## **Supporting Information**

## Three Dimensional Nanocomposite of Reduced Graphene Oxide and Hexagonal Boron Nitride as an Efficient Metal-Free Catalyst for Oxygen Electroreduction

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## **Experimental Details:**

## (a) Synthesis of Graphene Oxide (GO)

Graphene oxide was synthesized using a modified Hummer's method [49]. Briefly, 2.0 g graphite powder and 1.0 g NaNO<sub>3</sub> were mixed with 46 mL concentrated H<sub>2</sub>SO<sub>4</sub>. Afterwards, above mixture stirred together for 30 minutes and at vigorous condition 6.0 g KMnO<sub>4</sub> was slowly added under ice bath to prevent the temperature below the room temperature. Next, the mixtures was stirred and held at 35°C for 30 minute. Then 92 mL de-ionized water (DI) water was slowly added into system. Again stir the solution for 15 minute, after that 80 mL warm DI water was added. To reduce excess KMnO<sub>4</sub>, a proper amount of 3% H<sub>2</sub>O<sub>2</sub> aqueous solution was dropped into reaction until no bubbles were observed. The obtained mixture was centrifuged and the product was washed with 5% HCl to remove the residual metal impurities and finally with DI water up to neutral pH. As synthesized GO was collected by using freeze-drying.

Table S1. Comparison of experimental conditions, ORR activities and onset potentials forgraphene based electrocatalysts

Catalyst	Preparation Method Used	Electrolyte	Reference electrode employed	Onset Potential (V vs RHE) <sup>a</sup>	Kinetic current density at 1600 rpm (mA cm <sup>-2</sup> ) <sup>a</sup>	References
Cu <sub>3</sub> N@CNT	Atomic layer deposition (ALD)	0.1 M KOH	Hg/HgO	0.66	N/A	15
CoP- nanocrystals	Hydrotherma l	0.1 M KOH	RHE	0.80	N/A	16
Chemically drilled MWNT	Chemical drilling	0.1 M HClO <sub>4</sub>	RHE	0.73	1.1 (@ 0.2 V)	17
TDMAC- reduced graphene oxide	Physiochemi cal process	0.1 M KOH	Ag/AgCl	0.76	2.7 (@ -0.2 V)	18
N, S co-doped carbon	CO impregnation	0.1 M KOH	Ag/AgCl	0.83	2.3 (@ 0.3 V)	19
N, P, S- tridoped graphene	Thermal annealing	0.1 M KOH	SCE	0.68	N/A	20
N doped- reduced graphene oxide	Ultrasonoche mical	0.1 M KOH	NHE	0.87	2.0 (@ 0.2 V)	21
rGO/Co <sub>3</sub> O <sub>4</sub>	One-pot reaction	0.1 M KOH	Hg/HgO	0.72	N/A	22
Xerogel carbon/ PANFe	Pyrolysis	0.1 M H <sub>2</sub> SO <sub>4</sub>	NHE	0.67	N/A	23
C-N/ graphene compo.	Carbonizatio n of polypyrrole	0.1 M KOH	Ag/AgCl	0.80	N/A	24
Py-N doped graphene	CVD	0.1 M KOH	Ag/AgCl	0.80	N/A	25
X-graph. nanoplatelets	Ball milling	0.1 M KOH	Ag/AgCl	0.83	N/A	26

N-doped graphene film	Organic synthesis route	0.1 M KOH	Ag/AgCl	0.86	1.1 (@ 0.2 V)	27
N-doped graphene oxide	Hydrotherma l	0.1 M KOH	Ag/AgCl	0.79	N/A	28
N-doped graphene oxide	Hydrotherma l	0.1 M KOH	SCE	0.80	N/A	29
B,N doped graphene quantum dots/graphene nanoplates	CVD	0.1 M KOH	Ag/AgCl	0.998	4.5 (@ 0.2 V)	30
B/N substituted carbon ribbons	Thermal reduction	0.1 M KOH	Ag/AgCl	1.00	3.5 (@ 0.2 V)	31
h-BN nanosheets supported on Au	Spin coating	0.5 M H <sub>2</sub> SO <sub>4</sub>	Ag/AgCl	0.70	1.6 (@ 0.2 V)	47
rGO/BN composite	Hydrotherm al method	0.1 M KOH	Ag/AgCl	0.798	3.0 (@ 0.2 V)	Present study

<sup>(a)</sup> All potential have been mentioned against reversible hydrogen electrode (RHE) using standard conversion factor.

Figure S1. SEM image comparison of rGO/BN catalyst



**Figure S1**. (a-d) A typical SEM images comparison of GO-750, GOBN3-750, GOBN7-750 and GOBN10-750 respectively.

Catalyst	Onset (V vs RHE)	E <sub>1/2</sub> (V vs RHE)	Mass activity (mA/mg)
GO-750	0.73	0.57	40.12
GOBN3-750	0.725	0.52	48.98
GOBN5-750	0.798	0.64	155.46
GOBN7-750	0.72	0.51	39.9
GOBN10-750	0.74	0.59	60.79
Comm. Pt/C	1.0	0.88	227.4 (at 0.9 V)

Table S2. Comparison of ORR activities of various electrocatalysts

**Table S2**. The onset potential, half wave potential (V vs RHE) and mass activity (mA/mg) comparison of various rGO/BN nanocomposite catalyst with commercial Pt/C (20 wt %).

Figure S2. SEM image of GOBN composite



**Figure S2.** A low-magnification SEM image comparison of GOBN5 nanocomposite, before (left) and after (right) heat treatment at 750°C.

Figure S3. RRDE studies for GOBN5-750 catalyst



**Figure S3**. Disk current (bottom) and the corresponding ring current (top) for GOBN5-750 catalyst using RRDE at 1600 rpm in  $O_2$ -saturated 0.1 M KOH solution; (geo: geometric current density, sweep rate 10 mV/s).

Figure S4. Comparative ORR polarization curves for different rGO/BN catalysts with at various rotating speed



**Figure S4**. ORR polarization curves for (a) GO-750, (b) GOBN3-750, (c) GOBN7-750 and (d) GOBN10-750, in presence of  $O_2$ -saturated 0.1 M KOH at 25°C. (geo: geometric current density, sweep rate 10 mV/s).

Figure S5. Morphology comparison of GOBN5-750 catalyst after durability test



**Figure S5**. Comparative SEM images of GOBN5-750 electrocatalyst (a) before and (b) after durability test at 10000 cycles.