Electronic Supplementary Information

Dicobalt phosphide nanoparticles encased in boron and nitrogen co-doped graphitic layers as novel non-precious metal oxygen reduction electrocatalysts in alkaline media

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Experimental and characterization details

Materials Cyanamide (50 wt%), cobalt nitrate hexahydrate and 4-hydroxyphenylboronic acid (HPBA) were purchased from Aladdin Industrial Inc. Nafion (5 wt%) were purchased from Sigma–Aldrich. 20 wt% Pt/C commercial electrocatalysts were purchased from Johnson Matthey. All other chemicals were purchased and used without any further purification. The double distilled water was used for solution preparation.

Synthesis of catalysts

For the synthesis of BNC/Co_2P-2, 1.05 g cobalt nitrate hexahydrate, 4.5 mL double distilled water, 0.1 mL phosphoric acid, 3 mL cyanamide and 0.2 g HPBA were mixed under stirring, and then the mixed solution was heated to 80 ºC until completely dry to form royalblue powders. The obtained powders were calcined at 800 ºC with a heating rate of 4 ºC min^{-1} in a tubular furnace protected by N_2 for 3 h. After etched in 2 M H_2SO_4 at 80 ºC for 8 h, washed with double distilled water and ethanol, and finally dried, BNC/Co_2P-2 was obtained. The BNC/Co_2P-1 and BNC/Co_2P-3 samples were prepared with the same synthesis conditions as that for BNC/Co_2P-2, except using different addition of HPBA, 0.1 and 0.3 g, respectively. NC/Co_2P was prepared on the same process without addition of HPBA. Sample BNC was synthesized using 3 mL cyanamide, 0.1 mL phosphoric acid and 0.2 g HPBA as the precursors. Meanwhile, sample CoO/$Co_3(BO_3)_2$ was synthesized using 1.40g cobalt nitrate hexahydrate, 0.1 mL phosphoric acid and 0.2 g HPBA as the precursor.

Characterization

Transmission electron microscopy (TEM) images recorded on a high-resolution Hitachi JEM-2100 system equipped with an EDX analyzer operating at 200 kV. The X-ray diffraction (XRD)

patterns were measured using an X-ray D/max-2200vpc (Rigaku Corporation, Japan) instrument operated at 40 kV and 20 mA using Cu Kα radiation (k = 0.15406 nm). The specific surface areas of the samples are analyzed with a surface area analyzer (ASAP 2020, Micromeritics, USA) using physical adsorption/desorption of N_2 at the liquid-N_2 temperature. The X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 spectrometer (Thermo Electron Corp.) with Al Kα radiation (1486.6 eV) as the excitation source.

Electrochemical Measurements

Rotating disk electrode (RDE) voltammetry experiments were performed using a PARSTAT 2273 Electrochemistry Workstation. Rotating ring-disk electrode (RRDE) voltammetry experiments were performed using a speed control unit-Princeton Applied Research Model 636 Electrode Rotator and a PINE RRDE with Glassy carbon (GC) disk and Pt ring. Three-electrode system was used, which was composed of an Ag/AgCl electrode as the reference electrode, a platinum electrode as the counter-electrode and a GC electrode as the working electrode.

All electrochemical measurements were performed at room temperature in O_2-saturated 0.1 M KOH solution. The working electrode was polished with 1, 0.3 and 0.05 μm alumina powders, respectively, then ultrasonically cleaned with ethanol and double distilled water and dried in nitrogen. GC disk electrode was modified by the catalysts with the loadings of 213.3 μg cm^{-2} (5 mm diameter for RDE and 5.61 mm diameter for RRDE). All the modified electrodes were dried in air.

The 0.1 M KOH solution was saturated with oxygen by bubbling O_2 for 15 min prior to each ORR test. The LSV curves were recorded from 0.2 to -0.7 V at a rotating speeds of 1600 rpm and a scanning rate of 5 mV s^{-1}. For the RRDE test, the disc electrode was scanned at 5 mV s^{-1} with a

rotation rate of 1600 rpm, while the ring electrode was held at 0.5 V. The chronoamperometric measurements were performed at -0.4 V.

The electron transfer number and the amount of HO_2^- generated during ORR from RRDE experiment were determined by equation given blow:

$$HO_2^-(\%) = \frac{200 I_R}{I_D N + I_R} \quad \textbf{Equation 1}$$

$$n = \frac{4 I_D}{I_D + I_R / N} \quad \textbf{Equation 2}$$

Where I_R is the ring current, I_D is the disk current, N is the collection efficiency with a value of 0.37.

Supplementary Results

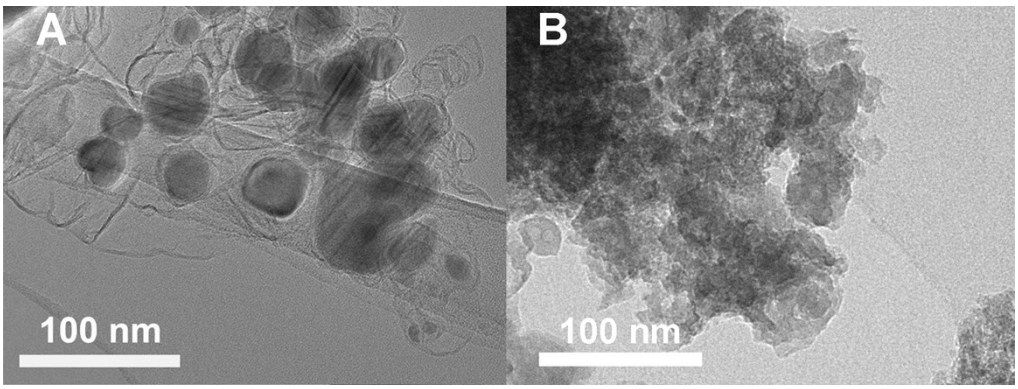


Fig. S1 TEM images of NC/Co_2P (A) and BNC (B).

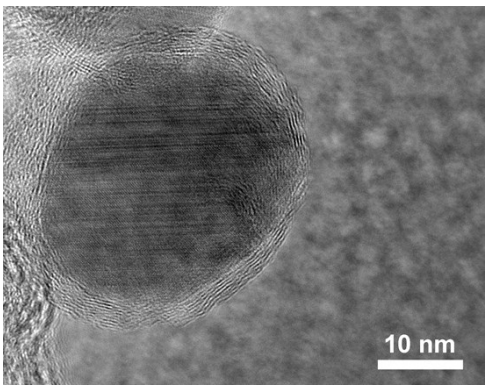


Fig. S2 HRTEM image of BNC/Co_2P-2.

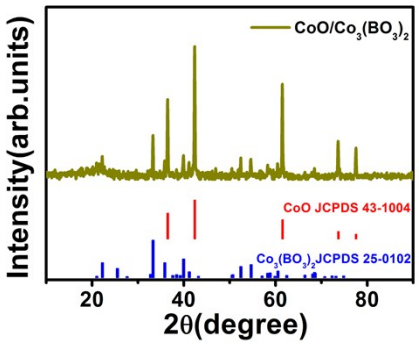


Fig. S3 XRD pattern of $CoO/Co_3(BO_3)_2$.

Table S1. The chemical structure and composition of the as-prepared materials

Catalyst	The addition of HPBA (g)	Elementary content (at %)						N 1s (at %)				B 1s (at %)	
		C	O	N	B	Co	P	N1	N2	N3	N4	B1	B2
$NC@Co_2P$	-	84.31	11.32	3.09	-	0.86	0.42	38.12	26.14	27.68	8.06	-	-
$BNC@Co_2P$-1	0.1	77.30	15.97	3.98	1.54	0.80	0.41	47.34	23.26	20.14	9.26	77.28	22.72
$BNC@Co_2P$-2	0.2	78.99	9.36	6.80	3.56	0.82	0.47	51.55	24.04	18.27	6.14	79.53	20.47
$BNC@Co_2P$-3	0.3	71.38	8.61	10.22	8.64	0.78	0.37	64.75	22.61	12.64	-	82.37	17.63

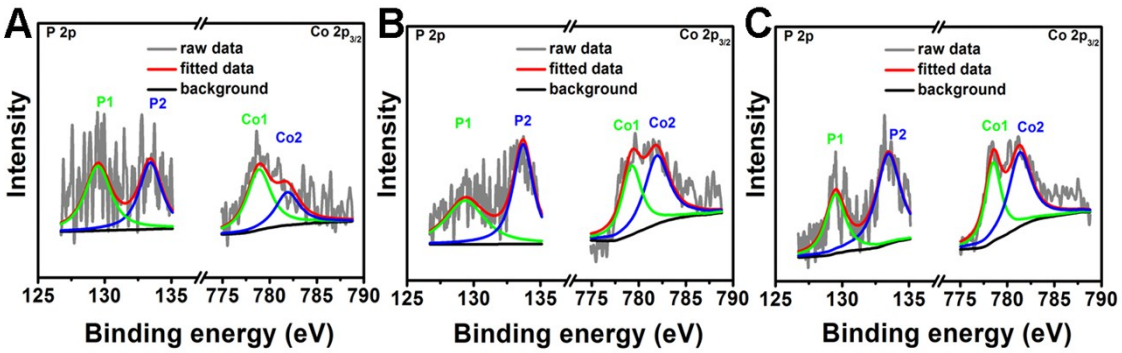
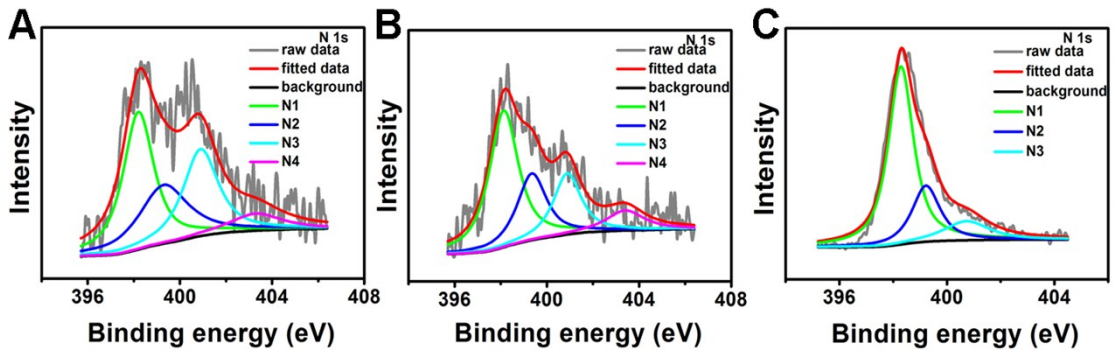


Fig. S4 XPS Co $2p_{3/2}$ and P 2p spectra of NC/Co_2P (A), BNC/Co_2P-1 (B) and BNC/Co_2P-3 (C).



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2 **Fig. S5** High-resolution N 1s XPS spectra of NC/Co_2P (A), BNC/Co_2P-1 (B) and BNC/Co_2P-

3 3 (C).

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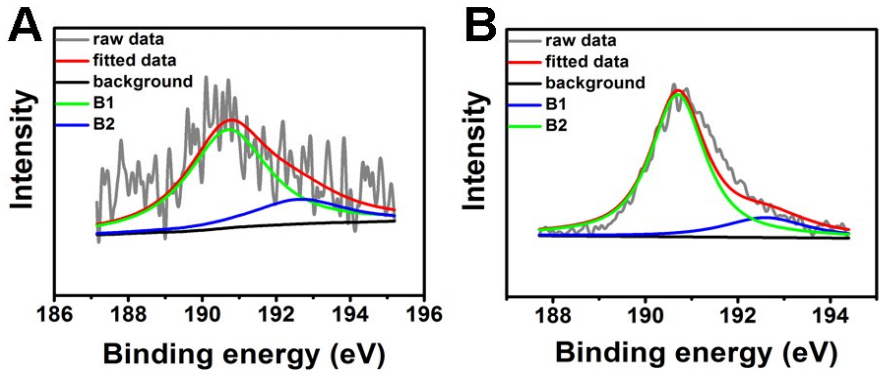

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6 **Fig. S6** High-resolution B 1s XPS spectra of BNC/Co_2P-1 (A) and BNC/Co_2P-3 (B).

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