Å<sup>-1</sup> were adopted as the convergence tolerance for energy difference between two consecutive self-

consistent calculations and residual force on each atom during structural relaxation, respectively. Through structural relaxation, the atomic arrangement on the interface formed by  $MoS_2$  fragment and  $SnO_2$  changes, and the O atom has the trend of substitution doping, indicating that the formation of heterostructure will produce certain defects, which are often the active sites for gas adsorption. For purpose of facilitating the actual calculation and comparison,  $NO_2$  adsorption was considered on the pure  $SnO_2$ ,  $MoS_2$ , and  $MoS_2/SnO_2$  heterostructure in this calculation, the adsorption energy ( $\Delta E_{ads}$ ) has been expressed as:

$$\Delta E_{ads} = E_{NO_2^*} - E^* - E_{NO_2}$$
 (S1) (S1)  $E_{NO_2^*}, E_{NO_2}, E_{NO_2},$ 

energies of the overall NO<sub>2</sub>-SnO<sub>2</sub> (or NO<sub>2</sub>-MoS<sub>2</sub>, NO<sub>2</sub>-MoS<sub>2</sub>/SnO<sub>2</sub>) system, isolated NO<sub>2</sub> molecule, and pure SnO<sub>2</sub> (or MoS<sub>2</sub>, MoS<sub>2</sub>/SnO<sub>2</sub>), respectively.



Fig. S1. The model of (a)  $SnO_2$ , (b)  $MoS_2$ , and (c)  $MoS_2/SnO_2$  heterostructure, respectively.



**Fig. S2**. The model of (a) SnO<sub>2</sub>, (b) MoS<sub>2</sub>, and (c) MoS<sub>2</sub>/SnO<sub>2</sub> heterostructure adsorbed with NO<sub>2</sub> gas molecules, respectively.



Fig. S3. Total density of states of (a)  $MoS_2$  and (b)  $SnO_2$ .

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Fig. S4 The SAED pattern of  $MoS_2/SnO_2$ . Bright rings results from the (210), (211), (310), and (222) planes of  $SnO_2$ , and the (203) plane of  $MoS_2$ .

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Fig. S5 (a) and (b) TEM elemental mapping images of  $MoS_2/SnO_2$ .

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Fig. S6 The XPS survey spectra of MoS<sub>2</sub>, SnO<sub>2</sub> and MoS<sub>2</sub>/SnO<sub>2</sub>, respectively.

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Fig. S7 Band alignment diagram for  $SnO_2/MoS_2$  (the working function ( $\Phi$  ( $SnO_2$ ) = 4.9 eV and  $\Phi$  ( $MoS_2$ ) = 5.79 eV).<sup>7,8</sup>



Fig. S8 Schematic description of the gas sensing installation.

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**Fig. S9** Gas responses of the MoS<sub>2</sub>/SnO<sub>2</sub> sensor upon exposure to 50 ppm NO<sub>2</sub> gas at 90 °C, 110 °C, 130 °C, 150 °C and 200 °C.





**Fig. S10** Comparisons of the MoS<sub>2</sub>/SnO<sub>2</sub>, SnO<sub>2</sub> and MoS<sub>2</sub> sensors response to 50 ppm NO<sub>2</sub> at: (a) 110 °C, (b) 130 °C and (c) 150 °C.





Fig. S11 Resistance of the  $MoS_2/SnO_2$  sensor from 1 ppm to 10 ppm  $NO_2$  at 130 °C.

#### Note S2. The calculated limit of detections (LOD)

The detection limit of this MoS<sub>2</sub>/SnO<sub>2</sub> sensor can be calculated as follows: <sup>1</sup>

$$S = AC^{\beta} + 1 \tag{S2}$$

Where A is the constant, C is the concentration of the target gas with the unit of ppm. The power exponent  $\beta$  is the parameter (usually from 0.5 to 1) depending on the charge of the surface species and the stoichiometry of the elementary reactions on the surface. When the relationship between the sensing signals and the concentrations is linear (shown in Fig. S12 b), the Eqn. (1) can be written as:

$$S = 0.726 \times C + 1$$
 (S3)

Therefore, the potential detection limit can be predicted from the Eqn. (2). If there is no noise, a slight change of the acquired signal can validate the existence of a gas when the ambient atmosphere is unchanged. Here, the detectable lower limit of the target gas concentration can be reasonably predicted on basis of the present signal-to-noise ratio.

In Fig.4 (e), the noise signal N is found to be ~ 0.02. The standard requirement of the detection limit is (S-1)/N>3. Consequently, the response signal must be larger than 0.06 or the value of the sensing signal must be >1.06. From the Eqn. (2), the corresponding concentration can be estimated to be ~ 80 ppb with a signal of 1.06 when the drift of the sensor baseline is significantly lower. It means the detection limit of concentration to NO<sub>2</sub> is ~ 80 ppb at 130 °C.



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**Fig. S12** (a) MoS<sub>2</sub>/SnO<sub>2</sub> sensor response from 1 ppm to 100 ppm NO<sub>2</sub> at 130 °C. (b) Response variations of the MoS<sub>2</sub>/SnO<sub>2</sub> sensor as a function of NO<sub>2</sub> concentration at 130 °C.

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Fig. S13 Dynamic sensing responses to 50 ppm  $NO_2$  under humid condition.

System	E*(eV)	$E_{NO2}(eV)$	$E_{NO2^*}$ (eV)	$\Delta E_{ads}(eV)$
SnO <sub>2</sub> +NO <sub>2</sub>	-392.82		-411.34	-0.12
MoS <sub>2</sub> +NO <sub>2</sub>	-271.85	-18.40	-290.42	-0.17
MoS <sub>2</sub> /SnO <sub>2</sub> +NO <sub>2</sub>	-1268.31		-1288.91	-2.20

Table S1. The calculation value of the adsorption energy of  $NO_2$  molecules

Table S2. Comparison of sensing performance based on nanostructure towards  $NO_2$  in the previous literatures.

Sample	NO <sub>2</sub> (ppm)	Working T (°C)	<b>Response Rg/Ra</b>	Ref
rGO/In <sub>2</sub> O <sub>3</sub>	0.5	150	22.3	9
α-Fe <sub>2</sub> O <sub>3</sub> /rGO	1	RT	1.24	10
ZnSe/ZnO	8	200	10.42	11
Cu-Fe <sub>2</sub> O <sub>3</sub>	10	300	1.4	12
MoSe <sub>2</sub> -graphene	25	RT	2.1	13
$MoS_2$	500	RT	3	14
MoS <sub>2</sub> /SnO <sub>2</sub>	1	130	1.94	<b>Present work</b>

**Table S3.** Comparison of limit of detections (LOD) based on nanostructure towards  $NO_2$  in the previous literatures.

Sample	LOD (NO <sub>2</sub> )	Working T (°C)	Ref
$MoS_2/SnO_2$	0.5 ppm	RT	15
$SnO_2/SnS_2$	1 ppm	80	16
SnO <sub>2</sub> -rGO	0.5 ppm	50	17
MoS <sub>2</sub> /graphene	0.2 ppm	200	18
$MoS_2$	20 ppb	200	19
MoS <sub>2</sub> /SnO <sub>2</sub>	80 ppb	130	Present work

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