

## Electronic Supplementary Information

### Novel C-rich Carbon Nitride for Room Temperature NO<sub>2</sub>

#### Gas Sensor

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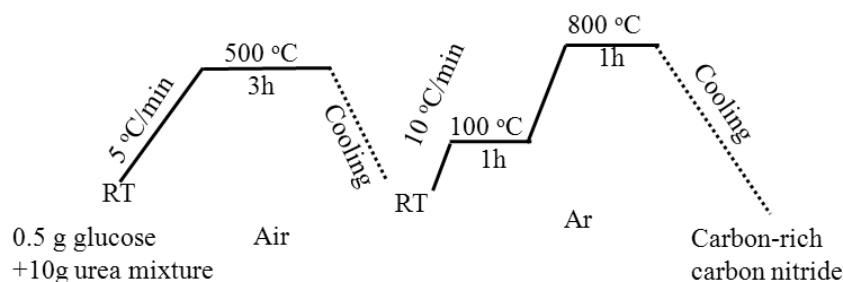
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#### 1. Synthesis of C-rich carbon nitride

As prepared C-rich carbon nitride was synthesized by two steps of thermal treatment of 0.5g glucose (from Sigma Aldrich ) and 10g urea (AR, Sinopharm Chemical Reagent Co., Ltd). Firstly, both of the precursors were dried at 60°C. Then, the precursors were mixed and grindled to uniform powders. After that, the powders were transferred to a crucible with a cover, to process the first thermal treatment of heating at 500°C for 3 hours under ambient pressure in air in Muffle Furnace (Isotemp Programmable Muffle Furnace 650-750 Series, Fisher Scientific). The obtained intermediate products then were subjected to the second thermal treatment in tube furnace under a protective flow of 100 sccm Ar. The thermal treatment process is shown as below. Finally, as prepared solid was suspended in N-Methyl pyrrolidone (NMP), the exfoliation of carbon nitride to carbon nitride sheet was achieved by accumulated 60 minutes 150 W horn sonication treatment in a program of 3s on and 3 s off in ice water bath. Then, the dispersion was continued to sonicating for further exfoliation using a Digital Sonifier (KQ3200DE, 400 W, 60%). The obtained black dispersion was washed with water to remove the NMP and dispersed in water, then subjected to centrifugation to remove any unexfoliated carbon nitride and small particles. The product obtained was steadily dispersed in water for further use.



**Scheme S1.** Process of preparation C-rich carbon nitride.

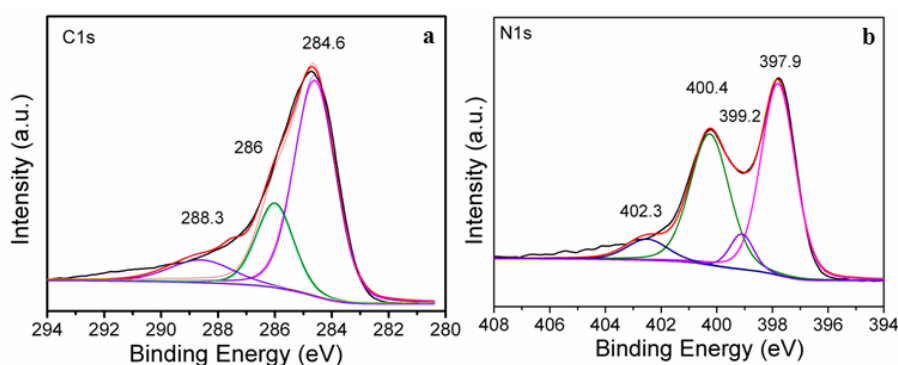
## 2. Characterization

The X-ray diffraction (XRD) measurements were performed with X'Pert-Pro MPD with Cu K $\alpha$  ( $\lambda=1.5406$  Å). The surface morphologies were determined by transmission electron microscopy (TEM) observed on Tecnai G2 F20 S-Twin (FEI, 200 kV). FESEM images were recorded by a Hitach S-4800 instrument. Chemical compositions and element binding energies were analyzed using X-ray photoelectron spectroscopy (XPS) on Perkin-Elmer RBD upgraded PHI-5000C ESCA system with Al K $\alpha$  x-ray as an excitation source. N<sub>2</sub> adsorption-desorption analyses were carried out at 77 K using Mocrumeritics Tristar II 3020.

## 3. Sensor Device Fabrication and Characterization

The preparation of sensor array is carried out by lithographing technology as the procedure described earlier.<sup>1</sup> Interdigitated electrodes (Au/Ti, 200/20 nm, respectively) were vacuum sputtering coating on a Si/SiO<sub>2</sub> (500 nm SiO<sub>2</sub> layer) substrate. Then the interdigitated electrodes with 5  $\mu$ m gap were defined using lift-off techniques. After that, a 50 nL C-rich carbon nitride nanosheets suspension (0.05 mg/ml) was drop-casted onto the top of the electrode gap using a microsyringe and dried at 60 °C. Finally, the electrodes were then annealed at 300 °C for 30 min under an inert gas to minimize the contact resistance between the C-rich carbon nitride sheets and the gold pads. The electrical properties (I–V curves) were measured with a Keithley 2602A System Source Meter (Keithley Instruments, Inc.) with potentials sweeping from -1 V to 1 V under different dilute gas.

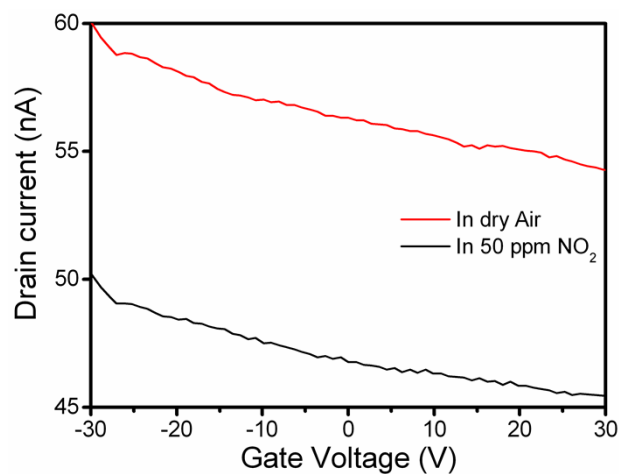
The sensors were wire-bonded on a CERDIP chip carrier and each sensor was connected in series with a load resistor. Gas-sensing measurements were performed with a WS-30A system (Weisheng Instruments Co., Zhengzhou, China). The system has a fan for rapid dispersion in a closed organic glass testing chamber (2.5L). The air (65% RH) was used both as a reference gas and as a diluting gas to obtain desired concentrations of the target gases. Typically, a certain volume of target gas was injected into the chamber directly by a microinjector. The gas was mixed with the air inside with the help of the fan. The concentration of target gas inside the detecting chamber was determined by the injected volume of the target gas. After the gas-sensing response turned to be in equilibrium, the target gas was released from chamber by inputting air. The sensor response sensitivity is defined as  $S = (R_a - R_g)/R_a$ , where  $R_a$  and  $R_g$  are the resistances of the sensor in the air and in the detected gases, respectively.



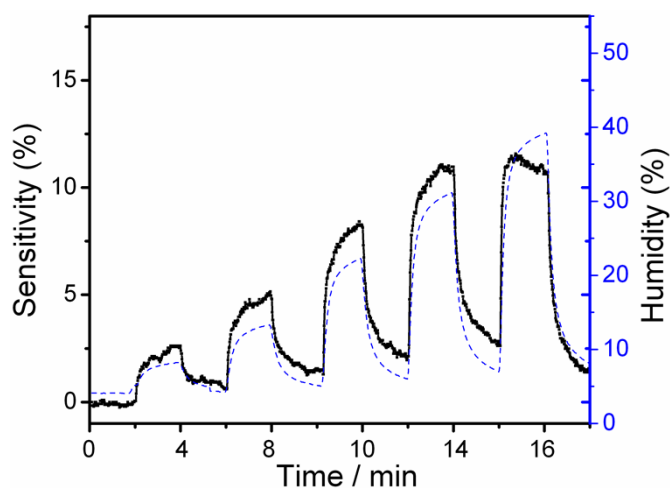
**Fig. S1** The XPS spectra of C-rich carbon nitride: (a) C 1s and (b) N 1s.

The C 1s spectrum in Fig. S1a shows the deconvoluted three peaks at 288.3 eV, 286 eV and 284.6 eV with peak area ratio of 1:0.33:0.24, corresponding to  $sp^2$ -bonded carbon in  $N-C=N$  groups (288.3 eV), C-N (286 eV), and  $sp^2$  C=C (284.6 eV). The content of  $sp^2$  C=C is much higher than that in  $g-C_3N_4$  with peak area ratio of 1:0.07:0.02<sup>2</sup>. Fig. S1b exhibits four peaks which are identified by the bonding state of the N atom in the composite. The peak signals are consistent with that of  $g-C_3N_4$ <sup>2</sup>. The main peak at 397.9 eV corresponds to  $sp^2$  hybridized aromatic N bonded to carbon atoms (C=N-C) existed in graphitic carbon nitride, also called pyridine N,

which was proved to be reactive by theories and experiments.<sup>3</sup>



**Fig. S2** The source-drain current ( $I_{sd}$ ) versus gate voltage ( $V_g$ ) of the C-rich carbon nitride FET device ( $V_{sd} = 0.1V$ ) in air and in 50 ppm  $NO_2$  gas.



**Fig. S3** Sensitivity of C-rich carbon nitride based sensor vs. different humidity.

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2 J. H. Liu, T. K. Zhang, Z. C. Wang, G. Dawson and W. Chen, *J. Mater. Chem.*, 2011, **21**, 14398.

3 Y. Zheng, Y. Jiao, M. Jaroniec, Y. G. Jin and S. Z. Qiao, *Small*, 2012, **8**, 3550.