Supplementary Information

Tuning the electrochemical properties of boron and nitrogen codoped nanodiamond rod array to achieve high performance for both electrooxidation and electro-reduction

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Fig. S1 Schematic diagram of the designed double-compartment cell for BDE-47 electro-reduction.

 Table S1 The B and N contents of different electrocatalysts.

| | BDD | NDD | BND1 | BND2 |
|-----------|-------|-------|-------|-------|
| B content | 1.89% | 0 | 1.96% | 1.90% |
| N content | 0 | 0.85% | 0.81% | 1.06% |



Fig. S2 Cyclic voltammograms of various electrodes in 0.1 M KOH electrolyte at a scan rate of 50 mV s⁻¹.



Fig. S3 The cyclic voltammograms of BDD/Si RA, BND4/Si RA, BND5/Si RA and BND1/Si RA for methanol oxidation in 0.1 M KOH electrolyte containing 1.0 M CH₃OH at a scan rate of 50 mV s⁻¹.

The BND/Si RAs with N content 0.2%, B/C = 0.01 (defined as BND4/Si RA) and N content 0.5%, B/C = 0.01 (defined as BND5/Si RA) in the precursors were prepared, and their cyclic voltammograms for methanol oxidation were shown in Fig. S3. It reveals the peak potential for methanol oxidation is positively shifted from 0.85 V on BDD/Si RA to 0.34 V on BND4/Si RA. When the N content increases from 0.3% to 0.7%, the peak potential is further positively shifted. Meanwhile, the current density is improved gradually.



Fig. S4 The cyclic voltammograms of BND3/Si RA and Pt/C@Si RA for methanol oxidation in 0.1 M KOH electrolyte containing 1.0 M CH₃OH at a scan rate of 50 mV s⁻¹.

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Fig. S5 In situ infrared spectrum of methanol electrooxidation at BND3/Si RA under different potentials in 0.1 M KOH.



Fig. S6 Pseudo-first-order plots of BDE-47 reduction on VA-BND3/Si RA under different potentials.



Fig. S7 Pseudo-first-order plots of BDE-47 reduction on Pd electrode under -0.80 V.