Electronic Supporting information (ESI) for

Carbothermal conversion of boric acid into boron-oxy-carbide

nanostructures for high-power supercapacitors

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S1. Experimental section

S 1.1 Materials

Boric acid (H₃BO₃), carbon black, acetonitrile, and N-methyl-2-pyrrolidone (NMP) were procured from Dae Jung Chemicals & Metals, South Korea. Cellulose and Polyvinylidene fluoride (PVDF) were acquired from Sigma Aldrich Ltd., South Korea. Tetraethylammonium tetrafluoroborate (TEABF₄) was purchased from Alfa Aesar Chemicals, South Korea. All the chemical reagents were research grade and used as acquired without any purification.

S 1.2 Preparation of boron-oxy-carbide via carbothermal reaction

The boron-oxy-carbide (BOC) was prepared via simple carbothermal reaction using boric acid and cellulose as the starting material. Briefly, 1 g of boric acid and 5 g of cellulose were ground until the formation of fine powders. These pre-mixed powders were annealed at 200 °C for 2 h, followed by gradual increase in temperature up to 900 °C for 6 h in an Argon atmosphere at the heating rate of 2.5 °C min⁻¹. After completion of this reaction, the furnace was allowed cool to reach room temperature naturally. The resulting black colored BOC powder was washed with double distilled water, and ethanol several times to remove the trace amount impurities and dried at 80 °C overnight. The bare B_2O_3 and carbon powders was obtained using the similar reaction without the use of cellulose and boric acid.

S 1.3 Instrumentation

The crystal structure and phase of BOC, carbon and B_2O_3 powders was acquired using an Empyrean X-ray diffractometer (XRD) instrument (Malvern Panalytical, UK) equipped with Cu-K α radiation ($\lambda = 1.54184$ Å) under a voltage of 40 kV and a current of 40 mA. The Raman spectrum was obtained using a LabRam HR Evolution Raman spectrometer (Horiba Jobin-Yvon, France). The Ar⁺ ion laser functioning at a power of 10 mW with an excitation wavelength of 514 nm was used in the Raman system. The functional groups present in boric acid, cellulose derived carbon, and BOC was analyzed using Nicolet 6700 FT-IR spectrometer from Thermo

Scientific. To measure the chemical and electronic state of each elements present in the assynthesized BOC, X-ray photoelectron spectroscopy (XPS) technique was performed using ESCA-2000 (VG Microtech Ltd). Using HR-TEM technique, the surface architecture of BOC was probed along with quantification of elements through conjugation of EDX analyzer from JEOL with JEM-2011 model. The morphology of cellulose derived carbon was examined by field-emission scanning electron microscopy (FE-SEM, TESCAN, MIRA3) coupled with an energy-dispersive x-ray spectroscopy (EDX) analyzer to quantify the elemental composition.

S 1.4 Fabrication and electrochemical analysis of boron-oxy-carbide symmetric supercapacitor (SSC)

The working electrodes were prepared via slurry coating method as reported in literatures¹. Here, the active materials (BOC – 85 wt.%), carbon black (10 wt.%) and polyvinylidene fluoride (PVDF) binder (5 wt.%) were mixed using NMP in an agate mortar until the formation of uniform slurry. After that, the slurry is coated onto the stainless-steel substrate of 15 mm diameter and dried at 80 °C in a vacuum oven to evaporate the solvent. The BOC symmetric supercapacitor (SSC) were fabricated in CR2032 type coin cell configuration using two ideal BOC electrodes separated by a Celgard membrane filled by 1 M TEABF₄/AN electrolyte. Finally, the BOC SSC was crimped using an electric coin cell crimping machine (MTI, Korea) in an argon filled glove box. Electrochemical characterizations such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge–discharge (CD) measurements were measured using an Autolab PGSTAT302N electrochemical workstation. The supercapacitor performance metrics such as device capacitance (C), columbic efficiency (η), energy density (E) and power density (P) of the BOC SSC device were calculated using the relations^{2,3}:

$$C = [(\int I \, dV) / (s \times \Delta V \times A)] \dots (1)$$

$$C = [(I \times \Delta t) / (\Delta V \times A)] \dots (2)$$

$$\eta \% = (t_d/t_c) \times 100 \dots (3)$$

$$E = 0.5 \times C \times \Delta V^2 \dots (4)$$

$$P = E / \Delta t \dots (5)$$

Here, "*C*" represents specific device capacitance of the of the BOC SSC, "*T*" denotes the applied current, " t_c and t_d " presents the time required for charging and discharging process, " Δt or t_d " is the time required to discharge from maximum to minimum voltage, "*A*" is the area of device, "s" denotes the scan rate and " ΔV " is the operating voltage window of BOC SSC.

S 1.5 Maximal power density calculation from EIS analysis

The maximal power density of the BOC SSC was determined from EIS analysis using the following relation⁴:

Here "V" represents the voltage window of BOC SSC and ESR is the equivalent series resistance.



Figure S1. Cyclic voltammetric profiles of BOC SSC over different operating volage windows recorded using a scan rate of 200 mV s⁻¹.

The operating voltage window (OVW) of any supercapacitor electrode or device is one of the prime factors determining their performance metrics such as capacitance, energy density, and power density⁵. To examine the operating voltage window (OVW) of BOC SSC, their CV profiles were measured at various OVWs (0 to 2.5 V) recorded at 200 mV s⁻¹ as shown in Figure S1. It showed that the BOC SSC capable of running over 2.0 V without any decomposition. When the operating voltage has been increased above 2.0 V the BOC SSC device undergoes parasitic reaction at the electrode and electrolyte interfaces⁶. Therefore, the OVW of the BOC SSC is limited to 2.0 V.



Figure S2. Gravimetric device capacitance of BOC SSC as a function of applied scan rates.

The specific device capacitance of BOC SSC as the function of applied scan rates is shown in Figure S2. It revealed that BOC SSC device possess the gravimetric capacitance of 11.95 F g⁻¹ at the scan rate of 5 mV s⁻¹. Added, the BOC SSC device delivered the gravimetric capacitance of 2.07 F g⁻¹ when the scan rate is increased up to 1000 mV s⁻¹ (50-fold). The observed decrease in specific device capacitance with an increase in scan rates is because of time constraints faced by electrolyte ions at much higher scan rates^{6,7}.



Figure S3. Nyquist plot of BOC SSC recorded with different device potentials.

The electrochemical impedance spectroscopy (EIS) of BOC SSC device were measured at various applied voltage from 0 to 2.5 V and the results are presented in the form of Nyquist plot is shown in Figure S3. When the increase in applied voltage (0.5 to 2.0 V) the Warburg line gets deviated from the imaginary axis suggesting the transition from capacitive to diffusion-controlled reaction occurred in the BOC SSC⁷. Further increase in applied voltage above 2.0 V, the BOC SSC shows the presence of parasitic reaction at the electrode and electrolyte interfaces⁸. This finding agrees well with the CV profiles given in Figure S1.



Figure S4. Bode phase angle plot of BOC SSC recorded with different device potentials.

The Bode phase angle plot of BOC SSC device were measured at various applied voltage from 0 to 2.5 V is shown in Figure S4. The phase angle of BOC SSC at the low-frequency region decreases from -68° (0.5 V) to -55.4° (2.0 V), which indicates that the more capacitive properties at lower cell voltage whereas an increase in voltage results in the transition from capacitive to pseudocapacitive nature⁹.



Figure S5. Gravimetric device capacitance of BOC SSC as a function of applied frequency.

Figure S5 portrays the device capacitance of BOC SSC as function of applied frequency derived from the EIS spectra. The device capacitance BOC SSC increases with a decrease in applied frequency and a maximum capacitance of about 7.98 F g^{-1} was obtained at a lower frequency of 0.01 Hz.



Figure S6. Gravimetric device capacitance of BOC SSC as a function of discharge currents.

The specific capacitance of BOC SSC as the function of applied current ranges (in the CD measurements) is provided in Figure S6. It revealed that the BOC SSC possess the gravimetric device capacitance of 11.26 F g⁻¹ at an applied current of 0.2 mA. Added, the BOC SSC still delivered the gravimetric device capacitance of 3.125 F g⁻¹ when the current is increased up to 25 mA (125-fold), suggesting their better rate capability. The much higher device capacitance at low applied current ranges is due to the better electrochemical reactions occurred between the electroactive materials and electrolyte ions at low current ranges¹⁰.



Figure S7. Nyquist plot of BOC SSC before and after cyclic tests over 10,000 cycles.

The Nyquist plot of BOC SSC device before and after 10,000 cycles is shown in Figure S7, which revealed the following changes:

- (i) The solution resistance (Rs) increased from 1.44 to 1.92 $\ensuremath{\Omega},$
- (ii) the charge transfer resistance increased from 2.81 to 3.9 $\ensuremath{\Omega}$, and
- (iii) the Warburg line moves towards the y-axis due to the diffusion of electrolyte ions.



Figure S8. Ragone plot of BOC SSC based on gravimetric metrics.



Figure S9. Digital photograph of the thermoelectric module integrated with the BOC SSC.

No.	SC material	Electrolyte	Voltage window	Specific capacitance	Energy density	Power density	Ref
1.	Graphene QD	EMIMBF ₄	0.0 to 3.0 V	468.1 μF cm ⁻²	1.7 mJ cm- ²	56.7 μW cm- ²	[11]
2.	Siloxene	TEABF ₄	0.0 to 3.0 V	2.18 mF cm ⁻²	9.82 mJ cm ⁻²	4.03 mW cm ⁻²	[4]
3.	PEDOT/Si	PYR ₁₃ TFSI	0.0 to 1.5 V	8-9 mF cm ⁻²	9 mJ cm ⁻²	0.8 mW cm ⁻²	[12]
4.	SiC NW	KC1	0.0 to 0.6 V	23 mF cm ⁻²	2.3 mJ cm ⁻²	1.1 mW cm ⁻²	[13]
5.	Si NW	PYR ₁₃ TFSI	0.0 to 4.0 V	30 µF cm ⁻²	0.19 mJ cm ⁻²	1-2 mW cm ⁻²	[14]
6.	Ti ₃ C ₂ Mxene	PVA/H ₂ SO ₄	0.0 to 0.6 V	0.87 mF cm ⁻²	1.7 μJ cm ⁻²	56.7 μW cm ⁻²	[15]
7.	SiC/Si NW	KC1	-0.2 to 0.6 V	1.7 mF cm ⁻²	0.85 mJ cm ⁻²	0.1 mW cm ⁻²	[16]
8.	Diamond/Si NW	PMPyrrTFSI	-2.5 to 1.5 V	$105 \ \mu F \ cm^{-2}$	84 μJ cm ⁻²	0.94 mW cm ⁻²	[17]
9.	Graphene	PVA/H ₂ SO ₄	0.0 to 1.0 V	2.4 mF cm ⁻²	1.36 mJ cm ⁻²	0.86 mW cm ⁻²	[18]
10.	SiC NW/SiC	KC1	-0.2 to 0.6 V	240 μF cm ⁻²	68 µJ cm ⁻²	4 μW cm ⁻²	[19]
11.	вос	TEABF ₄	0.0 to 2.0 V	7.26 mF cm ⁻²	14.53 mJ cm ⁻²	13.44 mW cm ⁻²	This Work

Table S1. Areal performance metrics of BOC SSC to that of recently reported SSC devices.

No	SC material	Electrolyte	Voltage window	Specific capacitance (F g ⁻¹)	Energy density (Wh kg ⁻¹)	Power density (W kg ⁻¹)	Ref
1.	Si nanowires	BMI-TFSI	-0.6 to 1.0 V	0.7	0.23	0.65	[20]
2.	Siloxene nanosheets	$TEABF_4$	0.0 to 3.0 V	4.06	5.08	375	[4]
3.	Ti ₂ CT _x	КОН	0.0 to 0.7 V	51	0.209	700	[21]
4.	Maxwell commercial	-	2.7 V	-	4.45	900	[22]
5.	Panasonic commercial	-	2.5 V	-	2.3	514	[22]
6.	Ti ₃ C ₂ T _x /MWCNT	Et ₄ NBF ₄	0.0 to 1.8 V	-	3	-	[23]
7.	MoS_2	LiCl -PVA	0.0 to 0.8 V	368	5.42	128	[24]
8.	Co ₃ O ₄	PVA- H ₃ PO ₄	0.25 to 0.6 V	762	3.01	1152	[25]
9.	LEPC/ PANI	H_2SO_4	0.0 to 0.8 V	184	3.0	41.6	[26]
10.	Porous carbon	КОН	-1.0 to 0.0 V	350.2	6.0	47.6	[27]
11.	Lignin/PAN derived carbon	КОН	0.0 to 1.0 V	129.23	4.49	2630	[28]
12.	вос	TEABF ₄	0.0 to 2.0 V	11.98	6.25	20833.33	This work

Table S2. Gravimetric performance metrics of BOC SSC to that of recently reported SSC devices.

S.No.	Hot side temperature (°C)	Cold side temperature (°C)	Temperature Difference, ∆T (°C)	Voltage (mV)	Current (mA)
1.	29	24	5	43.2	5.05
2.	35	25	10	75.4	11.5
3.	35	20	15	539	72
4.	40	20	20	610	81.7
5.	44	19	25	661	96.2
6.	53	25	30	1196	143.2

Table S3. Current and voltage outputs of commercial TE module.

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