

Electronic Supplementary Information

Phosphorus doped graphene nanosheets for room temperature NH₃ sensing

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Experimental details:

Chemicals. Triphenylphosphine and graphite were purchased from J&K Scientific Ltd. (Beijing) and used directly without further purification. Other reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. and used as received.

Preparation of graphene oxide (GO). The graphene oxide (GO) was prepared using a modified Hummers' method. The typical procedure is as follows: 10 g of natural graphite powder was dispersed into 50 mL of concentrated H₂SO₄ (98%) under vigorous stir, and then 9.5 g of K₂S₂O₈ followed by 9.5 g of P₂O₅ were added to this suspension. The suspension was then retained at 80 °C for 6 h and was centrifuged to gather the pre-oxidised graphite. After washing with water repeatedly, the pre-oxidised graphite was dried over night at 110 °C in an oven. The pre-oxidised graphite was then added to 450 ml of concentrated H₂SO₄ (98%) at 0 °C in an ice bath. Then, 50 g of KMnO₄ was added into this suspension slowly under vigorous stirring.

After stirring at 35 °C for 2 h, 1 L of demonized water was added slowly and the temperature was kept below 50 °C during this process. After stirring for 2 h, another 3 L of demonized water followed by 50 mL of H₂O₂ (30 %) were added into this suspension. After that, the obtained light yellow solution was stirred for 1 day and centrifuged, washed with 5 L of 10% HCl, and with 5 L of deionised water, and dried at 60 °C in an vacuum oven.

Preparation of rGO. For comparison, rGO was also prepared by the high-temperature annealing of GO at 400 °C under Ar atmosphere (25 ml/min). The as-prepared rGO was donated as rGO-400 in this work.

Characterization. The as-prepared P-GNS samples were characterized by X-ray diffraction (XRD, BRUKER D/max-2500), X-ray photoelectron spectroscopy (XPS, VGESCALAB 220i-XL), Fourier Transform Infrared spectroscopy (FTIR, BRUKER, TENSOR-27), Scan electron microscopy (SEM, JSM-6701F), and Laser Raman spectroscopy (Raman, HORIBA Jobin Yvon LabRAM HR800). A CHI 660E electrochemical workstation was used to measure the resistance of the P-GNS layer between the Pd interdigital electrodes on the ceramic substrate under air atmosphere and in NH₃ gas sensing process.

Gas sensing test. To measure NH₃ sensing property of P-GNS samples, an interdigital Pd electrode with a gap of about 0.2 mm were sputtered onto a ceramic substrate. 10mg of P-GNS powder was dispersed into 0.5 mL of ethanol under ultrasonication to form slurry, and this slurry was then dropped onto the Pd interdigital electrode on the ceramic substrate. A thin P-GNS layer between the Pd electrodes was formed after the evaporation of ethanol at 90 °C for 6 h in air. The as-prepared sensor was then introduced in an airtight chamber for the sensing test. Electrical measurements were carried out at room temperature under air atmosphere and NH₃ with various concentrations. The sensor resistance was measured by a CHI 660E electrochemical workstation in chronoamperometry with a constant voltage of 1

V for P-GNS-400, -500, -600, -800 and rGO-400. The sensor response to NH₃ is defined as $\text{Response} = (R_{\text{NH}_3} - R_{\text{Air}}) / R_{\text{Air}} \times 100\%$, where the R_{Air} is the baseline electrical resistance of the sensor in clean Air, and, the R_{NH_3} is the resistance in NH₃ with different concentrations.

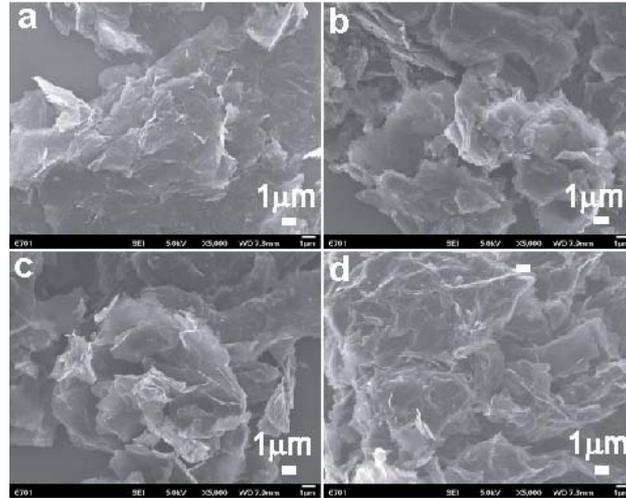


Figure S1. SEM images of (a) P-GNS-400, (b) P-GNS-500, (c) P-GNS-600, and (d) P-GNS-800. Heavily accumulation, due to the π - π interaction, between the graphene nanosheets can be observed from the SEM images of P-GNSs annealed at 400, 500, 600, and 800 °C.

Table S1 Atom contents of P-GNSs calculated from XPS analysis

	P-GNS-400	P-GNS-500	P-GNS-600	P-GNS-800
C	83.64	83.88	84.46	84.47
O	14.27	14.21	13.79	13.98
P	2.09	1.92	1.76	1.55

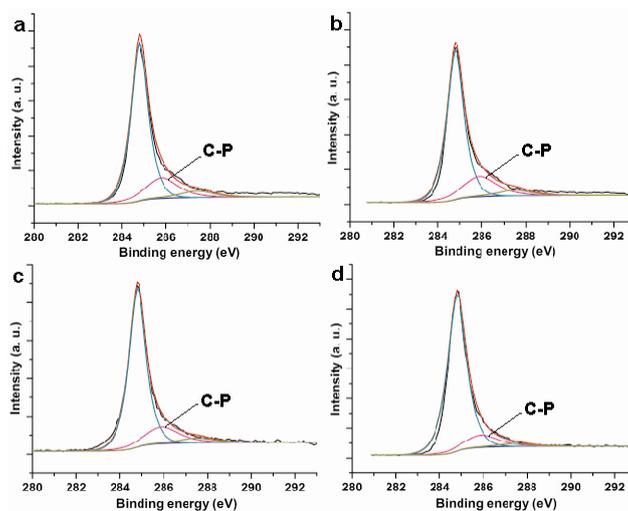


Figure S2 High resolution C 1s XPS spectra of P-GNSs annealed at (a) 400 °C, (b) 500 °C, (c) 600 °C, and (d) 800 °C.

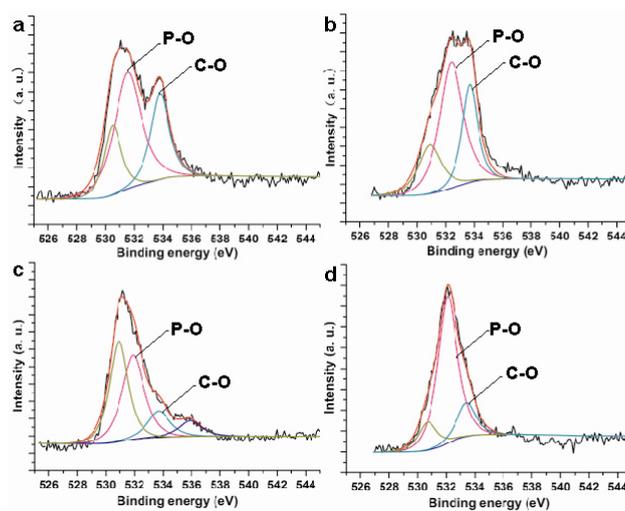


Figure S3 High resolution O 1s XPS spectra of P-GNSs annealed at (a) 400 °C, (b) 500 °C, (c) 600 °C, and (d) 800 °C.

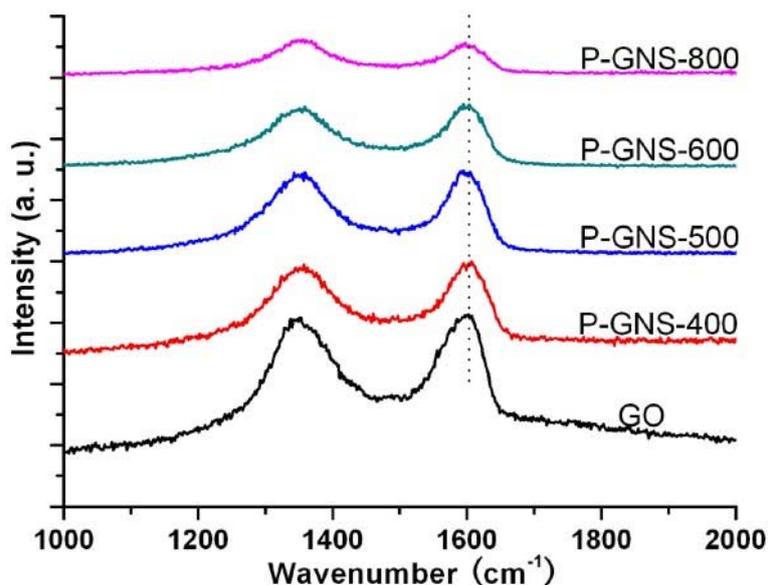


Figure S4 Raman spectra of GO, P-GNS-400, -500, -600, and -800. The Raman spectra of the as-prepared GO and P-GNSs were collected at an excitation wavelength of 532 nm under ambient conditions. In the Raman spectrum of GO, the peak at 1351 and 1601 cm^{-1} could be attributed to the D and G bands of GO, respectively. The D band refers to the structural defects and partially-disordered structures, while the G band refers to the E_{2g} vibration mode of sp^2 domain, defining the degree of graphitization. After doping of P atoms into graphene, the D and G bands still appeared at similar locations. A slightly red-shift of G band (from 1601 cm^{-1} to 1596 cm^{-1}) can be seen in the P-GNSs' Raman spectra, which is attributed to the P-doping.

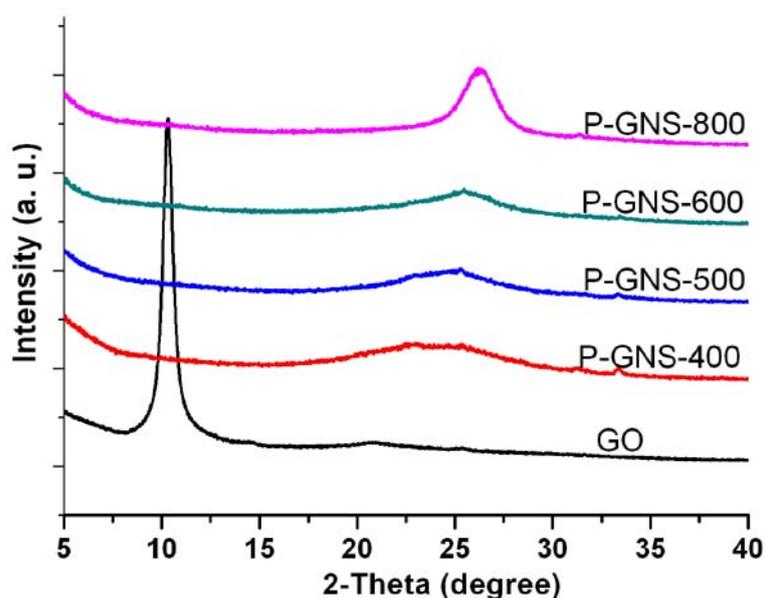


Figure S5 XRD patterns of GO, P-GNS-400, -500, -600, and -800. A strong diffraction peak located at $2\theta=10.3^\circ$ can be seen in the XRD pattern of GO. After doping of P atom into graphene networks via thermal decomposition at high temperatures, the diffraction peaks shifted to higher 2-Theta degree located at $23\sim 26^\circ$ and became broadening. The reason behind this phenomenon is that the interlayer distance of graphene sheets reduced with the gradually increased annealing temperatures during the thermal reduction of GO. And also, the P atoms that incorporated into the graphene networks and the residual oxygen groups might lead to XRD diffraction peak of the graphene broadening due to the lattice disordering. Since the P content and oxygen groups from P-GNSs increased with the decreasing of the annealing temperatures, the XRD diffraction peaks showed a broadening trend with the decreasing of the temperatures.

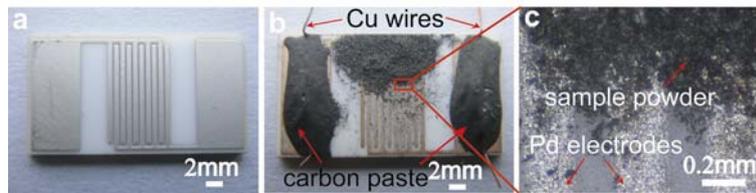


Figure S6 Photographs of (a) Pd interdigital electrode, (b) as-prepared sensor device, and (c) enlarged electrode-sample interface that highlighted in Fig. S6b.

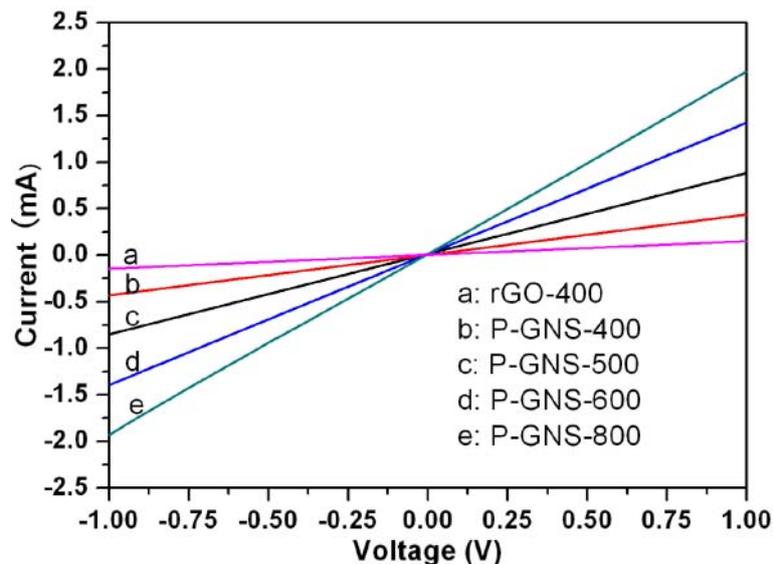


Figure S7 I-V curves of rGO-400, P-GNSs annealed at 400, 500, 600, and 800 °C. The gradually increasing currents from the I-V curves of P-GNSs from P-GNS-400 to P-GNS-800 imply that the resistance of the P-GNSs decreased with the increasing of

the annealing temperatures, which is due to the enhanced reduction degree of the graphene nanosheets.

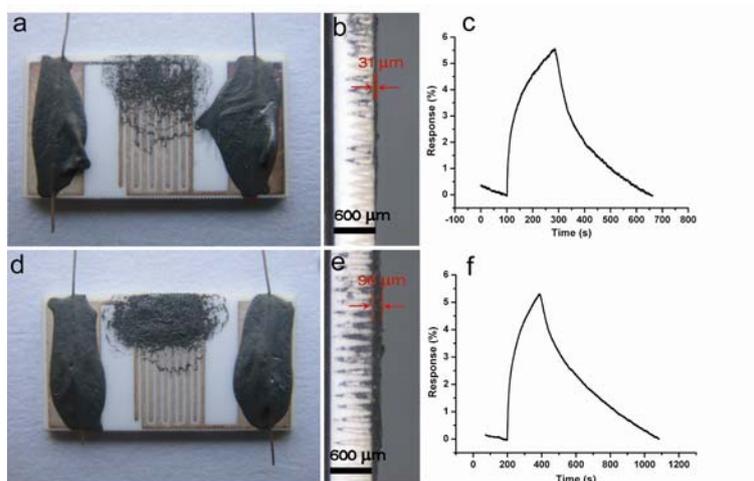


Figure S8 Photographs of (a) the as-prepared sensor device with a thin layer P-GNS-400 in 31 μm of thickness, (b) cross section of the sample layer, and (c) corresponding response of the thin layer P-GNS-400 to 100 ppm of NH₃; Photographs of (d) the as-prepared sensor device with a thick layer P-GNS-400 in 96 μm of thickness, (e) cross section of the sample layer, and (f) corresponding response of the thick layer P-GNS-400 to 100 ppm of NH₃; Comparing the response from the two sensor devices, we would find that the sensing results from P-GNS-400 layer in different thicknesses have some slight difference. The P-GNS-400 layer in 31 μm of thickness gave a higher response value (5.56%) and faster recovery time (270 s) compared to P-GNS-400 layer in 96 μm of thickness (response value: 5.41%, recovery time: 816 s). Therefore, the sensor device with P-GNS-400 in thinner thickness is more suitable for NH₃ sensing at room temperature.

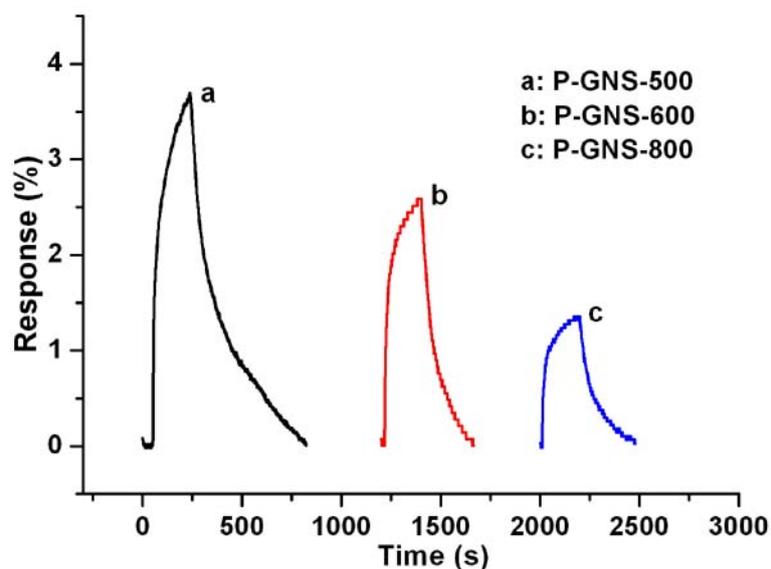


Figure S9 Sensing results of (a) P-GNS-500, (b) P-GNS-600, and (c) P-GNS-800 to 100 ppm of NH₃. A response value of 3.6%, 2.5%, and 1.3% was achieved for P-GNS-500, P-GNS-600, and P-GNS-800 to 100 ppm of NH₃, respectively. The decreasing response values compared to P-GNS-400 suggest a gradually reducing defect sites in the carbon skeleton of graphene upon the increasing annealing temperatures.

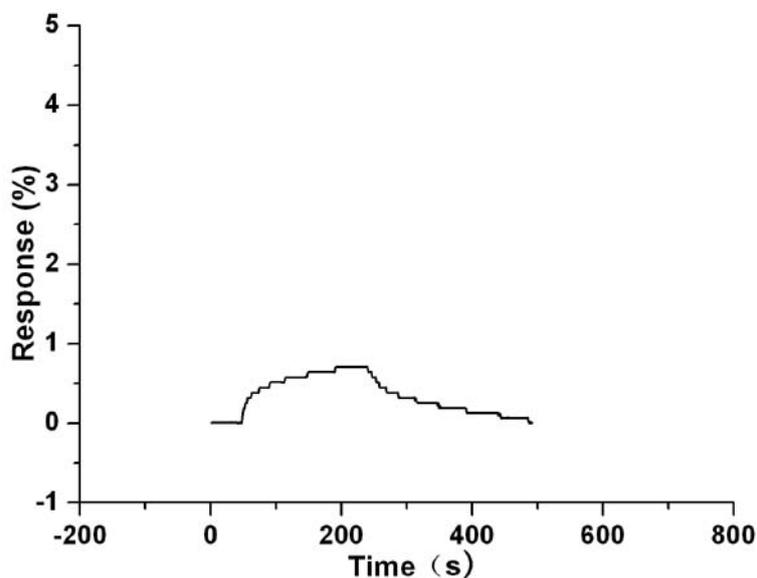


Figure S10 The response of rGO-400 to 100 ppm of NH₃.