Supplementary Information

Synthesis and Characterization of boron carbon oxynitride films with tunable composition using methane, boric acid and ammonia

Boitumelo J Matsoso[a,b], Kamalakannan Ranganathan[a, b], Bridget K Mutuma[a, b], Tsenolo Lerotholi[b], Glenn Jones[c,d] and Neil J Coville[a, b*]

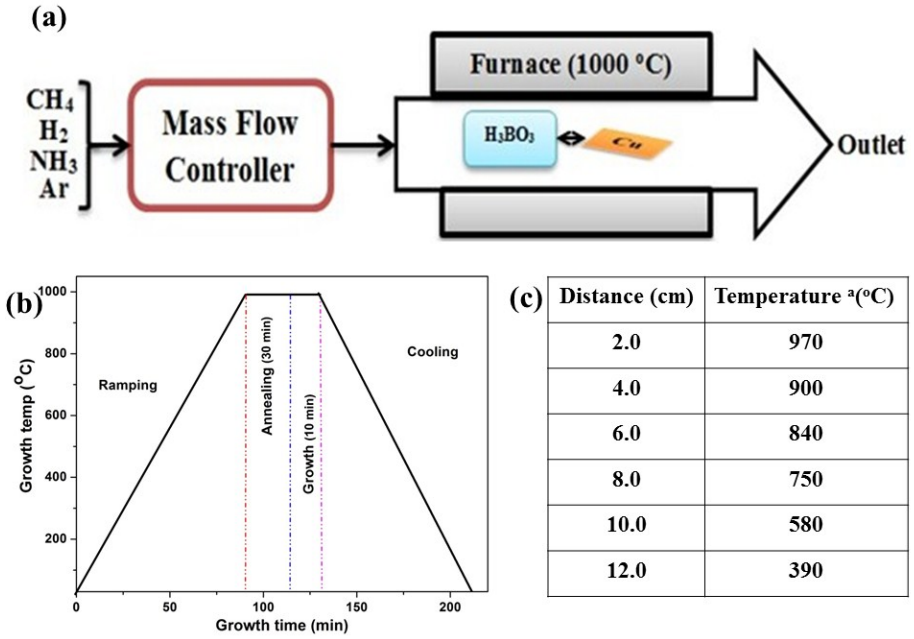
[a] DST-NRF Centre of Excellence in Strong Materials and [b] Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, 2050, Johannesburg, South Africa

[c]Department of Chemistry, University College London, Gordon Street, London, UK

[d]Johnson Matthey Technology Center, Blount's Court,, Sonning Common, Reading, RG4 9NH, UK.

Synthesis and transfer of BCNO films

Large area BCNO films were grown on a Cu substrate using an atmospheric pressure chemical vapour deposition method with CH_4, H_2, NH_3 (10% in Ar), and H_3BO_3 as precursor materials. Initially, the Cu foil was electrochemically cleaned for 90 sec in an aqueous mixture of 150 mL H_3PO_3, 150 mL ethanol, 30 mL iso-propanol and 3.0 g urea using a 12 V current[35]. The Cu foil was placed at the center of a 20 cm × 100 cm quartz tube, and a quartz boat containing 100 mg of H_3BO_3 was at placed different distances (2, 4, 6, 8, 10, and 12 cm) from the Cu substrate. H_3BO_3 placed at these distances allowed the vaporization temperature of H_3BO_3 to be varied from ~ 300^{o}C to ~ 1000 ^{o}C. The quartz tube was then inserted in a horizontal CVD furnace (Fig. S1), after which the furnace was heated to 1000 ^{o}C under H_2 and Ar atmospheres at the heating rate of 10 ^{o}C/min. After annealing for 30 min, growth of the BCNO films was achieved for 10 min by introducing 20 sccm CH_4 and 5 sccm NH_3 into the reaction chamber. For characterization purposes, the films were transferred onto a 300 nm SiO_2/Si substrate, TEM Cu grids, and fused silica substrates using the PMMA (4.6 % m/v in chlorobenzene) - assisted electrochemical delamination method[36]. The films were named according to the distance of the boric acid from the growth substrate in the reaction chamber, e.g. BCNO-2 stands for the BCNO films grown using boric acid placed at 2 cm distance from the Cu foil.



Distance (cm)	Temperature [a] (°C)
2.0	970
4.0	900
6.0	840
8.0	750
10.0	580
12.0	390

Figure S1: (a) CVD setup, (b) growth profile and (c) temperature profile for the growth of the BCNO films.

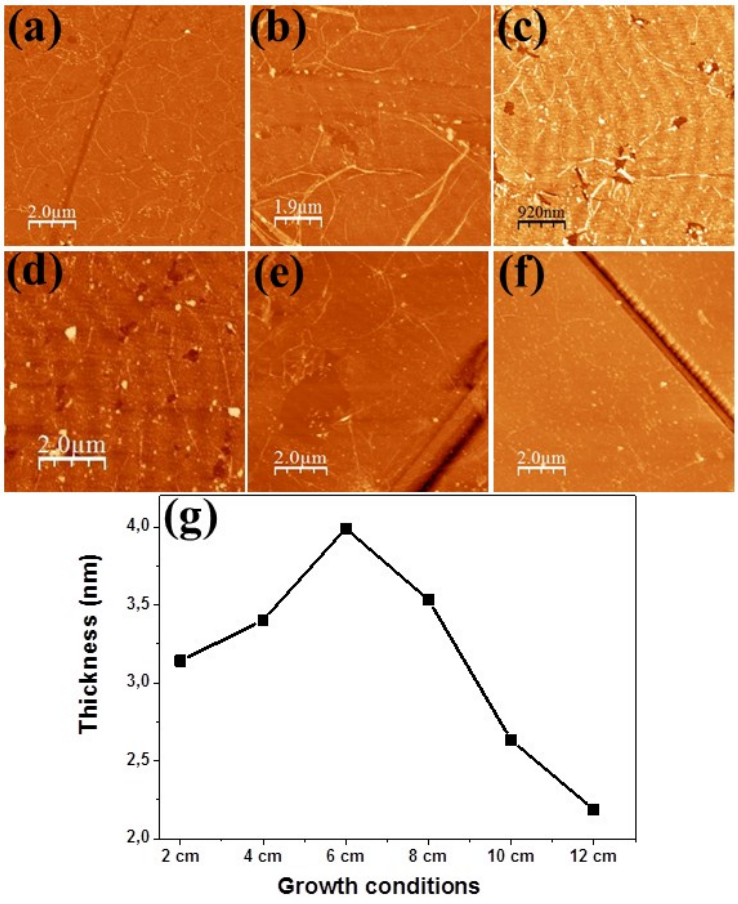


Figure S2: AFM topographic images (a – f) and estimated thickness plot (g) of BCNO films grown at 2 cm – 12 cm, respectively.

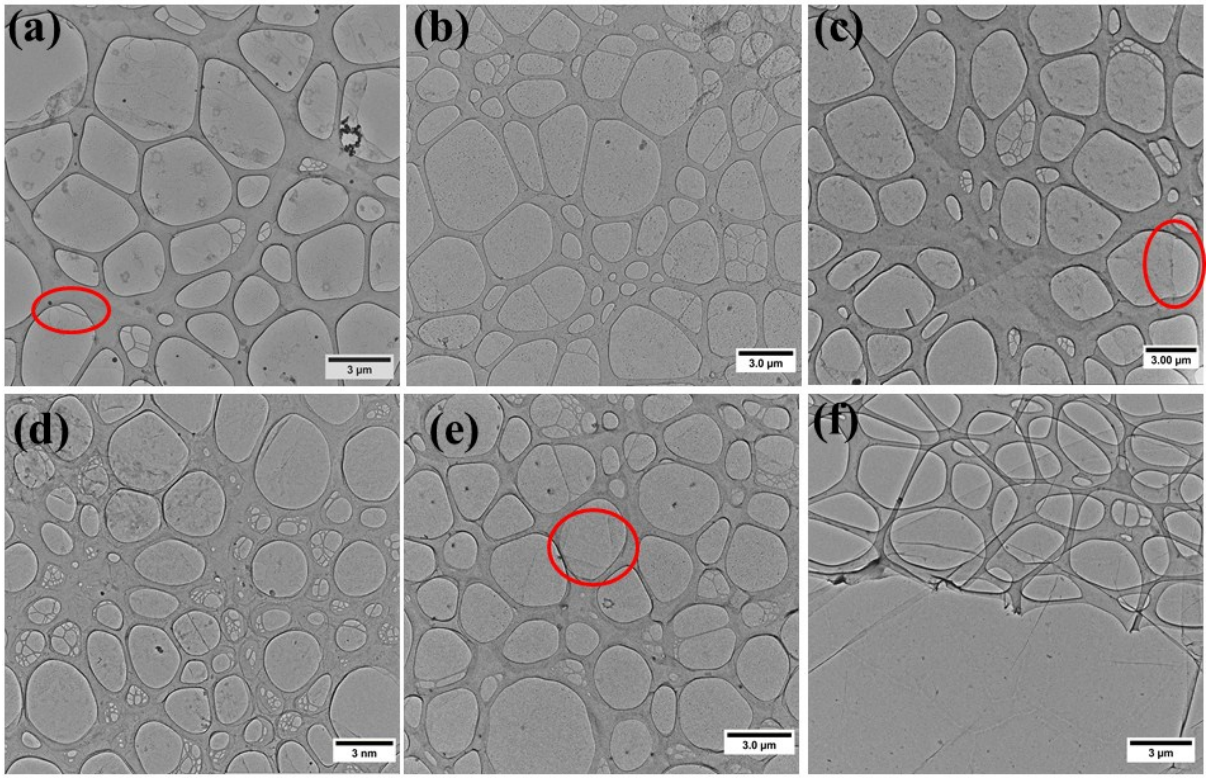


Figure S3: Low magnification TEM images of BCNO hybrid films grown at (a) 2 cm, (b) 4 cm, (c) 6 cm, (d) 8 cm, (e) 10 cm, and (f) 12 cm, respectively. Inset shows the TEM images of the respective BCNO films.

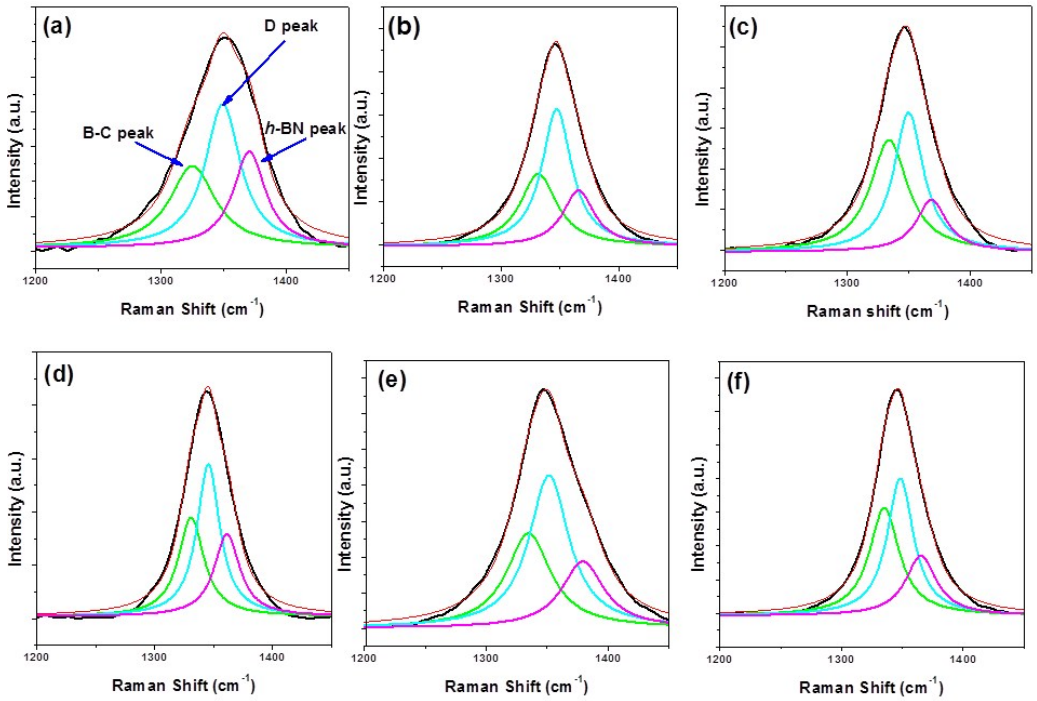


Figure S4: Deconvolution of defect induced D-bands for BCNO films grown at 2 cm -12 cm (a - f) showing the B-C, D, and the *h*-BN peaks, respectively.

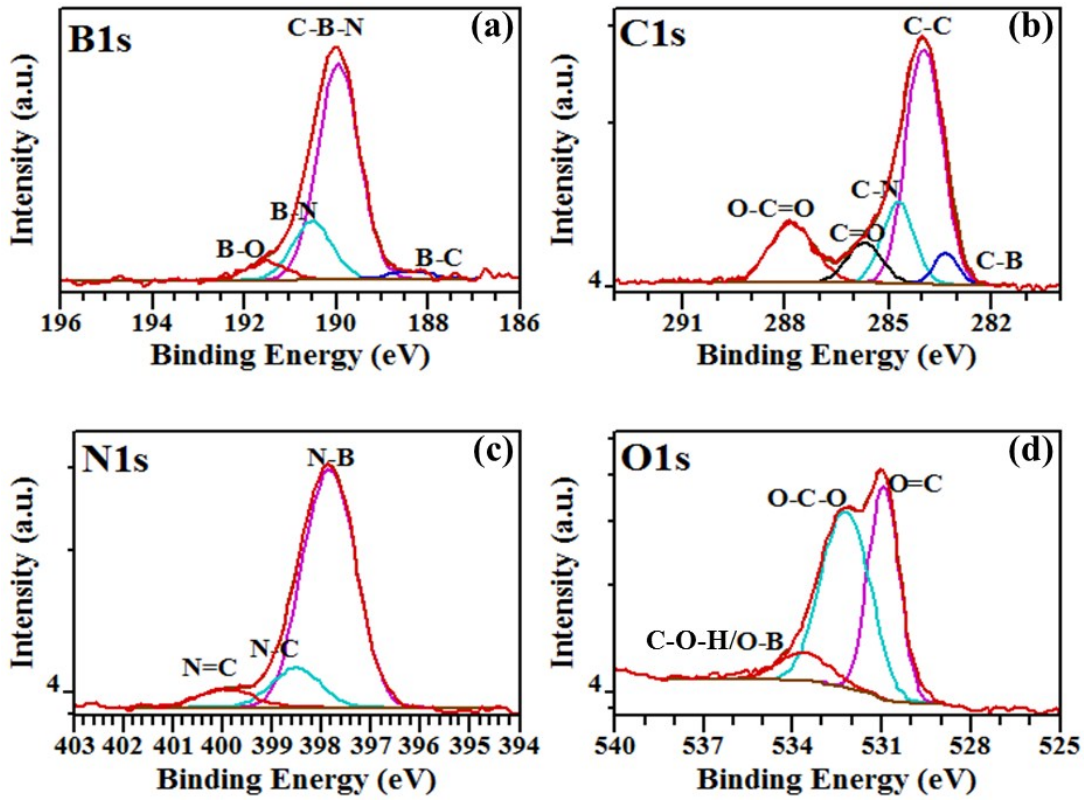


Figure S5: XPS spectra showing deconvoluted curves of (a) B1s, (b) C1s, (c) N1s, and O1s (d) of BN-doped graphene-BCN hybrid films grown at 4 cm using 100 mg H_3BO_3 and 20 sccm CH_4.

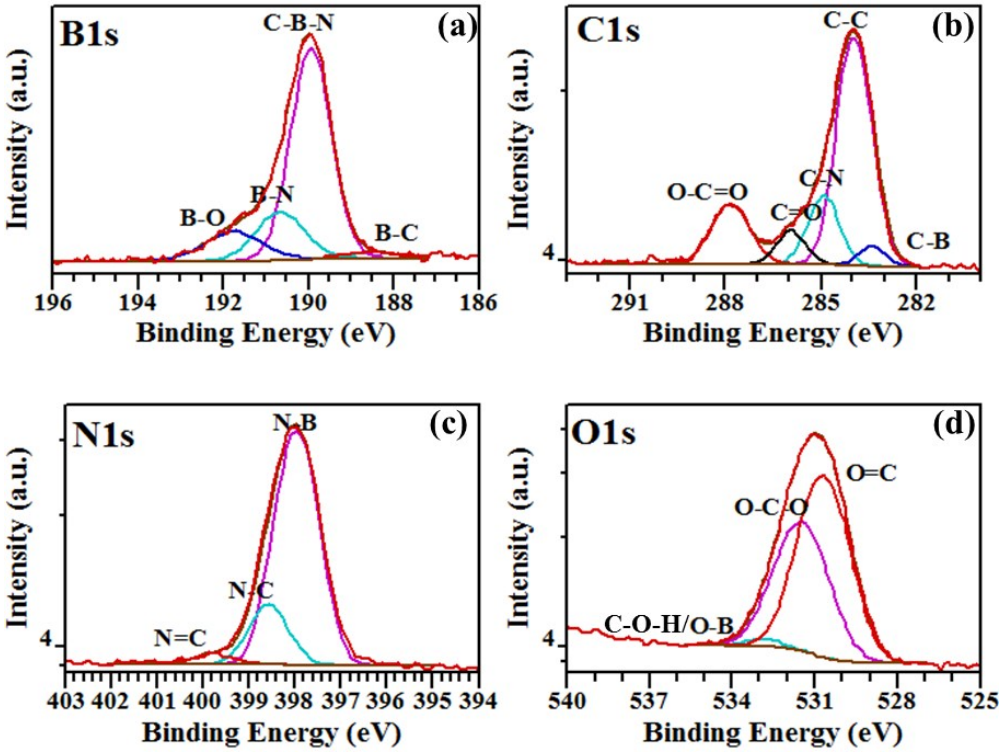


Figure S6: XPS spectra showing deconvoluted curves of (a) B1s, (b) C1s, (c) N1s, and O1s (d) of BN-doped graphene-BCN hybrid films grown at 6 cm using 100 mg H_3BO_3 and 20 sccm CH_4.

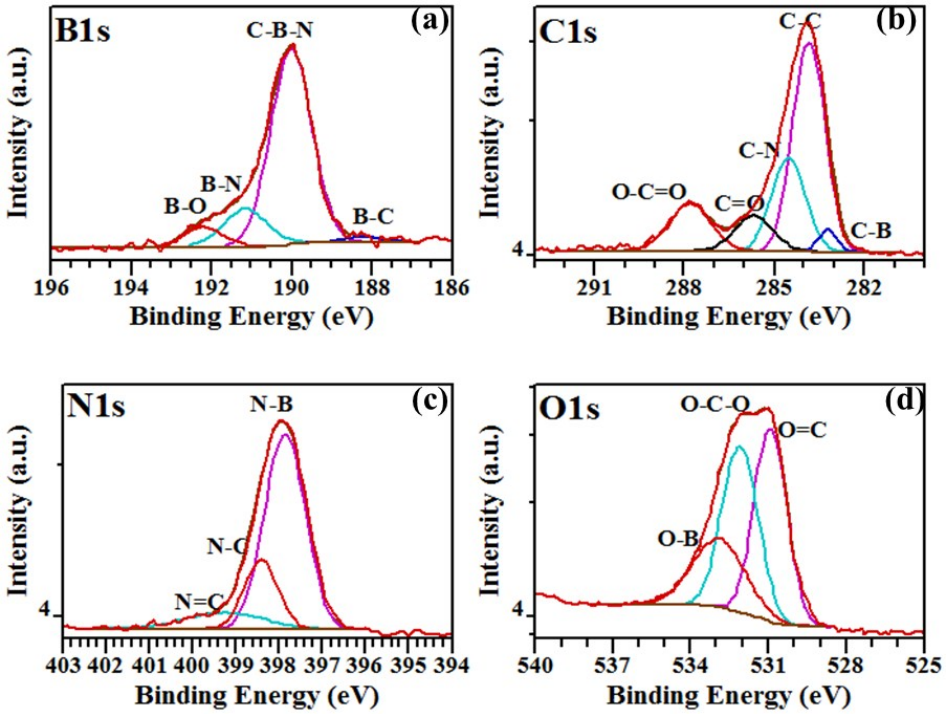


Figure S7: XPS spectra showing deconvoluted curves of (a) B1s, (b) C1s, (c) N1s, and O1s (d) of BN-doped graphene-BCN hybrid films grown at 8 cm using 100 mg H_3BO_3 and 20 sccm CH_4.

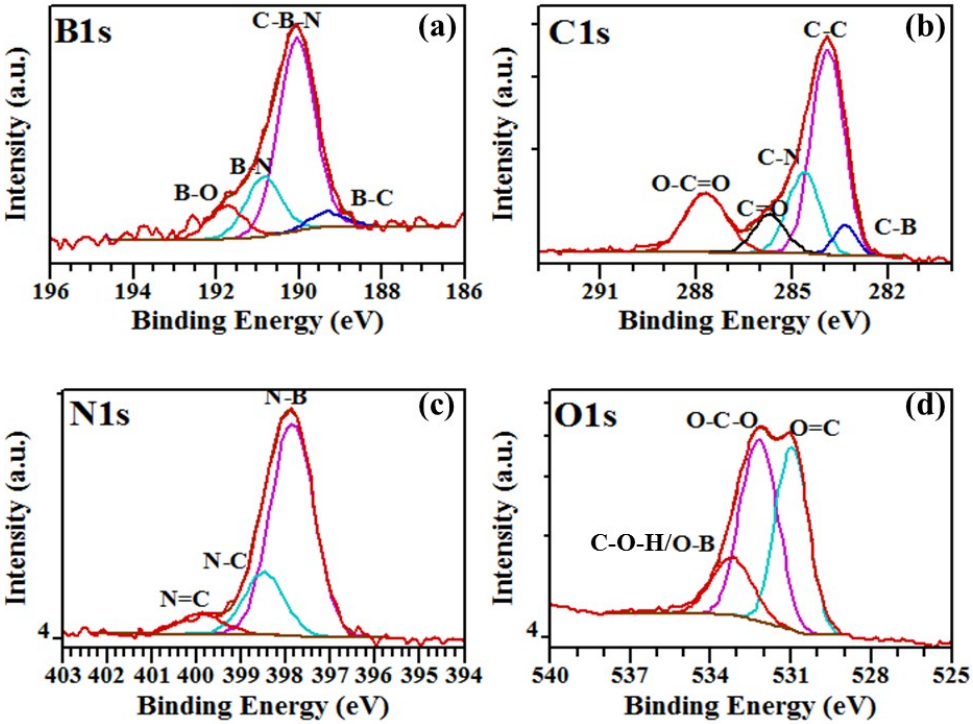


Figure S8: XPS spectra showing deconvoluted curves of (a) B1s, (b) C1s, (c) N1s, and O1s (d) of BN-doped graphene-BCN hybrid films grown at 10 cm using 100 mg H_3BO_3 and 20 sccm CH_4.

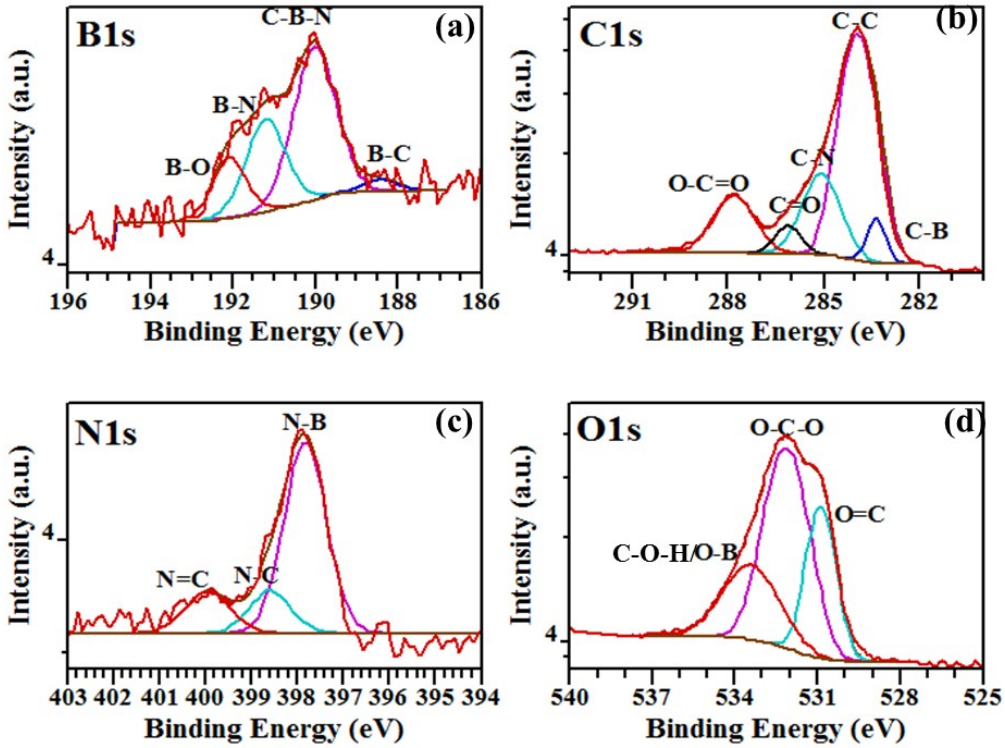


Figure S9: XPS spectra showing deconvoluted curves of (a) B1s, (b) C1s, (c) N1s, and O1s (d) of BN-doped graphene-BCN hybrid films grown at 12 cm using 100 mg H_3BO_3 and 20 sccm CH_4.

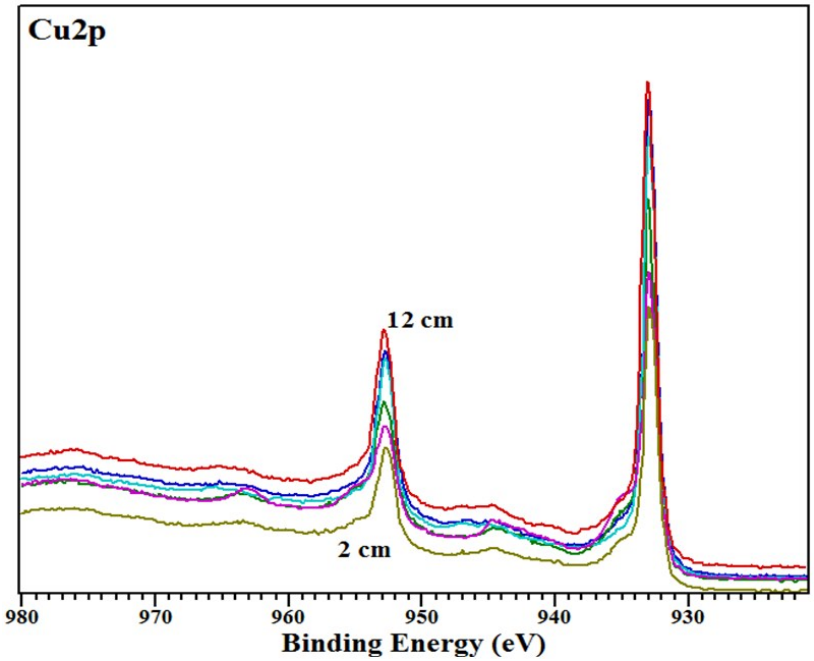


Figure S10: XPS spectra showing Cu2p of BCNO films grown at 2cm to 12 cm.

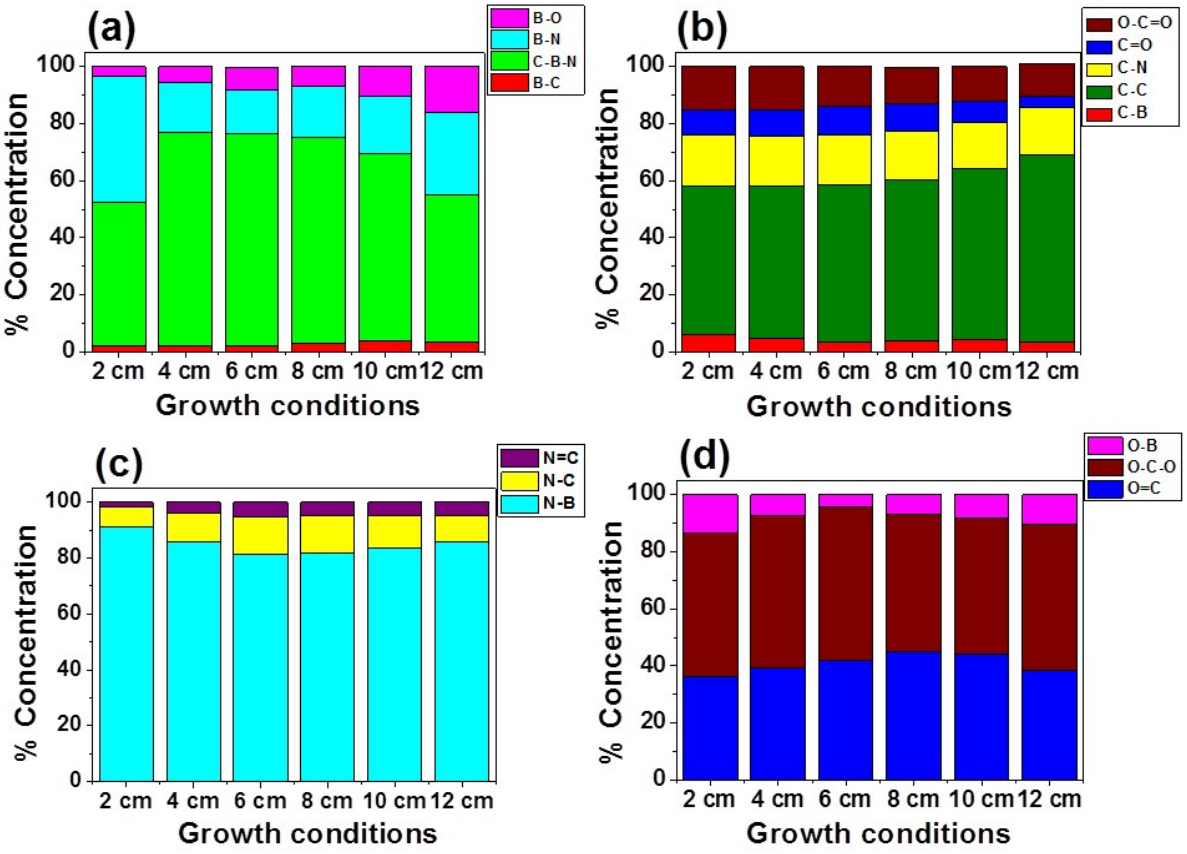


Figure S11: Evolution of bond concentration with increasing growth distance from the hot zone: a-d representing % concentrations of B, C, N and O atoms in (a) B1s, (b) C1s, (c) N1s and (d) O1s, respectively.

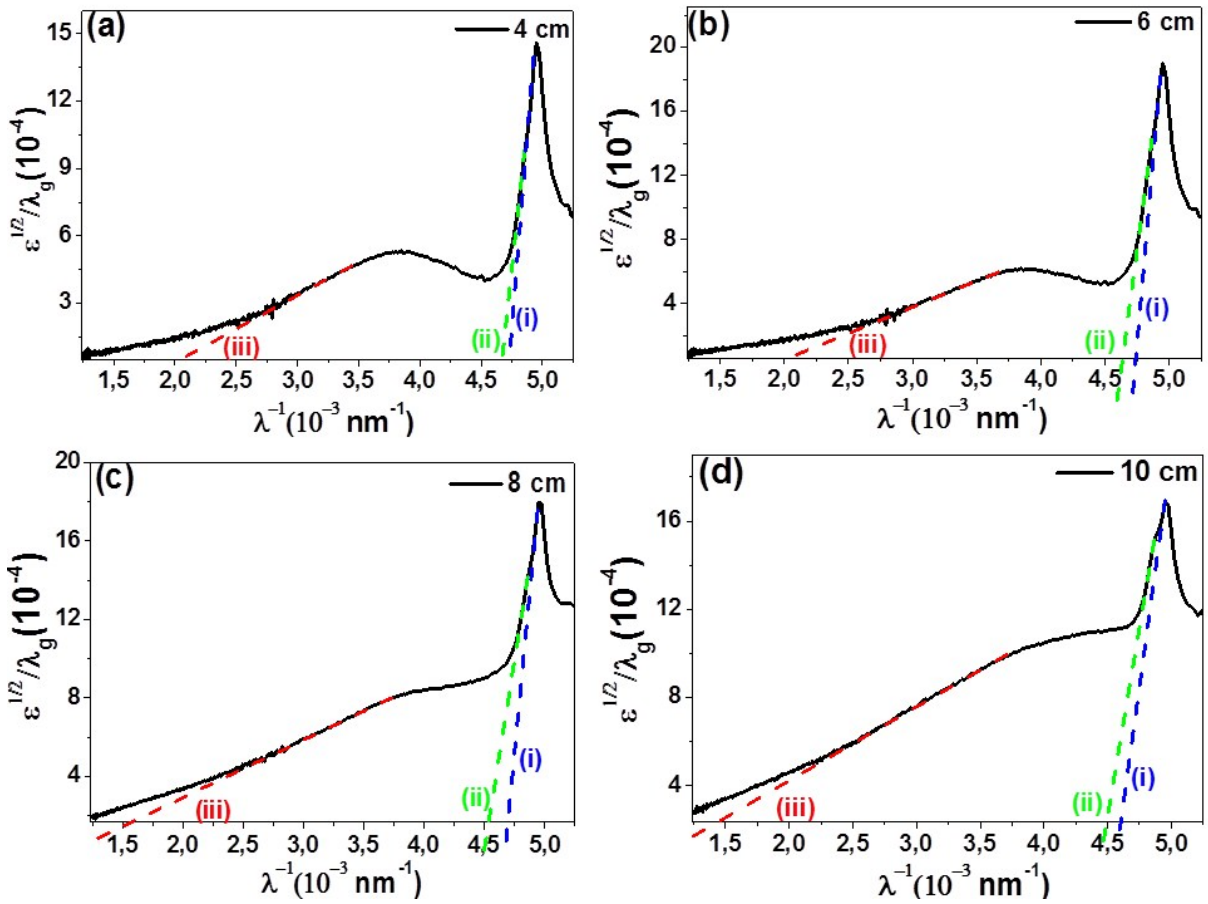


Figure S12: Tauc's plots of BCNO films grown at (a) 4 cm, (b) 6 cm, (c) 8 cm, and (d) 10 cm growth distances from the hot zone.

Table S1: Elemental ratio of all constituent atoms in the BCNO films

Growth distance	Elemental ratio (at. %)				
	B/N	B/C	N/C	B/O	O/C
2 cm	1,79	0,281	0,164	0,298	0,663
4 cm	1,01	0,408	0,0102	0,699	0,563
6 cm	1,40	0,695	0,495	1,083	0,642
8 cm	1,28	0,336	0,262	0,727	0,462
10 cm	1,12	0,138	0,124	0,288	0,498
12 cm	1,41	0,032	0,0225	0,0826	0,373