

## *Electronic Supplementary Information*

### **Nitrogen and silica co-doped graphene nanosheets for NO<sub>2</sub> gas sensing**

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## **Experimental details**

**Chemicals.** 3-Chloropropyltrimethoxysilane, 1-methylimidazole, and graphite were purchased from J&K Scientific Ltd. (Beijing) and used without further purification. All 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 from the natural graphite powder using the modified Hummers' method<sup>1</sup>. In a typical procedure, 12 g of graphite powder was dispersed into 50 mL of concentrated H<sub>2</sub>SO<sub>4</sub> under vigorous stir, and then 10 g of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> followed by 10 g of P<sub>2</sub>O<sub>5</sub> were added slowly to this suspension. The suspension was then retained at 80 °C for 6 h and the solid was recovered by centrifugation. After washing with water repeatedly, the pre-oxidised graphite was dried over night at  $T = 110$  °C in an oven. The pre-oxidised graphite was then added to 460 ml of concentrated H<sub>2</sub>SO<sub>4</sub> which was kept at 0 °C in

an ice bath. And then, 60 g of  $\text{KMnO}_4$  was added into this suspension slowly under vigorous stirring. After reaction at 35 °C for 2 h, 1 L of deionised water was added slowly and the temperature was kept below 50 °C during this process. After stirring for 2 h, another 3 L of deionised water followed by 50 mL of  $\text{H}_2\text{O}_2$  (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 a vacuum oven.

**Preparation of graphene oxide-ionic liquid (GO-IL) composite.** The ionic liquid precursor **3** was synthesized according to the literature<sup>2</sup>. 6 mmol of 3-chloropropyltrimethoxysilane and 6 mmol of 1-methylimidazole were mixed together with 20 ml of dried toluene firstly. The ionic liquid precursor **3** was obtained after stirring the above solution at 110 °C for 12 h. After that, the yellow-coloured ionic liquid precursor **3** was washed with diethyl ether for five times and dried at 40 °C in a vacuum oven for further use. The graphene oxide-ionic liquid (GO-IL) composite was synthesized via grafting the as-obtained ionic liquid precursor **3** with the hydroxyl group on the surface of GO. In a typical procedure, 1 mmol of ionic liquid precursor **3** was added into 10 ml of 3 mg/ml GO suspension in DMF. Then, this suspension was heated to 120 °C and kept for 24 h under vigorous stirring. The as-synthesized GO-IL was then recovered by centrifugation, washed with ethanol five times, and dried at 80 °C for further use.

**Preparation of nitrogen and silica co-doped graphene nanosheets (NSi-GNS).** The nitrogen and silica co-doped graphene nanosheets (NSi-GNS) were prepared through the high-temperature annealing of GO-IL under Ar atmosphere. In a typical process, 100 mg of GO-IL was put in a quartz vessel and heated to 400 °C with a temperature elevating rate of 20 °C/min, and kept at 400 °C for 30 min under Ar atmosphere. The other NSi-GNS samples annealed at 600 °C and 800 °C were also prepared in the control experiments, using the same temperature elevating rate under Ar atmosphere (25 ml/min). These as-prepared NSi-GNSs are donated as NSi-GNS-400,

NSi-GNS-600, and NSi-GNS-800 in this work, respectively.

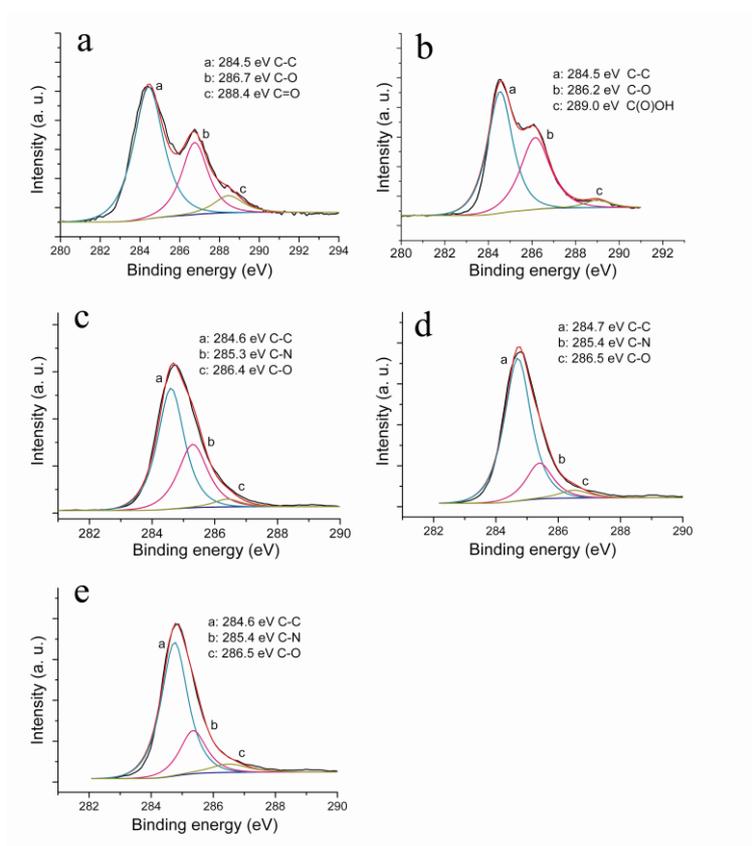
**Preparation of rGO.** For comparison, rGO was also prepared by the high-temperature annealing of GO at 400 °C under Ar atmosphere (25 ml/min).

**Characterisation.** The as-prepared NSi-GNS samples were characterised 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), Scanning Electron Microscopy (SEM, Hitachi S-4800), and Laser Raman spectroscopy (Raman, HORIBA Jobin Yvon LabRAM HR800). A CHI 660D electrochemical workstation was used to measure the resistance of the NSi-GNS layer between the Ag electrodes under air atmosphere and in NO<sub>2</sub> gas sensing process.

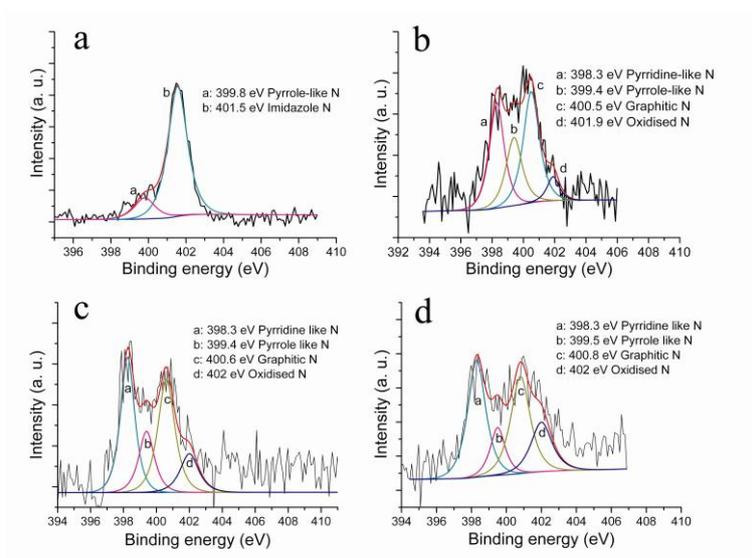
**Gas sensing test.** To measure the NO<sub>2</sub> gas sensing property of NSi-GNS samples, two parallel Ag electrodes (4 mm × 5 mm) with a distance of about 2 mm were sputtered onto a glass substrate (12 mm × 5 mm). 10 mg of NSi-GNS powder was dispersed into 0.5 ml of ethanol under ultrasonication to form slurry, and this slurry was then dropped between the two Ag electrodes on the glass substrate. A thin NSi-GNS layer between the two Ag electrodes was formed after the evaporation of ethanol. The as-prepared sensor was then introduced in an airtight chamber for the sensing test and the introduced sensor was allowed to carry out electric measurement in a controlled atmosphere. Electrical measurements were carried out at room temperature under air atmosphere and NO<sub>2</sub> with various concentrations. The sensor resistance was measured by a CHI 660D electrochemical workstation in chronoamperometry with a constant voltage of 10 V. The sensor response to NO<sub>2</sub> is defined as  $\text{Response} = (R_{\text{NO}_2} - R_{\text{Air}}) / R_{\text{Air}} \times 100\%$ , where the  $R_{\text{Air}}$  is the baseline electrical resistance of the sensor in clean Air, and, the  $R_{\text{NO}_2}$  is the resistance in NO<sub>2</sub> with different concentrations.

**Table S1.** The C, O, Cl, N and Si contents in GO, GO-IL, and NSi-GNSs calculated from the corresponding XPS spectra.

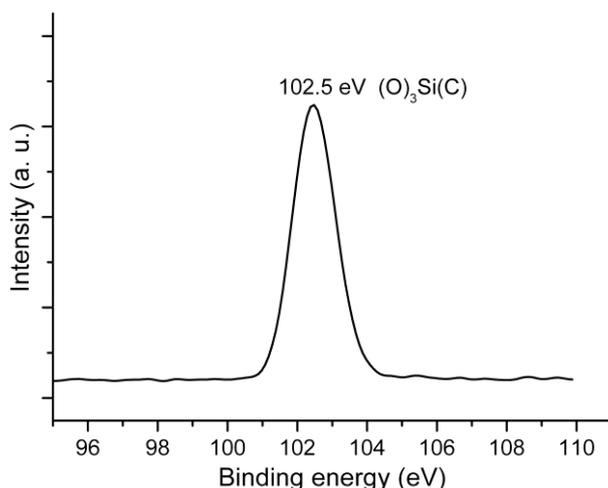
	C	O	Cl	Si	N
GO	40.88 %	59.12 %	-	-	-
GO-IL	51.43 %	21.04 %	6.70 %	10.79 %	4.45 %
NSi-GNS-400	82.55 %	9.62 %	-	5.42 %	2.40 %
NSi-GNS-600	78.58 %	12.48 %	-	6.59 %	2.35 %
NSi-GNS-800	76.74 %	13.70 %	-	7.60 %	1.97 %



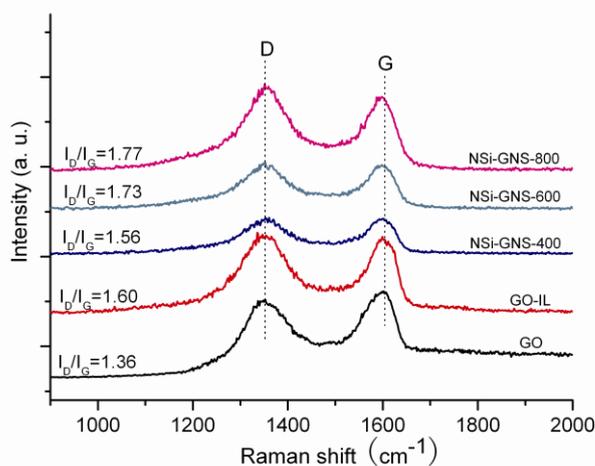
**Figure S1.** High resolution C 1s XPS spectra of (a) GO, (b) GO-IL, (c) NSi-GNS-400, (d) NSi-GNS-600, and (e) NSi-GNS-800, respectively.



**Figure S2.** High resolution N 1s XPS spectra of (a) GO-IL, (b) NSi-GNS-400, (c) NSi-GNS-600, and (d) NSi-GNS-800, respectively.

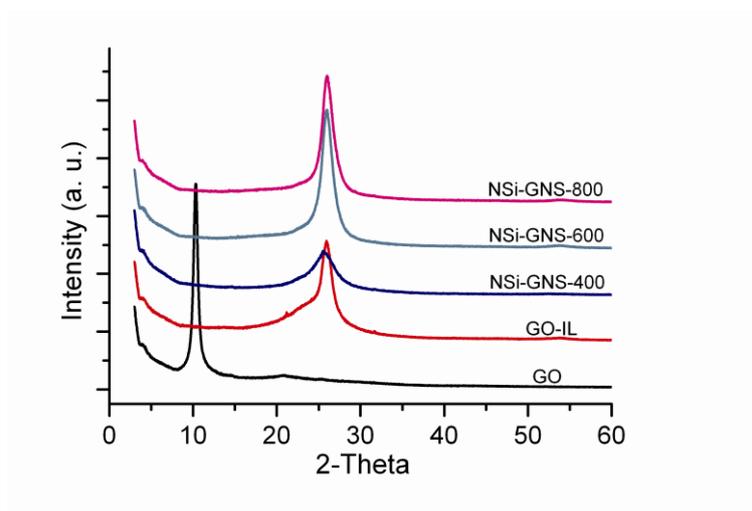


**Figure S3.** High resolution Si 2p XPS spectrum of GO-IL.

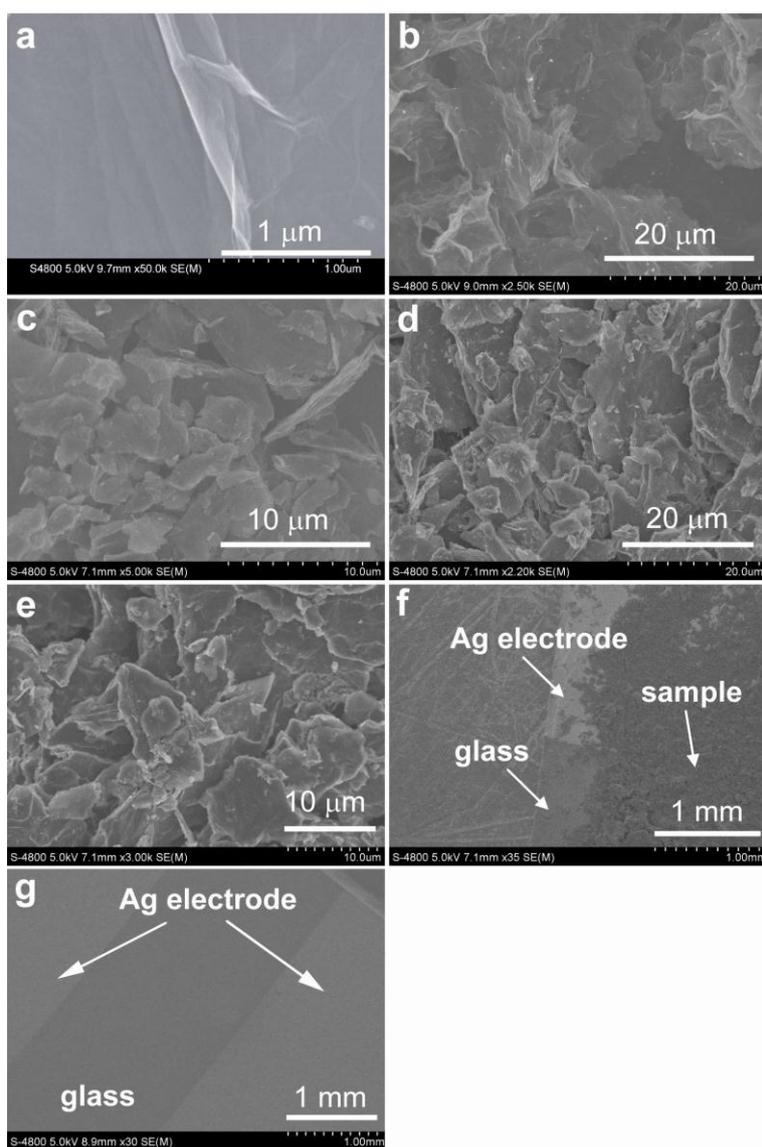


**Figure S4.** Raman spectra of GO, GO-IL, and NSi-GNSs annealed at 400 °C, 600 °C, and 800 °C. The Raman spectra of the as-prepared GO, GO-IL, and NSi-GNSs were collected at an excitation wavelength of 532 nm under ambient conditions. In the Raman spectrum of GO, the peaks at 1351 and 1601  $\text{cm}^{-1}$  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 grafting of ionic liquid precursor **3** onto GO, the D and G bands appeared at the same location while the  $I_D/I_G$  increased from 1.36 to 1.60 compared to GO. It indicated an increasing disorder of GO-IL. A red shift of G band can be seen in the NSi-GNSs' Raman spectra, which is attributed to the N-doping. In addition, the intensity ratio of  $I_D/I_G$  from NSi-GNSs

increased with the increased annealing temperature, suggesting that the incorporation of N and Si atoms into the graphene networks would result in the severe disorder.



**Figure S5.** XRD spectra of GO, GO-IL, and NSi-GNSs annealed at 400, 600, and 800 °C, respectively. A strong diffraction peak located at  $2\theta = 10.4^\circ$  and a weak and wide signal appeared at  $2\theta = 21.1^\circ$  in the XRD spectrum of GO. However, the diffraction peaks moved to  $2\theta = 26.1^\circ$  in GO-IL and NSi-GNS samples. Since the bigger  $2\theta$  refers to the narrower interlayer distance of GO, the gradually-increased  $2\theta$  value indicates that the post-treatment with ionic liquid precursor **3** and the high-temperature annealing would lead to the partial reduction of GO, and thus result in a decreased interlayer distance.



**Figure S6.** The SEM images of (a) GO on a silica substrate; (b) rGO annealed at 400 °C, and NSi-GNS samples annealed at (c) 400, (d) 600, and (e) 800 °C on the sensor electrodes. The SEM images of (f) the sensor fringe with both sample and Ag electrode exposed and (g) the bare sensor electrodes are shown.

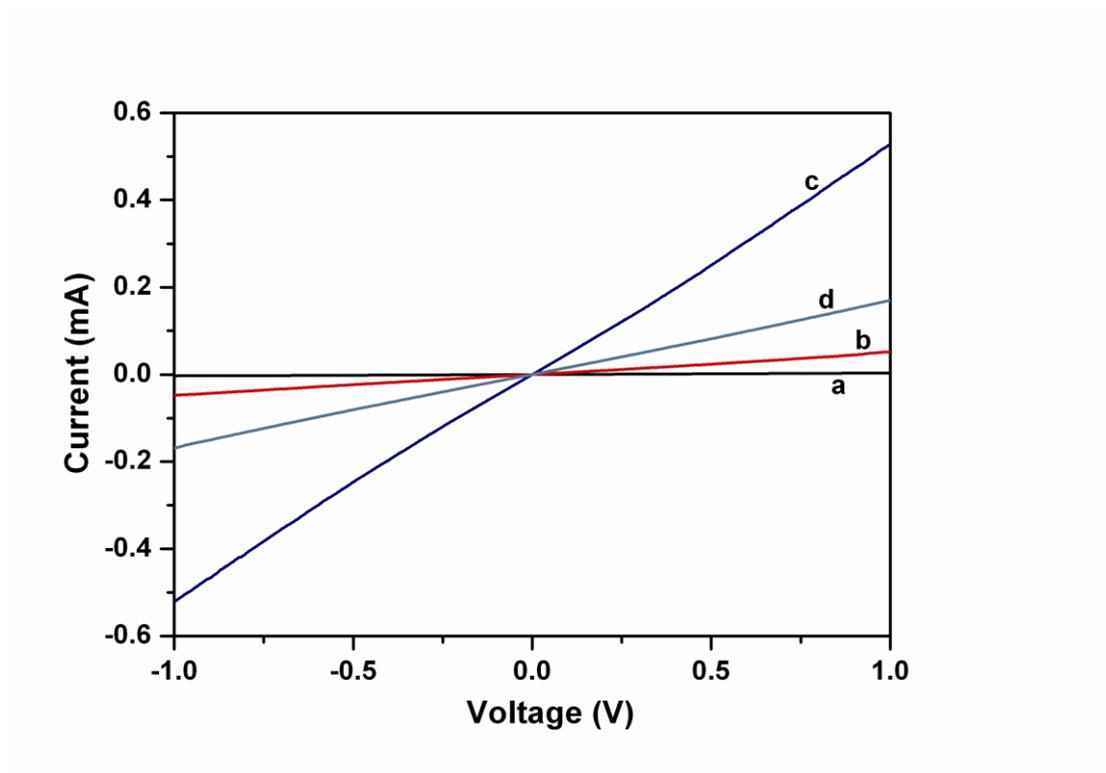
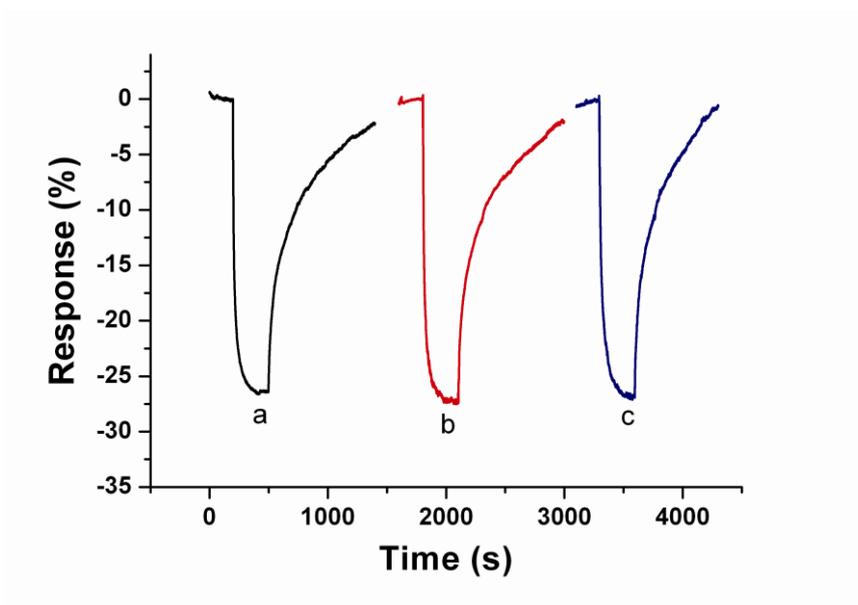
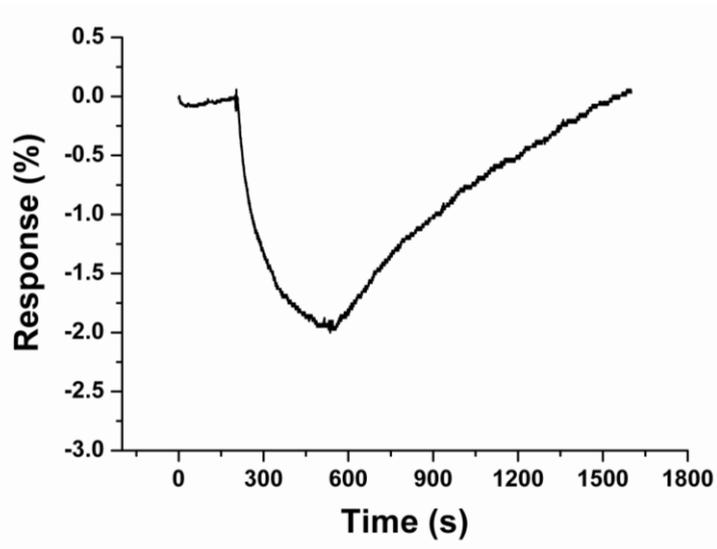


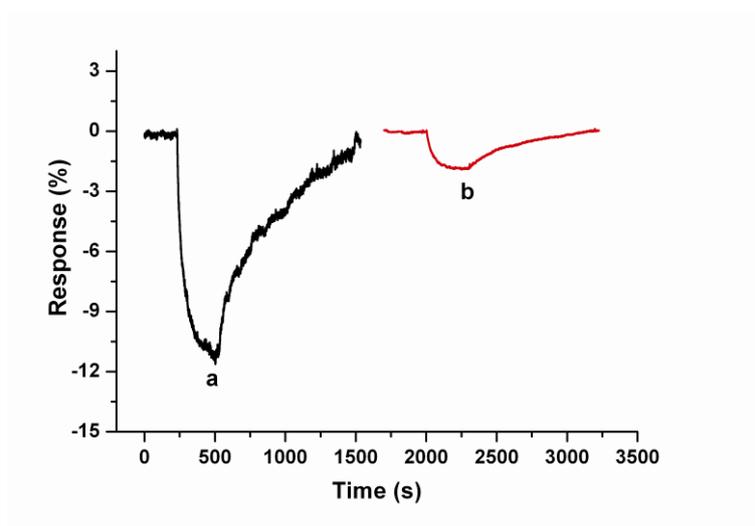
Figure S7. I-V curves of the gas sensors prepared with NSi-GNSs annealed at a) 400, b) 600, c) 800, and with rGO annealed at d) 400 °C.



**Figure S8.** The response results of NSi-GNS-400 to 21 ppm of NO<sub>2</sub> obtained from different sensors. The similar response values suggest the excellent reproducibility of the sensors.



**Figure S9.** The response of rGO to 21 ppm of NO<sub>2</sub>.



**Figure S10.** The response of (a) NSi-GNS-600 and (b) NSi-GNS-800 to 21 ppm of NO<sub>2</sub>. A response value of -11.3% and -1.88% were observed for NSi-GNS-600 and NSi-GNS-800 in 21 ppm of NO<sub>2</sub>, respectively.

## References

1. W. S. Hummers Jr. and R. E. Offeman, *Journal of American Chemical Society*, 1958, **80**, 1339-1339.
2. X. X. Zheng, S. Z. Luo, L. Zhang and J. P. Cheng, *Green Chemistry*, 2009, **11**, 455-458.