# **Supporting Information**

## UV assisted ultrasensitive trace NO<sub>2</sub> gas sensing based on few-layer MoS<sub>2</sub> nanosheet-ZnO nanowire heterojunctions at room temperature

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#### **Materials Preparation**

#### ZnO nanowire

Zinc oxide nanowires were synthesized via a facile hydrothermal method as follows. In the first step, ZnO nanparticles (ca. 40 nm in diameter) dispersed in ethanol solvent were prepared by the method proposed in our previous work.<sup>1</sup> In a typical procedure, zinc acetate dihydrate (Zn (CH<sub>3</sub>COO)<sub>2</sub>.2H<sub>2</sub>O, 20 mg) was used as a starting material, and then mixed and dissolved in 40 ml ethanol, followed by a dropwise addition of 10 ml ethanolamine ( $C_2H_7NO$ ) serving as a stabilizer. The mixture was then stirred at 60 °C for 2 h to yield a stable and homogenous solution, which served as a precursor solution. Subsequently, the ammonia or glacial acetic acid was then added into the precursor solution under stirring drop by drop until the pH value reached 9. Afterwards, the treated precursor solution was spin-cast several times onto a 1cm×1cm glass plate, followed by a 350 °C annealing for 20 min to form ZnO nanoparticles. These ZnO nanoparticles could be easily collected by a mild sonication and washing several times with water and ethanol, and then dispersed in ethanol for further processing. To form a layer of crystal seeds, the obtained ZnO nanoparticles were then spray-coated onto a clean polydimethylsiloxane (PDMS) substrate. A subsequent 150 °C annealing was carried out to ensure particle adhesion to the substrate surface. Then hydrothermal ZnO nanowire growth was proceeded by suspending the treated substrate in an open beaker filled with an aqueous solution of zinc nitrate hydrate (0.025M) and methenamine at 90 °C for about 4 h.<sup>2</sup> Thirdly, the PDMS substrate was removed by chloroform solution at 60 °C. The left solution was centrifuged, washed by deionized water and ethanol several times, and then dried. Eventually, the obtained ZnO nanowires were dispersed in ethanol by an ultrasonic cell crusher (TL-250Y) at a power of 150 W four three hours to prepare ZnO sensor, or collected after a drying.

#### MoS<sub>2</sub>/ZnO composites

 $MoS_2$  bulk (purchased from Sigma-Aldrich) was dispersed in ethanol/water solution (volume ratio of 1:3) by the ultrasonic cell crusher at a power of 150 W overnight to obtain few-layer  $MoS_2$  nanosheets. Then prescribed weight of ZnO nanowires were added into above solution under sonication for another five hours. The resultant products were eventually obtained by centrifugation, washing with water and ethanol several times, and a drying.

For example, to obtain  $MoS_2/ZnO$  composite solution (0.5mg/ml: 0.25mg/ml), we take 5 mg ZnO nanowires into pretreated 20 ml  $MoS_2$  ethanol/water solution (0.5 mg/ml) and then sonicate the obtained mixture with TL-250Y for another five hours. As the high energy of ultrasonication leads to the formation of high-energy *S*-vacancies<sup>3</sup> within  $MoS_2$  nanosheets, ZnO nanowire will contact intimately with activated  $MoS_2$  nanosheets after further ultrasonication treatment.

#### **Test Apparatus and Device Fabrication**

The test apparatus was schematically shown in **Figure S1a**. In brief, the as-prepared sensors were mounted into a seamless metal chamber (10 cm × 3 cm × 0.5 cm) and then purified by nitrogen to ensure a negligible inner humidity at room temperature. Within this chamber, an UV LED light (365 nm, 1W) was fixed above the sensors at a distance of 4 mm for on/off illumination test. During the test process, the total gas flow rate was set at 1000 ml/min unchanged with high-purity nitrogen as the background gas for dilution and degassing. Gas concentration is coordinated by a mass flow controller (MT50-4J, Beijing Metron Instruments Co. Ltd., China) through tuning the flow ratio of target gas and background gas. The humidity in the test chamber is measured at 14%RH with a hygrometer. The dynamic resistance transients are collected by Keithley 2700 and displayed in PC with the aid of relevant hardware and software.



Figure S1. Test setup and gas sensors: (a) schematic image of test apparatus, (b) real image of IDEs, (c) profile and (d) top illustrations of prepared sensors.

The planar interdigital electrodes (IDEs) (**Figure S1b**) with an active area of 1.1 cm×0.7 cm, both the finger gap and width of 50  $\mu$ m, and 200 nm/100 nm thick Au/Ti layers sputtered onto SiO<sub>2</sub>/Si substrate. To prepare gas sensors, sensitive materials are spray-coated onto the IDEs, followed by a drying for three hours in a vacuum oven at 70 °C. The profile and top illustrations of the sensors are exhibited in **Figure S1c** and **1d**, respectively.

To conveniently evaluate the sensing performance, sensing response is defined as  $\Delta R/R_0 = (R_t - R_o)/R_o$ , wherein  $R_o$  is the steady resistance before gas exposure, and  $R_t$  the resistance at any time *t* during the test. Sensitivity is defined as the slope of the linear fitting line between

response and gas concentration. The response time is defined as the time required to reach 90% of the total resistance variation after a target gas is injected, and the recovery time as the time necessary to recover to 10% of the total variation when the target species is terminated.

#### **Characterization Instruments**

Morphological images were gathered by a field emission scanning electron microscope (FESEM, S-4800, HITACHI, Japan) operated at acceleration voltage of 5 kV. Transmission electron microscopic (TEM) features were collected on a JEOL-2010 TEM operated at 200 kV. X-ray photoluminescence spectroscopy (XPS) measurements were performed on an Omicron Nanotech operated at 15 kV and 20 mA current using monochromatic Al Ka X-ray source. X-ray diffraction spectrum (XRD) was measured by PANalytical X'pert HighScore XRD instrument with a CuK $\alpha$ radiation source. Raman spectrum was obtained on a Raman microscope spectrometer (Raman, Renishaw Invia Reflex) in the backscattering configuration using a 514.5 nm laser excitation with 10 mW at the samples. The current-voltage characteristics of the prepared sensors were obtained by Keithley 4200 Semiconductor Characterization System. The temperature distribution on the surface of ZnO and MoS<sub>2</sub>/ZnO sensors was investigated via a thermal infrared imager (ThermoVision A40, resolution: 0.1 °C). UV-Visual absorption spectrum was obtained by UV-VIS-NIR Spectrophotometer (UV-3600, Shimadzu). The work function of sensing materials was measured from ultraviolet photoelectron spectroscopy (UPS, ThermoFisher Scientific) at a biased voltage of -5 V. He-1 (21.2 eV) was utilized as a photon source for the UPS measurement.



Figure S2. SEM images of (a) MoS<sub>2</sub>/ZnO composites and (b) further magnification of circular region in (a). Inset



shows individual ZnO nanowire.

Figure S3. XPS spectra of ZnO and MoS<sub>2</sub>/ZnO composites: (a) ZnO survey, (b) MoS<sub>2</sub>/ZnO survey, (c) Zn 2p, (d)

Mo 3d, (e) O 1s and (f) S 2p.



Figure S4. Raman spectra of ZnO and MoS<sub>2</sub>/ZnO composites.



Figure S5. Transfer characteristics of (a) MoS<sub>2</sub> and (b) MoS<sub>2</sub>/ZnO field effect transistors, and response transients

of (c) ZnO and (d)  $MoS_2/ZnO$  sensors toward 10 ppm  $NO_2$ .



Figure S6. (a) HAADF-STEM image of MoS<sub>2</sub>/ZnO sample and the corresponding EDS mapping images of (b)Mo,

(c) S, (d) Zn and (e) O.



Figure S7. Dynamic resistance transient of ZnO sensor as a function of NO<sub>2</sub> concentration under UV illumination.



Figure S8. Dynamic resistance transient of MoS<sub>2</sub>/ZnO sensors as a function of NO<sub>2</sub> concentration under UV

illumination.



Figure S9. Response transients of two MoS<sub>2</sub> sensors on exposure to 50 ppb NO<sub>2</sub> under UV illumination.



Figure S10. Relationship between response and  $NO_2$  concentration for two  $MoS_2/ZnO$  sensors under UV illumination.



Figure S11. Time-resolved (a) resistance and (b) response of two  $MoS_2/ZnO$  sensors in  $N_2$  and air under UV illumination, (c-f) dynamic response of four new  $MoS_2/ZnO$  sensors in  $N_2$  and air under UV illumination.



Fig. S12. Temperature investigation in sensing layer (a) before and (b) after 3h UV illumination.



Fig. S13 UV-Visual absorption spectra of (a) ZnO and (c) MoS2 together with the Kubelka-Munk transformed

reflectance spectra of (b) ZnO and (d)  $MoS_2$ 



Fig. S14 Intensity-Kinetic Energy curves of (a) ZnO nanowire and (b) MoS2 nanosheet for work function

estimation

### References

- 1 Y. Zhou, G. Xie, T. Xie, H. Yuan, H. Tai, Y. Jiang, and Z. Chen, *Appl. Phys. Lett.*, 2014, **105**, 033502.
- 2 L. E. Greene, M. Law, J. Goldberger, F. Kim, J. C. Johnson, Y. Zhang, R. J. Saykally and P. Yang, Angew. Chem. Int. Edit., 2003, 42, 3031-3034.
- 3 D. Burman, S. Santra, P. Pramanik, and P. K. Guha, Nanotechnology, 2018, 29, 115504.