Supporting Information

Direct Synthesis of Bulk Boron-Doped Graphitic Carbon

Nicholas P. Stadie, Emanuel Billeter, Laura Piveteau, Kostiantyn V. Kravchyk, Max Döbeli, and Maksym V. Kovalenko

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Table S1. Acquisition parameters for ^{11}B MQMAS NMR (Figure 5)

Magnetic Field (T)	16.4
Temperature (K)	298
Rotor Diameter (mm)	2.5
Pulse Sequence	mp3qdfs (Bruker)
Number of Scans	1664
Recycle Delay (s)	0.6
Spectral Width (kHz)	Direct Dimension: 100 Indirect Dimension: 125
Spinning Frequency (kHz)	20
Acquisition Length (points)	Direct Dimension: 1024 Indirect Dimension: 256
Rotor Cycles for Synchronization	40
Indirect Dimension Increment (μs)	8.0
Split-t_1 Increment (μs)	6.2
^{11}B Excitation Pulse Width [π/2] (μs)	4.5
Double Frequency Sweep Length (μs)	12.5
^{11}B Selective Pulse Width [π] (μs)	42

Table S2. Acquisition parameters for ^{11}B MAS NMR (Figure S7)

Magnetic Field (T)	16.4
Temperature (K)	298
Rotor Diameter (mm)	2.5
Pulse Sequence	hahnecho (Bruker)
Number of Scans	304
Recycle Delay (s)	1
Spectral Width (kHz)	100
Spinning Frequency (kHz)	20
Acquisition Length (points)	2048
^{11}B 90° Pulse Width [π/2] (μs)	22

Table S3. Acquisition parameters for ^{13}C MAS NMR (Figure S1)

Magnetic Field (T)	16.4
Temperature (K)	298
Rotor Diameter (mm)	2.5
Pulse Sequence	zg30 (Bruker)
Number of Scans	936
Recycle Delay (s)	120
Spectral Width (kHz)	178.6
Spinning Frequency (kHz)	20
Acquisition Length (points)	2048
^{13}C 90° Pulse Width [π/2] (μs)	3.4

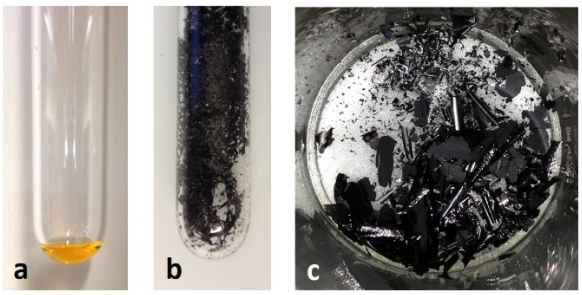

Figure S1. Photographs of (a) precursor solution (BBr_3 and C_6H_6), (b) as-carbonized BC_3', and (c) collected/washed BC_3' after direct synthesis for 1 h at 800 °C.

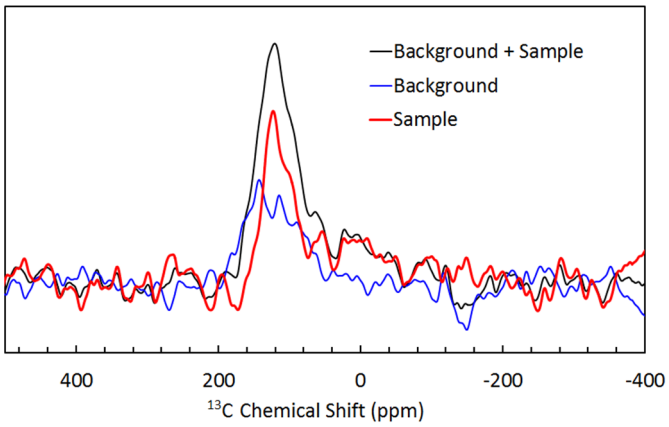

Figure S2. ^{13}C MAS NMR spectrum of directly-synthesized BC_3' deconstructed to show the background contribution from the probe.

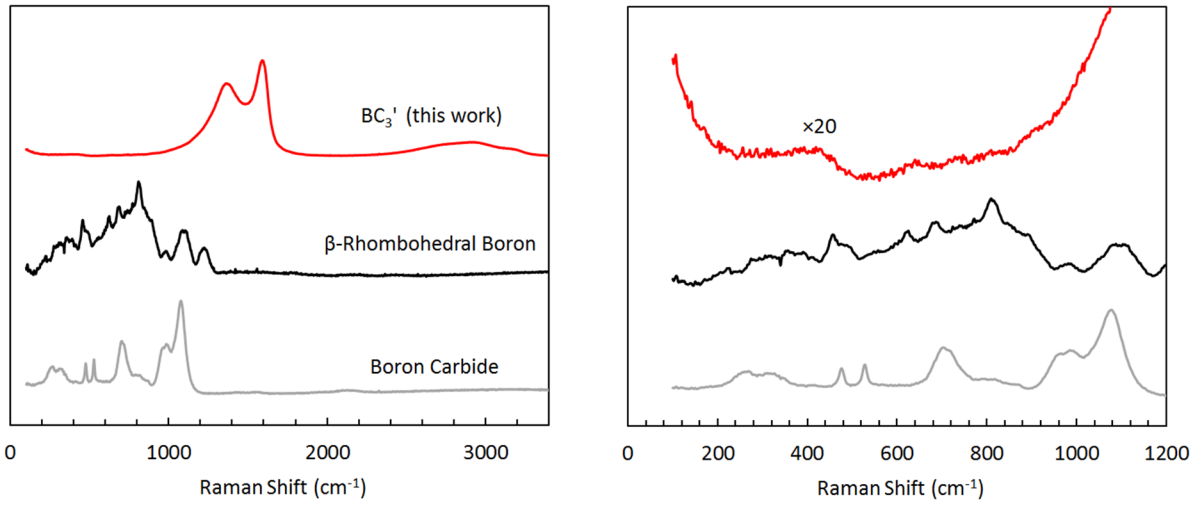

Figure S3. Raman spectra of boron carbide and β-rhombohedral boron reference samples in comparison to directly-synthesized BC_3'.

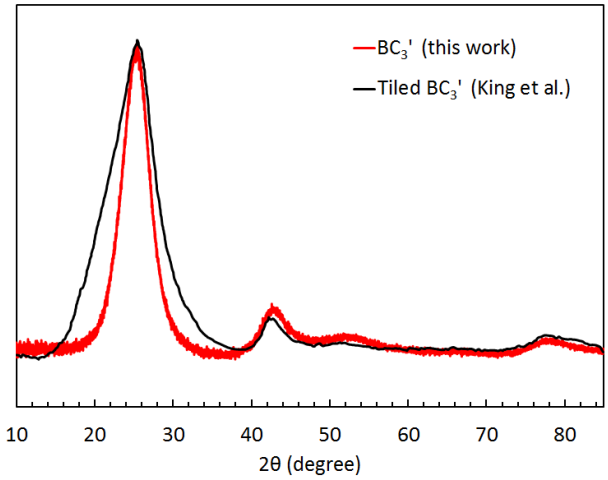

Figure S4. XRD pattern of tiled BC_3'[S1] in comparison to directly-synthesized BC_3', both synthesized at 800 °C under "optimal" heating ramps (6 °C/h and 60 °C/h, respectively).

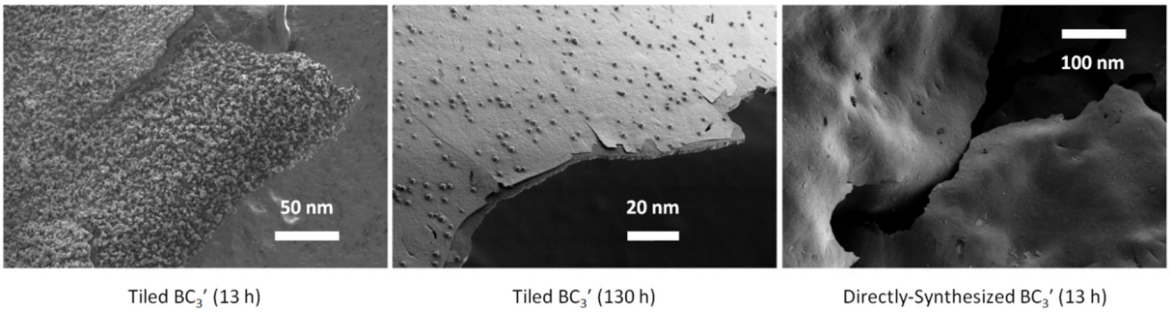

Figure S5. SEM micrographs of tiled BC_3' (obtained after 13 h or 130 h, this work) in comparison to directly-synthesized BC_3' (obtained after 13 h, this work).

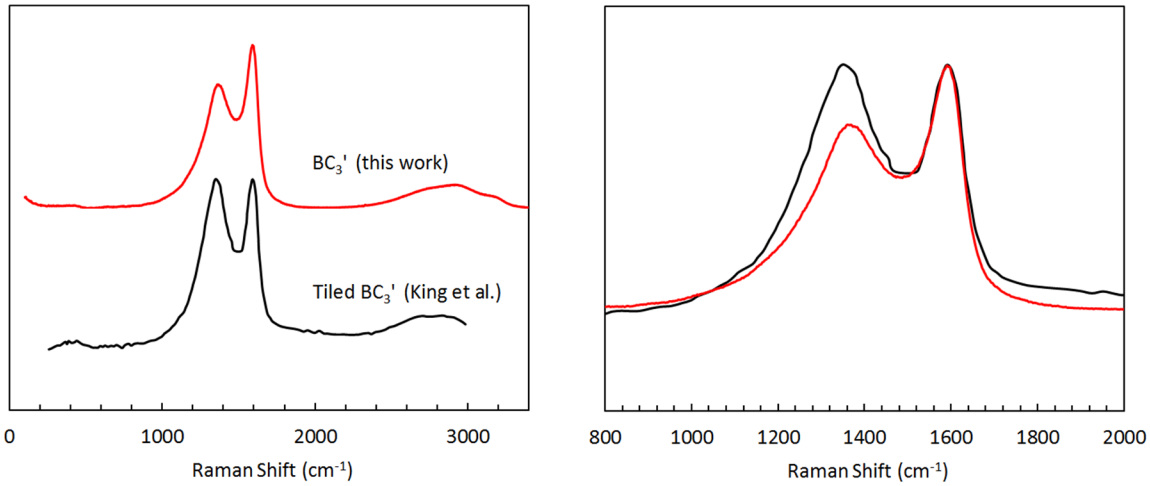

Figure S6. Raman spectrum of tiled BC_3'[S1] in comparison to directly-synthesized BC_3'.

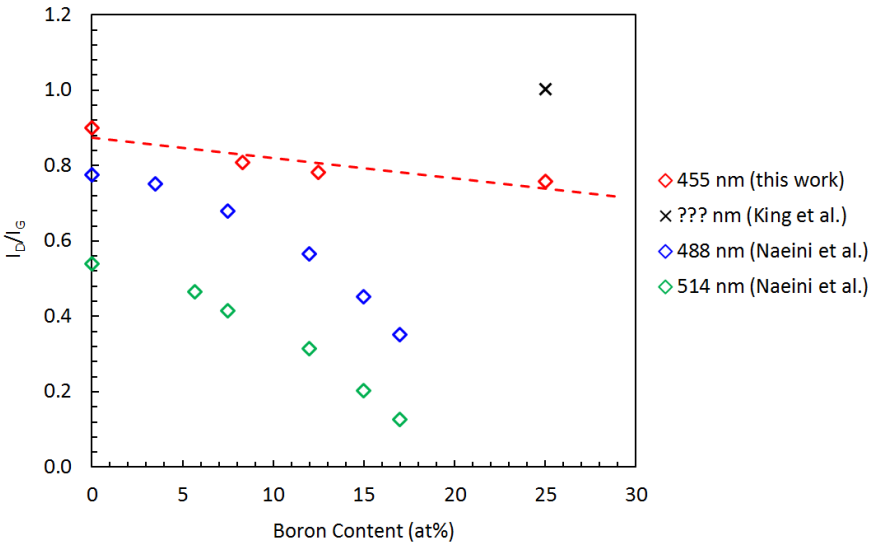

Figure S7. Raman spectroscopy analysis of the I_D/I_G ratio as a function of boron content and excitation wavelength in thin-film BC_x' [S3] in comparison to directly-synthesized BC_x'.

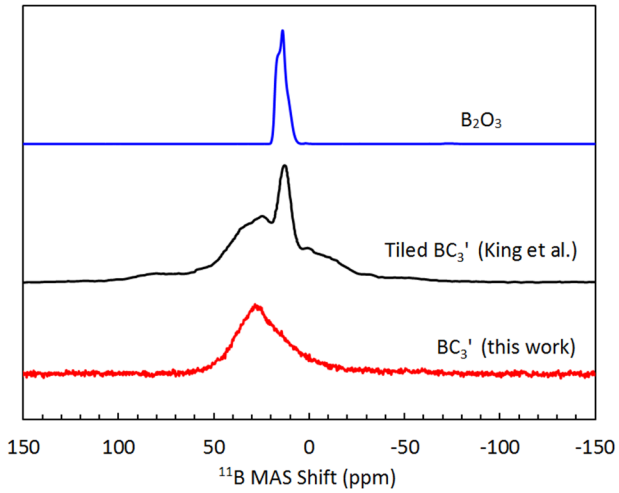

Figure S8. ^{11}B MAS NMR spectra of boron trioxide (B_2O_3)[S2] and tiled BC_3'[S1] in comparison to directly-synthesized BC_3' (this work).

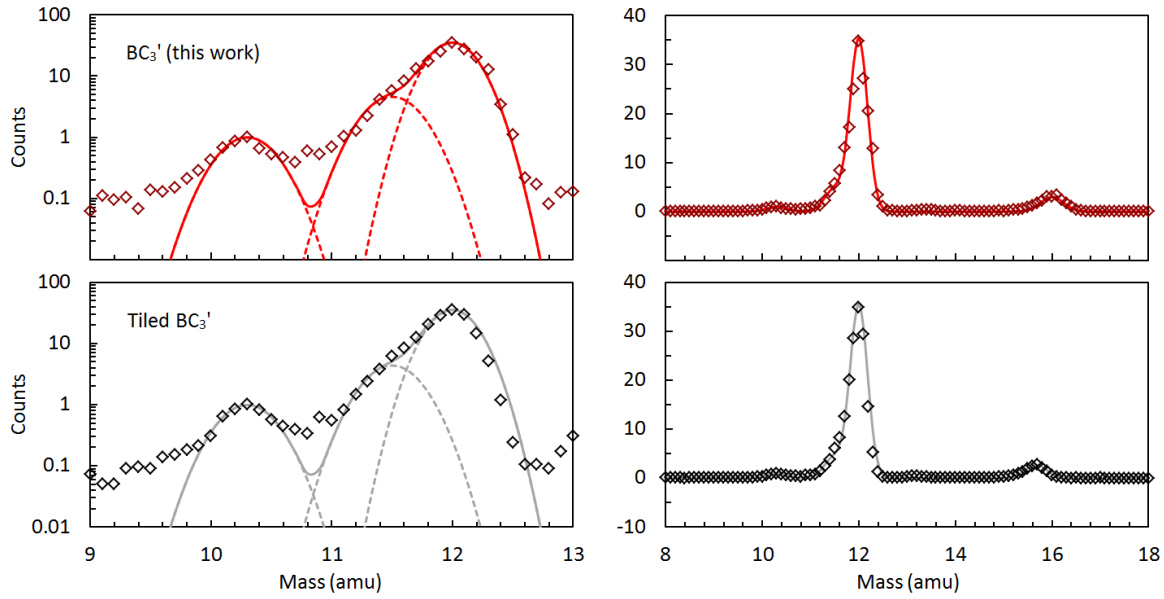

Figure S9. Representative ERDA spectrum of tiled BC_3' (synthesized herein, following the route described elsewhere[S1]) in comparison to directly-synthesized BC_3' (this work).

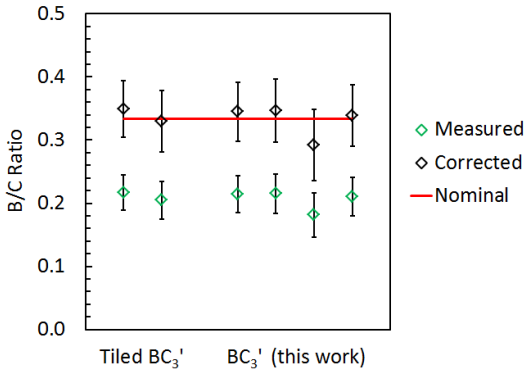

Figure S10. ERDA composition of tiled BC_3' and directly-synthesized BC_3' (as in Figure S8).

Supporting References:

(S1) King, T. C.; Matthews, P. D.; Glass, H.; Cormack, J. A.; Holgado, J. P.; Leskes, M.; Griffin, J. M.; Scherman, O. A.; Barker, P. D.; Grey, C. P.; Dutton, S. E.; Lambert, R. M.; Tustin, G.; Alavi, A.; Wright, D. S., Theory and Practice: Bulk Synthesis of C_3B and its H_2- and Li-Storage Capacity. *Angew. Chem. Int. Ed.* **2015**, 54, 1-6.

(S2) Kroeker, S.; Stebbins, J. F., Three-Coordinated Boron-11 Chemical Shifts in Borates. *Inorg. Chem.* **2001**, 40 (24), 6239-6246.

(S3) Naeini, J. G.; Way, B. M.; Dahn, J. R.; Irwin, J. C., Raman scattering from boron-substituted carbon films. *Phys. Rev. B* **1996**, 54 (1), 144-151.