Supplementary data

Ternary Heteroatom (B, P, N) Co-doped Graphene for High-Performance Supercapacitors

Amanpreet Kaur, O.P. Pandey and Loveleen K. Brar*

Department of Physics and Material Science, Thapar Institute of Engineering and Technology, Patiala, Punjab, India, 147004

*Corresponding author- Dr. Loveleen Kaur Brar

Email- brarloveleen@thapar.edu

Phone: +91-9417991799

1st Author: Amanpreet Kaur

Email- amanpreetk199595@gmail.com

Co Author: Dr. O.P. Pandey

Email- oppandey@thapar.edu

S1. GO

S1.1 Synthesis

Graphene oxide (***GO***) was prepared from graphite powder using a two-step, slight modified Hummers method [1]. In the first step, for the preoxidation of graphite, the required amount of graphite powder along with equal amounts of P_2O_5 and $K_2S_2O_8$ were dispersed in concentrated H_2SO_4. This was followed by stirring for 4.5 hours at 80 °C. After adding DI water (320 ml), the product was washed and dried at 80 ºC. In the second step, pre-oxidized graphite powder was added to concentrated H_2SO_4 (80 ml), and $KMnO_4$ (10 g) was added slowly while stirring for 2.5 hours. Then, DI water was added and the mixture was stirred further for 2 hours. Finally, diluted H_2O_2 was added, followed by washing with HCl (10%) and DI water. The end product was dried at 80 ºC.

S1.2 Structural Characterization *GO*

Synthesized ***GO*** was characterized by XRD, SEM and XPS techniques to confirm its formation from graphite. The XRD patterns of synthesized ***GO*** is depicted in Fig. S1(a). The characteristic peak of ***GO*** at $2\theta = 10.9^{o}$ indicated the (001) crystalline plane, signifying the successful preparation of ***GO*** from graphite [2]. Scherrer's equation was used to determine the thickness of 4-5 layers in the synthesized ***GO*** samples from this peak. The peaks appearing at $2\theta = 42.7^{o}$ and $2\theta = 78.07^{o}$ were attributed to the

(10) and (110) planes and indicated multi-layered ***GO*** [1,3]. The structural morphology of ***GO*** studied by SEM is shown in Fig. S1(b) showed agglomerated sheets indicating strong van der Waals interactions. The atomic concentration of C and O for ***GO*** from XPS is displayed in Table 1. Fig. S1(c) and S1(d) show deconvoluted C1s and O1s high-resolution spectra of ***GO***. The presence of C-O, C=O and O-C=O bonds also confirmed the formation of ***GO*** from graphite.

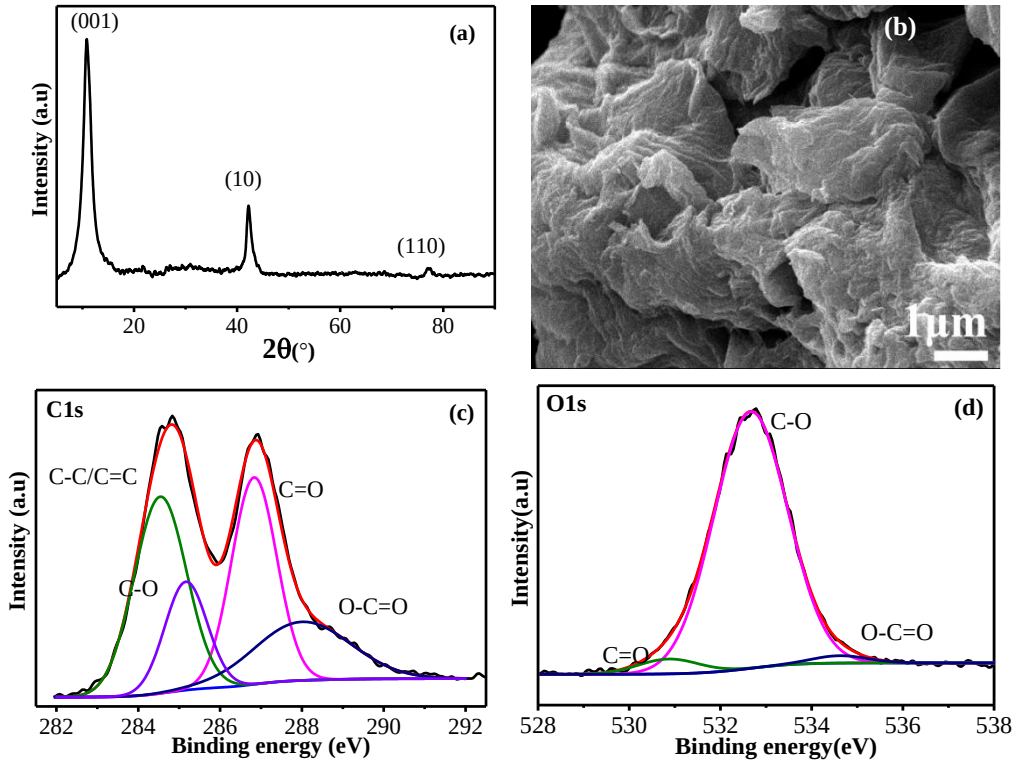

Fig. S1. (a) XRD (b) SEM image (c) High resolution spectra of C1s and (d) O1s obtained from XPS of synthesized ***GO***.

S2. Electrode formation

S2.1 Supercapacitor measurements

Working electrode fabrication on GCE : Synthesized sample (1mg) was mixed in 250 µl of ethanol followed by 10-minute ultrasonication. Addition of 40 µl of Nafion®117 (Sigma Aldrich) was done followed by 30-minute ultrasonication. 20 µl of the dispersed solution was drop cast on a GCE with 0.07065 cm^2 cross-section area and dried overnight.

Working electrode fabrication on Graphite felt: 1×1 cm^2 graphite felt was cleaned with acetone, ethanol solution and DI water, followed by ultrasonication, respectively. After drying, 4 mg of synthesized sample mixed with 500 µl ethanol with addition of 20 µl of Nafion®117 followed by ultrasonication was poured on both sides of graphite felt. Finally modified graphite felt was dried at 90º C in oven.

Fabrication of symmetric and asymmetric cell

To fabricate symmetric supercapacitor cells, CR2032-type stainless steel (304 grade) coin cells were utilized, sourced from Beyond Battery, ANR Technologies, Singapore. The coin cell assembly comprises key components including a cathode cap, spacer, spring, and anode cap. For device fabrication, the active material coated onto a graphite felt current collector was employed as the working electrode.

Graphite felt electrodes with a circular area of 7.065 cm^2 were fabricated following the procedure described in Section (*Working electrode fabrication on Graphite felt*). For the symmetric configuration (***BPNG2//BPNG2***), both electrodes were made from the same ***BPNG2*** material. A Whatman filter paper (Grade 1), pre-soaked in 1 M H_2SO_4, functioned as the separator between the two electrodes. The coin cell components were assembled with the graphite felt -based electrodes and the electrolyte-saturated separator placed in proper alignment. The final assembly was sealed using a hydraulic press under a pressure of approximately 15 $kg \cdot cm^{-2}$ to ensure reliable contact and mechanical integrity.

The cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS) techniques were employed to evaluate the supercapacitive behavior of the assembled symmetric and asymmetric coin cells. The specific capacitance (C, in F/g) was determined from the GCD profiles using the following equation:

$$E = \frac{C\ X\ \Delta V^2}{2} \qquad \text{S1}$$

and

$$P = \frac{E}{\Delta t} \qquad \text{S2}$$

Where C is the specific capacitance calculated from GCD curves, ΔV is the potential window and Δt (h) is the discharge time.

S3. FESEM

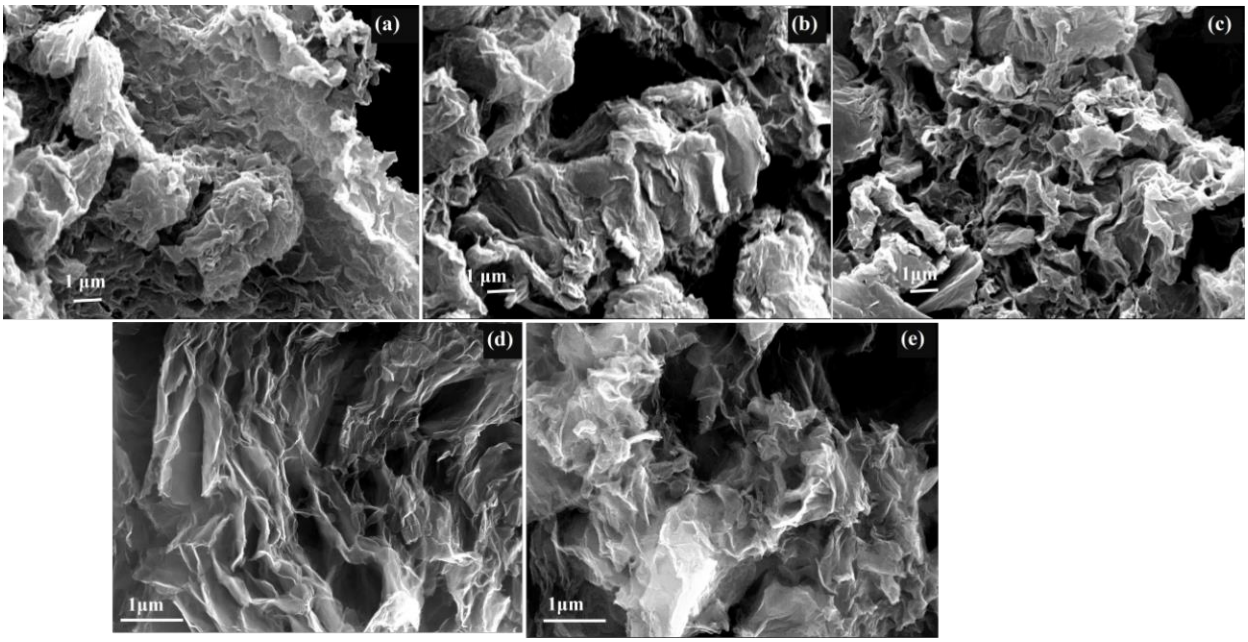

Fig. S2. SEM images of (a) ***BG***, (b) **NG**, (c) ***PG*** and FESEM images of (d) ***BNG***, and (e) ***BPG*** samples **.**

S4. XPS

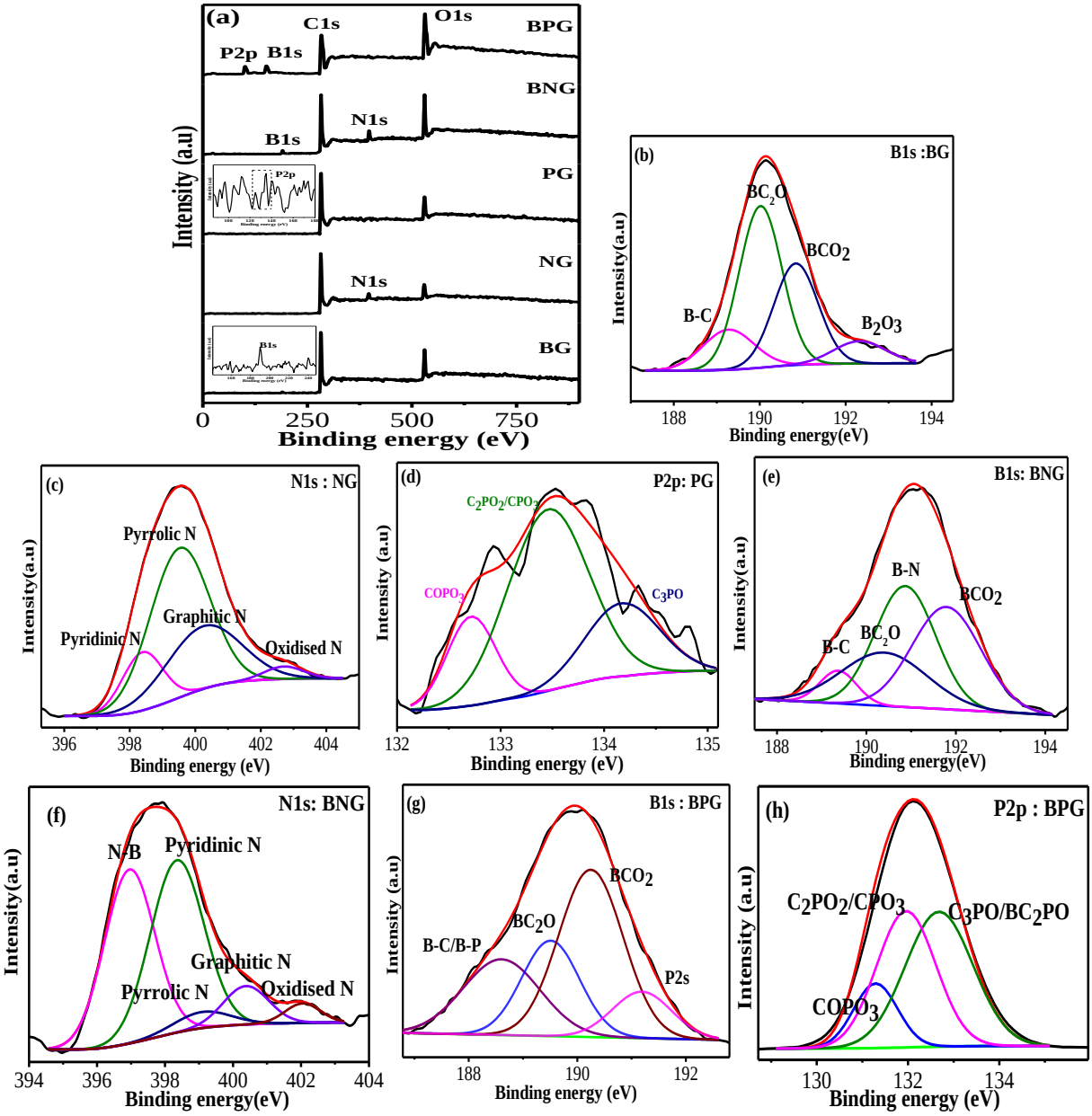

Fig. S3. (a) Survey spectra, (b-h)High resolution spectra for ***BG, NG, PG, BNG***, and ***BPG*** samples.

Table S1. XPS parameters obtained from deconvoluted high resolution spectra's of B1s, NIs and P2p for synthesized ***BG, NG, PG***, ***BNG***, and ***BPG*** samples.

	Gp.	BG(%)	PG(%)	NG(%)	BNG(%)	BPG(%)
B1s	B-C	12.89	-	-	6.00	-
	B-C/B-P	26.79	-	-	-	23.48
	BC_2O	55.49	-	-	22.68	22.17
	B-N		-	-	36.32	-
	BCO_2		-	-	34.99	43.33
	B_2O_3	4.83	-	-	-	-
N1s	N-B	-	-	-	41.00	-
	Pyridinic N	-	-	14.31	43.30	-
	Pyrrolic N	-	-	54.29	4.20	-
	Graphitic N	-	-	28.44	8.10	-
	Oxidized N	-	-	2.95	3.20	-
P2p	$COPO_3$	-	17.09	-	-	26.29
	CPO_3/C_2PO_2	-	60.96	-	-	58.32
	C_3PO	-	21.93	-	-	--
	C_3PO/BC_2PO	-		-	-	15.40

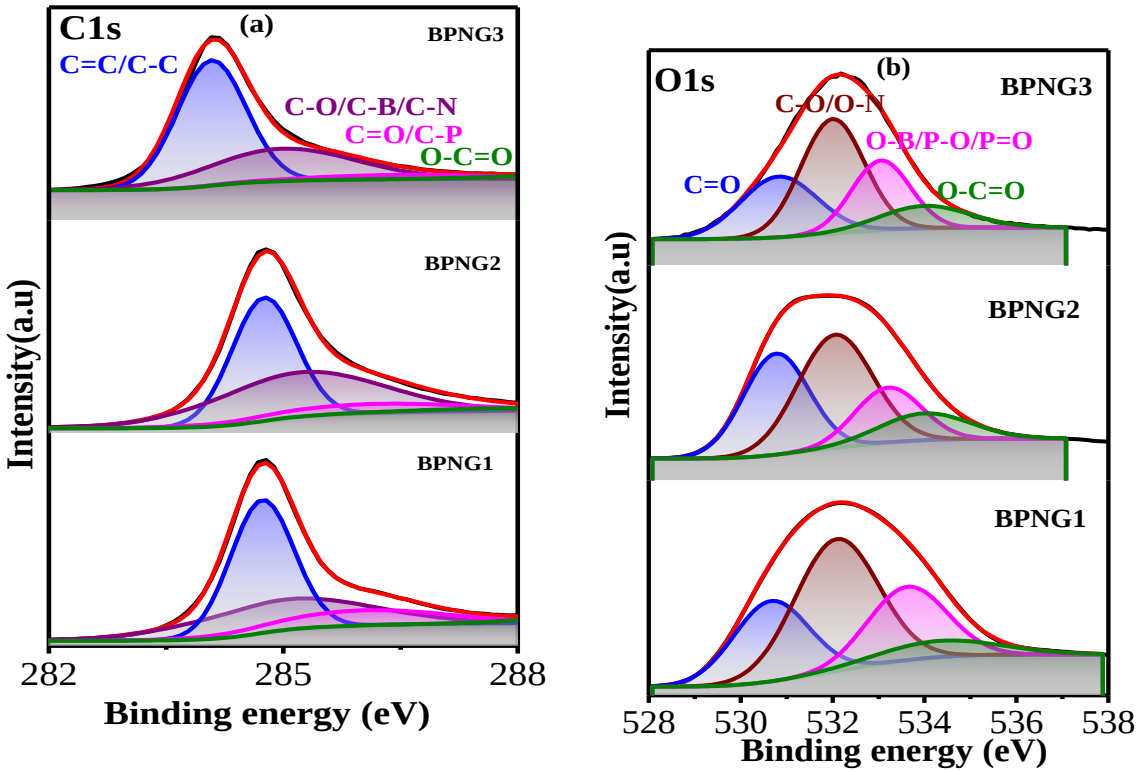

Fig. S4. High resolution spectra of (a) C1s and (b) O1s for ***BPNGn (n=1-3)*** samples.

Table S2. XPS parameters obtained from deconvoluted high resolution spectra's of C1s and O1s for synthesized ***BPNGn*** samples.

C1s	**BPNG1**	**BPNG2**	**BPNG3**	**O1s**	**BPNG1**	**BPNG2**	**BPNG3**
C-C/C=C	31.73	44.98	60.21	C=O	24.48	31.37	25.96
C-B/C-O/C-N	50.43	42.06	32.53	C-O/O-N	44.21	39.89	40.31
C=O/C-P	15.36	10.13	5.38	O-B/P-O/P=O	23.37	17.25	22.57
O=C-O	2.48	2.83	1.87	O=C-O	7.94	11.49	11.15

S5. Raman

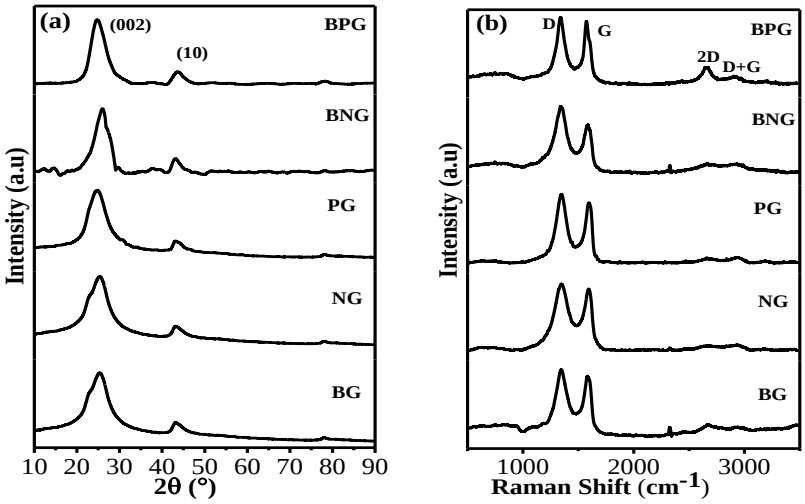

Fig. S5. (a) XRD and (b) Raman plot for ***BG, NG, PG, BNG***, and ***BPG*** samples.

S6. EIS

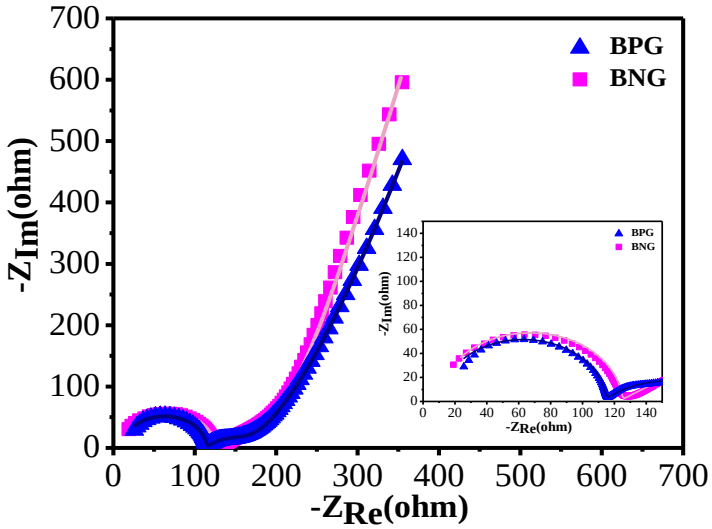

Fig. S6. EIS responses for ***BNG*** and ***BPG*** samples in 0.1 M KCl electrolytic solution containing 5 mM of $Fe(CN)_6^{3-/4}$

References

1 A. Mirmohseni, M. Azizi, M. Saeed and S. Dorraji, *Prog. Org. Coatings*, 2019, **131**, 322–332.

2 Y. Chen, L. Sun, Z. Liu, Y. Jiang and K. Zhuo, *Mater. Chem. Phys.*, 2019, **238**, 121932.

3 B. E. Warren, *Phys. Rev.*, 1941, **59**, 693–698.