

Supporting Information

Pt and black phosphorus co-modified WS₂ flower-like composites for fast NO₂ gas detection at low temperature

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Preparation of BP nanosheets

Black phosphorus (BP) was prepared by the chemical vapor transport (CVT) technique. Red phosphorus (RP) powder was heated continuously at 100 °C for 20-30 min to remove moisture. Firstly, the dried RP powder was milled roughly to achieve a uniform grain size of 300-500 nm. Subsequently, a mixture of 0.5 g tin particles and 0.3 g iodine particles was added to the ground RP powder to obtain finer grains with a grain size of approximately 100-200 nm. The fine RP powder was placed in a quartz tube, and then a complete vacuum was reached in the quartz tube by pumping. The quartz tube was sealed by using a hydrogen and oxygen flame gun. After that, the quartz tube was placed in the tubular furnace. The furnace temperature was raised from room temperature to 600 °C with a heating rate of 0.8 °C/min, and holding 130-160 min. Then, the furnace naturally cooled down to room temperature to get BP crystals. The as-fabricated products were washed with ethanol repeatedly to remove the residual RP. The final BP products were obtained by drying in a vacuum.

Preparation and quantification of target gas

The gas source includes the gases of NO₂, CH₂O, CH₄, and CO with a purity of ≥ 99.9%, and the liquids with a concentration of 25% ammonia (NH₃·H₂O) and 95% ethanol (C₂H₅OH). For the gas source, taking NO₂ as an example, the NO₂ gas was injected into the gas chamber with different concentrations (ppm) via a rubber plug by using a gas microsyringe, which can accurately control the quantity of the NO₂ gas injected. The volume of the gas chamber is about 15 L. The concentration of the NO₂ gas in the chamber was calculated according to the volume ratio of the injected gas to that of the chamber. The sensor was biased 0.5, 1.0, and 1.5 V to achieve the operating temperature of 31, 50, and 79 °C, respectively. The relative humidity in the

chamber was about 32%.

For the liquid gas source, the target gas concentrations of NH_3 and $\text{C}_2\text{H}_5\text{OH}$ were calculated from the saturated vapor pressure of the target gas. Suppose that the volume of the test chamber is 1 L. The saturated vapor pressure of the target gas is calculated first, and then according to the saturated vapor pressure value, we can roughly estimate that 100 ppm target gas corresponds to how much volume of saturated vapor in 1 L test chamber. The other gas concentrations can be converted by equal proportion. The saturated vapor pressure is usually calculated by the Antoine equation as described below: $\lg P = A - B/(C + t)$, where P (mmHg) is saturated vapor pressure, t ($^{\circ}\text{C}$) is temperature, and A , B , and C is Antoine constants, respectively. Antoine constants can be found elsewhere.

Gas-sensing measurements

To realize the gas-sensing measurements for the WS_2 , BP-WS_2 , $\text{BP-WS}_2/\text{Pt}$ sensors, a home-made gas detection system was built, as shown in Fig. 2. The two-wire resistance measurement method was used to determine the resistance of the sensors. The test system is composed of E36103A programmable DC power supply, a closed gas testing chamber, Agilent 34970A data acquisition unit, and computer-controlled software system.

The target gas measurement employs static gas distribution method. During the testing process, the corresponding amounts of NO_2 , CH_2O , CH_4 , CO , NH_3 , and $\text{C}_2\text{H}_5\text{OH}$ gas were injected into the closed gas test chamber using a microsyringe. Under the action of the fan, the target gas is quickly and evenly dispersed throughout the gas chamber. When the test gas is adsorbed onto the sensing materials, the resistances of sensing materials will change, and subsequently the measured electronic signals are outputted. At this time, the computer-controlled software records the gas-sensing responses through the data collector.

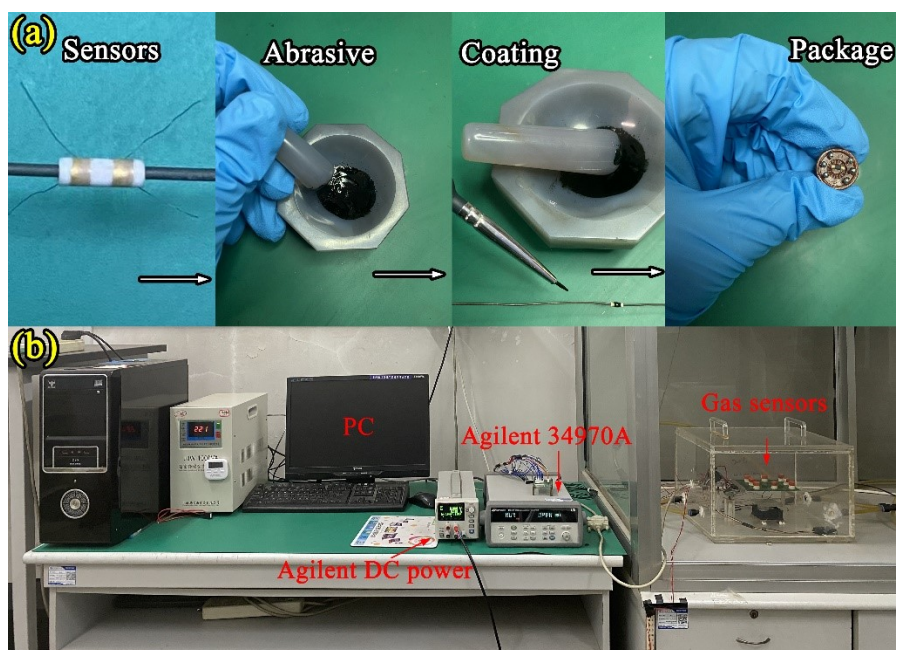


Fig. S1. Physical photos of the sensor package and measurement system.

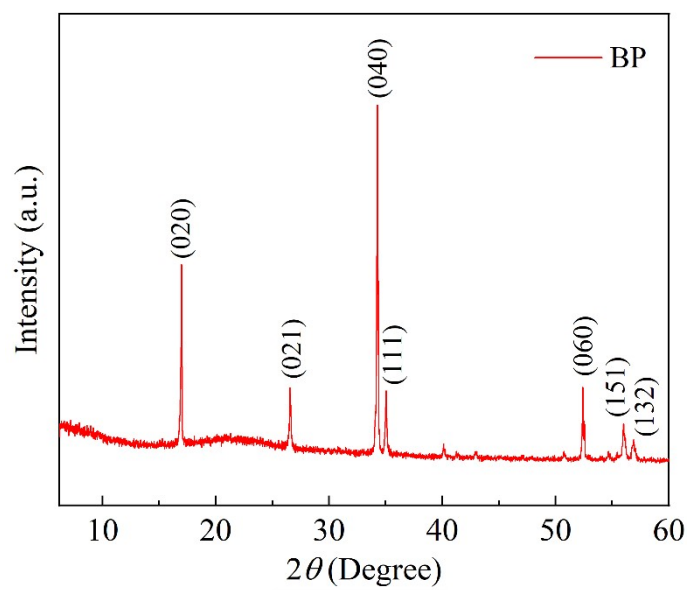


Fig. S2. XRD pattern of BP powder at room.

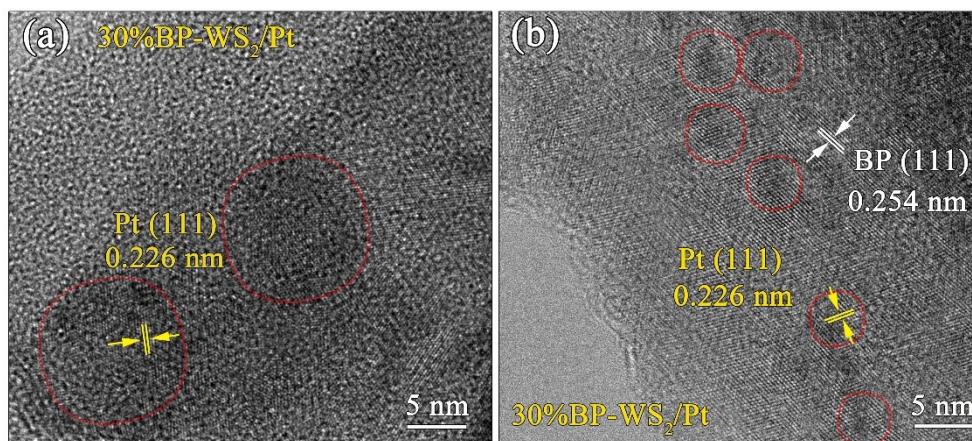


Fig. S3. HRTEM images of 30%BP-WS₂/Pt sample.

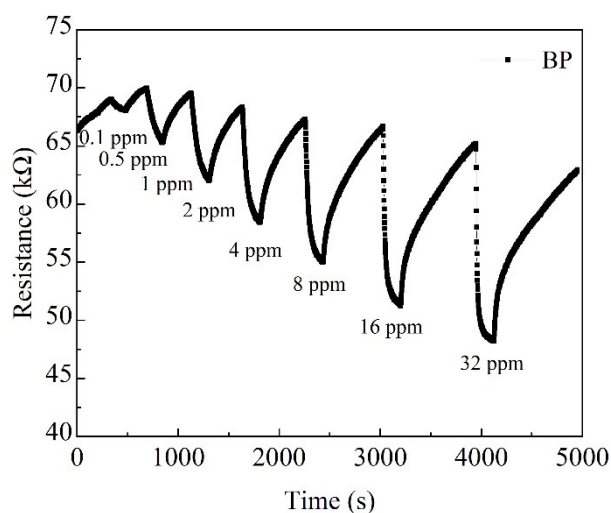


Fig. S4. Dynamic resistance curve of the BP sensor with increasing NO₂ concentration at 50 °C.

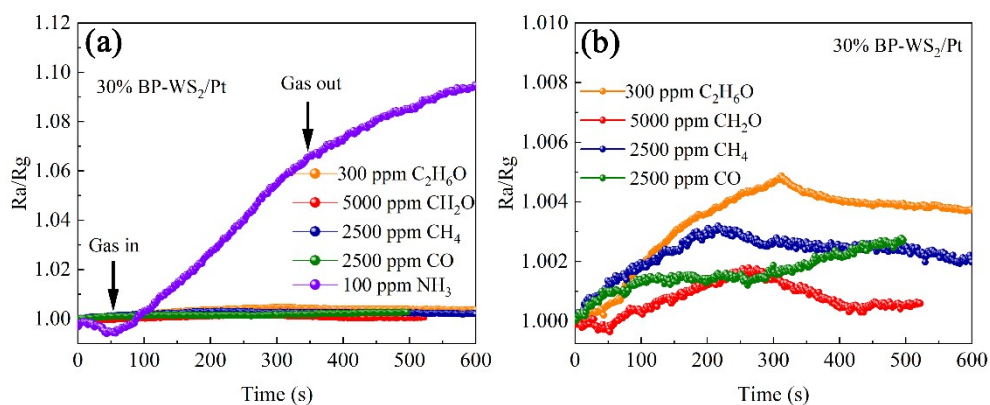


Fig. S5. (a) Gas response of the 30%BP-WS₂/Pt sensor towards different interference gases and (b) the enlarged gas response shown in figure (a).

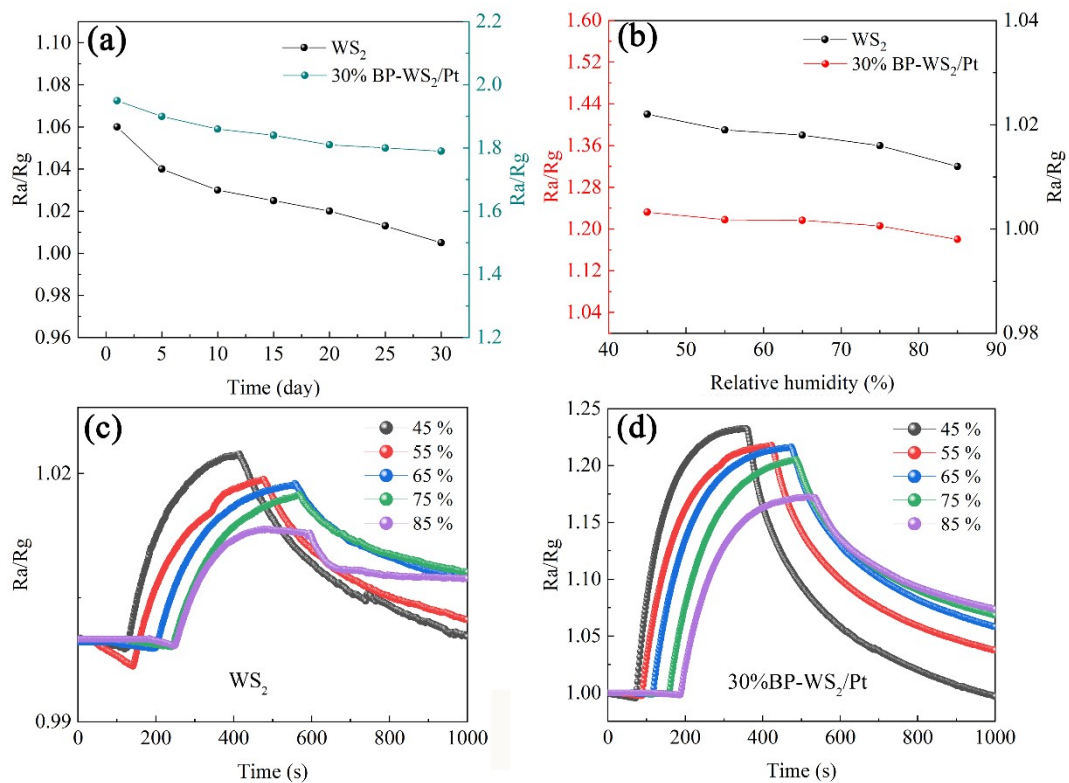


Fig. S6. (a) Long-term stability to 32 ppm NO₂ and (b) gas responses at different RH values of the WS₂ and 30%BP-WS₂/Pt sensors to 1 ppm NO₂; dynamic response curves of (c) the WS₂ and (d) 30%BP-WS₂/Pt sensors to 1 ppm NO₂ under different RH conditions.

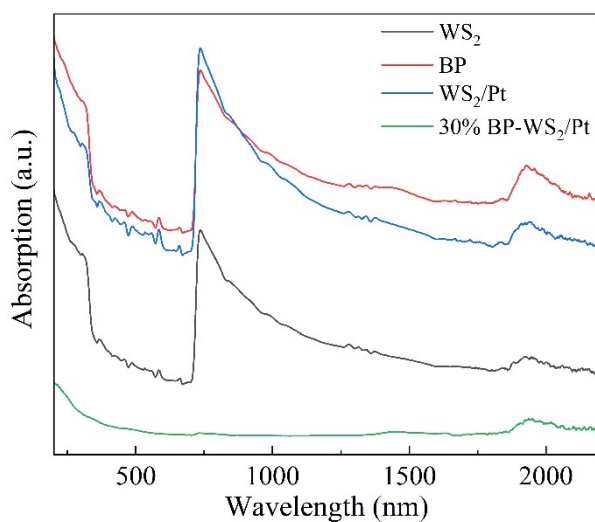


Fig. S7. UV-vis diffuse reflectance spectra of WS₂, BP, WS₂/Pt, and 30%BP-WS₂/Pt.

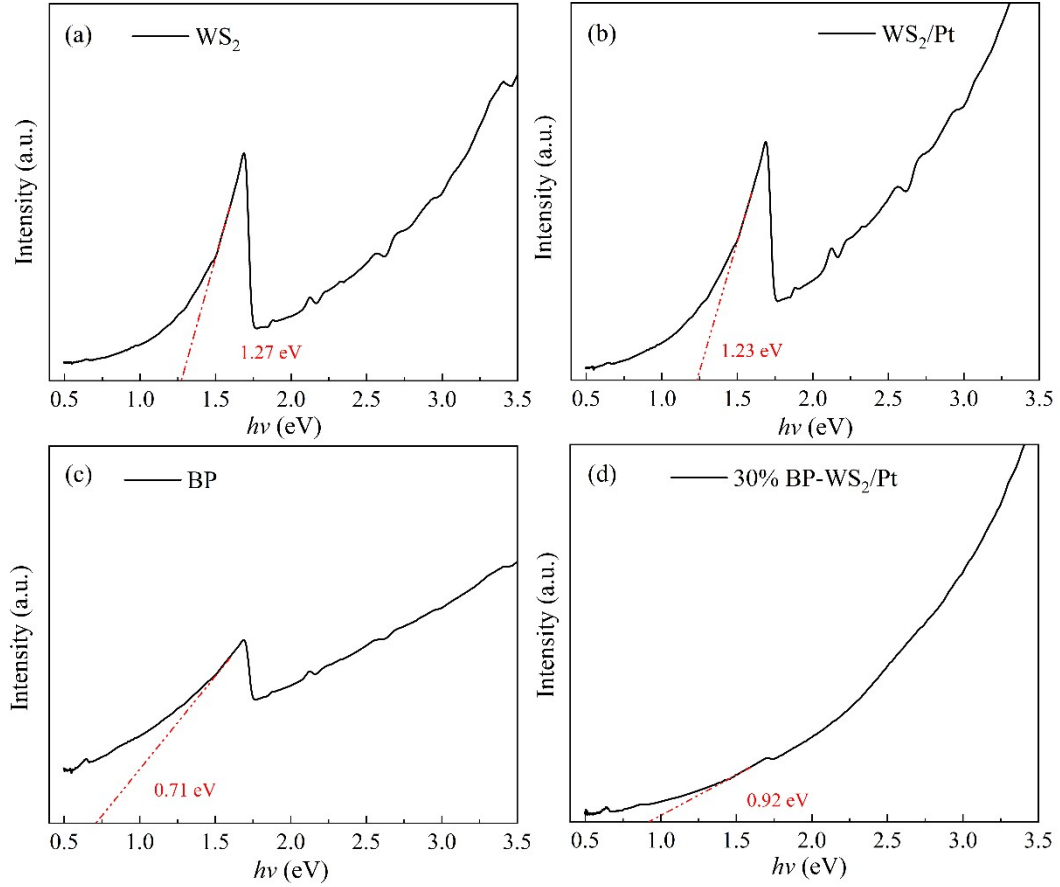


Fig. S8. Band gap of (a) WS₂, (b) WS₂/Pt, (c) BP, and (d) 30%BP-WS₂/Pt samples calculated using UV-vis data.

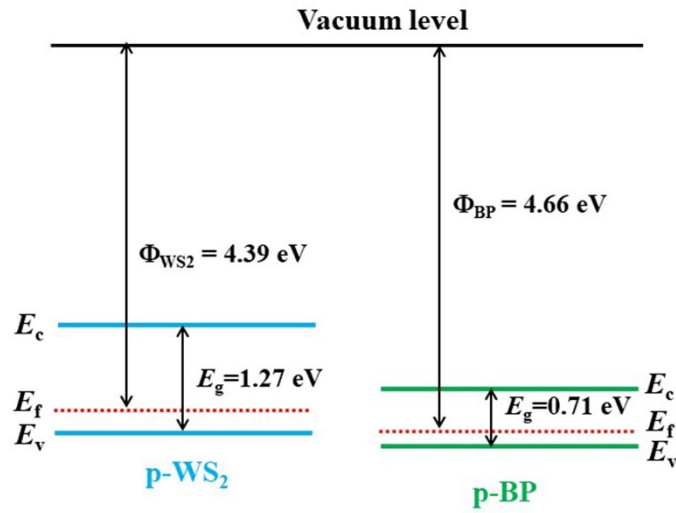


Fig. S9. Energy band diagrams of WS₂ and BP before contact.