Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Supplementary Material for

Zinc Oxide-Black Phosphorus Composites for Ultrasensitive Nitrogen Dioxide Sensing

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This document includes:

Materials and methods

Preparation of the ZnO Hollow Spheres

The aqueous solution (20 mL) of zinc acetate dehydrate ($Zn(Ac)_2 \cdot 2H_2O$, 0.3512 g) and trisodium citrate dehydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$, 0.12 g) were kept with mild magnetic stirring for 10 min. Then aqueous solution (20 mL) of urea ($CO(NH_2)_2$, 0.48 g) was slowly added into the above solution while stirring. The final aqueous solution was transferred into 100 mL capacity Teflon-lined autoclave, sealed tightly and put it into a microwave digestion system (Ethos One, Milestone Inc., Italy). The microwave hydrothermal process was carried out at 180 °C for 30 min, which was allowed to cool down naturally. The precipitates were filtered using a vacuum filtration and then were washed with distilled water for several times prior to dry in oven at 80 °C for 8 h. Finally, the products were calcined at 500 °C for 3 h.

Preparation of ZnO-BP Composites

Black phosphorous powder (2 mg, purchased from Nanjing XFNANO Materials Tech Co., Ltd) was immersed in N-methyl pyrrolidone (NMP, 10 mL) and sealed. After sonicating (80 W, 45 °C) for 70 min, ZnO hollow spheres (22 mg) were added to the above solution and sonicating for 20 min. Sequentially, the resulted powder was collected and filtered using a vacuum filtration assembly on a polytetrafluoroethylene (PTFE) membrane filter of 0.2 µm pore size. The filtered film was then thoroughly washed three times by ethanol to remove the solvent residue. Finally, the as-prepared products were collected and vacuum dried at 60 °C for 6 h.

Preparation of graphene oxide (GO)

GO was prepared from natural graphite powder through a modified Hummers method.[1,2] In a typical synthesis, graphite (1 g) was added into of H_2SO_4 (23 mL), followed by stirring at room temperature ($T = 25 \pm 5$ °C) and 40 ± 5% humidity for 24 h. After that, $NaNO_3$ (100 mg) was introduced into the mixture and stirred for 30 min. Subsequently, the mixture was kept below 5 °C by ice bath, and $KMnO_4$ (3 g) was slowly added into the mixture. After being heated about to 35 °C, the mixture was stirred for another 30 min. After that, water (46 mL) was added into above mixture during a period of 25 min and the mixture was heated to 95 °C under stirring for 15 min. Finally, water (140 mL) and H_2O_2 (10 mL) were added into the mixture to stop the reaction. The unexploited graphite in the mixture was removed by using 60 min centrifugation at 8000 rpm. The obtained suspension with GO (1 mg/mL) was then used for the following experiment.

Preparation of ZnO-GO Composites

The synthesis procedures were the same as that of ZnO-BP composites mentioned above, except for GO and distilled water instead of BP and NMP. The detailed parameters and morphologies for the synthesis of ZnO are given in Table S1 and Figure S1, respectively.

Sensor Fabrication and Measurement

The gas-sensing properties of sensors were measured using a CGS-8 gas-sensing characterization system (purchased from Beijing ELITE Tech Co., Ltd). The obtained samples were coated onto an Al_2O_3 tube, which a pair of Au electrodes previously printed. Pt-lead wires attaching to the Au electrodes were used for connecting with measurement instrument. A small nickel-chromium alloy coil was inserted into the ceramic tube to provide the operating temperature. After drying under an infrared lamp for 10 min, the tube was then aged in the gas sensor system at 100 °C for 12 h. The response (R) of the sensor was defined as R_g/R_a and R_a/R_g for oxidizing gas and reducing gas, respectively, where Ra and R_g stand for the electrical resistances of sensor in air and in the target gas. The response and recovery time are defined as the time taken by sensor to attain 90% of the final value and the time taken to regain 10% of the base value, respectively.

Characterization

The crystal structures and morphologies of the obtained samples were characterized by X-ray diffraction (XRD, Rigaku), using a monochromatized Cu target radiation resource (λ = 1.5418 Å, operated at 40 kV). The surface morphologies of the samples were inspected using a FEI Nano SEM 450 scanning electron microscopy (SEM) at an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) images were recorded on a FEI Tecnai G20 transmission electron microscope under a working voltage of 200 kV equipped with energy dispersive X-ray (EDX) spectrometer. X-ray photoelectron spectroscopy (XPS) experiments were measured using an ESCAlab250 Analytical XPL Spectrometer with a monochromatic Al Kα source. Height and phase measurements were performed using ~300 kHz Si cantilevers in Non-Contact mode on an Asylum Cypher AFM. Images were taken in the repulsive phase regime using at least 512 samples per line. The scanning rate was 1.5 Hz or lower. Raman shift spectra were taken on a XPLORA PLUS with 514 nm wavelength incident laser light.

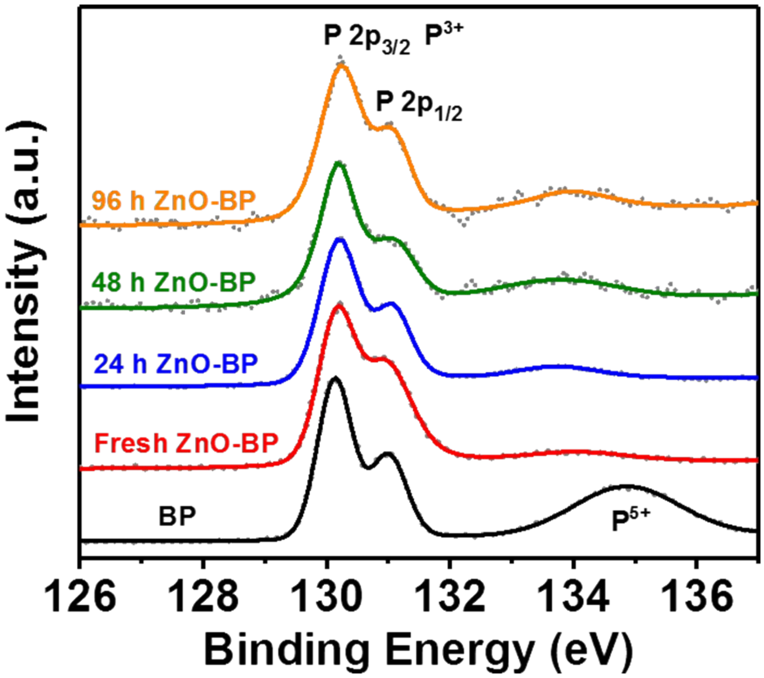

Fig. S1 P 2p core-level XPS for both fresh ZnO-BP and after 24 hours, 48 hours, and 96 hours.

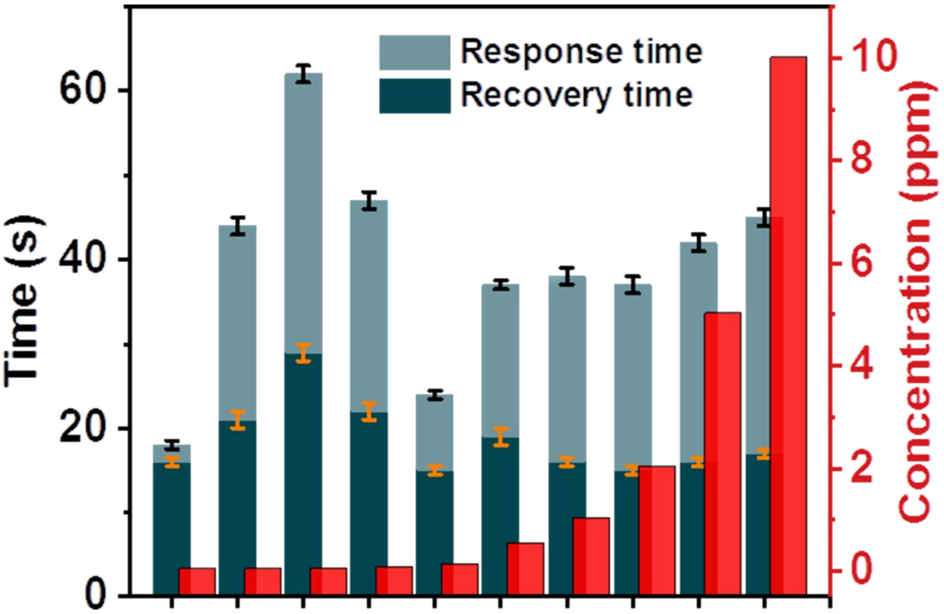

Fig. S2 Response and recovery time of the ZnO-BP gas sensor to different concentrations NO_2 at 160 °C.

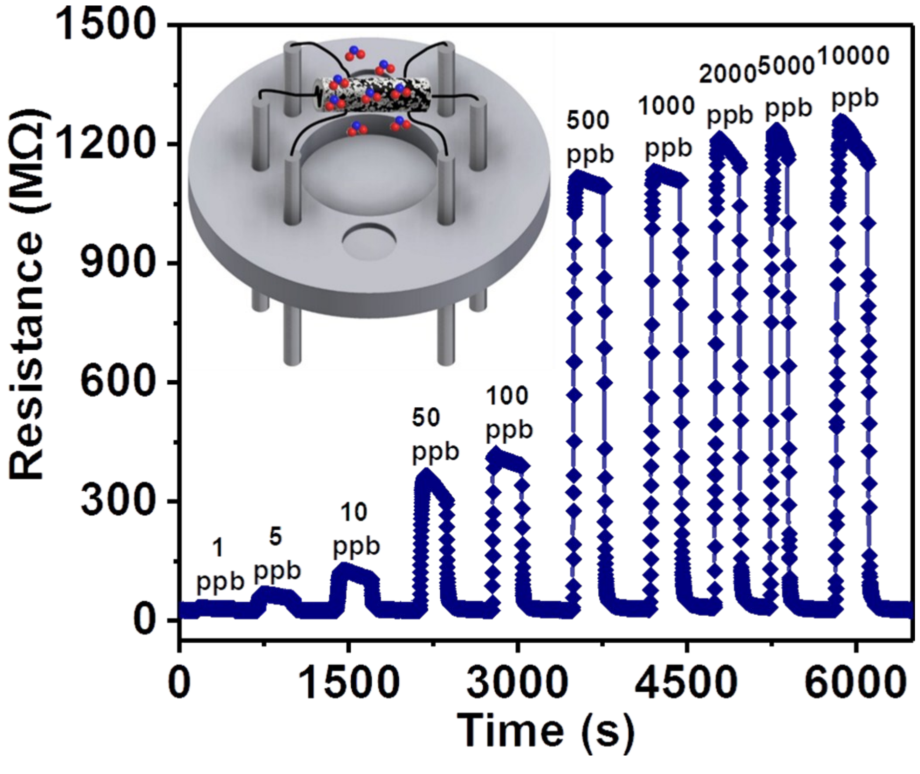

Fig. S3 Dynamic response-recovery curves of ZnO-BP sensor to different NO_2 concentrations at 160 °C.

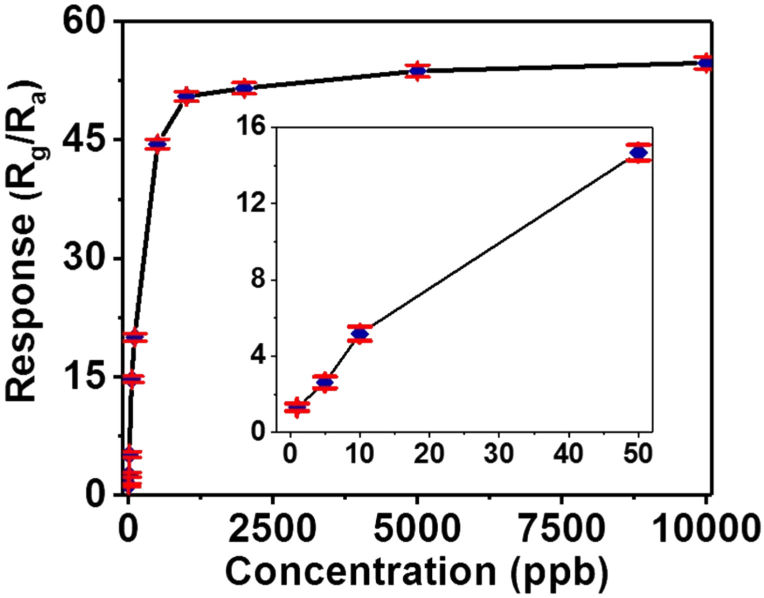

Fig. S4 Response of ZnO-BP sensor as a function of NO_2 concentrations (1-10000 ppb) at 160 °C, the inset shows the response at low NO_2 concentrations (1-50 ppb).

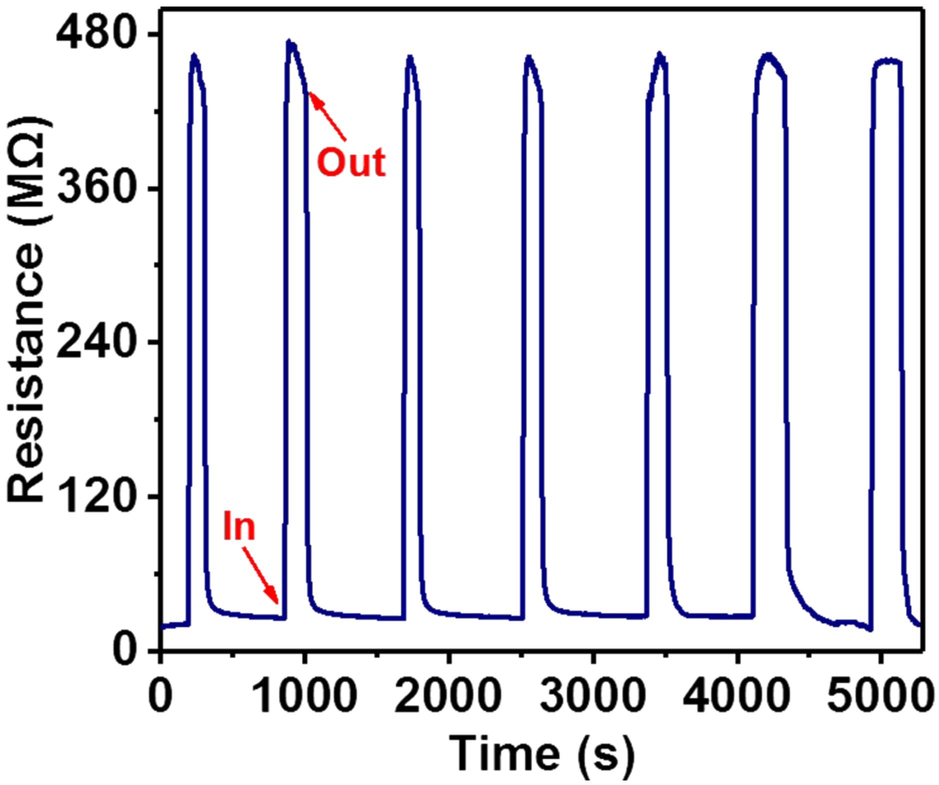

Fig. S5 The reproducibility of the ZnO-BP sensor upon seven cycles to 100 ppb NO_2 at 160 °C.

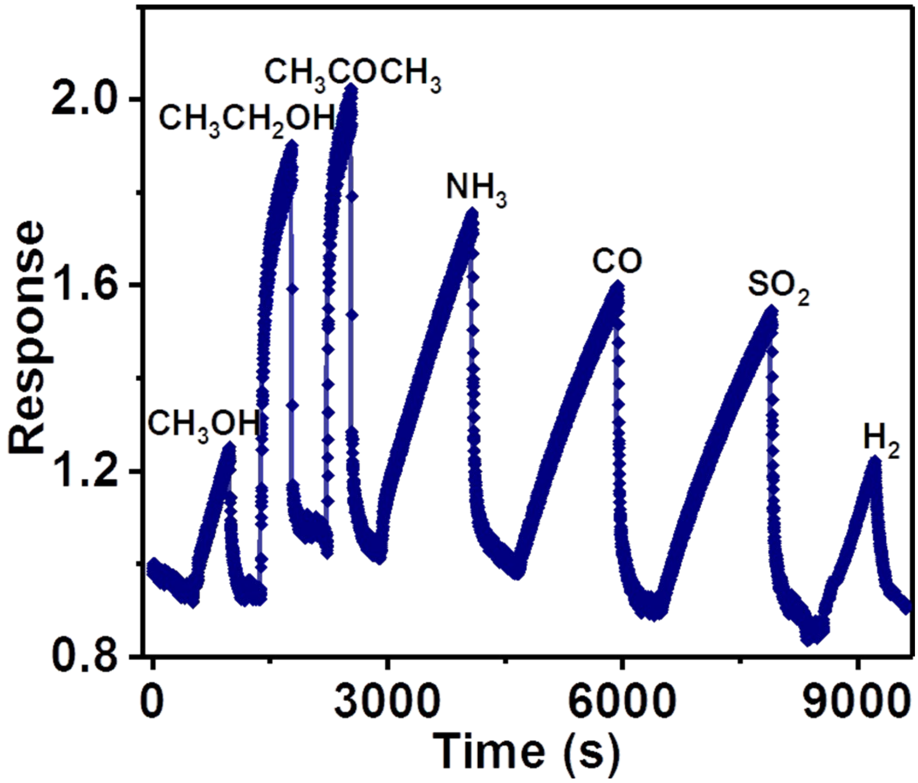

Fig. S6 Dynamic response curves of the sensor based on ZnO-BP to 1 ppm various gases (CH_3OH, CH_3CH_2OH, CH_3COCH_3, NH_3, CO, SO_2, and H_2) at 160 °C.

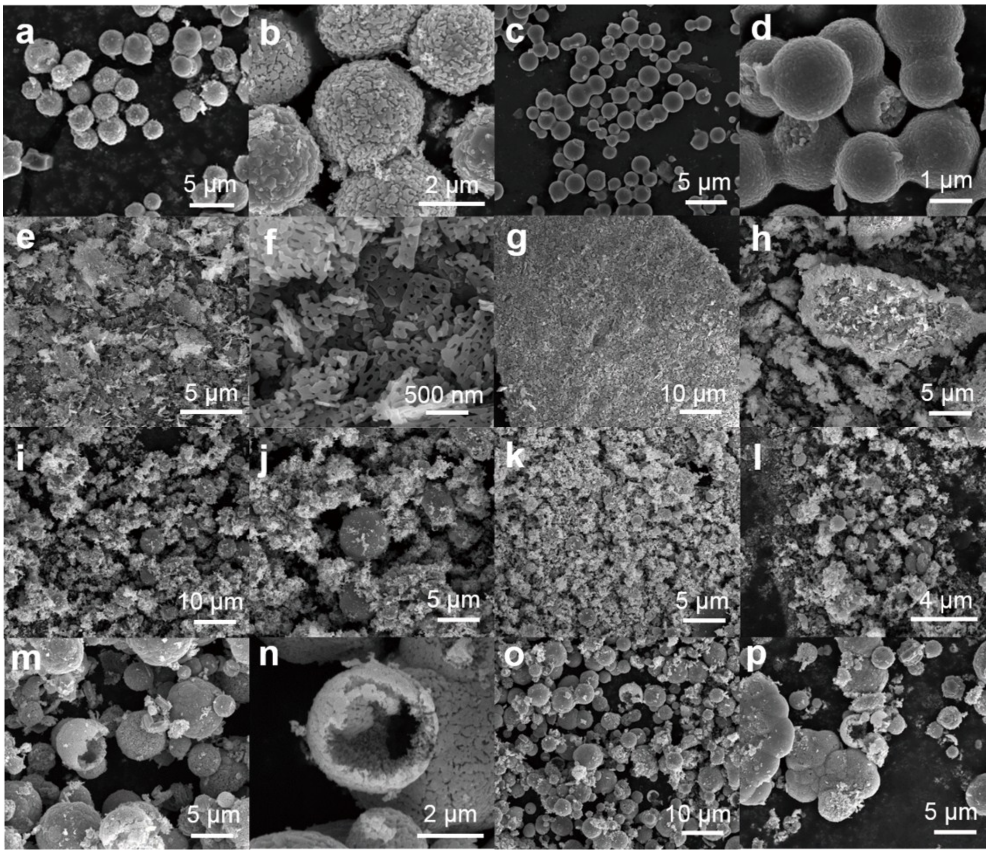

Fig. S7 SEM images of (a) and (b) ZnO hollow spheres; (c) and (d) ZnO-1; (e) and (f) ZnO-2; (g) and (h) ZnO-3; (i) and (j) ZnO-4; (k) and (l) ZnO-5; (m) and (n) ZnO-6; (o) and (p) ZnO-7.

Table S1. Parameters for ZnO synthesis.

Sample	$CO(NH_2)_2$ [g]	$C_6H_5Na_3O_7{\cdot}2H_2O$ [g]	H_2O [ml]	Time [min]	Temperature [°C]
ZnO	0.48	0.12	40	30	180
ZnO-1	0.00	0.12	40	30	180
ZnO-2	0.48	0.00	40	30	180
ZnO-3	0.48	0.12	40	30	90
ZnO-4	0.48	0.12	40	30	110
ZnO-5	0.48	0.12	40	30	130
ZnO-6	0.48	0.12	40	30	200
ZnO-7	0.48	0.12	40	30	220

REFERENCES

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2 S. Liu, J. Q. Tian, L. Wang and X. P. Sun, *Carbon,* **2011**, *49*, 3158.