

## Supporting Information

### Effective construction of B, N co-doped 3D porous carbon metal-free oxygen reduction reaction catalyst by secondary pyrolysis strategy

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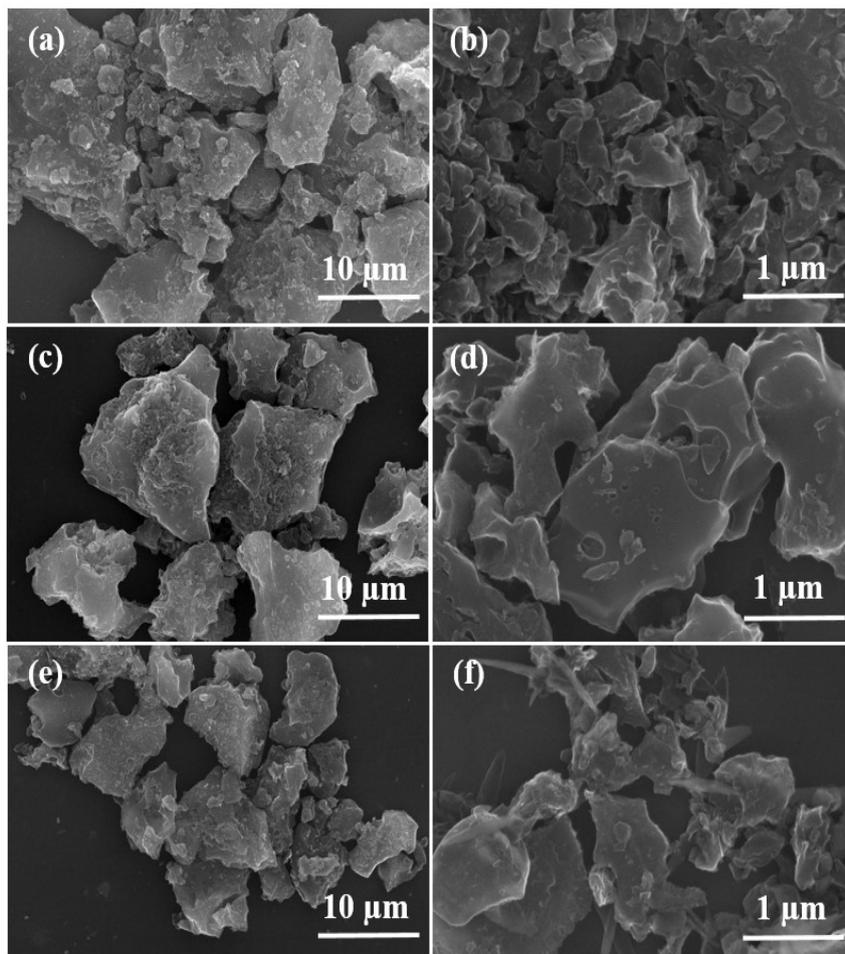
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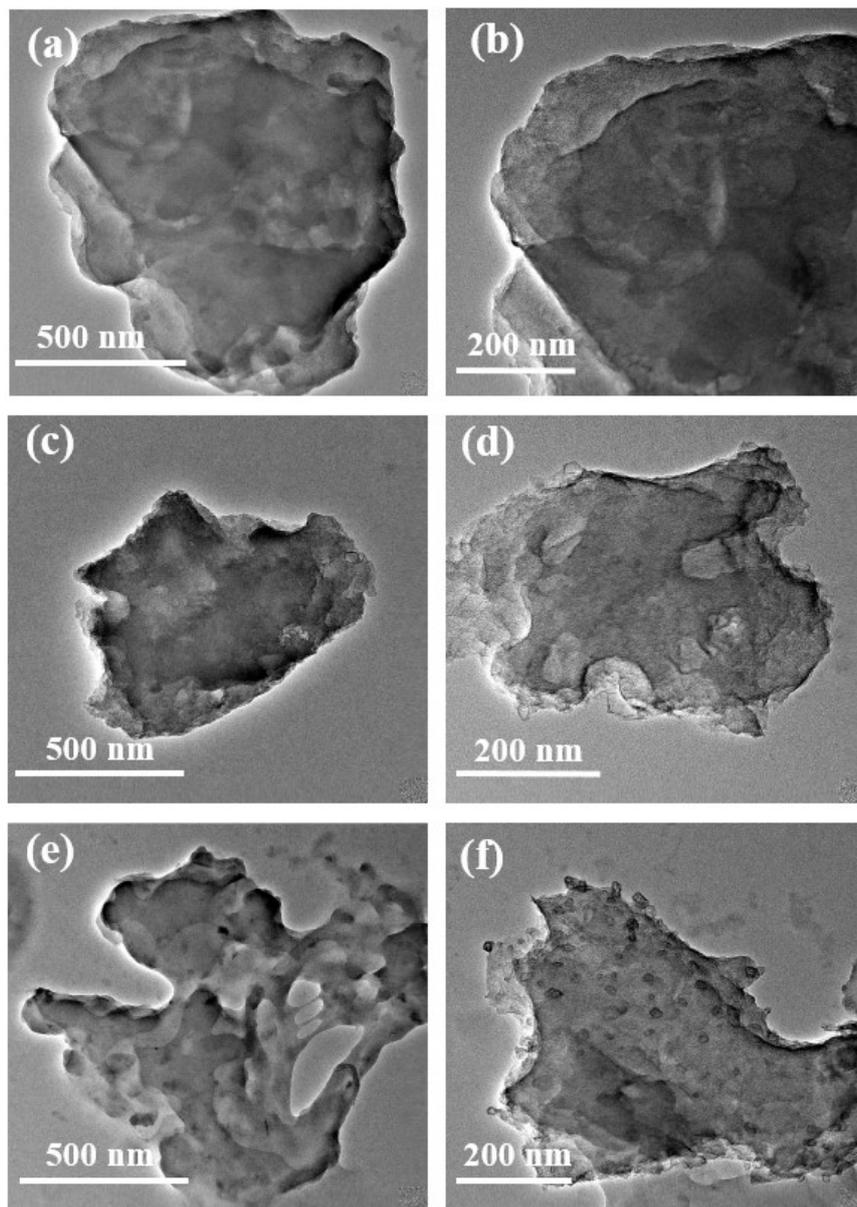
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**Figure S1.** SEM images of (a-b) BNC-pre, (c-d) BNC-one, and (e-f) NC catalysts.



**Figure S2.** TEM images of (a-b) BNC-pre, (c-d) BNC-one, and (e-f) NC catalysts.

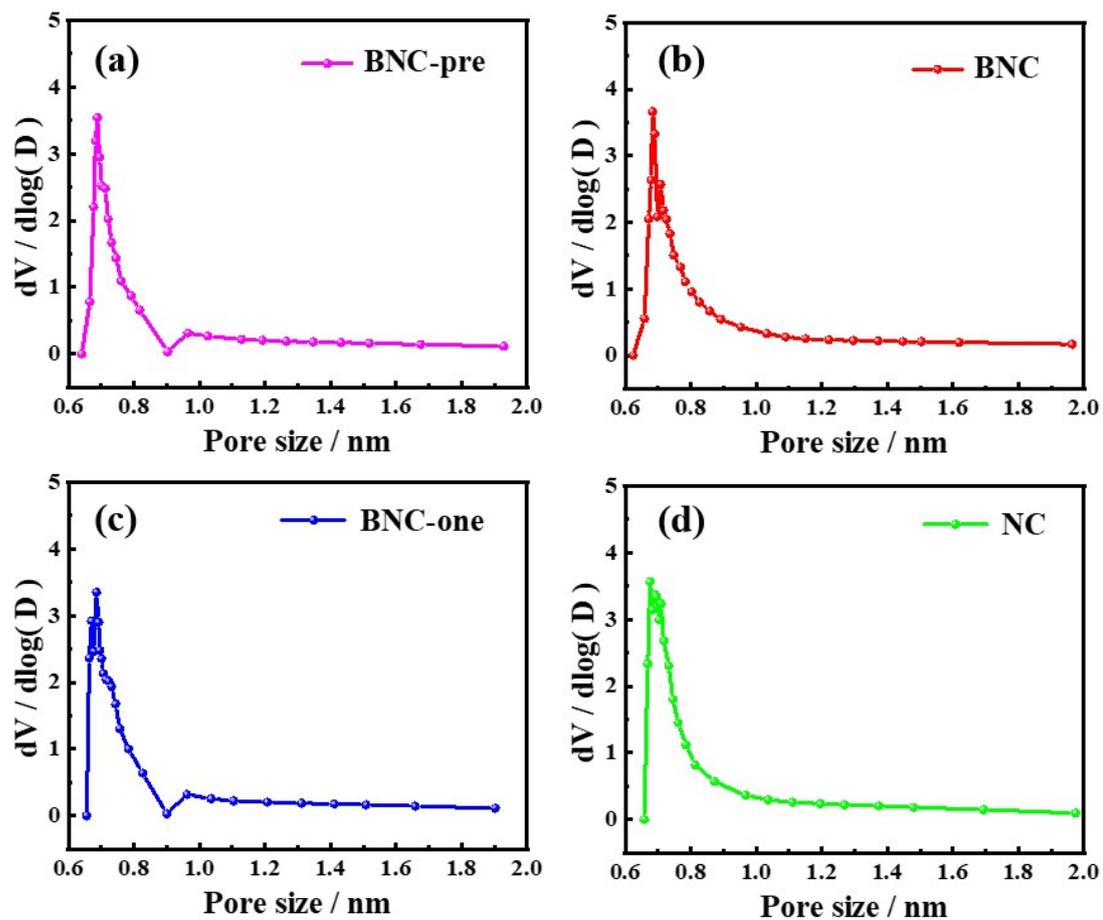
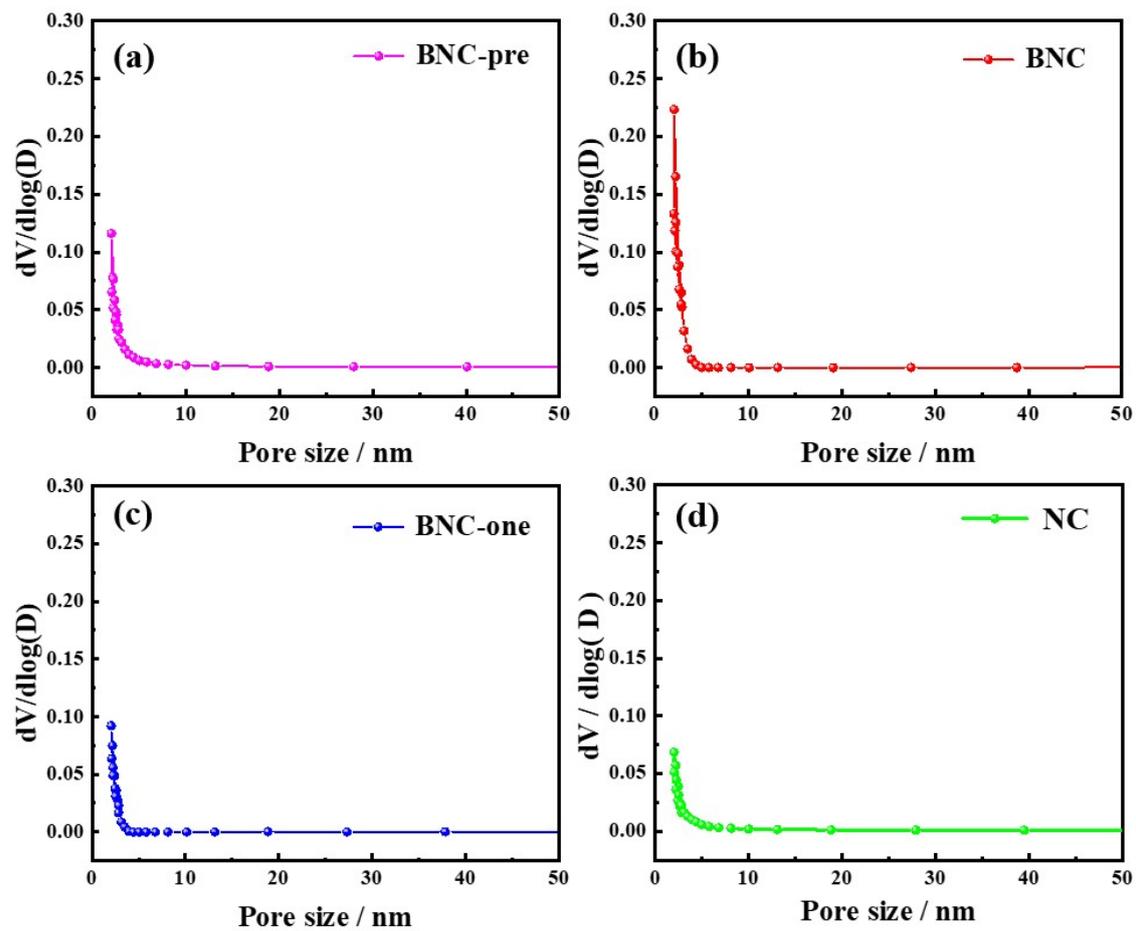
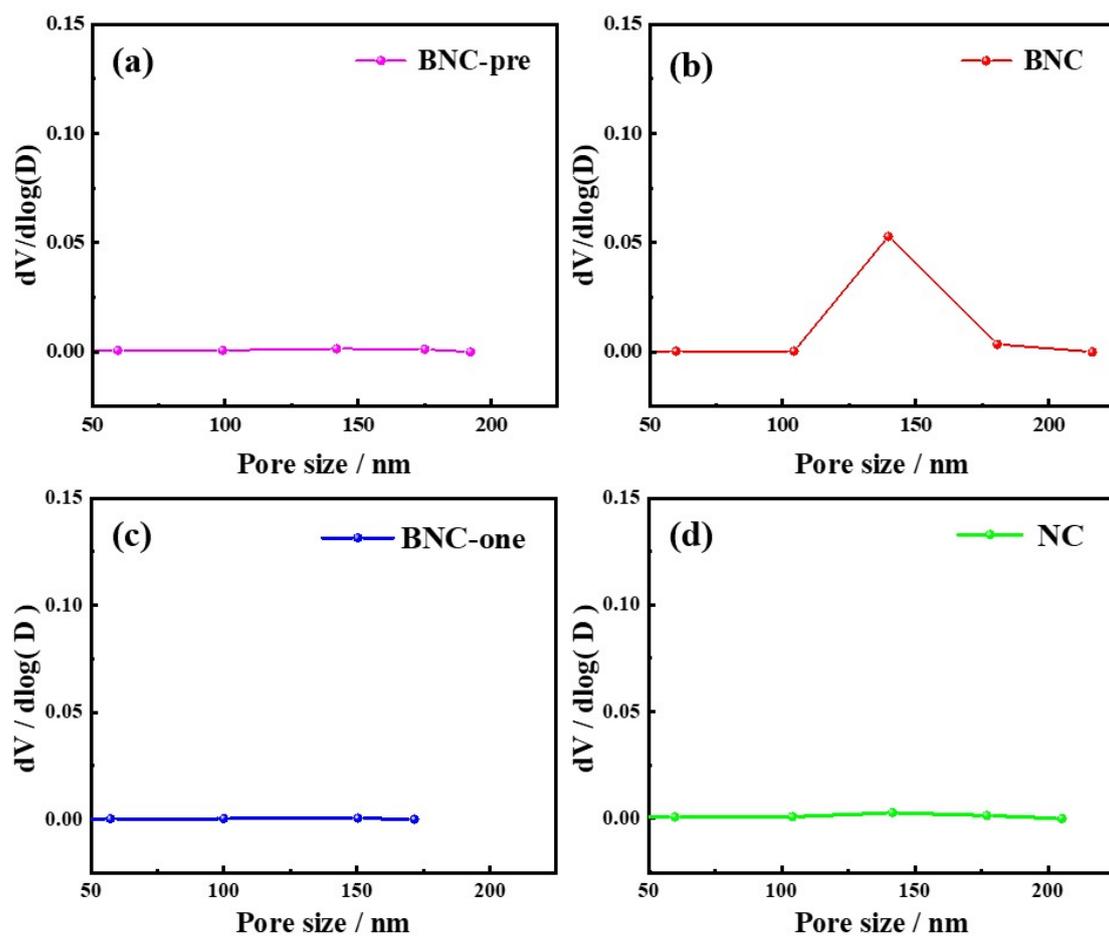


Figure S3. Micropore distribution curves of BNC-pre, BNC, BNC-one, and NC catalysts.



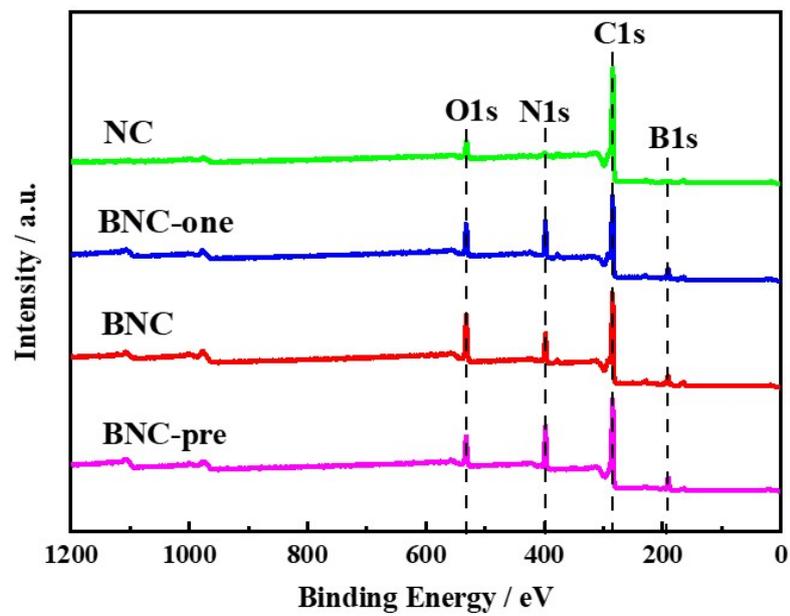
**Figure S4.** Mesoporous distribution curves of BNC-pre, BNC, BNC-one, and NC catalysts.



**Figure S5.** Macropore distribution curves of BNC-pre, BNC, BNC-one, and NC catalysts.

**Table S1.** The parameters of porous structures based on BET data for the prepared samples.

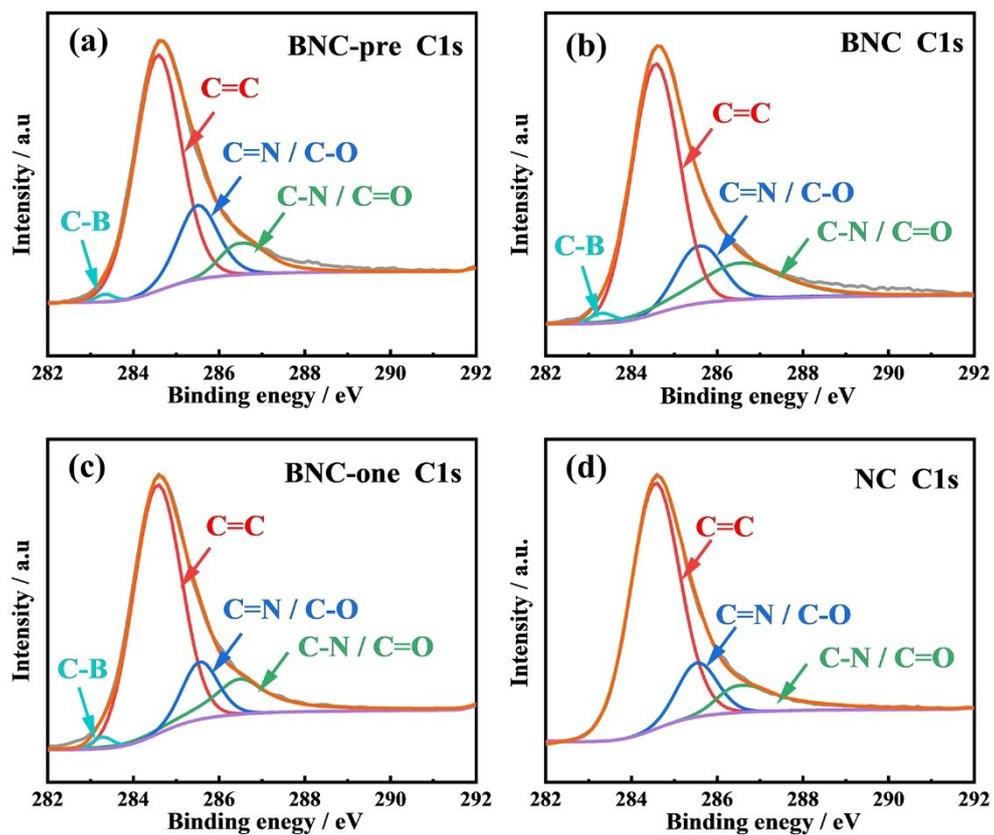
Samples	Specific surface area ( $\text{m}^2 \text{g}^{-1}$ )	Total pore volume ( $\text{cm}^3 \text{g}^{-1}$ )
BNC-pre	1228.5	0.776
BNC	1539.7	1.56
BNC-one	1299.9	0.656
NC	1405.9	0.889



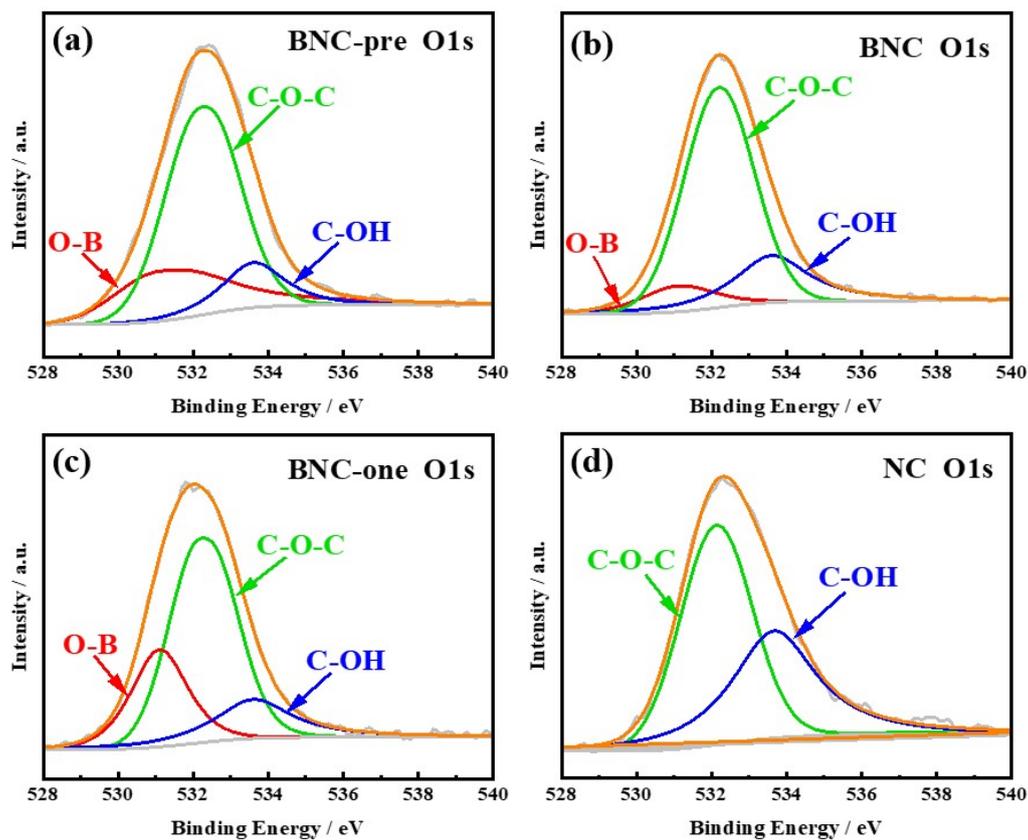
**Figure S6.** XPS spectra of BNC-pre, BNC, BNC-one, and NC catalysts.

**Table S2.** The element contents (at. %) of C, N, B, and O of BNC-pre, BNC, BNC-one, and NC catalysts based on the XPS.

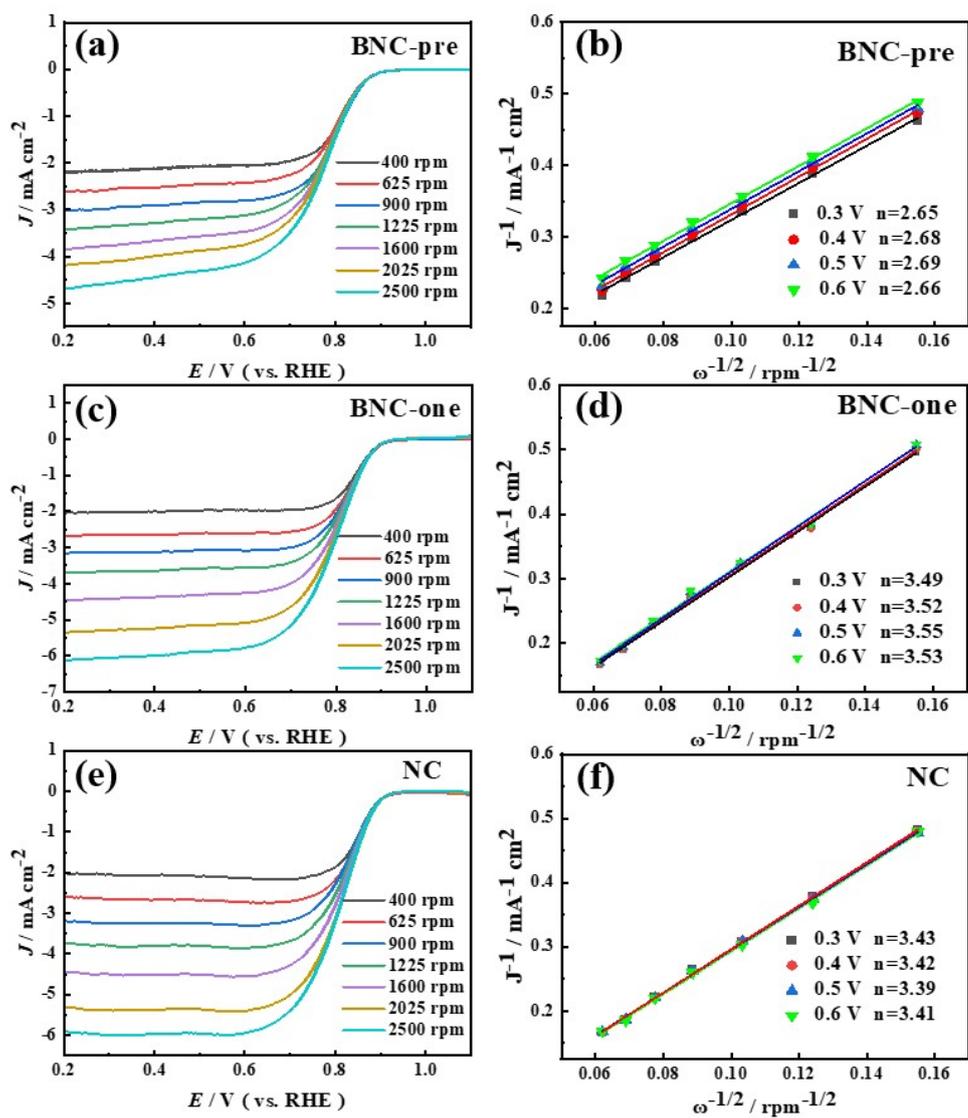
Element	BNC-pre	BNC	BNC-one	NC
C (at. %)	59.82	59.79	60.87	90.77
N (at. %)	15.27	11.30	14.23	3.30
B (at. %)	17.07	15.92	15.00	/
O (at. %)	7.83	12.99	9.90	5.93



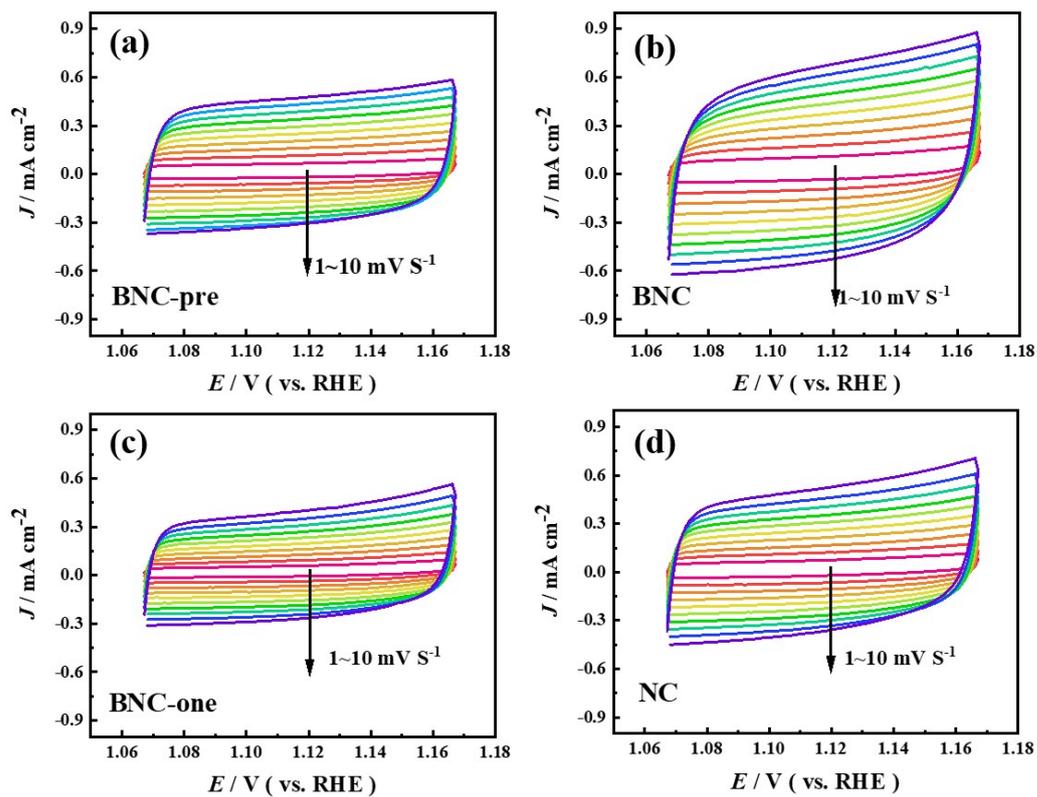
**Figure S7.** C 1s XPS spectra of (a) BNC-pre, (b) BNC, (c) BNC-one, and (d) NC catalysts.



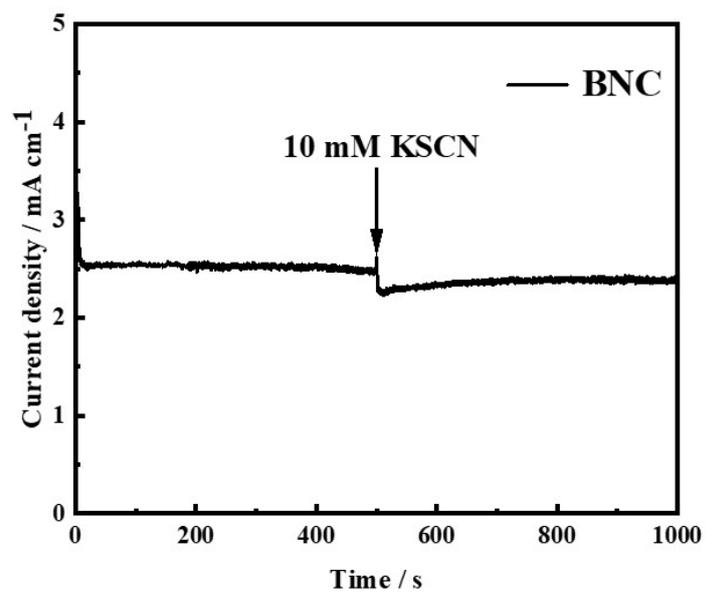
**Figure S8.** O 1s spectra of BNC-pre, BNC, BNC-one, and NC catalysts.



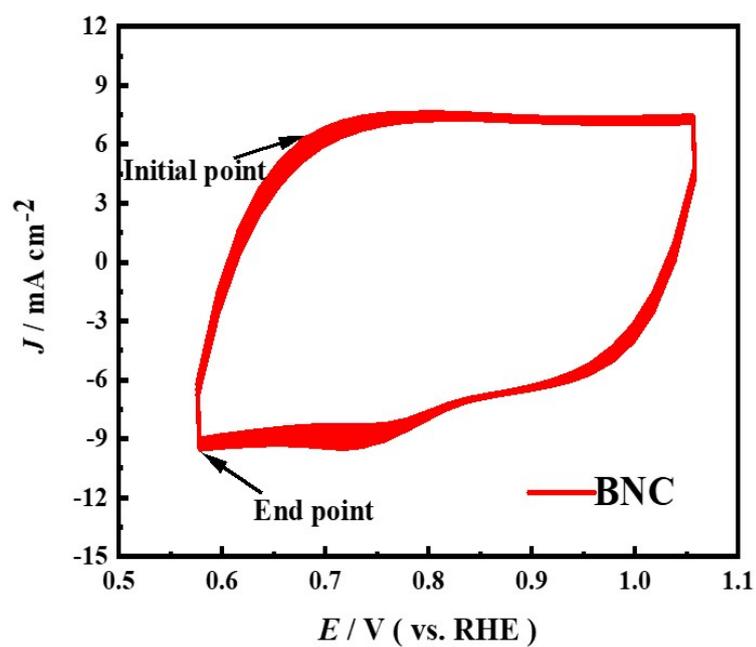
**Figure S9.** (a, c, e) ORR polarization curves of BNC-pre, BNC-one, and NC recorded at different rotation speeds. (b, d, f) Linearly fitted K-L curves at different potential of BNC-pre, BNC-one, and NC.



**Figure S10.** The CV curves at various scan rate ( $1\text{-}10 \text{ mV s}^{-1}$ ) of (a) BNC-pre, (b) BNC, (c) BNC-one, and (d) NC.



**Figure S11.** Chronoamperometric response of BNC in O<sub>2</sub>-saturated 0.1 M KOH with the addition of KSCN (resulting in an electrolyte with 0.01 M KSCN).



**Figure S12.** ORR cyclic measurements of BNC at a scan rate of  $100 \text{ mV s}^{-1}$  for 10000 cycles.