

Supporting Information

Boron-doped onion-like carbon with enriched substitutional boron: relationship between electronic property and catalytic performance

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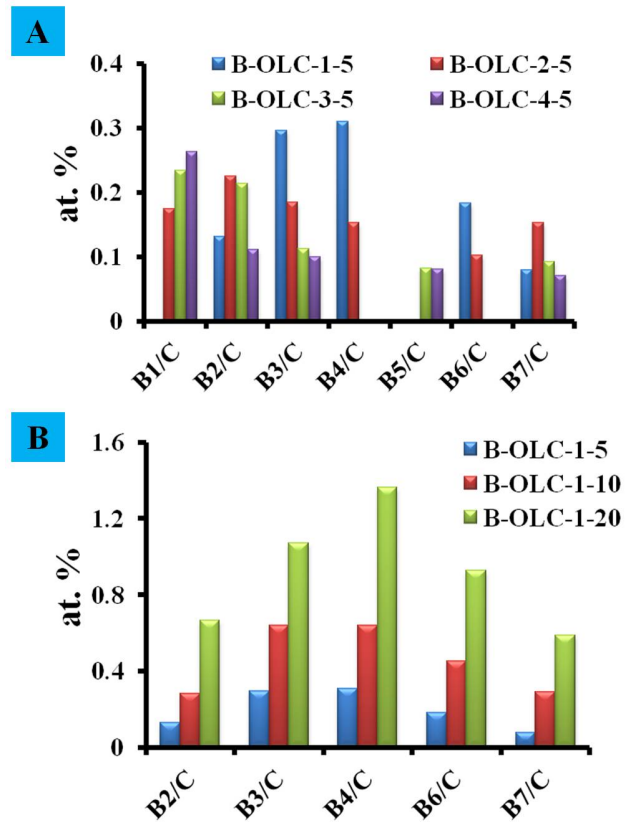


Fig. S1 (A)-(B) the detailed B_x/C species distribution diagram of the various B-OLC samples.

Table S1. Distribution of element species obtained from the deconvolution of the C1s and B1s Peaks by XPS. ^(a)

Entry	Binding energy (eV)	FWHM (eV)	Bx/C	At. %					
				B-OLC-1-5	B-OLC-2-5	B-OLC-3-5	B-OLC-4-5	B-OLC-1-10	B-OLC-1-20
boron atom cluster (B1)	~186.5	1.25	B1/C	---	0.174	0.234	0.27	---	---
B ₄ C (B2)	~187.6	1.35	B2/C	0.132	0.225	0.214	0.111	0.284	0.65
substitutional boron species BC ₃ (B3)	~188.8	1.39	B3/C	0.296	0.184	0.112	0.1	0.641	1.06
BC ₂ O (B4)	~190.1	1.45	B4/C	0.31	0.153	---	---	0.641	1.354
B-N (B5)	~190.7	1.49	B5/C	---	---	0.082	0.081	---	---
BCO ₂ (B6)	~191.3	1.54	B6/C	0.183	0.102	---	---	0.451	0.92
B ₂ O ₃ (B7)	>192.8	1.54	B7/C	0.08	0.153	0.092	0.071	0.294	0.58
Total boron	186.5~194.5	1.2~1.6	Total B/C	1.0	0.99	0.73	0.63	2.31	4.57

(a) The fitting is performed by fixing the peak maximum within ± 0.1 eV for all spectra and applying a full width half-maximum (FWHM) of 1.2-1.6 eV. The value of the mixed Gaussian-Lorentzian is maintained at 30 %.

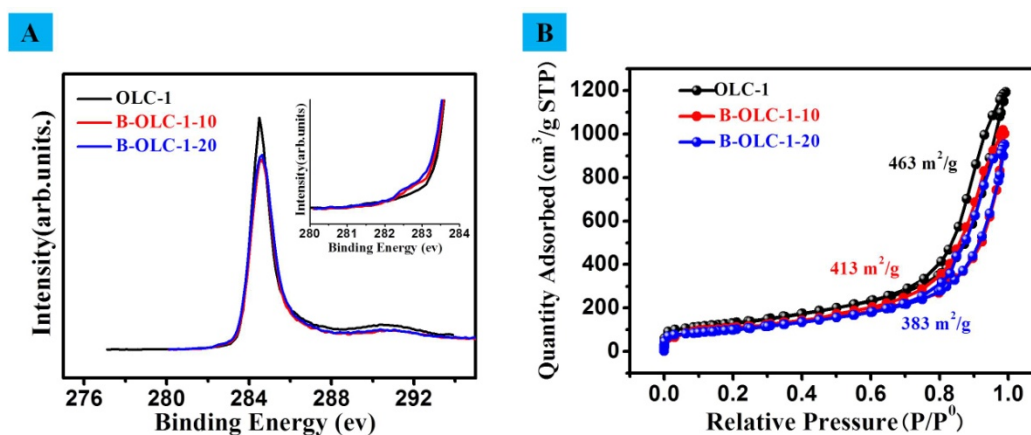


Fig. S2 (A) XPS C1s spectra of the representative samples. (B) Nitrogen adsorption-desorption isotherm distribution of the representative samples.

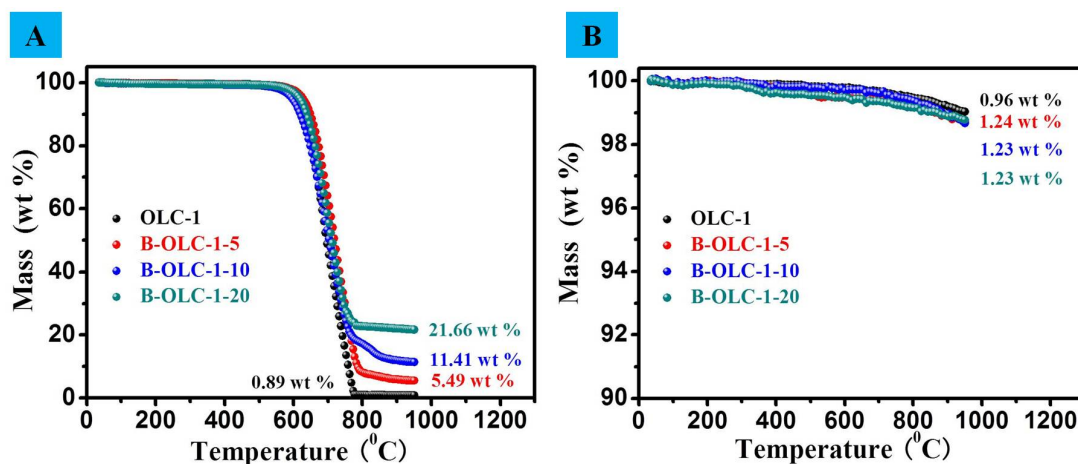


Fig. S3 TG profiles of various un-doped and doped OLC samples at a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$ under different atmospheres. (A) dry air, (B) argon gas.

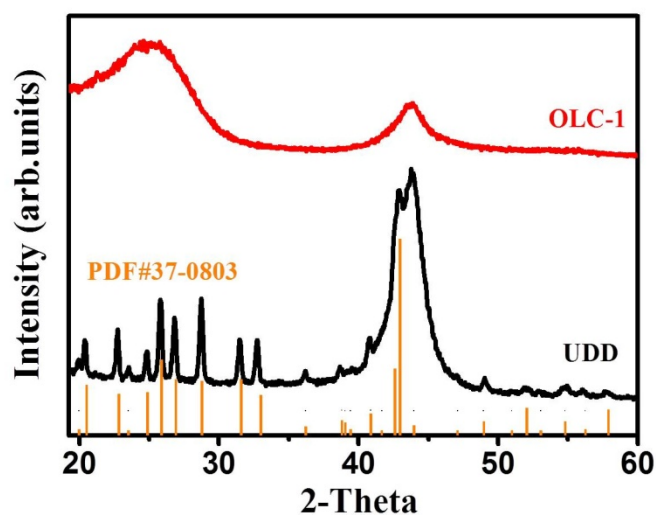


Fig. S4 XRD patterns of UDD and OLC-1. The orange histogram represents the unpurified BaK_xSO_4 (NO. PDF#37-0803) contamination in the commercial UDD.

The combustion residue of pure OLC is about 0.89 wt%, which is mainly attributed to the unpurified BaK_xSO_4 in the origin commercial UDD. Besides, the contaminations in the commercial UDD involve $\text{Fe} < 50 \text{ ppm}$, $\text{Cr} < 10 \text{ ppm}$, $\text{Al} < 50 \text{ ppm}$, $\text{Cu} < 10 \text{ ppm}$, $\text{Mg} < 10 \text{ ppm}$, $\text{Ti} < 10 \text{ ppm}$ and $\text{Ca} < 50 \text{ ppm}$, which are tested by inductively coupled plasma emission spectrometer (ICP).

Table S2. Work functions and valence band edges of various pristine and low doped-OLC samples obtained by UPS.

Sample	OLC-2	B-OLC-2-5	OLC-3	B-OLC-3-5	OLC-4	B-OLC-4-5
Preparation Temperature (°C)	1800	1800	2100	2100	2400	2400
Work Function (eV)	4.72	4.75	4.96	4.99	5.24	5.26
Valence Band Edge(eV)	1.35	1.37	1.42	1.43	1.50	1.50
The content of BC ₃ species	-----	~0.18	-----	~0.11	-----	~0.1

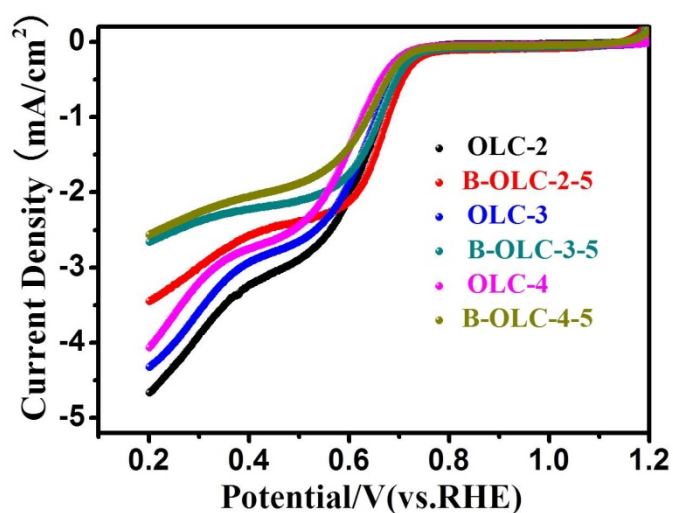


Fig.S5 Rotating disk electrode (RDE) voltammograms recorded with OLC-2, B-OLC-2-5, OLC-3, B-OLC-3-5, OLC-4 and B-OLC-4-5 in O₂-saturated 0.1 M KOH at 900 rpm, scan rate: 5 mV s⁻¹