### **Electronic supplementary information**

# "Protrusions" or "holes" in graphene: which is better choice for sodium ion storage? †

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† Dedicated to Prof. Yoshio Bando on the occasion of his 70th birthday.

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### **Experimental Procedures**

#### Synthesis of phosphorus-doped graphene (GP).

In the first step, Graphene oxide (GO) was obtained from a graphite powder by using a modified Hummers method.<sup>[1]</sup> And then GP was prepared by thermal annealing of GO and 1,2-Bis(diphenylphosphino)methane (BPM). Namely, 50 mg of GO and 250 mg of BPM were mixed into 80 mL of ethanol solution at room temperature under stirring, followed by drying at 60 °C overnight in a vacuum oven. As-made GO/BPM mixture was then annealed in a tube furnace with argon as a protective gas at 800-900 °C for 1.5 h under a flow rate of 150 mL/min.

#### Synthesis of nitrogen-doped graphene (GN).

In the first step, Graphene oxide (GO) was obtained from a graphite powder by using a modified Hummers method.<sup>[1]</sup> And then 50 mg of the pristine graphene oxide was loaded in a ceramic boat in a SiC tube furnace followed by heat treatment of at 600 °C for 1.5 h in a gas mixture of NH<sub>3</sub> (~99.0%) and Ar (1:2 v/v) with a total flow rate of 150 mL/min.

#### Characterization.

JEOL 3000F and 2100F microscopes were used to analyze the final product morphologies, while a Hitachi S4800 electron microscope operating at 15 kV was utilized to take scanning electron microscopy (SEM) images. In order to record the XRD patterns, a Philips X Pert PRO MPD Xray diffractometer operated at 35 kV and 45 mA under Cu K $\alpha$  radiation was used. XPS measurements were carried out on an ESCALab220i-XL spectrometer by using a twin-anode Al Ka (1486.6 eV) X-ray source. All the spectra were calibrated to the binding energy of the C 1s peak at 284.6 eV. The background pressure was ~3×10<sup>-7</sup> Pa. Raman spectra were taken on a Horiba Jobin-Yoon T6400 Raman spectrometer with an excitation laser wavelength of 514.5 nm.

#### Electrochemical tests.

The electrochemical properties of samples were studied on a Hokudo Denko Charge/Discharge instrument by using a 2032-type coin cell. Na metal foil was selected as the reference and counter electrode. The electrolyte was 1 M NaPF<sub>6</sub> in ethyl carbonate (EC) and diethyl carbonate (DEC) (EC : DEC = 1 : 1 in v/v). 15 wt % AB was used as a conductive agent and 5 wt % PVDF as a binder. A Cu foil was used as current collector. The cells were assembled in a glove box filled with pure argon gas. Galvanostatic discharge/charge measurements were performed in a potential range of 3 V-50 mV vs Na<sup>+</sup>/Na.

#### Construction of GP and GN nanosheet-based SIBs.

*In situ* transmission electron microscopy (TEM) observations were conducted in a JEOL-3100 FEF equipped with an Omega filter and a "Nanofactory Instruments AB" scanning tunneling microscopy (STM)-TEM holder. In order to build up a test cell, individual GP or GN nanosheets

were attached to the gold wire, which was further attached to the piezo-manipulator. A small piece of sodium foil was also attached to another gold wire as a reference and counter electrode. Before insertion of the holder into the TEM, a piece of sodium foil naturally covered with a  $Na_xO$  layer was placed on the surface of metal gold tip. Isolated GP or GN were then chosen. The sodiation was carried out at a negative bias in the range of -3 V to 0 V with respect to the Na metal.

#### **DFT calculations.**

The DFT calculations were performed on the MagicCubic of Shanghai Supercomputer Center. The first principles calculations were carried out with the Vienna *ab initio* simulation package (VASP),<sup>[2]</sup> where projected-augmented-wave (PAW) potential was adopted.<sup>[3, 4]</sup> The functional of Perdew, Burke, and Ernzerhof (PBE) and the generalized gradient approximation (GGA)<sup>[5]</sup> were employed in the calculations. We use a  $3\times3\times1$  mesh in the irreducible Brillouin Zone for structure relaxation and  $6\times6\times1$  mesh for self-consisted calculations. In all the calculations the energy cutoff was set as 400 eV. The forces were relaxed lower than 0.02 eV/Å.

## **Results and Discussion**

Pnictogen	d (PN-C) (Å)	d (out of plane) (Å)	charge transfer (e)
N2 (pyrrolic)	1.40	-	1.06
N3 (pyridinc)	1.40	-	1.05
Р	1.76	1.54	2.39
As	1.90	1.88	1.07
Sb	2.10	2.31	2.02
Bi	2.20	2.48	1.99

**Table S1.** Geometric Parameters of Pnictogen doped Graphene.<sup>[6]</sup>

<b>Table S2.</b> Energies of Formation of Each Pnictogen doped Graphene Structures. <sup>16</sup>
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Formation				Pnic	tongen		
Energies	N2	N3	Р	As	Sb	Bi	Monovacancy
$E_{f}(eV)$	0.95	0.86	2.95	4.06	5.38	6.15	7.66



Figure S1. Schematic illustrations of pictogen doped graphene ( $C_{48}N$ ,  $C_{49}P$ ,  $C_{49}As$ ,  $C_{49}Sb$ ,  $C_{49}Bi$ ) and their corresponding PDOS, respectively.



Figure S2. (a) The HAADF-STEM image and (b) the corresponding P-elemental map of a GP nanosheet.



**Figure S3.** (a) Schematic illustration of three N-doping configurations in GN. N1, N2 and N3 represent graphitic N, pyrrolic N, and pyridinic N, respectively. (b-d) HAADF-STEM image and the corresponding C- and N-elemental maps of a GN nanosheet.



**Figure S4.** Galvanostatic charge/discharge profile of a GP anode during the 1<sup>st</sup> cycle.



Figure S5. HRTEM image of a GP nanosheet at the sodiation state after cycling.



**Figure S6.** a) HRTEM image of the used onion-like acetylene black (AB) carbon sphere after 1<sup>st</sup> discharging in SIBs. b) Contrast profiles along the red line indicate interlayer spacing of the sample.



**Figure S7.** *In situ* TEM observation of the electrochemical process within an individual GN nanosheet-based sodium battery. a) Low-magnification TEM image of a built-in individual nano-SIBs GN nanosheet device in the microscope. b) Schematic illustration of the *in situ* TEM electrochemical experimental setup, consisting of a GN nanosheet, Au rod, and Na metal covered with a Na<sub>2</sub>O layer. A negative bias is applied to the GN terminal to initiate sodiation. c) Schematic illustration and HRTEM images of the GN edge structural evolution during the sodiation process. d) Schematic illustration and HRTEM images of surface structural evolution of GN during the discharging process.



**Figure S8.** Calculated one-Na-insertion-GP structures based on DFT. GP nanosheet with one C atom substituted by P is doped with one Na.



**Figure S9.** Calculated one-Na-insertion-GN structures in four N-doped systems based on DFT. GNs with three/four C atoms substituted by N are doped with one Na.



Figure S10. Illustration of the one-Na-atom-insertion process for two dominant N-doping configurations in GN, namely  ${}^{a}C_{46}N_{3}$  (pyridinic N) and  ${}^{b}C_{46}N_{3}$  (pyrrolic N).



**Figure S11.** a) Calculated potential curves of the GP configurations based on DFT. In the  $C_{47}P_3$  system, 19 Na atoms can be inserted during sodiation; b) Calculated Na chemical potential profiles of Na atoms for the dominant doping forms in the GN systems:  ${}^{a}C_{46}N_3$  (pyridinic N) and  ${}^{b}C_{46}N_3$  (pyrrolic N).



**Figure S12.** Theoretical sodiation capacities and storage mechanisms of bilayer GP. (a) Illustration of the Na atoms adsorption and insertion process for a dominant P-doping form in GP:  $C_{94}P_6$ ; (b-c) electronic structure of: pristine  $C_{94}P_6$  and  $C_{94}P_6Na$ , respectively

#### References

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