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Supporting Information

For

## Boron-doped Graphene as Electrocatalytic Support for Iridium Oxide for Oxygen Evolution Reaction

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Figure S1 Comparison of Raman spectra for GO (red line), rGO (black line) and B-rGO (purple

line) with  $I_d/I_g$  ratio



**Figure S2** SEM images of B-rGO **a**) low magnification and **b**) high magnification. **c**) EDX elemental mapping of IrO<sub>2</sub>-B-rGO at 20 kV



**Figure S3** TEM images of **a**) IrO<sub>2</sub>-rGO and **b**) size distribution of IrO<sub>2</sub> nps deposited on rGO sheets. **c**) TEM image of IrO<sub>2</sub>-B-rGO (Enlarged image of IrO<sub>2</sub> nps showing lattice fringes of IrO<sub>2</sub>). **d**) TEM image of comm. IrO<sub>2</sub>



**Figure S4 a)** Survey scan of GO (brown line) and IrO<sub>2</sub>-rGO (orange line), and XPS deconvoluted spectra for **b**) GO (C1s), **c**) B-rGO (C1s), **d**) Ir powder (Ir 4f), **e**) IrO<sub>2</sub>-rGO (C 1s) and **f**) IrO<sub>2</sub>-rGO (Ir 4f)



Figure S5 Deconvoluted Ir4f spectra for IrO<sub>2</sub>-rGO and IrO<sub>2</sub>-B-rGO with contribution of Ir<sup>0</sup>

There is an additional way to deconvolute the Ir 4f peaks in IrO<sub>2</sub>-B-rGO, i.e. inclusion of the contribution from metallic Ir, Ir<sup>0</sup>. **Figure S5** shows the revised XPS deconvolution for IrO<sub>2</sub>-B-rGO and IrO<sub>2</sub>-rGO with inclusion of Ir metal peaks. Considering the reported XRD of Ir (111) plane in Ir<sup>0</sup>, a high intensity sharp peak at 40.1° is reported <sup>1</sup>, which is near IrO<sub>2</sub> (200) plane at 40.7 ° (**Figure S6**). This states the possibility of the presence of metallic Ir in the sample. However, bearing in mind the area ratio of the deconvoluted peaks, it can be deduced that Ir<sup>IV</sup> is dominant.

Elements	IrO <sub>2</sub> -B-rGO (At. conc. from XPS)		
В	1.94		
С	36.93		
0	44.82		
Ir	16.10		

Table S1 Elemental composition of IrO2-B-rGO-19.6, estimated from XPS spectra

Table S2 Ir 4f peak positions and peak shift obtained from XPS spectra

Sample	Ir 4f <sup>7/2</sup> / eV	Ir 4f <sup>5/2</sup> / eV	Peak Shift from Rutile type unsupported IrO <sub>2</sub> <sup>2</sup> / eV
Ir powder	60.9	63.9	0.9
IrO <sub>2</sub> -rGO	61.4	64.4	0.4
IrO <sub>2</sub> -B-rGO	61.2	64.2	0.6
Rutile type unsupported IrO <sub>2</sub>	61.8	64.8	0.0



Figure S6 XRD patterns of the catalyst and the initial precursors, GO (purple line), IrO<sub>2</sub>-rGO (black line), B-rGO (red line), IrO<sub>2</sub>-B-rGO (blue line)



Potential (V) vs RHE Figure S7 LSV profiles of B-rGO with various GO: BA weight ratio in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte solution

	GO : BA (wt./wt. %)					
Elements	1:1		1:3		1:5	
	At. %	Wt. %	At. %	Wt. %	At. %	Wt. %
В	2.82	2.33	2.69	2.34	2.14	1.87
С	88.92	86.66	85.92	82.86	84.58	80.37
0	8.14	10.57	10.77	13.84	11.96	15.15

Table S3 Elemental composition of B-rGO, estimated from SEM-EDX analysis



**Figure S8** LSV curve of comm. IrO<sub>2</sub> (purple line) in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution between 1.20 to 1.65 V vs RHE (the Ir loading amount of comm. IrO<sub>2</sub> is 284  $\mu$ g cm<sup>-2</sup>) and its comparison with the synthesized catalyst IrO<sub>2</sub>-B-rGO-19.6 (green line) and IrO<sub>2</sub>-rGO-11.7 (black line)



Figure S9 LSV profiles of IrO<sub>2</sub>-rGO (with 11.7 wt.% Ir) and IrO<sub>2</sub>-B-rGO with different Ir content (3.3, 7.1 and 19.6. wt. %)

Catalyst	Catalyst loading (wt. %)	Particle Size (nm) (by TEM)	Active Surface area (m <sup>2</sup> g <sub>Ir</sub> <sup>-1</sup> ) (by TEM)
IrO <sub>2</sub> -B-rGO1	3.3	$1.6 \pm 0.3$	10.6
IrO <sub>2</sub> -B-rGO2	7.1	$1.5 \pm 0.3$	24.4
IrO <sub>2</sub> -B-rGO3	19.6	$1.6 \pm 0.4$	63.1
IrO <sub>2</sub> -rGO	11.7	$1.5 \pm 0.4$	40.1

Table S4 Particle size and active surface area (calculated from TEM image)



Figure S10 The calculated Tafel slopes for OER on the IrO<sub>2</sub> nps on the B-doped and undoped catalysts, calculated from their LSV profiles

Table S5	Calculated	Tafel slopes	for IrO <sub>2</sub> -	-B-rGO with	different	Ir content
						1

Catalyst (Ir wt. %)	Tafel slope (mV dec <sup>-1</sup> )
IrO <sub>2</sub> -B-rGO-3.3	142.0
IrO <sub>2</sub> -B-rGO-11.7	104.2
IrO <sub>2</sub> -B-rGO-19.6	124.8
IrO <sub>2</sub> - rGO -11.7	176.5



**Figure S11 a)** Accelerated durability test profiles for IrO<sub>2</sub>-B-rGO-19.6 and IrO<sub>2</sub>-rGO-11.7 (before (solid line) and after 1000 cycles (dashed line))



**Figure S11 b)** Chronopotentiometry profiles for IrO<sub>2</sub>-B-rGO and IrO<sub>2</sub>-rGO catalysts at 10 mA cm<sup>-2</sup> (inset: magnified image at time scale of 60 min)



Figure S11 c) ADT studies of B-rGO in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution between 1.20 and 1.65 V vs RHE

## **References:**

- 1 Y. Lee, J. Suntivich, K. J. May, E. E. Perry and Y. Shao-Horn, J. Phys. Chem. Lett., 2012, 3, 399–404.
- 2 V. Pfeifer, T. E. Jones, J. J. Velasco Vélez, C. Massué, M. T. Greiner, R. Arrigo, et al., Phys. Chem. Chem. Phys., 2016, 18, 2292–2296.