**Table S1 Crystallographic data**

| Compound | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Empirical formula | $C_{30}H_{22}CoN_5O_{6.50}$ | $C_{36}H_{30}Co_3N_6O_{18}$ | $C_{102}H_{84}Cl_2Co_4N_{28}O_{17}$ | $C_{27}H_{21}CoN_7O_5$ |
| Formula weight | 615.46 | 1011.45 | 2280.59 | 582.44 |
| Crystal system | Trigonal | Monoclinic | Monoclinic | Monoclinic |
| Space group | R-3 | P2(1)/c | P2(1)/c | C2/c |
| *a*(Å) | 26.658(8) | 7.565(3) | 13.850(3) | 29.174(10) |
| *b*(Å) | 26.658(8) | 29.760(10) | 13.682(3) | 13.803(4) |
| *c*(Å) | 20.810(9) | 17.084(6) | 26.863(7) | 13.380(4) |
| *α*(º) | 90 | 90 | 90 | 90 |
| *β*(º) | 90 | 101.521(4) | 97.757(4) | 112.762(5) |
| *γ*(º) | 120 | 90 | 90 | 90 |
| *V*(Å$^3$) | 12807(9) | 3769(2) | 5044(2) | 4969(3) |
| *Z* | 18 | 4 | 2 | 8 |
| $D_{calcd}$(g·cm$^{-3}$) | 1.436 | 1.783 | 1.502 | 1.557 |
| μ(mm$^{-1}$) | 0.657 | 1.397 | 0.782 | 0.746 |
| $R_{int}$ | 0.0416 | 0.0634 | 0.0368 | 0.0315 |
| Final R indicaes [I>2σ(I)] | $R_1$ = 0.0419 $wR_2$= 0.1134 | $R_1$ = 0.0397 $wR_2$ = 0.0989 | R1=0.0594, wR2 = 0.1678 | $R_1$=0.0465 $wR_2$=0.1327 |
| R indices(all data) | $R_1$ = 0.0443 $wR_2$ = 0.1155 | $R_1$ = 0.0480 $wR_2$ = 0.1035 | R1=0.0662, wR2 = 0.1734 | $R_1$=0.0507 $wR_2$=0.1376 |
| Goof | 1.024 | 1.005 | 1.085 | 0.913 |

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$, $wR = \{\sum[w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2]\}^{1/2}$

**Table S2 Selected bond lengths(Å)and bond angles(º)of compound 1**

| | | | | | |
|---|---|---|---|---|---|
| Co(1)-O(4A) | 2.0181(15) | Co(1)-O(3B) | 2.0262(14) | Co(1)-O(2) | 2.0515(14) |
| Co(1)-N(3) | 2.1306(16) | Co(1)-N(1) | 2.1688(17) | | |

| | | | |
|---|---|---|---|
| O(4A)-Co(1)-O(3B) | 120.04(6) | O(4A)-Co(1)-O(2) | 90.55(6) |
| O(3B)-Co(1)-O(2) | 149.03(5) | O(4A)-Co(1)-N(3) | 93.80(6) |
| O(3B)-Co(1)-N(3) | 90.62(6) | O(2)-Co(1)-N(3) | 92.14(6) |
| O(4A)-Co(1)-N(1) | 86.80(6) | O(3B)-Co(1)-N(1) | 86.81(6) |
| O(2)-Co(1)-N(1) | 90.47(6) | N(3)-Co(1)-N(1) | 177.31(6) |

Symmetry Code:A, -y-1/3,x-y+1/3,z+1/3 ; B, y-1/3,-x+y-2/3,-z+1/3

**Table S3 Selected bond lengths(Å)and bond angles(°)of compound 2**

| | | | | | |
|---|---|---|---|---|---|
| Co(1)-O(8) | 2.0272(17) | Co(1)-O(14) | 2.039(2) | Co(1)-O(13) | 2.045(2) |
| Co(1)-O(1) | 2.0945(17) | Co(1)-N(6) | 2.111(2) | Co(2)-O(4A) | 2.0578(19) |
| Co(2)-O(9) | 2.0668(17) | Co(2)-O(7B) | 2.0757(16) | Co(2)-N(4C) | 2.1329(19) |
| Co(2)-O(2B) | 2.1475(19) | Co(3)-O(11D) | 2.0892(16) | Co(3)-O(12) | 2.0924(16) |
| Co(3)-O(6E) | 2.1213(16) | Co(3)-N(5F) | 2.1386(19) | Co(3)-O(15) | 2.1400(19) |
| Co(3)-O(6G) | 2.1667(17) | | | | |

| | | | |
|---|---|---|---|
| O(8)-Co(1)-O(14) | 90.51(8) | O(8)-Co(1)-O(13) | 86.43(9) |
| O(14)-Co(1)-O(13) | 174.20(11) | O(8)-Co(1)-O(1) | 163.82(7) |
| O(14)-Co(1)-O(1) | 88.43(7) | O(13)-Co(1)-O(1) | 93.14(8) |
| O(8)-Co(1)-N(6) | 99.71(8) | O(14)-Co(1)-N(6) | 99.42(10) |
| O(13)-Co(1)-N(6) | 85.96(11) | O(1)-Co(1)-N(6) | 96.39(7) |
| O(4A)-Co(2)-O(9) | 90.85(8) | O(4A)-Co(2)-O(7B) | 86.98(8) |
| O(9)-Co(2)-O(7B) | 176.99(7) | O(4A)-Co(2)-N(4C) | 105.73(8) |
| O(9)-Co(2)-N(4C) | 89.18(7) | O(7B)-Co(2)-N(4C) | 89.40(7) |
| O(4A)-Co(2)-O(2B) | 157.18(7) | O(9)-Co(2)-O(2B) | 91.08(7) |
| O(7B)-Co(2)-O(2B) | 91.73(7) | N(4C)-Co(2)-O(2B) | 97.03(8) |
| O(11D)-Co(3)-O(12) | 98.50(7) | O(11D)-Co(3)-O(6E) | 92.70(7) |
| O(12)-Co(3)-O(6E) | 168.79(6) | O(11D)-Co(3)-N(5F) | 87.76(7) |
| O(12)-Co(3)-N(5F) | 87.34(7) | O(6E)-Co(3)-N(5F) | 93.60(7) |
| O(11D)-Co(3)-O(15) | 90.42(7) | O(12)-Co(3)-O(15) | 91.36(7) |
| O(6E)-Co(3)-O(15) | 88.07(7) | N(5F)-Co(3)-O(15) | 177.59(8) |
| O(11D)-Co(3)-O(6G) | 169.18(6) | O(12)-Co(3)-O(6G) | 92.32(7) |
| O(6E)-Co(3)-O(6G) | 76.49(7) | N(5F)-Co(3)-O(6G) | 92.38(7) |
| O(15)-Co(3)-O(6G) | 89.70(7) | | |

Symmetry Code: A, x-1,y,z-1; B, x-1,-y+1/2,z-1/2; C, -x+1,-y,-z+1; D, -x+2,-y+1,-z+1; E, -x+3,y+1/2,-z+3/2; F, x+1,-y+1/2,z+1/2; G, x,-y+1/2,z-1/2.

**Table S4 Selected bond lengths(Å)and bond angles(º)of compound 3**

| | | | | | |
|---|---|---|---|---|---|
| Co(1)-O(5A) | 2.002(3) | Co(1)-O(1B) | 2.039(3) | Co(1)-N(12) | 2.157(3) |
| Co(1)-N(11C) | 2.174(3) | Co(1)-Cl(1) | 2.3647(12) | Co(2)-O(6A) | 2.010(3) |
| Co(2)-O(4) | 2.048(3) | Co(2)-N(6) | 2.162(3) | Co(2)-N(5C) | 2.166(3) |
| Co(2)-Cl(1) | 2.3839(12) | | | | |

| | | | |
|---|---|---|---|
| O(5A)-Co(1)-O(1B) | 150.23(11) | O(5A)-Co(1)-N(12) | 90.34(12) |
| O(1B)-Co(1)-N(12) | 91.57(12) | O(5A)-Co(1)-N(11C) | 90.46(12) |
| O(1B)-Co(1)-N(11C) | 86.75(12) | N(12)-Co(1)-N(11C) | 177.85(12) |
| O(5A)-Co(1)-Cl(1) | 107.99(8) | O(1B)-Co(1)-Cl(1) | 101.51(9) |
| N(12)-Co(1)-Cl(1) | 93.89(9) | N(11C)-Co(1)-Cl(1) | 87.76(10) |
| O(6A)-Co(2)-O(4) | 152.28(11) | O(6A)-Co(2)-N(6) | 90.38(12) |
| O(4)-Co(2)-N(6) | 92.96(12) | O(6A)-Co(2)-N(5C) | 89.22(12) |
| O(4)-Co(2)-N(5C) | 87.09(12) | N(6)-Co(2)-N(5C) | 179.23(14) |
| O(6A)-Co(2)-Cl(1) | 107.69(8) | O(4)-Co(2)-Cl(1) | 99.83(9) |
| N(6)-Co(2)-Cl(1) | 89.99(9) | N(5C)-Co(2)-Cl(1) | 90.75(10) |

Symmetry Code: A : -x,y-1/2,-z+1/2 ; B, x+1,y,z ; C, x,-y+3/2,z+1/2 ;

**Table S5 Selected bond lengths(Å)and bond angles(º)of compound 4**

| | | | | | |
|---|---|---|---|---|---|
| Co(1)-O(2A) | 1.987(2) | Co(1)-O(3) | 2.0055(19) | Co(1)-O(4B) | 2.027(2) |
| Co(1)-N(4C) | 2.161(2) | Co(1)-N(5) | 2.173(2) | | |

| | | | |
|---|---|---|---|
| O(2A)-Co(1)-O(3) | 134.76(10) | O(2A)-Co(1)-O(4B) | 97.13(10) |
| O(3)-Co(1)-O(4B) | 128.10(10) | O(2A)-Co(1)-N(4C) | 96.15(9) |
| O(3)-Co(1)-N(4C) | 88.10(8) | O(4B)-Co(1)-N(4C) | 87.38(8) |
| O(2A)-Co(1)-N(5) | 86.29(9) | O(3)-Co(1)-N(5) | 91.62(8) |
| O(4B)-Co(1)-N(5) | 90.31(9) | N(4C)-Co(1)-N(5) | 176.83(9) |

Symmetry Code: A, -x+1/2,y+1/2,-z+3/2; B, -x+1/2,-y-1/2,-z+1; C, x+1/2,-y-1/2,z+1/2.

**Table S6 Electrocatalytic parameters of CoNC-A and CoNC-B**

| | CoNC-A | CoNC-B | Pt/C |
|---|---|---|---|
| $E_{onset}$/V | 0.893 | 0.962 | 0.968 |
| $E_{1/2}$/V | 0.785 | 0.808 | 0.799 |
| $J_L$/ mA·cm$^{-2}$ | 5.46 | 5.29 | 5.09 |

**Table S7. $E_{onset}$ and $E_{1/2}$ of CoNC-B and the reported carbon nanomaterials derived from some Co-MOFs in alkaline electrolyte**

| Co-MOFs | Onset potentials (V) | Half Wave potential (V) | Ref. |
|---|---|---|---|
| [$Co_3(tpt)_2(Hbpt)_3$]·0.5DMDP | 0.962 | 0.808 | This work |
| Co-doped ZIF-8 | 0.93 | 0.80 | 34 |
| CPM-24 | - | 0.76 | 50 |

| | | | |
|---|---|---|---|
| $Co^{II}(pybz)_2 \cdot 2DMF$ | 0.94 | 0.81 | 51 |
| $[Co_2(\mu_3\text{-}OH)(bib)(bpt)] \cdot H_2O$ | 0904 | 0.795 | 70 |
| $[Co_3(\mu_2\text{-}OH)_4(I)_2] \cdot 2H_2O$ | 0.95 | 0.80 | 74 |
| $[Co(im)_4 \cdot DMA]$ | 0.83 | 0.77 | 75 |
| Co-Ade-MOFs | 0.91 | 0.81 | 76 |

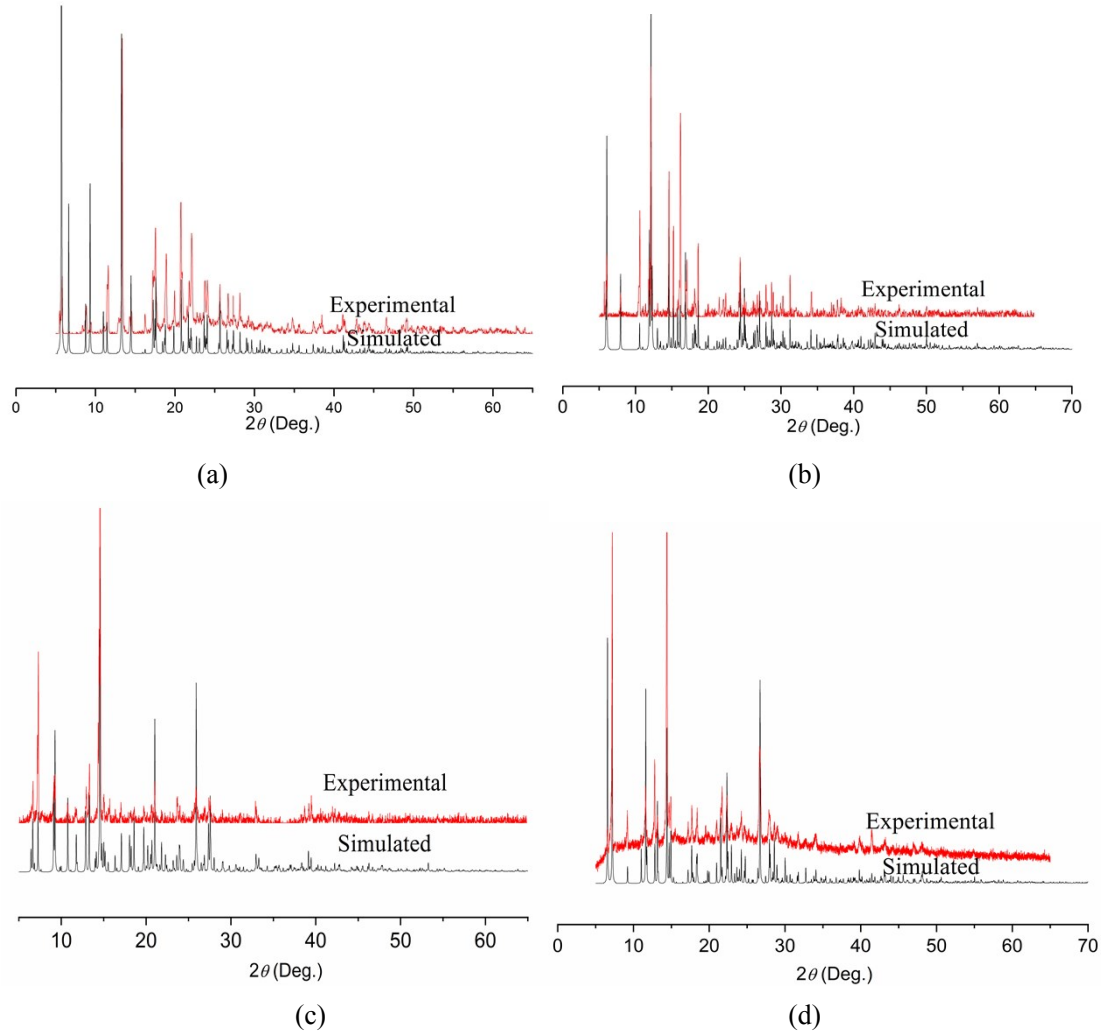



Fig. S1 Experimental X-ray powder pattern and simulated powder pattern based on the results from single-crystal X-ray diffraction for compounds 1(a),2(b),3(c) and 4(d)

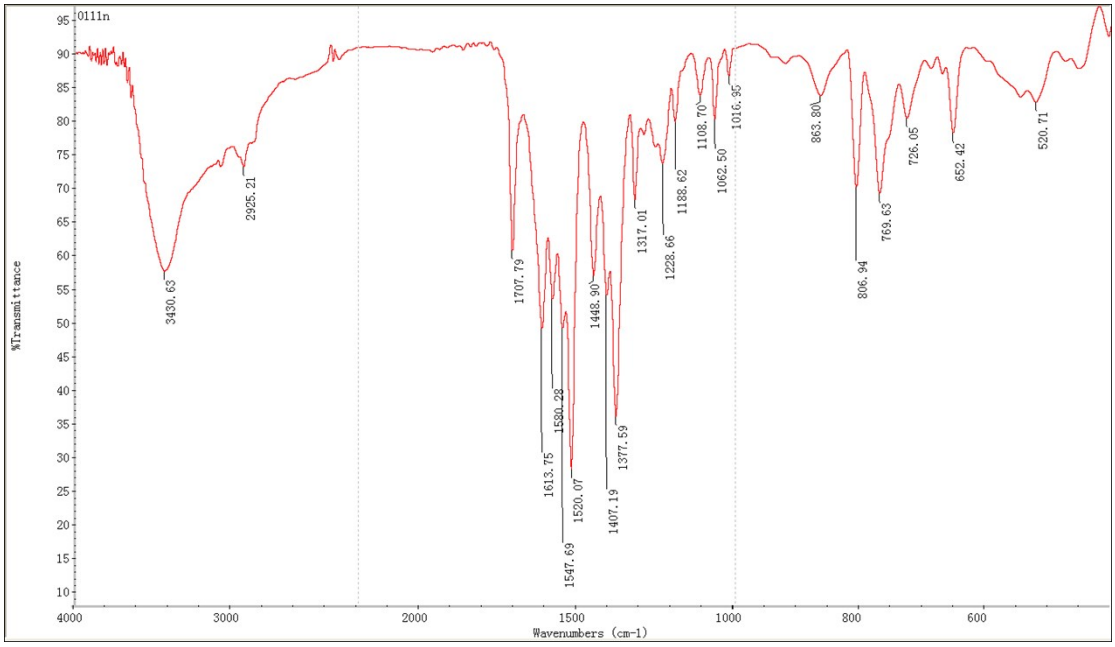



Figure.S2. IR of compound **1**

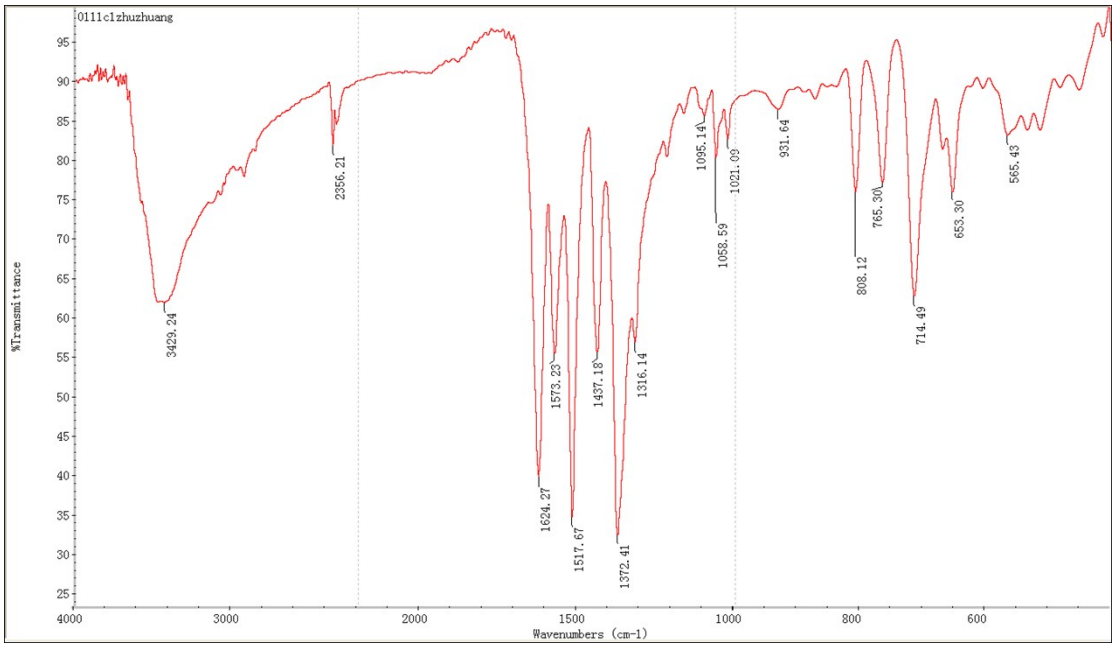



Figure.S3. IR of compound **2**

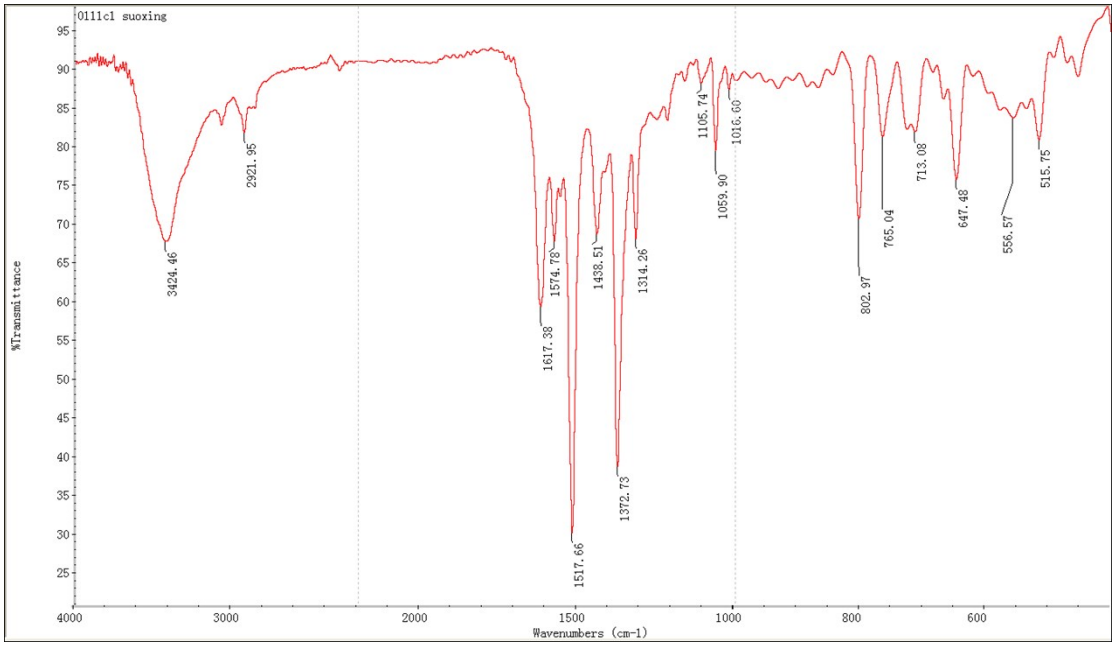



Figure.S4. IR of compound **3**

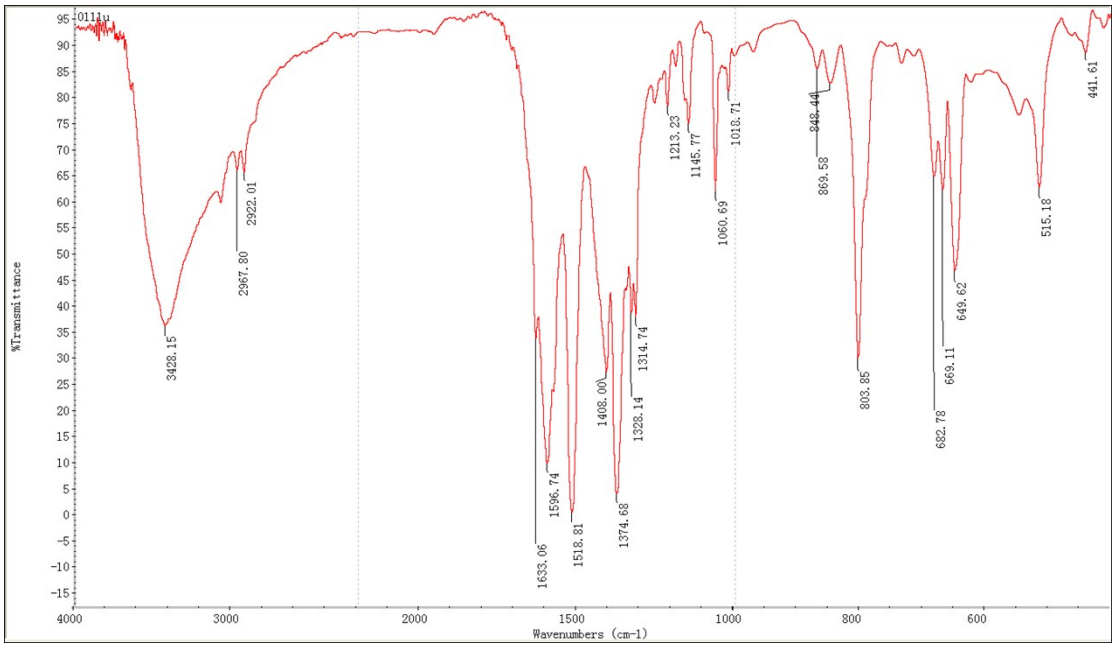



Figure.S5. IR of compound **4**

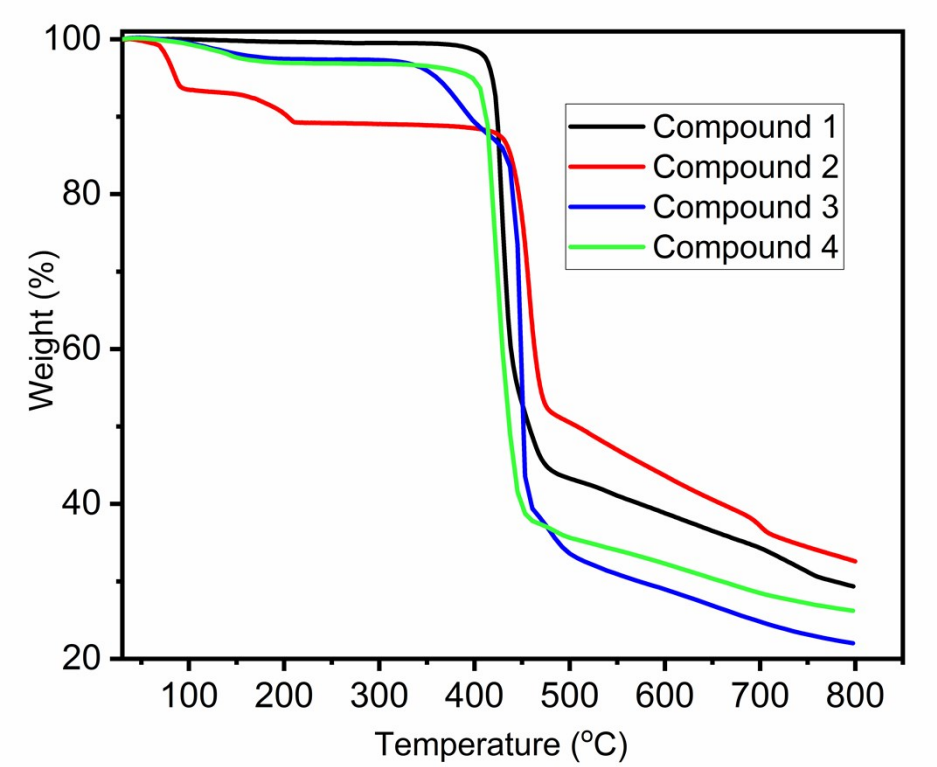
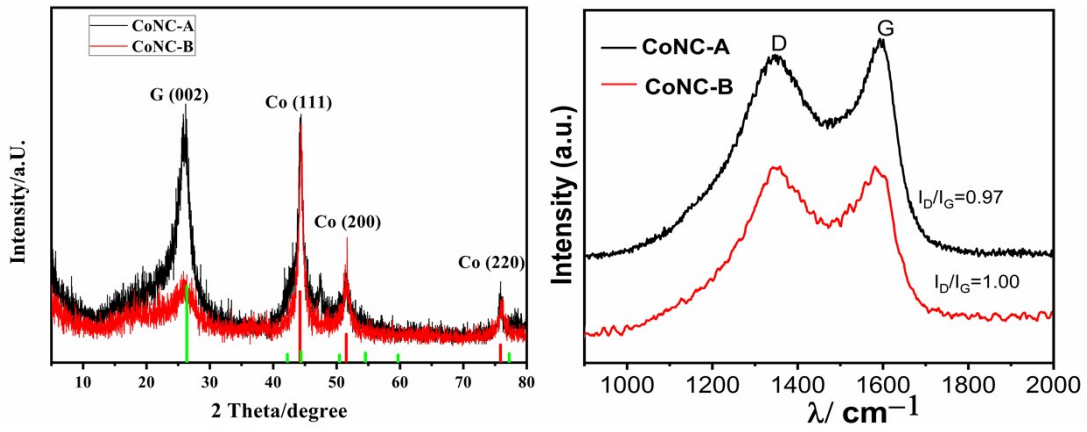
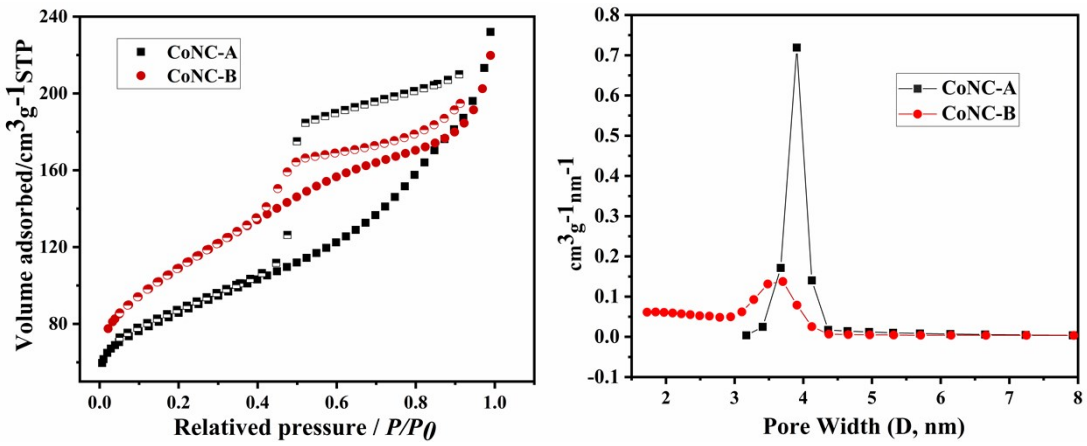



Fig. S6 The TG curve of compounds **1**-**4** under $N_2$ atmosphere at a heating rate of 10 K·min$^{-1}$.



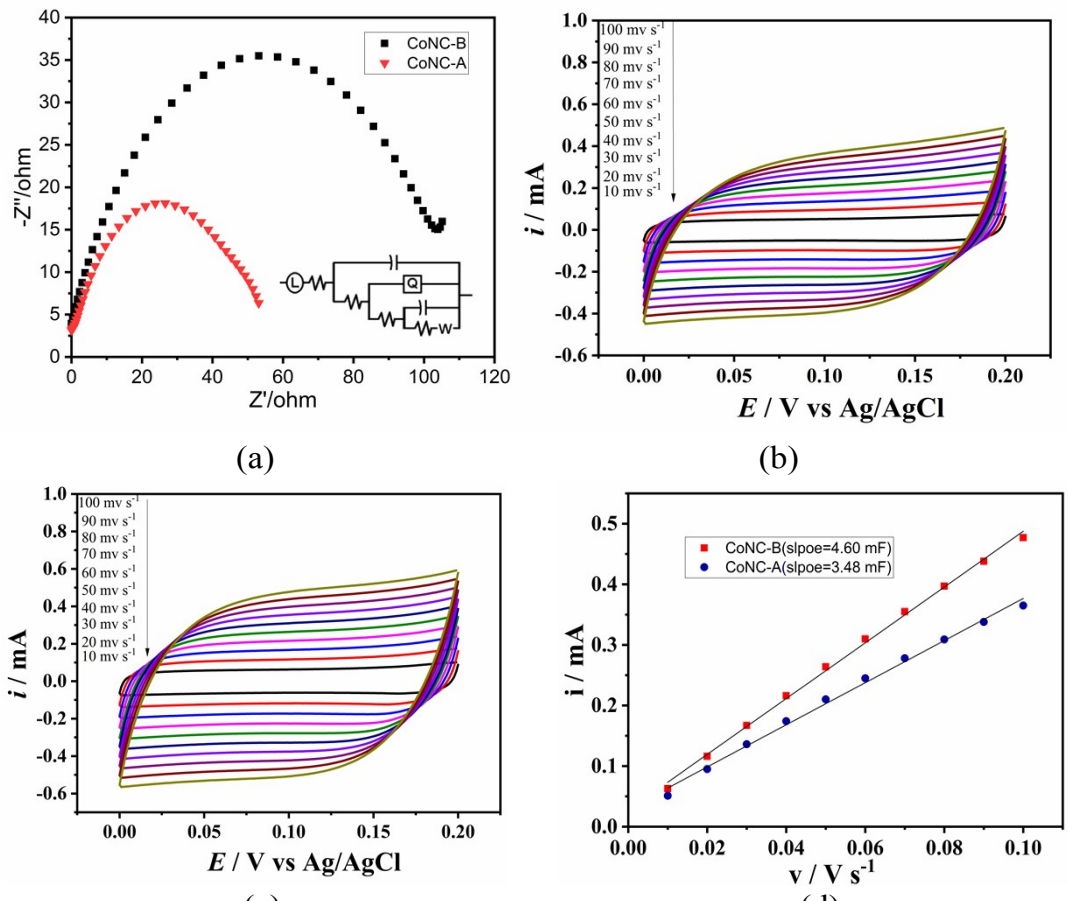

(a) (b)

Fig. S7. (a) Powder XRD patterns (a) and Raman ($\lambda_{ex}$ = 532 nm) spectra (b) of CoNC-A and CoNC-B




(a) (b)

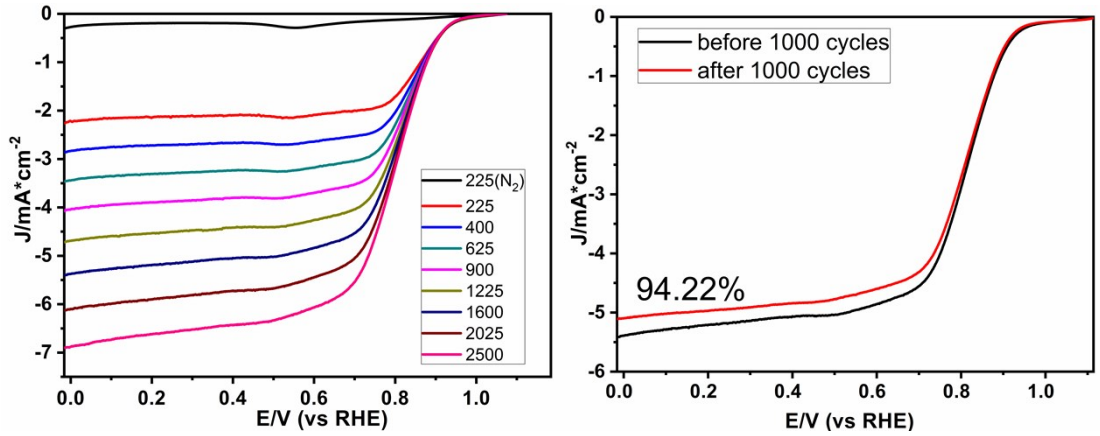
Fig. S8. (a)$N_2$ adsorption and desorption isotherms for CoNC-A and CoNC-B materials. (b) Corresponding pore size distribution plots.




(a) (b)

(c) (d)

Fig. S9 (a) the EIS results. Nyquist plots recorded at 0.75 V (vs Ag/AgCl). CV scans for the CoNC-A (b) and CoNC-B (c). (d) Plot of the current density versus scan rate for the electrocatalysts.




(a) (b)

Fig. S10(a) LSV curves (5mv/s) of CoNC-B at various rotating speeds in $N_2$ and $O_2$-saturated 0.1 M KOH. (b) LSV curves (5 mV/s ) of CoNC-B before and after 1000 potential cycles in $O_2$-saturated 0.1 M KOH solution.at a RDE rotation rate of 1600 rpm.

## 1. Calculating the electron transfer number (n).

The electron transfer numbers (n) were determined by the Koutecky-Levich equation:

$$\frac{1}{J}=\frac{1}{J_L}+\frac{1}{J_K}=\frac{1}{B\omega^{\frac{1}{2}}}+\frac{1}{J_K}$$

$$B=0.62\mathrm{n}FC_0D_0^{\frac{2}{3}}V^{-\frac{1}{6}}$$

Where J is the measured current density, $J_K$ and $J_L$ are the kinetic and limiting current densities, ω is the angular velocity of the disk, n is the overall number of electrons transferred in oxygen reduction, F is the Faraday constant (96485 $C\cdot mol^{-1}$), $C_0$ is the bulk concentration of $O_2$ ($1.2\times10^{-6}$ $mol\cdot cm^{-3}$), $D_0$ is the diffusion coefficient of $O_2$ in 0.1 M KOH ($1.9\times10^{-5}$ $cm^2\cdot s^{-1}$), and V is the kinematic viscosity of the electrolyte (0.01 $cm^2\cdot s^{-1}$), and k is the electron transfer rate constant.

The electron transfer number (n) were calculated by the results of the rotating ring-disk electrode (RRDE) test with the following equations:

$$n = 4 \times \frac{I_D}{I_D + \frac{I_R}{N}}$$

Where $I_D$ is the disk current, IR is the ring current, and N is the ring collection efficiency and N=0.37.

## 2. The equation about the measured potentials converted to the reversible hydrogen electrode (RHE):

All the potentials in this work were converted into reference potential of reversible hydrogen electrode (RHE) by the conversion formula as follows:

$$RHE = E_{Ag/AgCl} + 0.059pH + 0.2224V - 0.059 \lg a(Cl^-)$$

Where $E_{Ag/AgCl}$ represents potential which is measured by silver chloride electrode as reference electrode. 0.2224V is the standard electrode potential of silver chloride electrode at 25℃. The $a(Cl^-)$ is the concentration of $Cl^-$ in saturated silver chloride electrode (3.4M).