Supporting Information

Tuning local electronic structure of single-site Ni catalyst by co-doping 3D graphene framework with B/N atoms toward enhanced CO_2 electroreduction

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Supplementary experimental section:

Chemicals

1,4-benzenediboronic acid (BDBA, 97%) and o-phenylenediamine (oPD, 99.5%) were purchased from Aladdin Reagent Co., Ltd.. Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, 98%), potassium bicarbonate ($KHCO_3$, 99.5%), hydrogen peroxide (H_2O_2, 30%), and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd.. Nafion solution (5 wt%) was obtained from Alfa Aesar Chemical Reagent Co., Ltd. All the chemicals were used as received without any further purification. The water used in the synthesis and testing was deionized (DI) with a resistivity of 18.2 MΩ·cm.

Material characterizations

Scanning electron microscopy (SEM) images were taken on a Zeiss Supra 40 field-emission scanning electron microscope at 5 kV. Transmission electron microscopy (TEM) images were taken on a Hitachi Model H-7700 microscope at 100 kV. Atomic resolution aberration-corrected high-angle annular dark-field scanning TEM (HAADF-STEM) images were recorded on JEOL JEM-ARM200F TEM/STEM with a spherical aberration corrector. The corresponding elemental energy-dispersive X-ray spectroscopy (EDS) was collected on an FEI Talos F200X high-resolution transmission electron microscope. High-resolution X-ray photoelectron spectra (XPS) were collected on Thermo ESCALAB 250Xi photoelectron spectrometer, using non-monochromatized Al-Kα X-ray (1486.6 eV) as the excitation source. The spectra were corrected by referencing C 1s to 284.8 eV. Powder X-ray diffraction (XRD) patterns were performed using a Philips X'Pert Pro Super X-ray diffractometer with Cu-Kα radiation (λ = 1.54178 Å). The inductively coupled plasma-atomic emission spectrometry (ICP-AES) was taken on a Thermo Fisher iCAP7400 spectrometer. Brunauer–Emmett–Teller (BET) surface areas of the prepared samples were obtained using nitrogen adsorption-desorption isotherms with a ASAP 2460 adsorption apparatus (Micromeritics, USA).

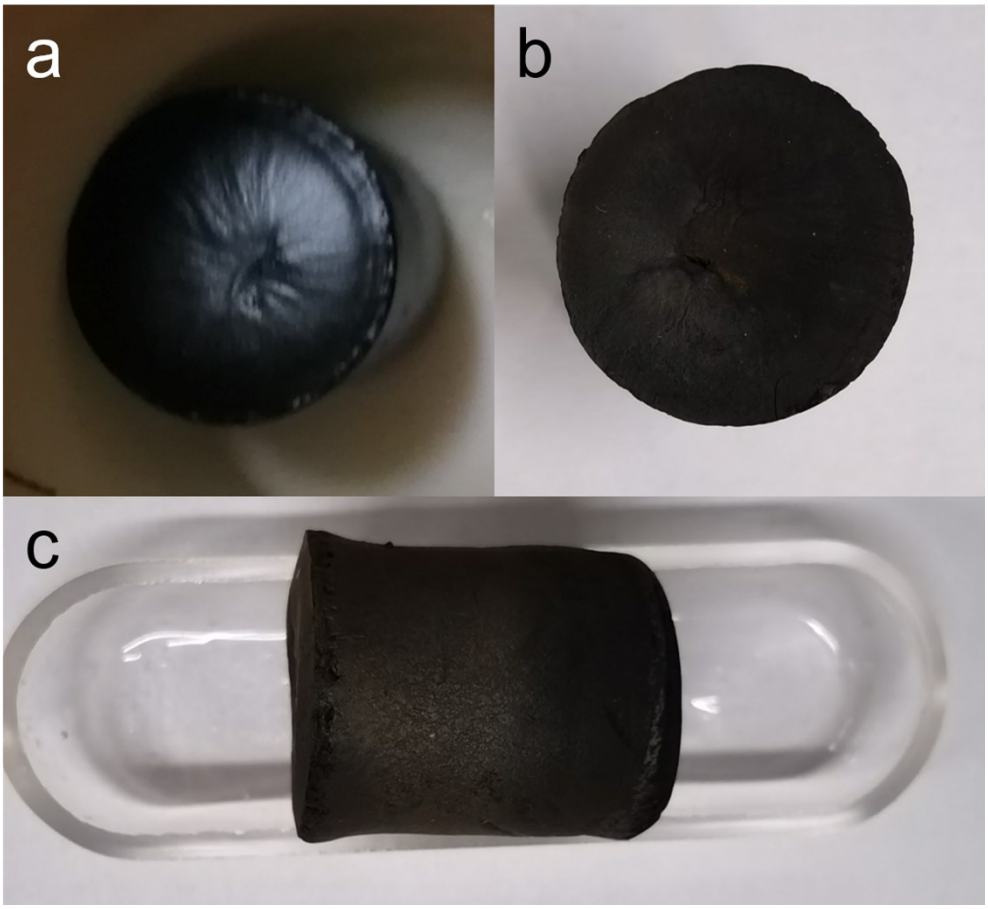

Fig. S1 Photograph of 3D porous graphene framework hydrogel with the B, N-containing polymer and Ni sites. (a) After hydrothermal. (b-c) After directional freezing dry.

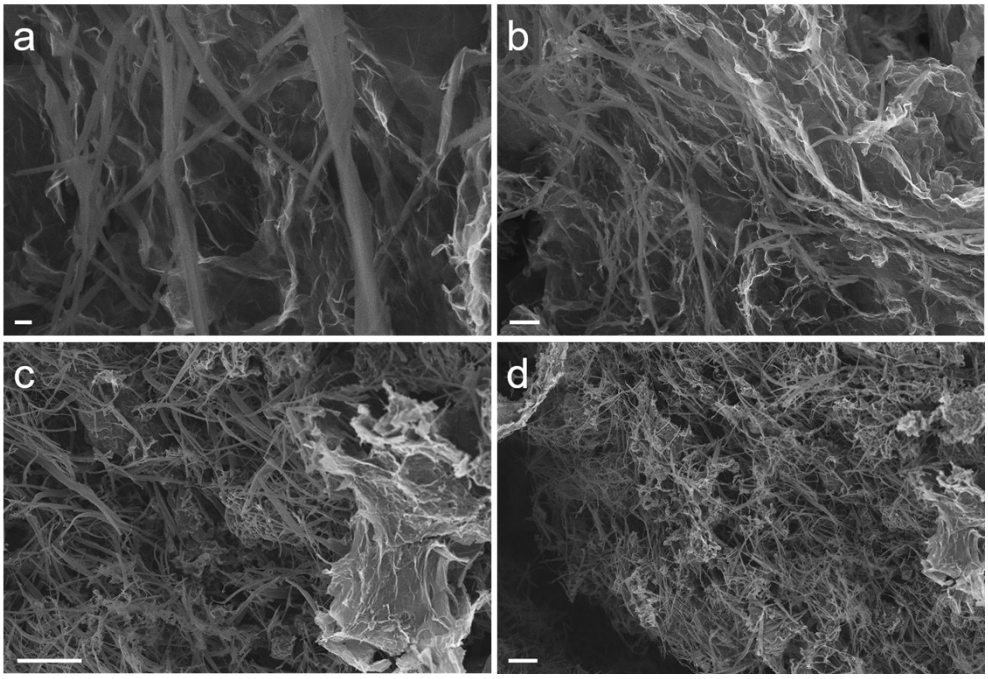

Fig. S2 SEM images of the graphene framework loading with Ni sites and the polymer nanofibers derived from the polymerization of oPD monomer. The scale bars are (a) 200 nm, (b) 1 μm, and (c, d) 10 μm.

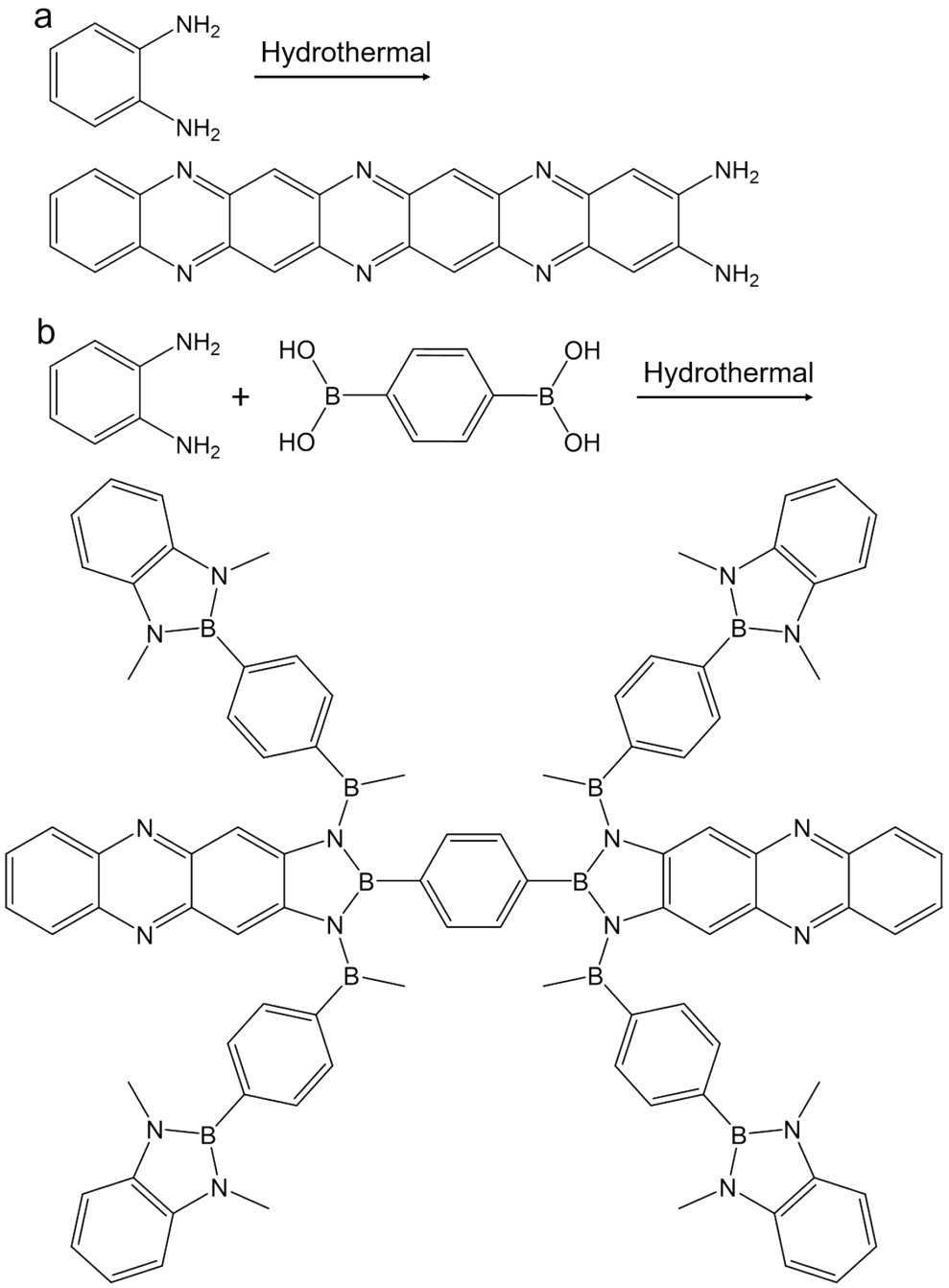

Fig. S3 The chemical reactions for (a) oPD self-polymerization, and (b) oPD and BDBA copolymerization.

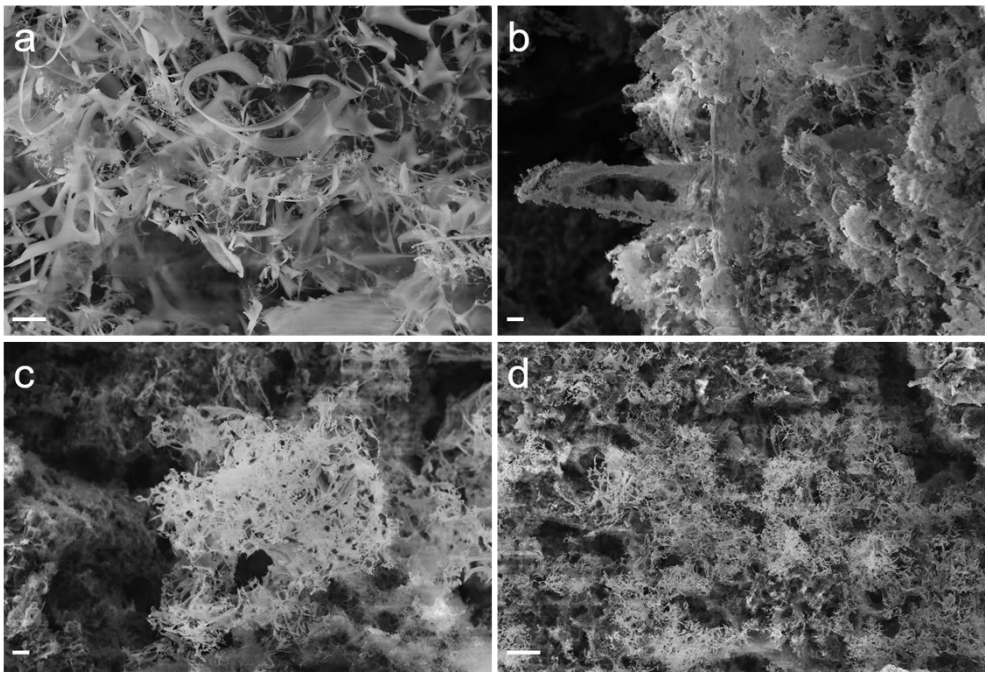

Fig. S4 SEM images of the graphene framework loaded with Ni sites and the polymer nanofibers derived from the polymerization of oPD and BDBA monomer. The scale bars are (a, b) 1 μm, (c) 2 μm, and (d) 10 μm.

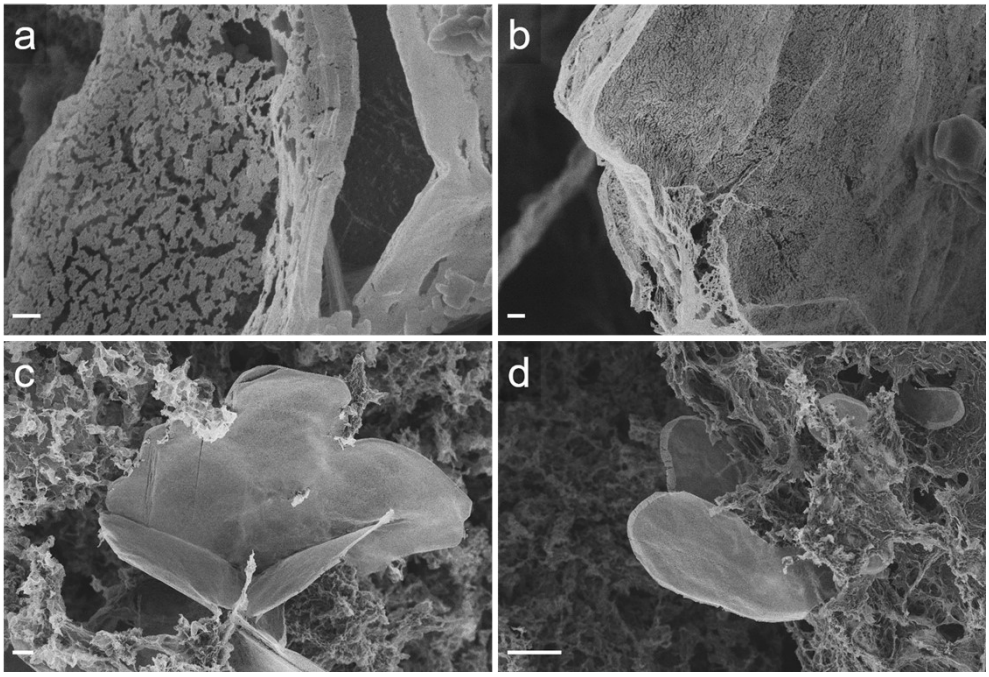

Fig. S5 SEM images of the graphene framework loaded with Ni sites and the polymer nanofibers derived from the polymerization of BDBA monomer. The scale bars are (a, b) 200 nm, (c) 2 μm, and (d) 10 μm.

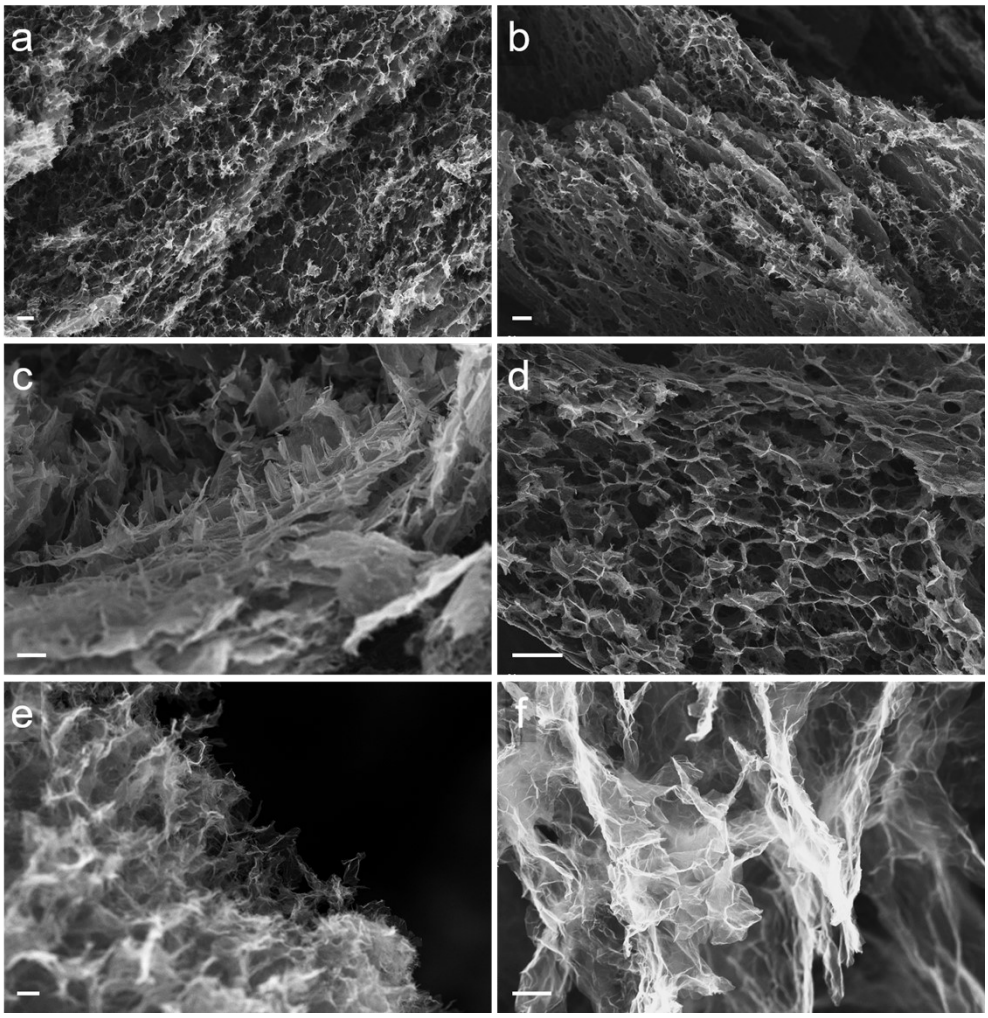

Fig. S6 SEM images of the Ni-B_2N_4 sample. The scale bars are (a) 10 μm, (b, d) 20 μm, (e) 2 μm, and (f) 1 μm.

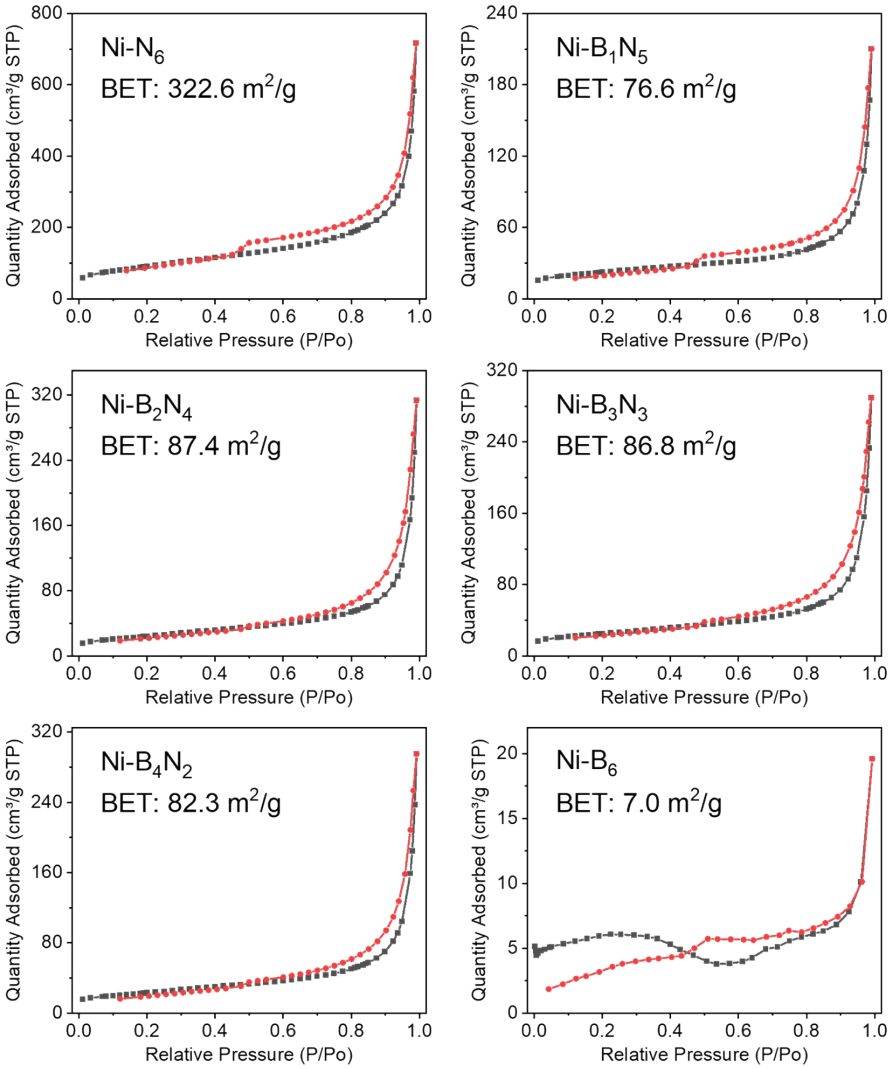

Fig. S7 The Brunauer–Emmett–Teller (BET) surface area analysis for Ni-B_xN_{6-x} (x=0-6) samples.

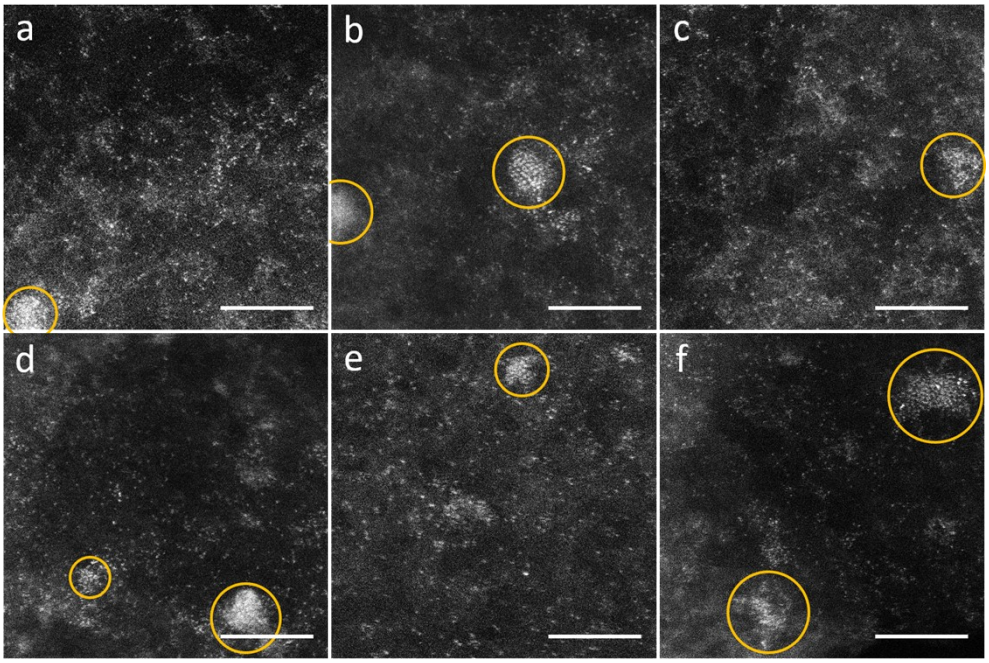

Fig. S8 Aberration-corrected HAADF-STEM images of the Ni-N_6 sample in multiple areas. The Ni nanoclusters and nanoparticles are marked by yellow circles. The scale bar is 5 nm.

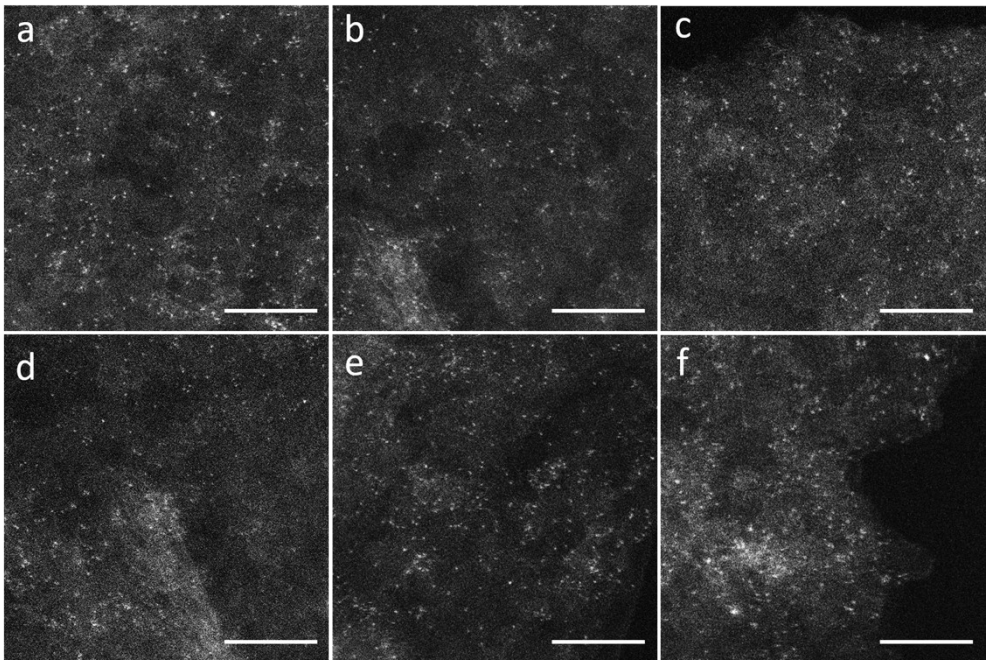

Fig. S9 Aberration-corrected HAADF-STEM images of the Ni-B_2N_4 sample in multiple areas. The scale bar is 5 nm.

Table S1. The loading amounts of Ni sites for Ni-B_xN_{6-x} (x=0-6) samples.

Sample	Ni content (wt %)
Ni-N_6	0.488
Ni-B_1N_5	0.495
Ni-B_2N_4	0.571
Ni-B_3N_3	0.524
Ni-B_4N_2	0.569
Ni-B_6	0.523

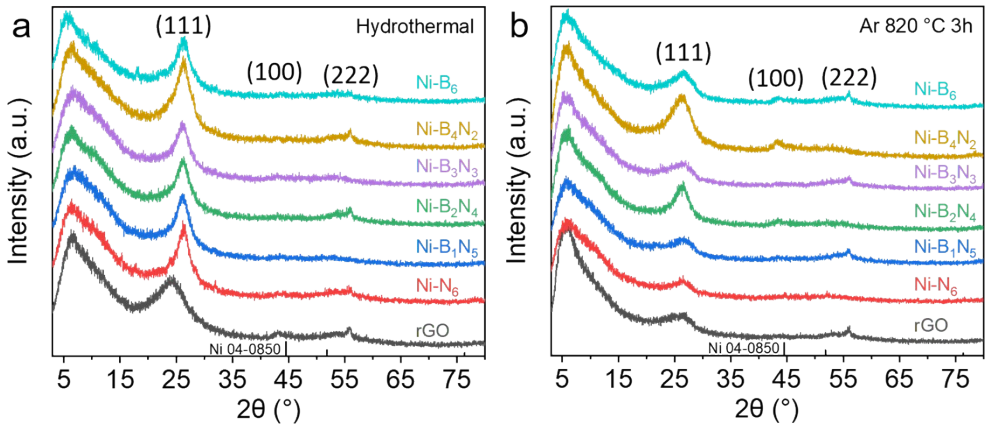

Fig. S10 (a) XRD patterns of the reduced graphene oxide (rGO) and Ni-B_xN_{6-x} (x=0-6) precursors obtained by the hydrothermal process. (b) XRD patterns of the rGO and Ni-B_xN_{6-x} (x=0-6) samples obtained by the pyrolysis under Ar atmosphere at 820 °C for 3 h.

Table S2. The doping percentages for B and N, as well as the B/N ratios in Ni-B_xN_{6-x} (x=0-6) samples.

Sample	B (mole %)	B (wt %)	N (mole %)	N (wt %)	Precursor molar ratio (B:N)	Practical molar ratio (B:N)
Ni-N_6	0	0	5.70	6.45		
Ni-B_1N_5	1.74	1.52	5.88	6.67	0.2	0.30
Ni-B_2N_4	1.97	1.73	4.49	5.09	0.5	0.44
Ni-B_3N_3	2.34	2.05	3.40	3.86	1	0.69
Ni-B_4N_2	3.93	3.43	4.64	5.24	2	0.85
Ni-B_6	3.45	3.02	0	0		

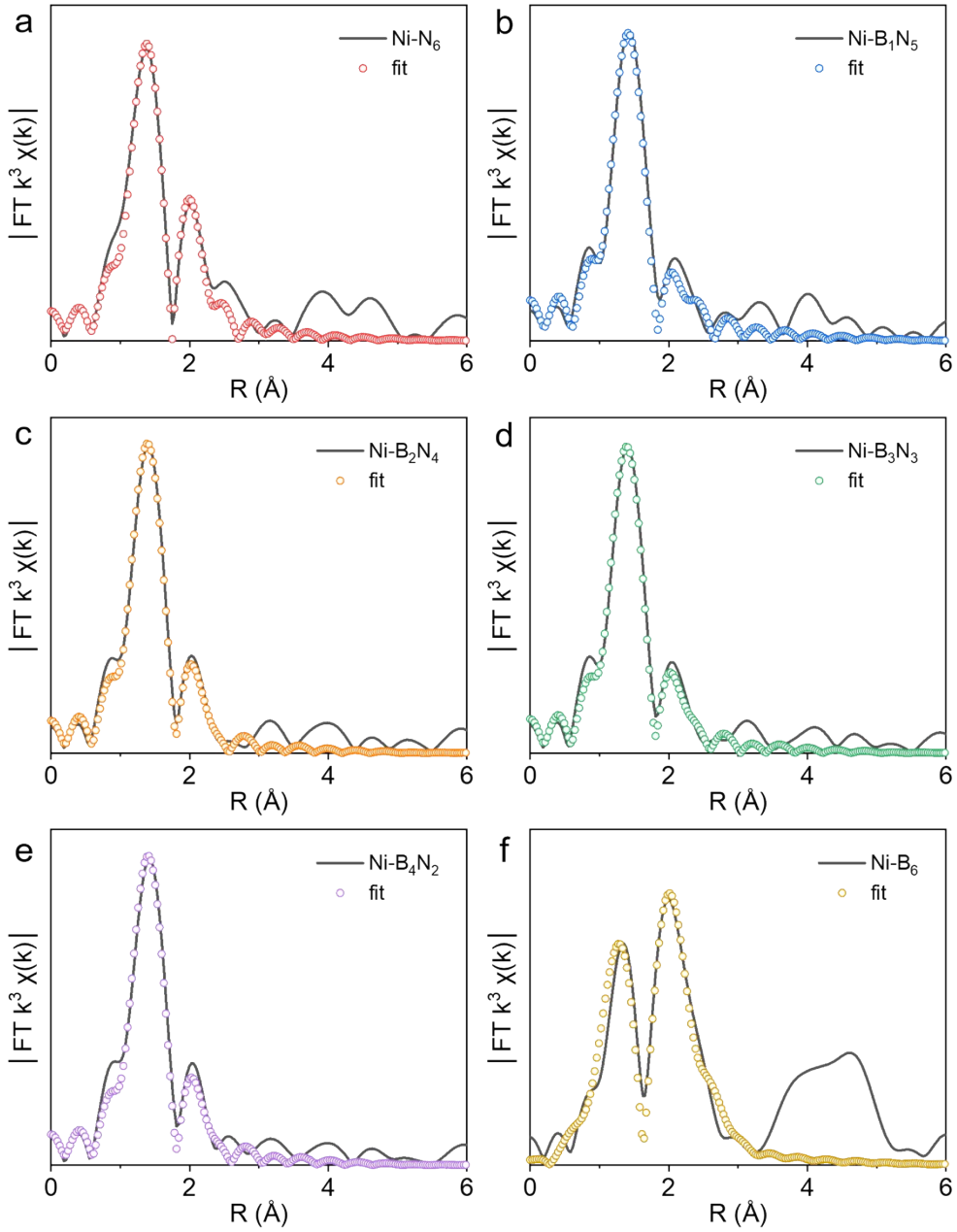

Fig. S11 EXAFS fitting and optimized model for Ni-B_xN_{6-x} (x=0-6) samples.

Table S3. Fitting results of Ni K-edge EXAFS data.

[a]CN, the coordination numbers; R, the bonding distance; σ^2, the Debye-Waller factor. NiPc refers to nickel phthalocyanine.

Sample	Scattering Path	CN	R(Å)	σ^2 (Å)
$Ni\text{-}N_6$	Ni-N/O/C	2.61 +/- 0.16	1.83 +/- 0.04	0.00442
	Ni-C	2.06 +/- 0.35	2.67 +/- 0.14	0.00301
$Ni\text{-}B_1N_5$	Ni-N/O/C	3.18 +/- 0.18	1.85 +/ 0.02-	0.00442
	Ni-B/C	0.89 +/- 0.41	2.69 +/- 0.02	0.00301
$Ni\text{-}B_2N_4$	Ni-N/O/C	3.27 +/- 0.12	1.87 +/- 0.03	0.00442
	Ni-B/C	1.19 +/- 0.24	2.67 +/- 0.01	0.00301
$Ni\text{-}B_3N_3$	Ni-N/O/C	3.00 +/- 0.13	1.85 +/- 0.03	0.00442
	Ni-B/C	1.13 +/- 0.30	2.67 +/- 0.01	0.00301
$Ni\text{-}B_4N_2$	Ni-N/O/C	2.81 +/- 0.15	1.85 +/- 0.03	0.00442
	Ni-B/C	1.02 +/- 0.34	2.66 +/- 0.01	0.00301
$Ni\text{-}B_6$	Ni-O/C	1.87 +/- 0.53	1.71 +/- 0.17	0.00442
	Ni-B/C	4.96 +/- 0.95	2.67 +/- 0.27	0.00301
Ni foil	Ni-Ni	12 (fixed)	2.48 +/- 0.01	0.00573
	Ni-Ni	6 (fixed)	3.52 +/- 0.01	0.00875
NiO	Ni-O	6 (fixed)	2.09 +/- 0.01	0.00614
	Ni-Ni	12 (fixed)	2.96 +/- 0.01	0.00860
NiPc	Ni-N	4 (fixed)	1.90 +/- 0.18	0.00332

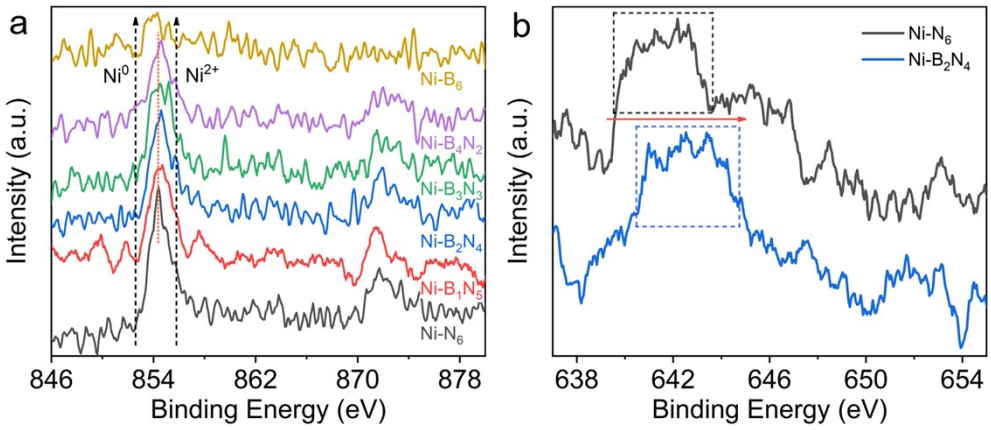

Fig. S12 (a) XPS spectra of Ni 2p for Ni-B_xN_{6-x} (x=0-6) samples. (b) Auger electron spectra of Ni for Ni-N_6 and Ni-B_2N_4.