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$_2$·6H$_2$O (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$_x$C samples

2 mmol CoCl$_2$·6H$_2$O (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 °C 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 °C at 2 °C/min for 2 h, and then heated to 800 °C for 4 h at 5 °C/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$_x$C 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$_x$C 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 °C 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 ($\lambda = 1.5418$ 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  |
|------------|-----|--------|--------|----|
| 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\textsubscript{2} sorption isotherm curves and corresponding (d-f) pore size distribution of the Co@NC samples.
Table S2. \( \text{N}_2 \) sorption data for the Co@N\textsubscript{x}C samples.

| Sample       | Surface (m\(^2\) g\(^{-1}\)) | Pore volume (cm\(^3\) g\(^{-1}\)) |
|--------------|-------------------------------|-----------------------------------|
| Co@N\textsubscript{0.07}C | 700.6                         | 1.36                              |
| Co@N\textsubscript{0.06}C | 632.6                         | 1.40                              |
| Co@N\textsubscript{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\textsubscript{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.