

## Supporting Information

**Title** Boron Doping and Defect-Engineering of Graphene Aerogels for Ultrasensitive NO<sub>2</sub> Detection

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*Characterizations:* Transmission electron microscopy (TEM) is performed on a JEOL 2010 microscope. Samples are prepared by sonicating aerogels in water or isopropanol and drop-casting onto a lacey carbon TEM grid. Raman spectroscopy is performed on a Renishaw inVia spectrometer with 514nm excitation laser. An FEI Sirion microscope with 5V accelerating voltage is used for scanning electron microscopy (SEM). X-ray diffraction (XRD) is taken on a Bruker AXS d8 Discover GADDS X-Ray diffractometer with CoKa (1.79Å) source. Textural properties are determined by Brunauer Emmett Teller (BET) and Barrett Joyner Halenda (BJH) methods using an ASAP 2020 surface area analyzer (Micromeritics Instrument Corp.) via nitrogen porosimetry. X-ray photoelectron spectroscopy (XPS) was performed on a PHI Quantum 2000 system using a focused monochromatic Al Ka x-ray (1486.7 eV) source for excitation and a spherical section analyzer. The instrument has a 16-element multichannel detection system. A 200 μm diameter x-ray beam was used for analysis. The x-ray beam is incident normal to the sample and the x-ray detector is at 45° away from the normal. The pass

energy was 23.5 eV giving an energy resolution of 0.3 eV that when combined with the 0.85 eV full width at half maximum (FWHM) Al Ka line width gives a resolvable XPS peak width of 1.2 eV FWHM. Deconvolution of non-resolved peaks was accomplished using Avantage software curve fitting routines using a smart background. XPS compositional analysis was accomplished by measuring the integrated XPS peak area and dividing by the respective atomic sensitivity factor and thus obtaining the atomic percent concentration with an accuracy of  $\pm 0.3\%$ . X-ray absorption spectroscopy (XAS) measurements were performed on the Resonant Elastic and Inelastic X-ray Scattering (REIXS, 10 ID-2) beamline at the Canadian Light Source. Electron yield and fluorescence yield measurements were performed at the B, C, and N k-edges; spectra were normalized to an I0 gathered from an upstream drain current. A background has been subtracted from the spectra by fitting to the pre-edge, and the spectrum scaled to an edge step of unity. Data presented here is the average of three spectra.

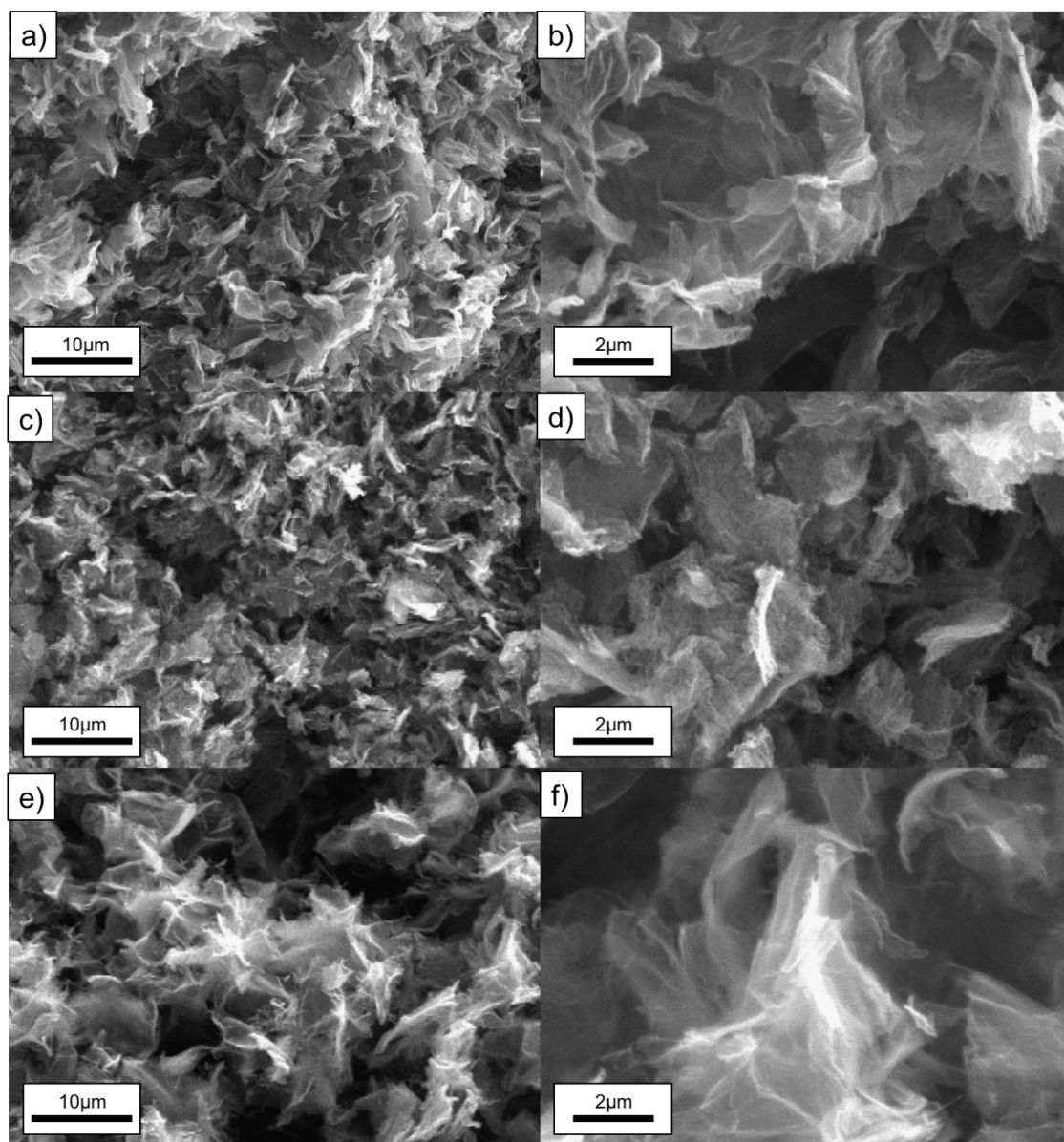
The sensing performance of the devices are quantified in terms of percentage response, response time, percentage recovery and recovery time. Percentage response is defined by the percentile resistance change when the sensor is exposed to an analyte gas as follows:

$$Response = \frac{|R_0 - R_g|}{R_0} \times 100\% \quad (1)$$

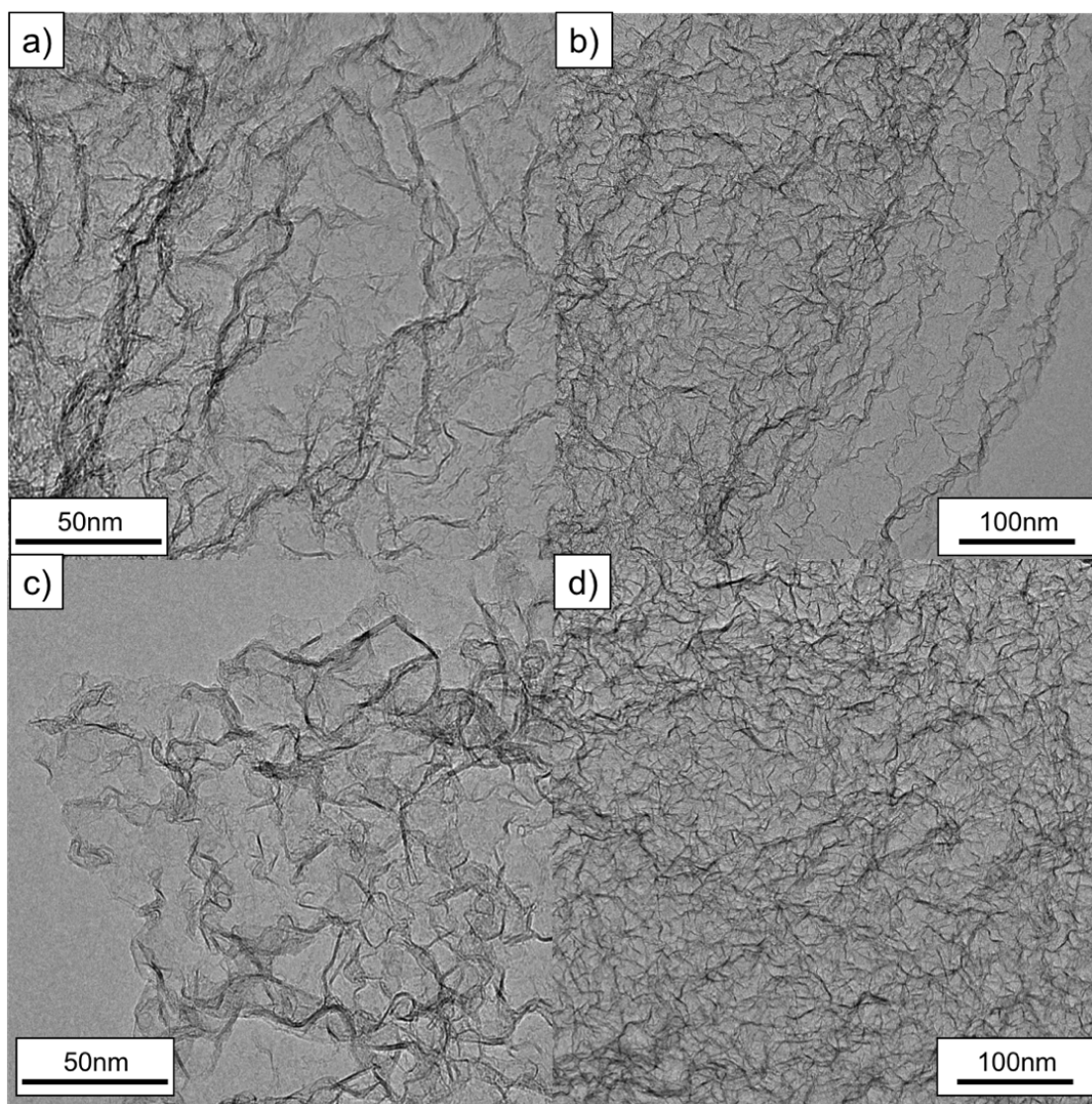
where  $R_0$  and  $R_g$  are the resistances of the sensor before and after exposure to the analyte gas, respectively. Percentage recovery is evaluated as follows:

$$Recovery = \frac{|R_a - R_g|}{|R_0 - R_g|} \times 100\% \quad (2)$$

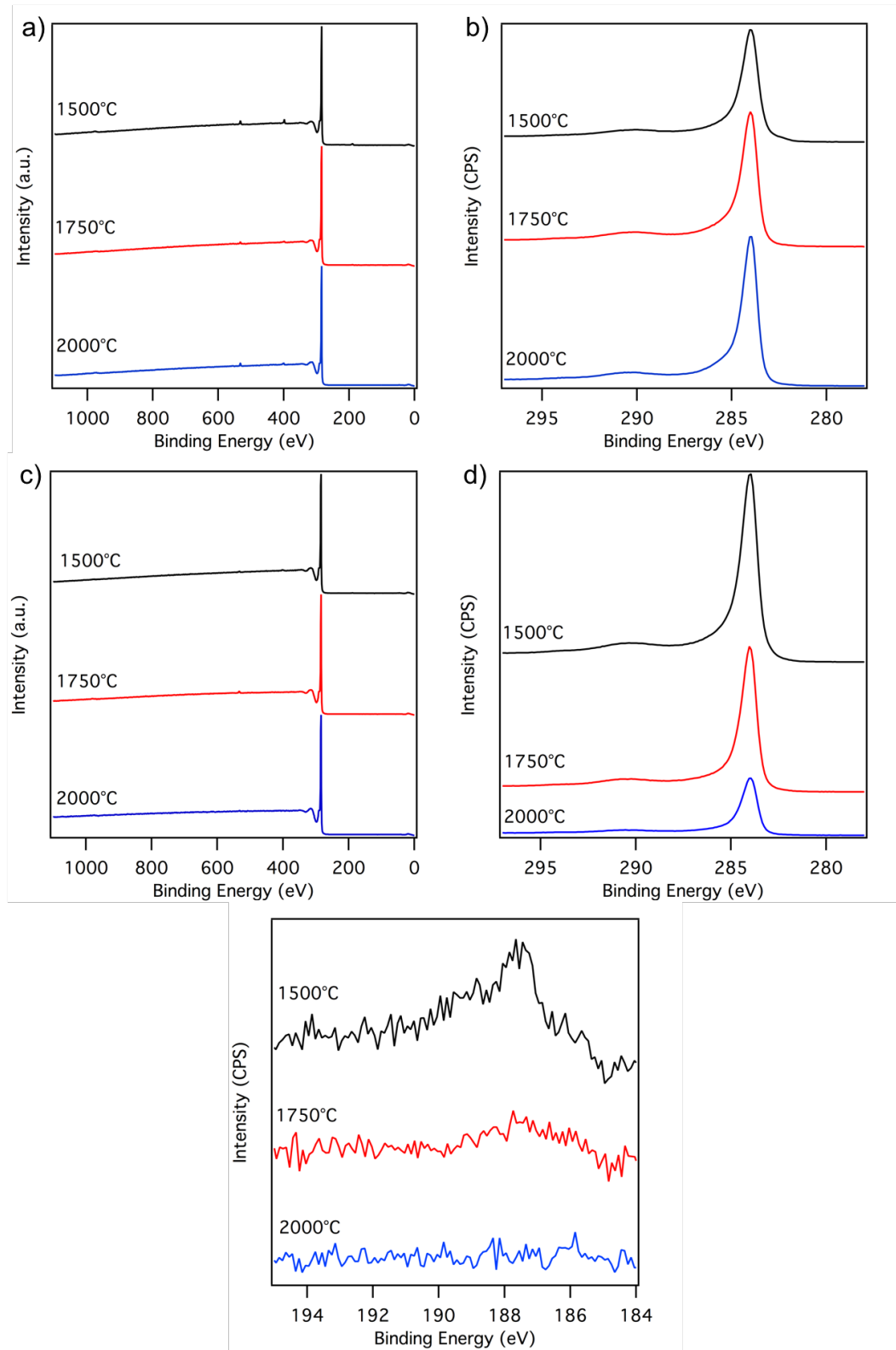
where  $R_a$  is the resistance of the sensor exposed to air for a given recovery time. The response time ( $t_{response}$ ) is defined as the time taken to reach 90% of the full response after the introduction of the target gas. The recovery time ( $t_{recovery}$ ) is defined as the time taken to return to 90% of the baseline resistance after the flow of target gas is stopped.



**Figure S1** SEM images of BPh<sub>3</sub>-GA's heated at 1500°C (a,b), and 1750°C (c,d), and precursor control GA (e,f).



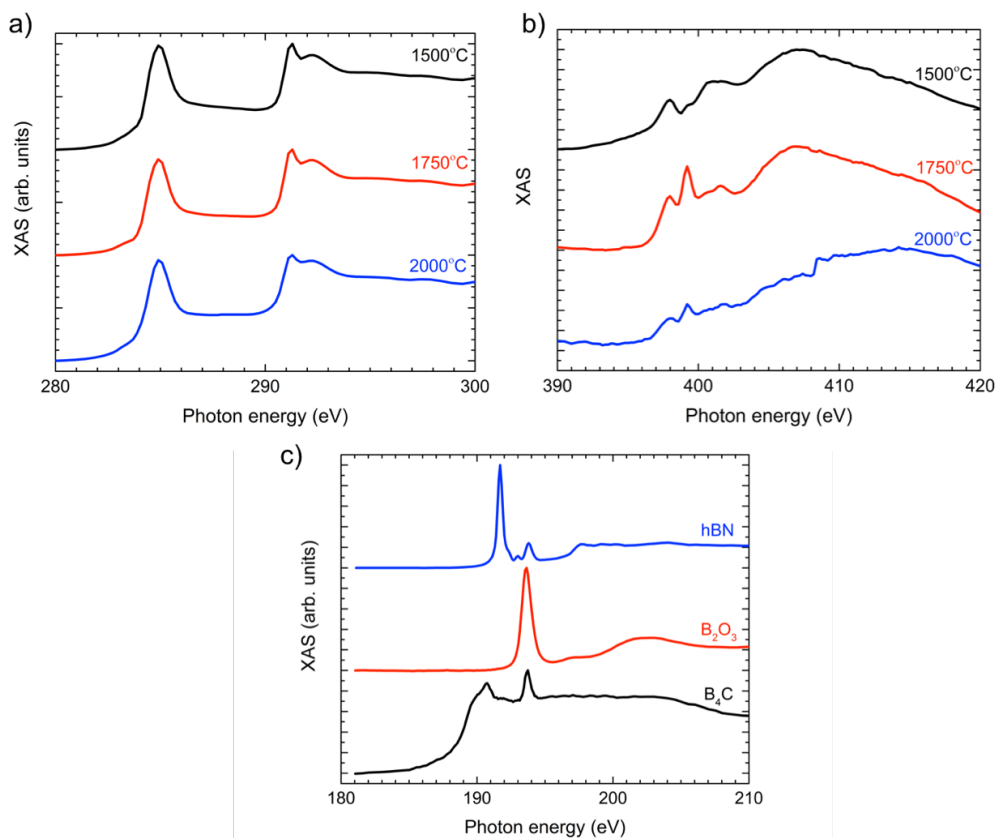
**Figure S2** TEM images of BPh<sub>3</sub>-GA's heated at 1500°C (a,b), and 1750°C (c,d), respectively.



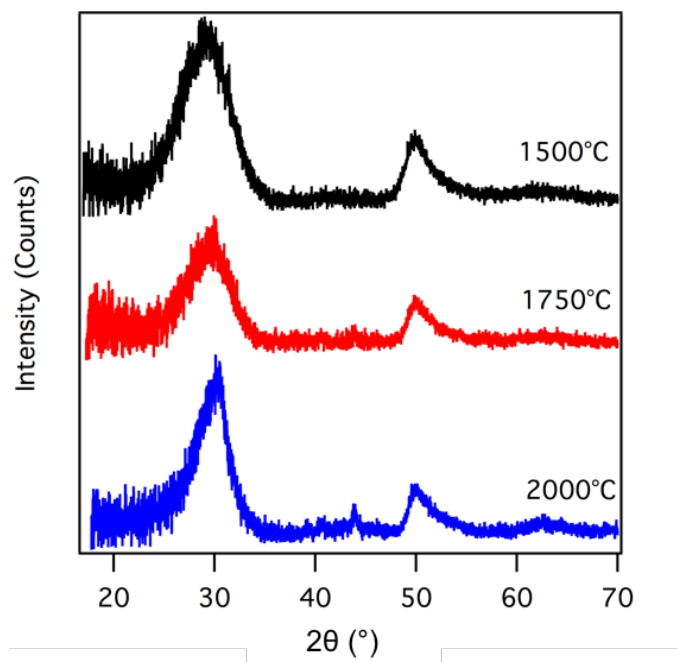
**Figure S3** (a,c) Survey Spectra and (b,d) C1s spectra of BPh<sub>3</sub>-GA samples and control GA samples, respectively. (e) B1s spectra of control GA samples.

Bonding Abundance (%)			
Bond Type	1500°C	1750°C	2000°C
B-C <sub>3</sub>	22.6	11.8	N/A
B-N <sub>3</sub>	33.0	52.9	N/A
BC <sub>2</sub> N/BN <sub>2</sub> C	24.5	11.3	N/A
BC <sub>2</sub> O	11.7	10.8	N/A
B <sub>2</sub> O <sub>3</sub>	6.3	4.8	N/A
B-B	1.8	8.4	N/A

**Table S1** Summary of B1s XPS deconvolutions of BPh<sub>3</sub>-GA samples heated to 1500, 1750 and 2000°C .



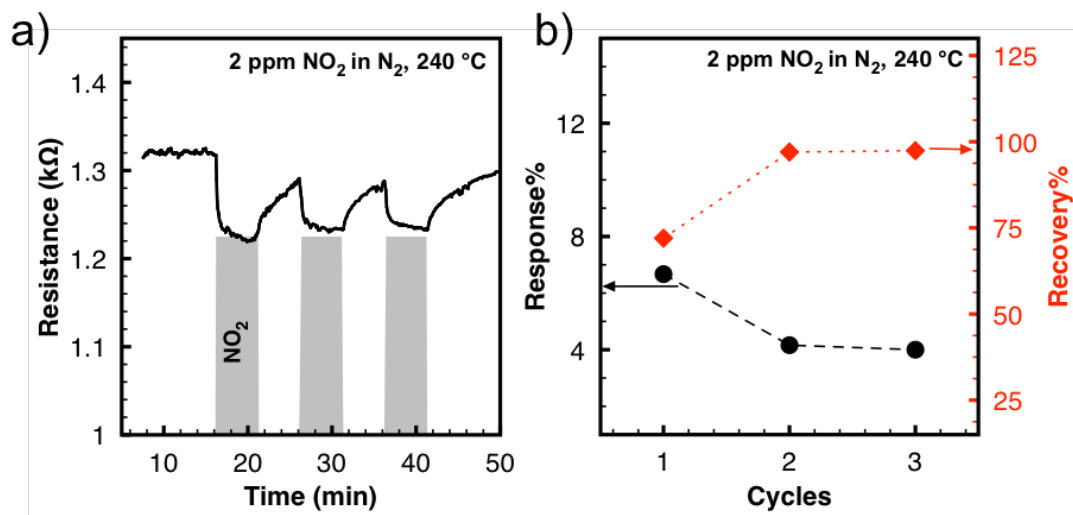
**Figure S4** (a) Carbon and (b) Nitrogen XAS spectra of BPh<sub>3</sub>-GA's fired at 1500°C, 1750°C, and 2000°C (c) Boron XAS spectra of h-BN, B<sub>2</sub>O<sub>3</sub> and B<sub>4</sub>C standards.



**Figure S5** X-Ray Diffractograms of BPh<sub>3</sub>-GA fired at 1500°C, 1750°C, and 2000°C.

Annealing Temperature (°C)	Sensitivity 2 ppm NO <sub>2</sub> (%)	Detection Limit to NO <sub>2</sub> (ppm)
<b>Control</b>	2.6	0.5
<b>1500</b>	2.6	0.05
<b>1750</b>	4.8	0.5
<b>2000</b>	<b>8.0</b>	<b>0.05</b>

**Table S2** Comparison of sensitivity and detection limit of control graphene aerogel and BPh<sub>3</sub>-GA's fired at increasing temperatures.



**Figure S6** (a) The reproducible resistance change of the BPh<sub>3</sub>-GA fired at 2000 °C sensor (b) the response % and recovery % changes during 3 cyclic exposures to 2 ppm NO<sub>2</sub> in N<sub>2</sub> at 240 °C.