Supporting Information

Highly efficient Co centers functionalized by nitrogen-doped carbon for the chemical fixation of CO_2

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Supplementary Methods

Materials and Methods

Materials

$CoCl_2 \cdot 6H_2O$ (Sinopharm Chemical Reagent Co., Ltd), 2-Methylglyoxaline (sigma-aldrich, Vetec™ reagent grade, 98%), urea (Sinopharm Chemical Reagent Co., Ltd); styrene oxide (Aladdin, AR, 99.00%). Other substrates were purchased from Aladdin Industrial Corporation. All the chemicals were directly used as received without any further purification.

Synthesis of Co@N_xC samples

2 mmol $CoCl_2 \cdot 6H_2O$ (475.86 mg) was dissolved in 100 mL ethanol. After stirring, 8.947 g of carbon nitriding powder was added, and 16 mmol 2-methyl imidazole (1.314 g) was added. Heat the mixture to 70 ℃ and stir it vigorously. The dried powder was placed into a crucible, capped, and put into a muffle furnace. Nitrogen was continuously injected into the pot. The temperature was raised to 400 ℃ at 2 ℃ /min for 2 h, and then heated to 800 ℃ for 4 h at 5 ℃ /min. Eventually, it was cooled naturally to room temperature and removed to obtain the black product, which was then ground into a powder. Different proportions of Co@N_xC were roasted with the program. During the preparation of Co@$N_{0.06}$C and Co@$N_{0.05}$C, only the dosage of carbon nitride powder was changed, which were 17.849 g and 44.735 g, respectively. There was no subsequent purification process for all samples.

The CO_2 cycloaddition with styrene oxide and its derivatives

Prepare 0.1201 g styrene oxide (1 mmol) in a flask, add 50 mg Co@N_xC catalyst and 0.0645 g TBAB (0.2 mmol), and add 2 mL acetonitrile. After three times of washing with CO_2, the reactants were reacted for 12 hours at a temperature of 60 ℃ in an atmosphere of 1 ATM CO_2. Samples were collected for GC-MS analysis after the reaction time of 4 h and 8 h separately. The samples of ethylene oxide substituted

reaction 1, 2, 3 were analyzed by ^{1}H NMR.

Characterization

Scanning electron microscopy (SEM) observations were recorded on a Nova NanoSEM 230 field emission scanning electron microscope (FEI, USA). The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were taken by a JEM-2100F microscope operated at an acceleration voltage of 200 kV. Powder X-ray diffraction (XRD) patterns were performed on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). X-ray photoelectron spectroscopy (XPS) experiments were performed at a Kratos Axis Ultra DLD spectrometer and ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific). The surface area was determined by a multipoint Brunauer-Emmett-Teller (BET) method, using an ASAP 2460 surface area and porosimetry analyzer. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were taken by a Titan 80-300 scanning/transmission electron microscope operated at 300 kV, equipped with a probe spherical aberration corrector. The sample The qualitative and quantitative analysis of each substance in the reaction system is by means of QP2010E gas chromatography - mass spectrometry (GC-MS) and AVANCE III HD 400 nuclear magnetic resonance (^{1}H NMR).

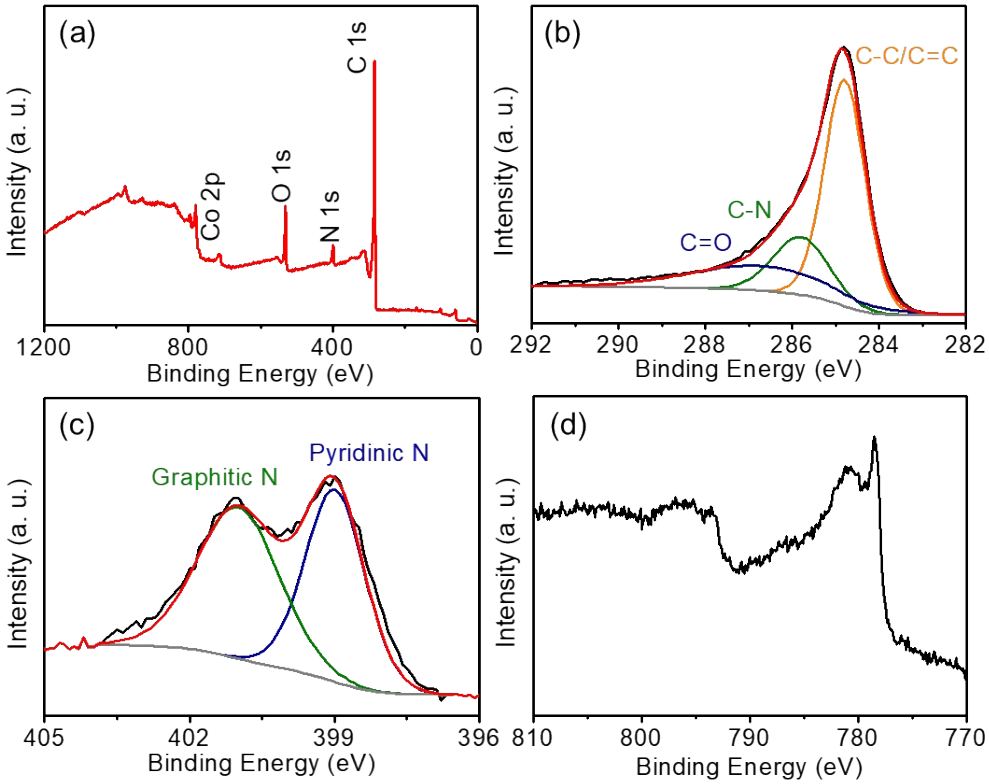

Figure S1. (a) The XPS survey spectrum, (b) C 1s, (c) N 1s and (d) Co 2p XPS spectra of $Co@N_{0.07}C$.

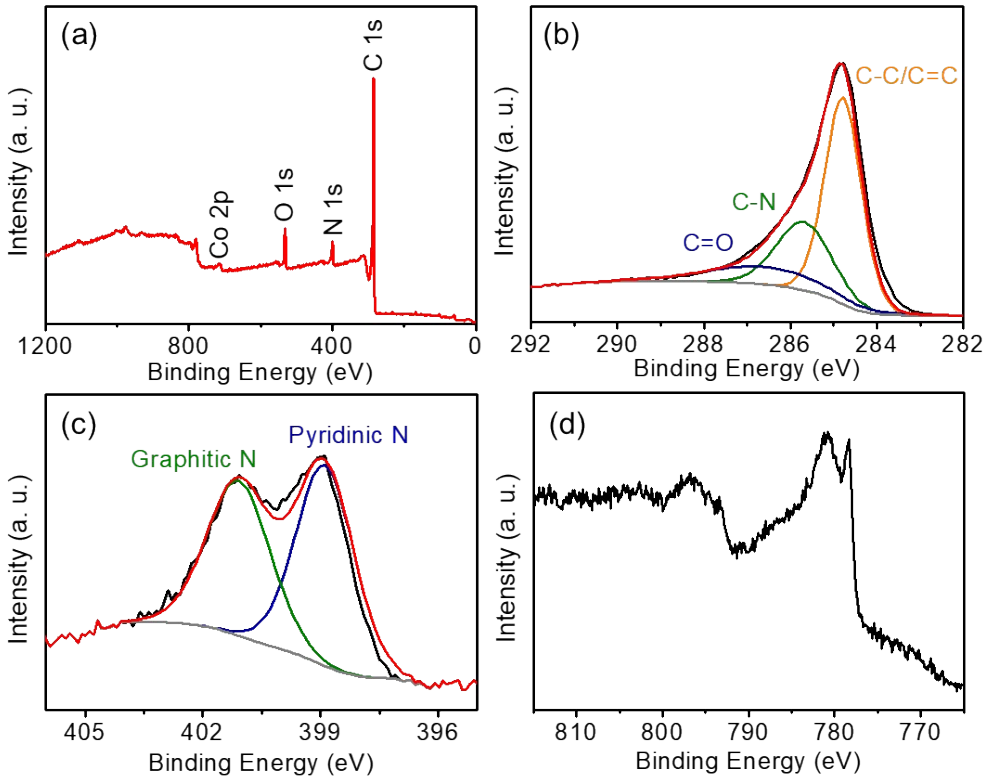

Figure S2. (a) The XPS survey spectrum, (b) C 1s, (c) N 1s and (d) Co 2p XPS spectra of $Co@N_{0.06}C$.

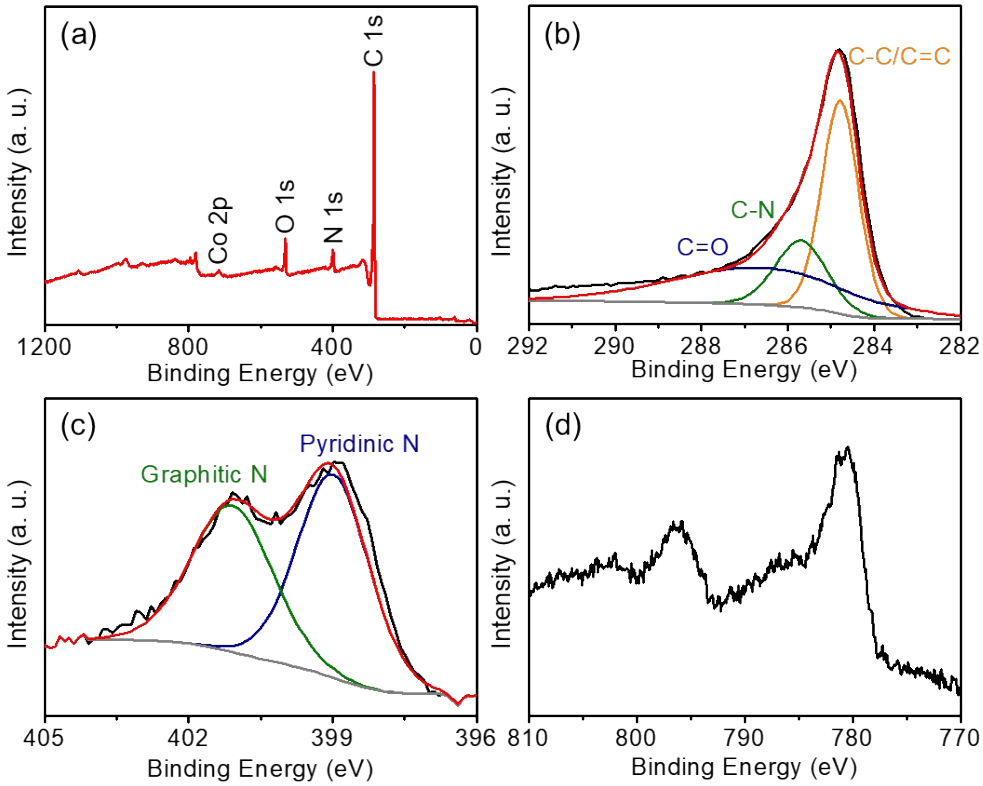

Figure S3. (a) The XPS survey spectrum, (b) C 1s, (c) N 1s and (d) Co 2p XPS spectra of $Co@N_{0.05}C$.

Table S1. Elemental analysis of Co, C, N and O based on the XPS analysis results.

Sample	Co	C	N	O
	Atomic percentage (at. %)			
$Co@N_{0.07}C$	6.09	81.58	6.49	5.83
$Co@N_{0.06}C$	5.09	82.79	6.23	5.89
$Co@N_{0.05}C$	6.67	79.64	4.28	9.41

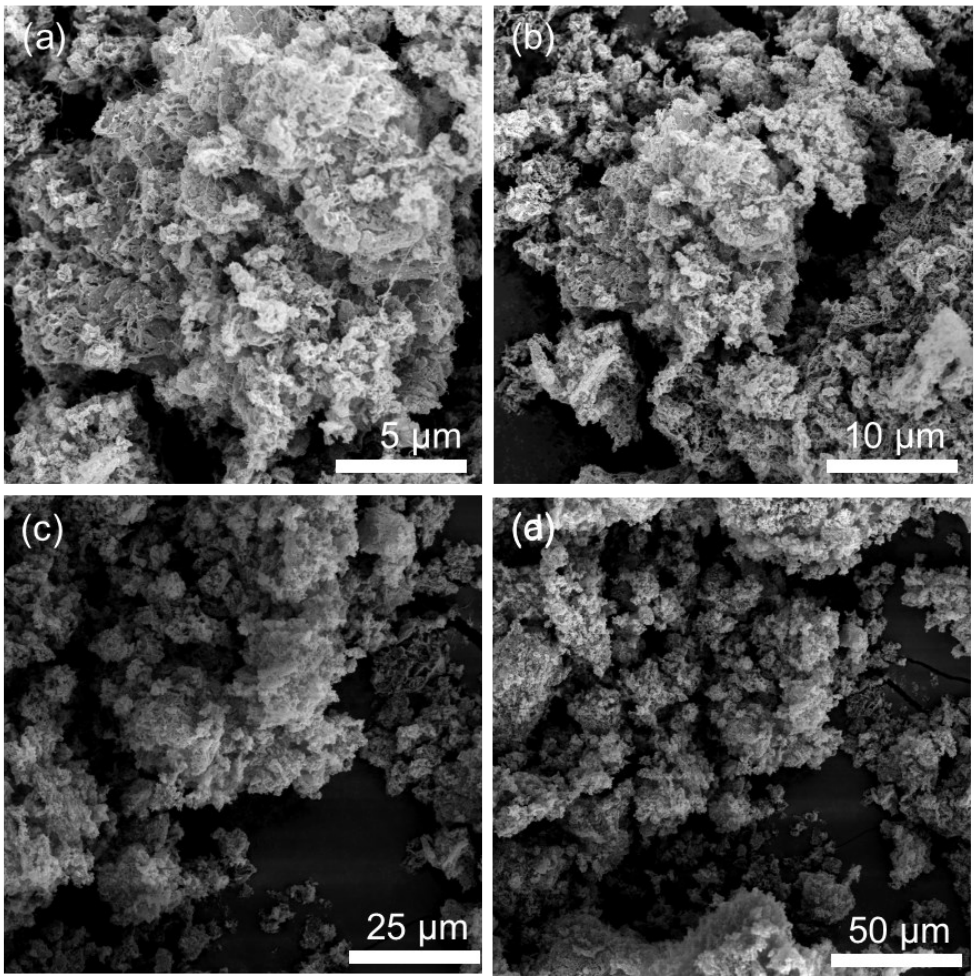

Figure S4. SEM images of the as-prepared Co@$N_{0.07}$C sample at different scales.

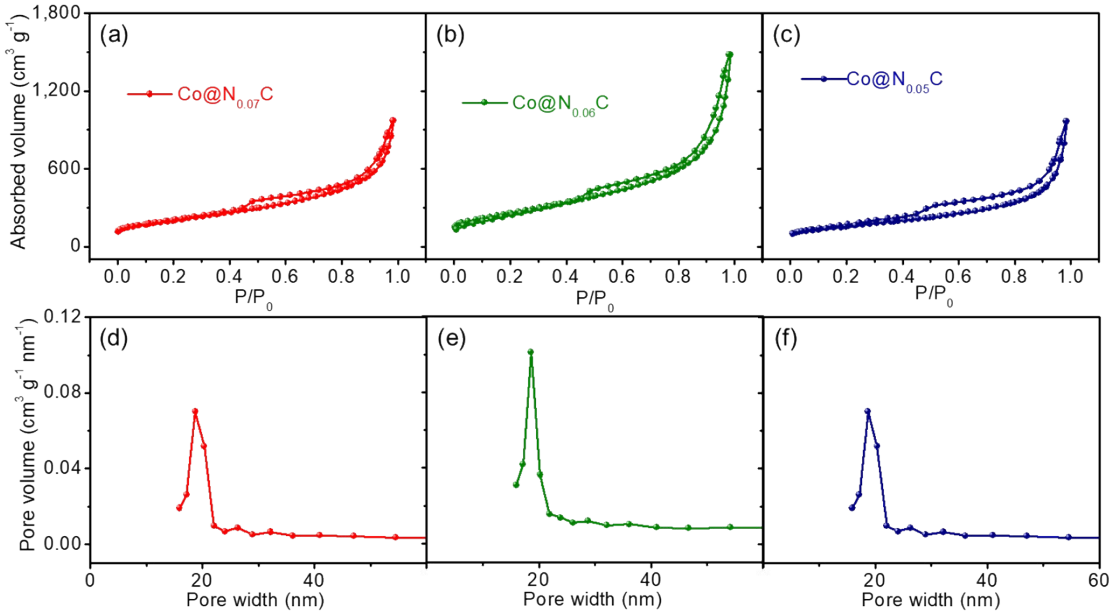

Figure S5. (a-c) N_2 sorption isotherm curves and corresponding (d-f) pore size distribution of the Co@NC samples.

Table S2. N_2 sorption data for the Co@N_xC samples.

Sample	Surface (m^2 g^{-1})	Pore volume (cm^3 g^{-1})
Co@$N_{0.07}$C	700.6	1.36
Co@$N_{0.06}$C	632.6	1.40
Co@$N_{0.05}$C	300.7	2.18

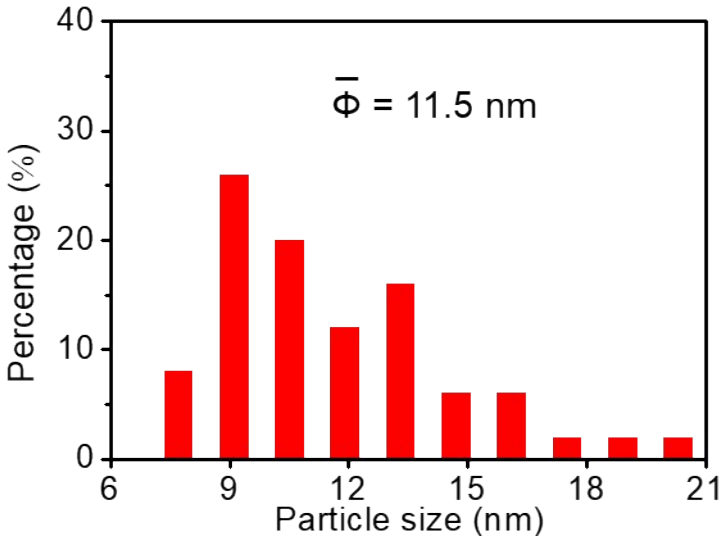

Figure S6. The particle size distribution of Co nanoparticles in the Co@$N_{0.07}$C sample.

Table S3. The Co content in the Co@NxC samples based on the ICP results

Sample	Co content (wt. %)
$Co@N_{0.07}C$	22.21
$Co@N_{0.06}C$	23.00
$Co@N_{0.05}C$	29.89

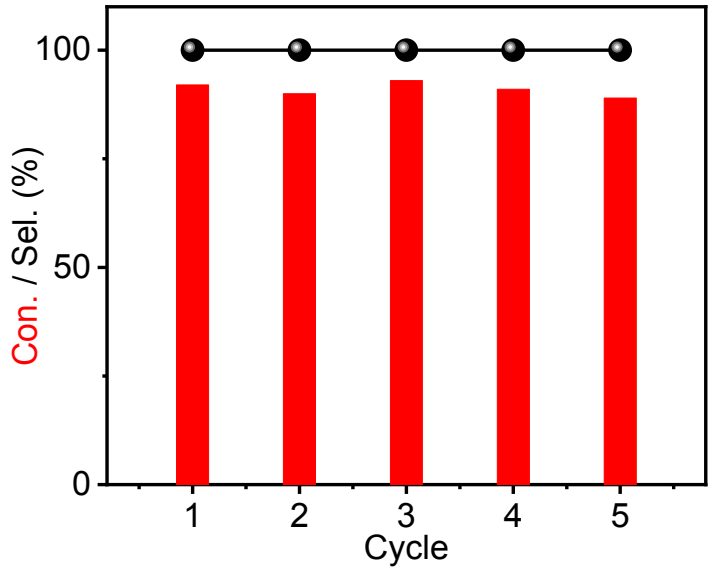

Figure S7. The recycle test of Co@$N_{0.07}$C catalyst in the reaction of CO_2 cycloaddition with styrene oxide.

Table S4. The recycle test of Co@$N_{0.07}$C catalyst in the reaction of CO_2 cycloaddition with styrene oxide.

Cycle	Con. (%)	Sel. (%)
1	92	>99
2	90	>99
3	93	>99
4	91	>99
5	89	>99

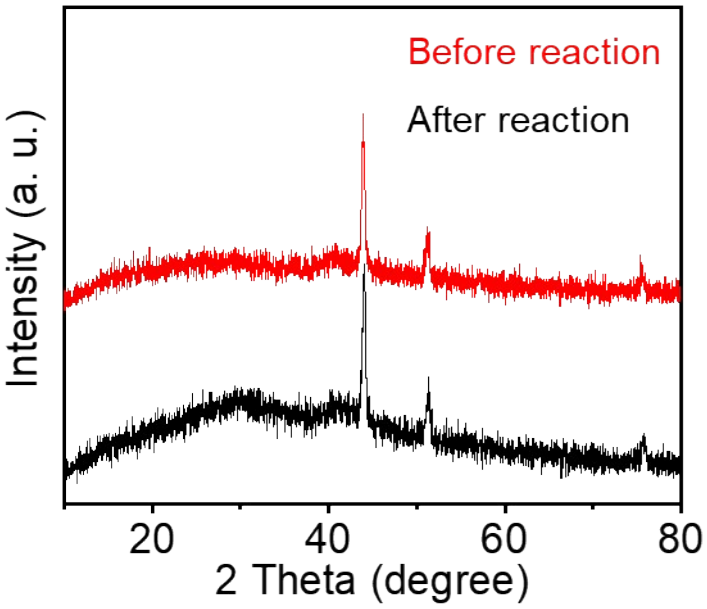

Figure S8. Powder XRD patterns of the Co@$N_{0.07}$C catalyst before and after the reaction.

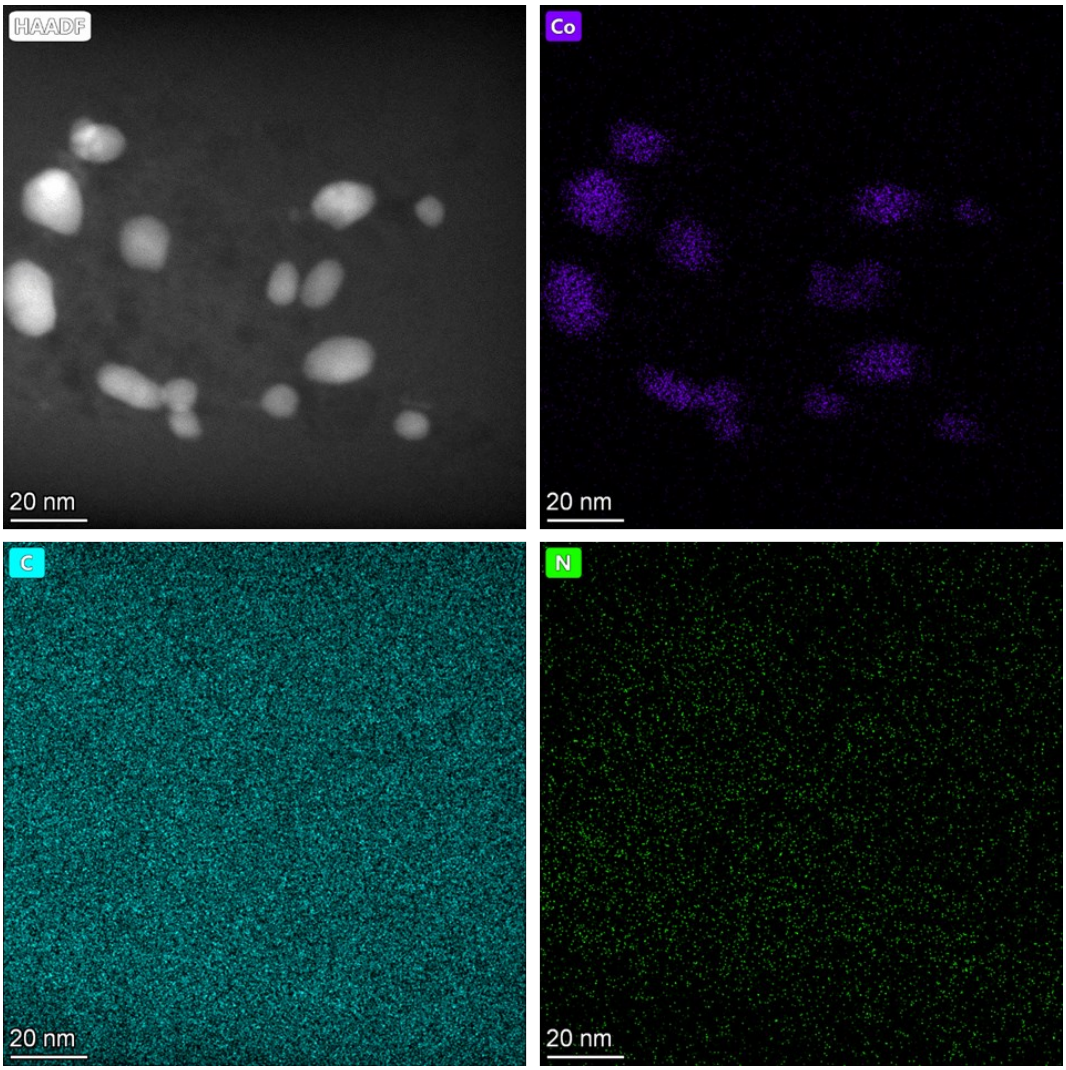

Figure S9. A HAADF image of Co@$N_{0.07}$C and the corresponding element mapping of Co, C and N respectively.