2D MOF Induced Accessible and Exclusive Co Single Sites for Efficient O-Silylation of Alcohols with Silanes

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Table of contents

1. Materials and Methods

Materials

Analytical grade Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$), Cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$), N,N-Dimethylformamide (DMF) and 2-methyl imidazole were obtained from Shanghai Chemical Reagents, China. Polyvinylpyrrolidone (PVP, average mol wt 40,000) was purchased from Sigma-Aldrich. Tetrakis(4-carboxyphenyl)porphyrin (TCPP, 97%) and Pyrazine (99%) were purchased from Innochem. All the materials were used as received without further purification.

Synthesis of Zn-TCPP nanosheets

A method was used according to a previous report with a tiny modification.[1] $Zn(NO_3)_2{\cdot}6H_2O$ (22.5 mg, 0.075 mmol), pyrazine (4.0 mg, 0.05 mmol) and PVP (100.0 mg) in 60 mL of the mixture of DMF and ethanol (V:V=3:1) were dissolved in a 100 mL capped vial. Then TCPP (20.0 mg, 0.025 mmol) dissolved in 20 mL of the mixture of DMF and ethanol (V: V=3:1) were added dropwise under stirring. After that, the solution was sonicated for 10 min. The vial was heated to 80 °C and then kept for 16 h. The resulting purple nanosheets were washed twice with ethanol and collected by centrifuging at 8,000 r.p.m. for 10 min. Finally, the obtained Zn-TCPP nanosheets were redispersed in 10 mL of ethanol.

Synthesis of 2D Zn_1Co_1-BMOF nanosheets

$Zn(NO_3)_2{\cdot}6H_2O$ (11.25 mg, 0.0375 mmol), $Co(NO_3)_2{\cdot}6H_2O$ (11.25 mg, 0.0375 mmol), pyrazine (4.0 mg, 0.05 mmol) and PVP (100.0 mg) were dissolved in 60 mL of a mixture of DMF and ethanol (V:V=3:1) in a 100 mL capped vial. Then TCPP (20.0 mg, 0.025 mmol) dissolved in 20 mL of the mixture of DMF and ethanol (V: V=3:1) were added dropwise under stirring. After that, the solution was sonicated for 10 min. The vial was heated to 80 °C and then kept for 24 h. The resulting purple nanosheets were washed twice with ethanol and collected by centrifuging at 8,000 r.p.m. for 10 min. Finally, the obtained Zn_1Co_1-BMOF nanosheets were redispersed in 10 mL of ethanol.

Synthesis of 2D Zn_1Co_2-BMOF nanosheets

$Zn(NO_3)_2 \cdot 6H_2O$ (11.25 mg, 0.0375 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (22.5 mg, 0.075 mmol), pyrazine (4.0 mg, 0.05 mmol) and PVP (100.0 mg) were dissolved in 60 mL of the mixture of DMF and ethanol (V:V=3:1) in a 100 mL capped vial. Then TCPP (20.0 mg, 0.025 mmol) dissolved in 20 mL of the mixture of DMF and ethanol (V: V=3:1) were added dropwise under stirring. After that, the solution was sonicated for 10 min. The vial was heated to 80 °C and then kept for 24 h. The resulting purple nanosheets were washed twice with ethanol and collected by centrifuging at 8,000 r.p.m. for 10 min. Finally, the obtained Zn_1Co_2-BMOF nanosheets were redispersed in 10 mL of ethanol.

Synthesis of 3D $Zn_1Co_{0.2}$-BMOF

A method was used according to a previous report with a tiny modification.[2] In a typical procedure, $Zn(NO_3)_2 \cdot 6H_2O$(0.558g) and $Co(NO_3)_2 \cdot 6H_2O$ (0.109g) were dissolved in 15ml methanol to form a clear solution, which was subsequently injected into 15ml of methanol containing 0.616g 2-methylimidazole(MeIM) under ultrasound for 10min at room temperature. The mixed solution was then transferred into 50ml Teflon-lined stainless-steel autoclaves and heated at 120°C for 2 h. The as-obtained precipitates were centrifuged and washed with ethanol several times and dried in vacuum at 70 °C for overnight.

Synthesis of Co SAs/2D N-C, Co NPs/2D N-C and 2D N-C

In a typical procedure, 10 mL ethanolic solution of Zn_1Co_1-BMOF nanosheets was dropped onto the carbon fiber paper and dried at room temperature naturally. Then, the carbon fiber paper loaded with Zn_1Co_1-BMOF nanosheets was heated to the desired temperature 800°C for 60min at the heating rate of 5°C/min under Ar atmosphere. After cooling to room temperature, the carbon fiber paper loaded with Co SAs/2D N-C nanosheets was sonicated for 30 minutes in ethanol. The obtained solution was centrifugated at 15,000 rpm for 5 min and dried in vacuum at 70 °C for overnight. In a control experiment, the Co NPs/2D N-C and 2D N-C were prepared through the aformentioned experiment procedure except using the 2D Zn_1Co_2-BMOF and 2D Zn-TCPP to replace Zn_1Co_1-BMOF nanosheets, respectively.

Synthesis of Co SAs/3D N-C

The corresponding $Zn_1Co_{0.2}$-BMOF sample was placed in a tube furnace and then heated to 800°C for 60min at the heating rate of 5°C/min under Ar atmosphere. After cooling down to room temperature, the mixture was stored in the glass bottle for further use.

Synthesis of Co NPs/XC-72 and Co_3O_4/XC-72

A method was used according to a previous report with a tiny modification.[3] To a screw-capped glass bottle equipped with a stirring bar were added 64 mg of cobalt sulphate (225 μmole), 100 mg tetrabutyl ammonium bromide (300 μmole) and 8 ml of deionized water. After adding deionized water solution of $NaBH_4$ (0.1 M) dropwise, the mixture was stirred at room temperature for 15 min and then aqueous solution was decanted off. The obtained CoNPs were redispersed in deionized water after washed with water and acetone for twice.

1g carbon black (Vulcan XC-72) was dispersed in a mixture of 2.5 ml ethanol and 2.5 ml deionized water. After 30 min vigorous stirring, 5 ml deionized water solution containing 1.5 mg Co (base on ICP-MS measurement) as-prepared CoNPs was added into the carbon suspensions under ultrasonication for an additional 30 min. Then the as-prepared product (Co NPs/XC-72) was collected after centrifugation. The Co_3O_4/XC-72 was synthesized by a similar procedure for the Co NPs/XC-72. Commercial nano-sized cobaltosic oxide (Co_3O_4) was used in this experiment.

Characterization

Powder X-ray diffraction patterns of samples were recorded on a Rigaku Miniflex-600 operated at 40 kV voltage and 15 mA current using a Cu K_α radiation (λ=0.15406nm). TEM images were recorded by a Hitachi-7700 working at 100 kV. The high-resolution TEM, HAADF-STEM images the corresponding Electron energy-loss spectroscopy were recorded by a FEI Tecnai G2 F20 S-Twin high-resolution transmission electron microscope working at 200 kV and on a JEOL JEM-ARM200F TEM/STEM with a spherical aberration corrector working at 300 kV. Through-focal HAADF series were acquired at nanometer intervals, with the first image under-focused (beyond the beam exit surface) and the final image over-focused (before the beam entrance surface). The images were then manually aligned to remove the effects of sample drift. X-ray Photoemission spectroscopy (XPS) measurements were performed at the Catalysis and Surface Science End station at the BL11U beamline of National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. The end station is comprised of four ultrahigh vacuum (UHV) chambers including analysis chamber, preparation chamber, molecular beam epitaxy (MBE) chamber, and a radial distribution chamber (RDC). The base pressures are 7×10^{-11}, 1×10^{-10}, 5×10^{-10} and 2×10^{-11} mbar, respectively. In addition, a quick sample load-lock system was attached to the RDC. The analysis chamber was equipped with a VG Scienta R4000 analyzer and a monochromatic Al *Ka* X-ray source. The sample was annealed at the preparation chamber and then transferred to the analysis chamber for characterization. The core-level spectra were measured using a monochromatic Al *Ka* X-ray source. For the core-level spectra, the binding energies were calibrated using the C 1s feature located at 285.0 eV as the reference. Soft X-ray absorption spectra (Soft-XAS, C K-edge and N-Kedge) were carried out at BL12B X-ray Magnetic Circular Dichroism (XMCD) station and BL10B photoemission end-station of National Synchrotron Radiation Laboratory (NSRL, Hefei in China) in TEY mode. The samples were coated on double-sided carbon tape for characterization. XAFS measurement and data analysis： XAFS spectra at the Co K-edge (7709 eV) were measured at the beamline 1W1B station of the Beijing Synchrotron Radiation Facility, China. The Co K-edge XANES data were recorded in a fluorescence mode. Co foil, CoO were used as references. The storage ring was working at the energy of 2.5 GeV with an average electron current of 250 mA. The hard X-ray was monochromatized with Si (111) double-crystals. The acquired EXAFS data were extracted and processed according to the standard procedures using the ATHENA module implemented in the IFEFFIT software packages. The k^3-weighted EXAFS spectra were obtained by subtracting the post-edge background from the overall absorption and then normalizing with respect to the edge-jump step. Subsequently, k^3-weighted χ (k) data in the k-space ranging from 2.0–12.0 $Å^{-1}$ were Fourier transformed to real (R) space using hanning windows (d_K = 1.0 $Å^{-1}$) to separate the EXAFS contributions from different coordination shells.

Typical procedure for the O-Silylation of Alcohols with Silanes

In this typical reaction, a mixture of silane (1.0 mmol) and alcohol (3.0 ml) with Co catalysts was stirred at room temperature under argon atmosphere for 2h. The Co catalysts were Co SAs/2D N-C (5.34mg, 0.14 wt% Co loading), Co SAs/3D N-C (5.0mg, 0.15 wt% Co loading), Co NPs/2D N-C (1.47mg, 0.51 wt% Co loading), Co NPs/XC-72 (5.0mg, 0.15 wt% Co loading) and Co_3O_4/XC-72 (5.0mg, 0.15 wt% Co loading), respectively. The yield was determined by GC analysis. All of the reaction yields reported were averaged values from 3 time experiments.

2. Supplementary Figures and Tables

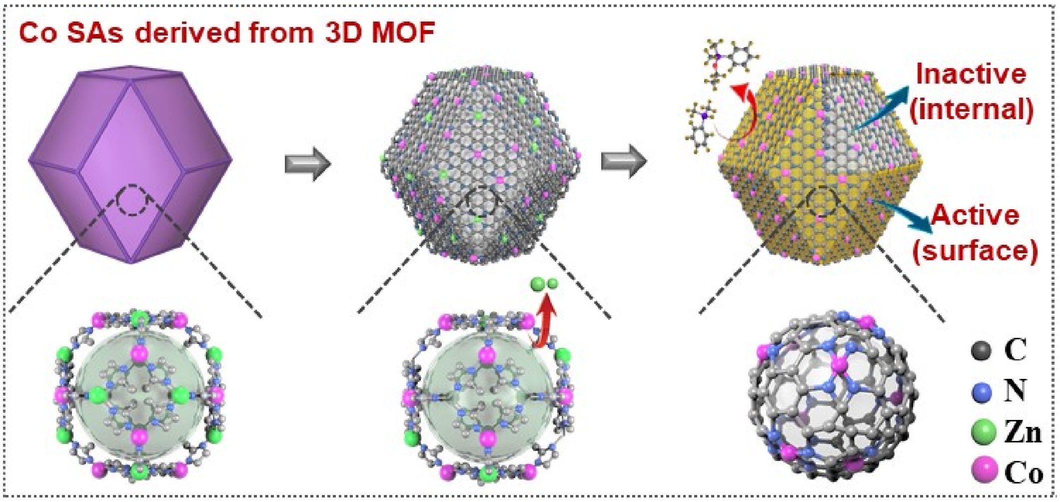


Figure S1. Proposed formation mechanisms for Co SAs/3D N-C.

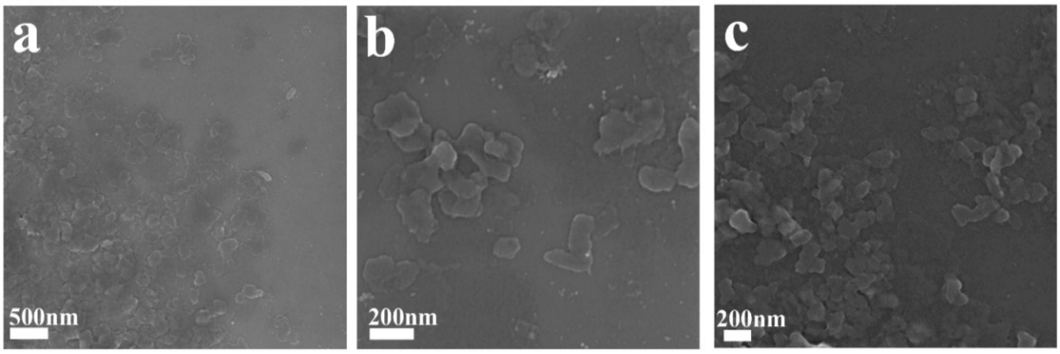


Figure S2. SEM images of a) 2D Zn_1Co_1-BMOF, b) 2D Zn_1Co_2-BMOF and c) 2D Zn-TCPP.

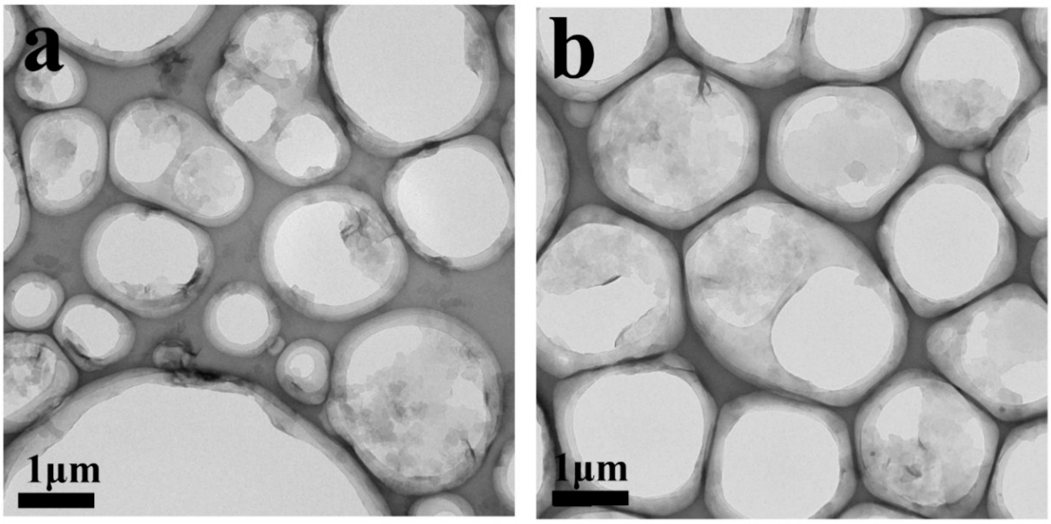


Figure S3. TEM images of a) 2D Zn$_1$Co$_2$-BMOF and b) 2D Zn-TCPP.

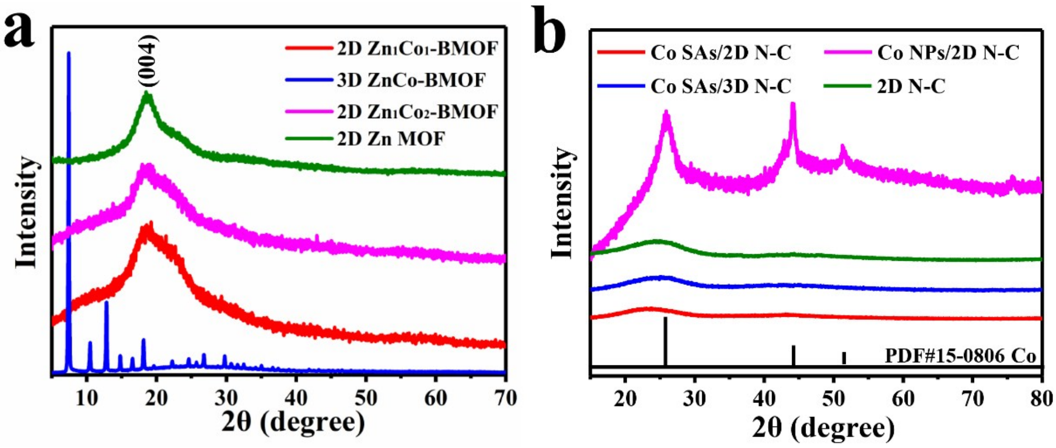


Figure S4. a) XRD patterns of as-prepared ZnCo-BMOF, b) Co SAs/2D N-C obtained from 2D Zn$_1$Co$_1$-BMOF, Co SAs/3D N-C obtained from 3D ZnCo-BMOF, Co NPs/2D N-C obtained from 2D Zn$_1$Co$_2$-BMOF and 2D N-C obtained from 2D Zn-TCPP.

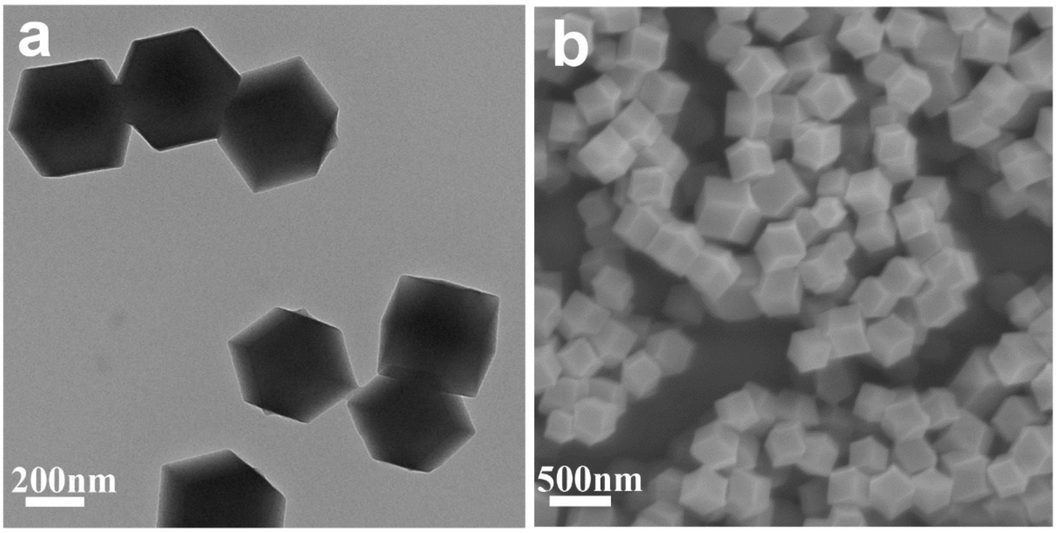


Figure S5. a) TEM and b) SEM images of 3D ZnCo-BMOF.

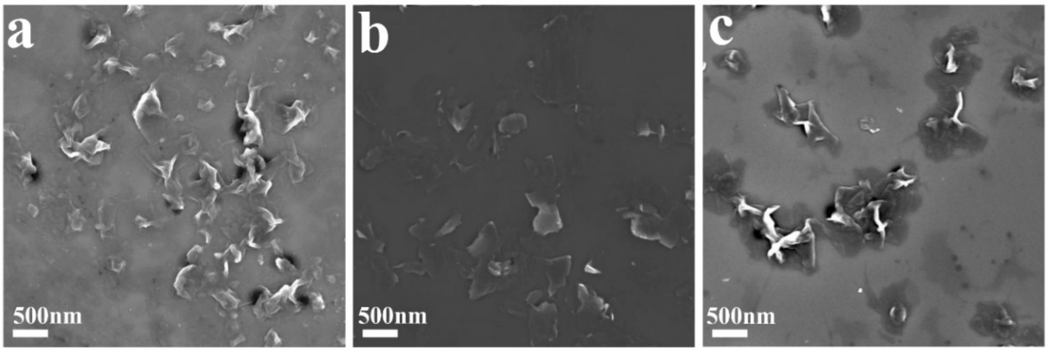


Figure S6. SEM images of a) Co SAs/2D N-C, b) Co NPs/2D N-C and c) 2D N-C.

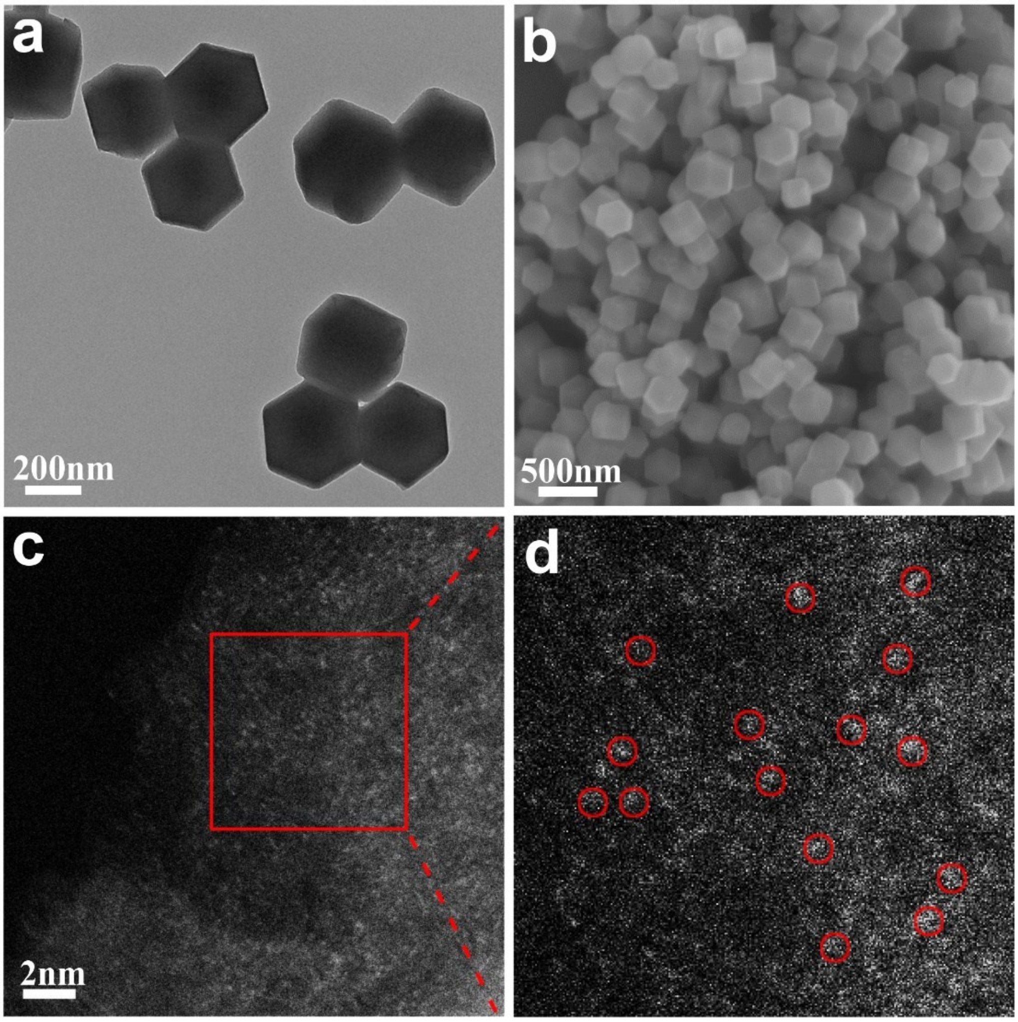


Figure S7. a) TEM and b) SEM images of Co SAs/3D N-C. c,d) Magnified HAADF-STEM images of Co SAs/3D N-C, showing that only Co single atoms are in Co SAs/3D N-C.

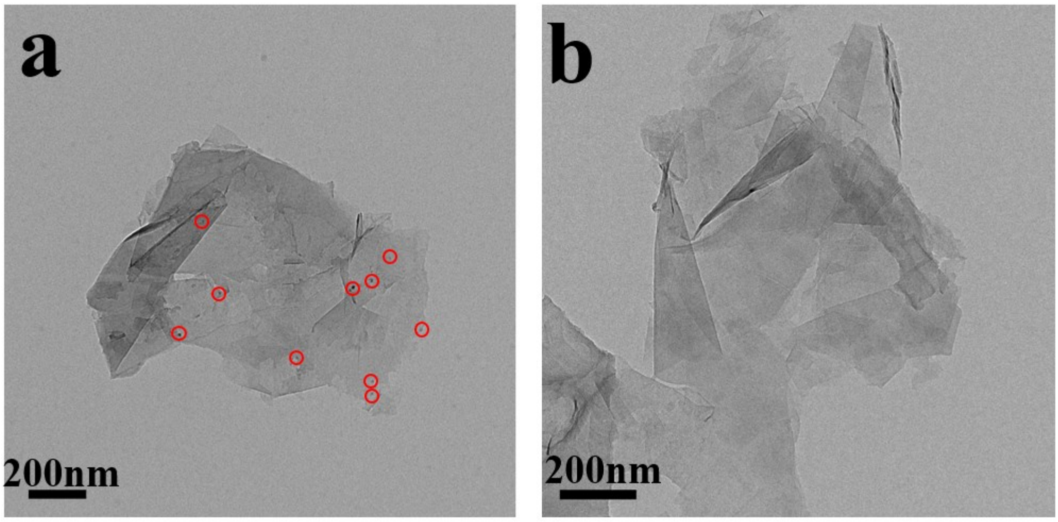


Figure S8. TEM images of a) Co NPs/2D N-C and b) 2D N-C.

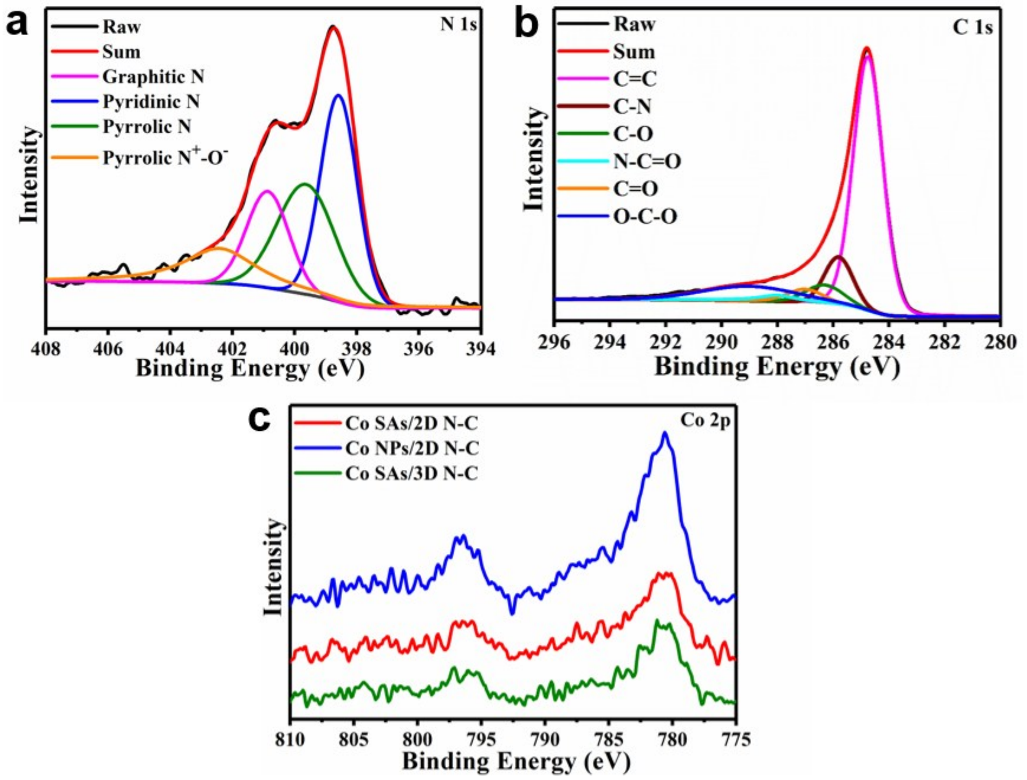


Figure S9. The XPS spectra of a) N 1s, b) C 1s and c) Co 2p of Co SAs/2D N-C.

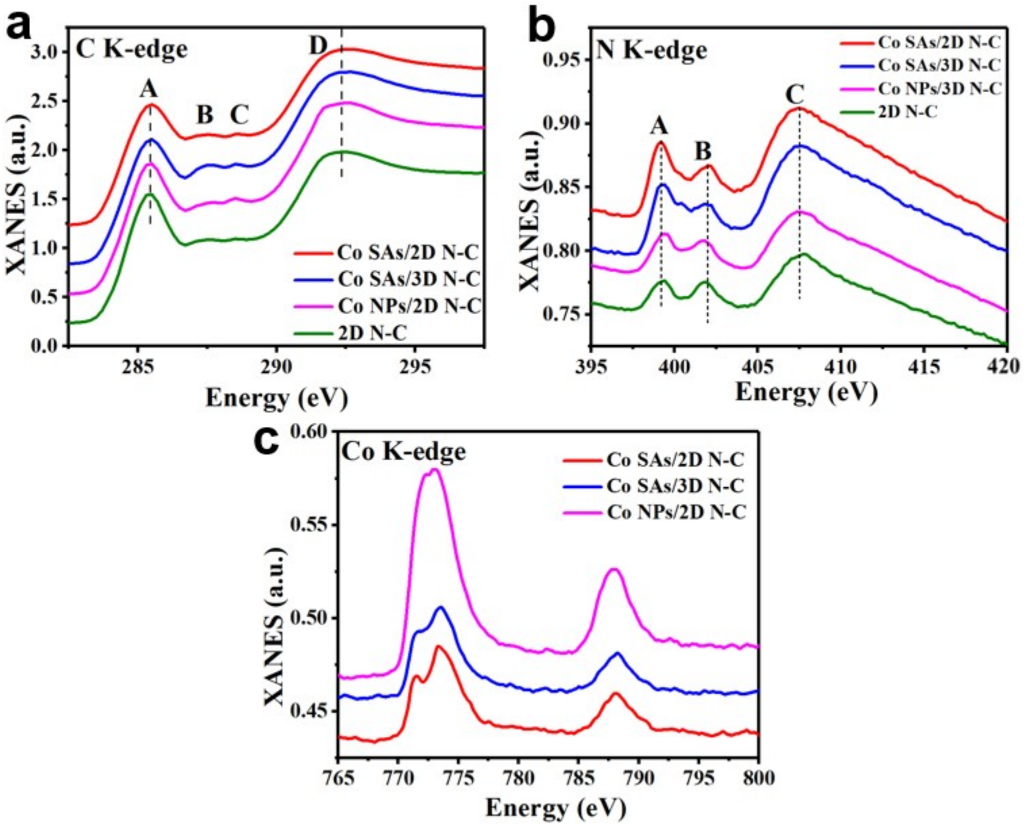


Figure S10. a) C K-edge, b) N K-edge and c) Co L-edge X-ray absorption spectroscopy (XAS) spectra of Co SAs/2D N-C, Co SAs/2D N-C, Co NPs/2D N-C and 2D N-C.

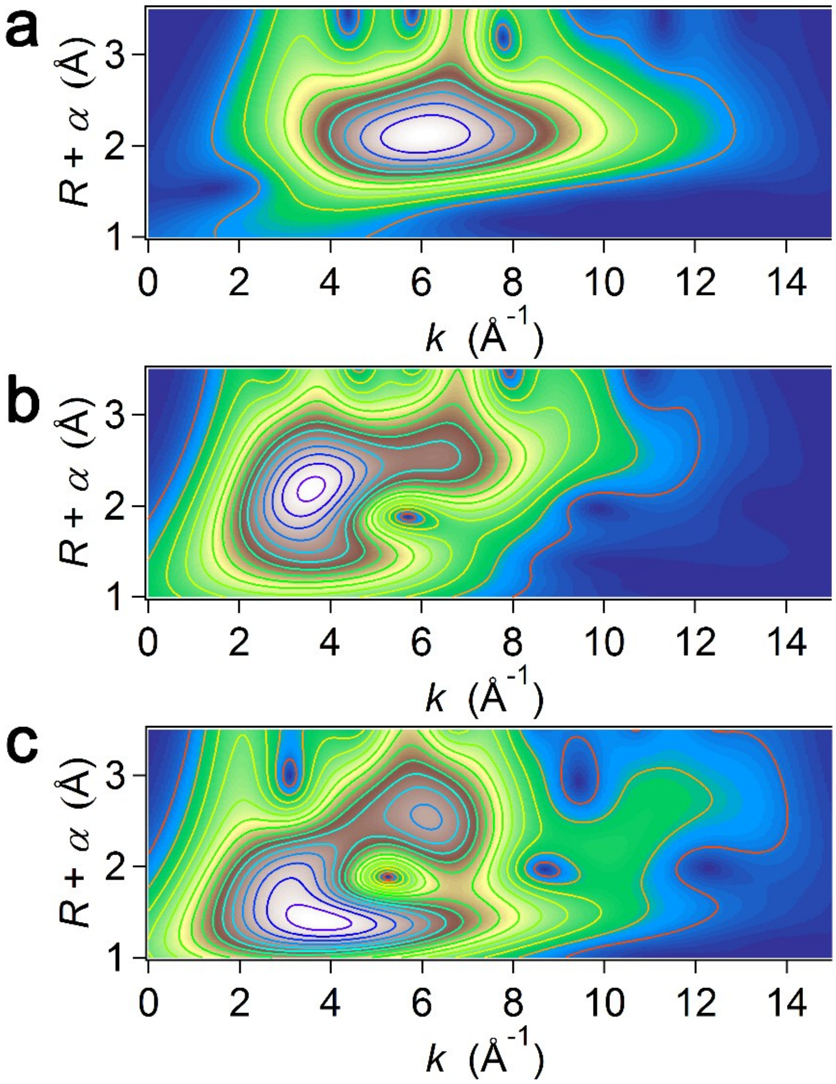


Figure S11. Wavelet transformed (WT) k^3-weighted χ(k)-function of the Co-K edge EXAFS spectra of Co foil, CoO and Co_3O_4.

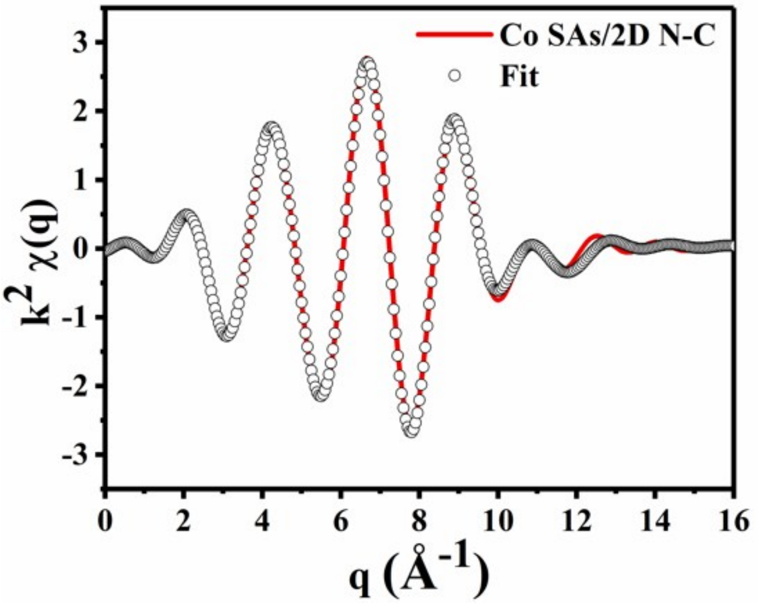


Figure S12. Inverse FT-EXAFS Fitting result of Co K-edge.

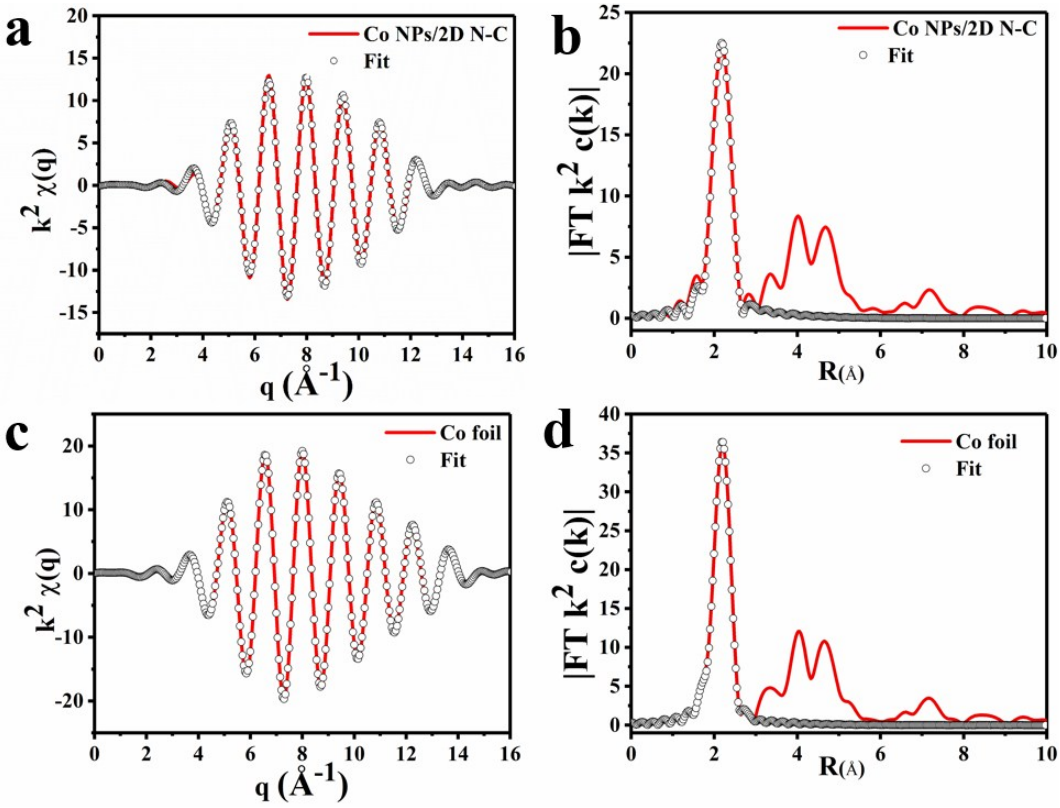


Figure S13. R space and inverse FT-EXAFS Fitting result of Co K-edge.

Co foil (FT range: 2.0-12.0 Å^{-1}; fitting range: 1.2-2.9 Å)

Co SAs/2D N-C (FT range: 2.0-12.0 Å^{-1}; fitting range: 1.4-2.4 Å)

Co NPs/2D N-C (FT range: 2.0-12.0 Å^{-1}; fitting range: 1.4-2.8 Å)

Table S1. Structural parameters of Co SAs/2D N-C, Co NPs/2D N-C and Co foil extracted from the EXAFS fitting. (S_0^2=0.76)

sample	**Scattering pair**	**CN**	**R(Å)**	**σ^2(10^{-3}Å^2)**	**ΔE_0(eV)**	**R factor**
Co-SAs/2D N-C	Co-N	4.1	1.93	7.9	-3.1	0.0045
Co-NPs/2D N-C	Co-Co	8.2	2.50	6.6	6.8	0.0049
Co foil	Co-Co	12*	2.50	6.5	7.7	0.0013

* This value was fixed during EXAFS fitting, based on the known structure.

Error bounds that characterize the structural parameters obtained by EXAFS spectroscopy were estimated as N ± 20%; R ± 1%; σ^2 ± 20%; ΔE_0 ± 20%.

S_0^2 is the amplitude reduction factor; CN is the coordination number; R is interatomic distance (the bond length between Co central atoms and surrounding coordination atoms); σ^2 is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances); ΔE_0 is edge-energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model). R factor is used to value the goodness of the fitting.

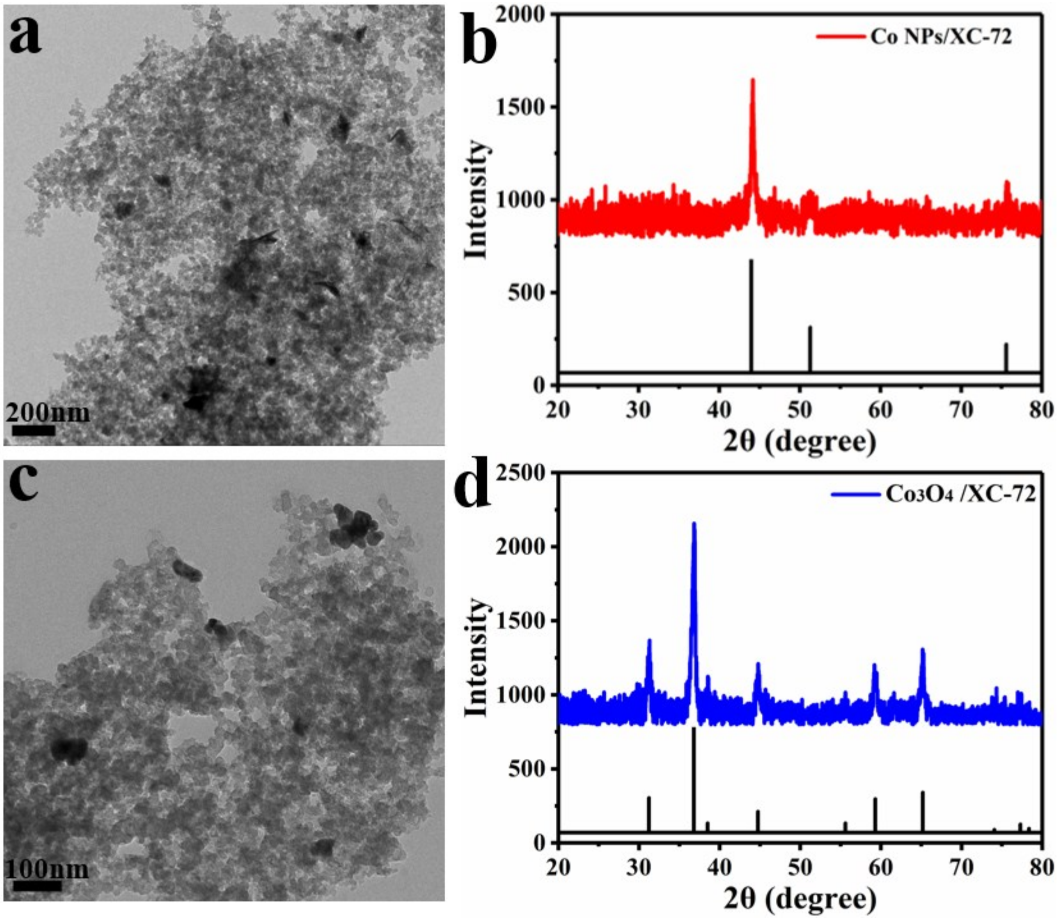
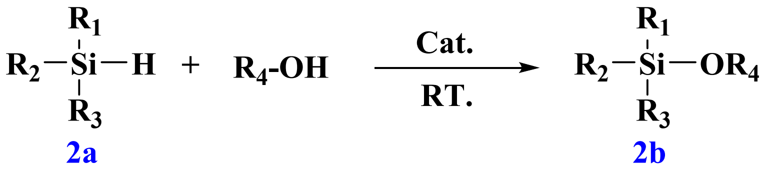


Figure S14.TEM images of a) Co NPs/XC-72, c) Co_3O_4/XC-72 and XRD patterns of b) Co NPs/XC-72, d) Co_3O_4/XC-72.

Table S2. Results of the oxidative coupling of silanes with alcohols catalysed by Co SAs/2D N-C



Entry	R_1	R_2	R_3	R_4	t(h)	Yield of 2b(%)
1	Ph	Me	Me	Et	2	97.5
2	Ph	Me	Me	n-Bu	2	97.2
3	Ph	Ph	H	Et	3	96.2
4	Ph	Ph	H	n-Bu	3	96.9
5	Ph	H	H	Et	3	95.6
6	Ph	H	H	n-Bu	3	95.7
7	Et	Et	Et	Et	2	95.1
8	Et	Et	Et	n-Bu	2	94.8

[a] Reaction conditions: silane (1.0 mmol) in alcohol (3 ml) with Co catalysts (5.34 mg) at 25°C;

[b] The products were identified by gas chromatography (GC).

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2. J. Yang, F. Zhang, H. Lu, X. Hong, H. Jiang, Y. Wu and Y. Li, *Angew. Chem. Int. Ed.*, 2015, **54**, 10889-10893.
3. A. Mondal, B. Adhikary and D. Mukherjee, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 2015, **482**, 248-257.