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Supporting Information
Dual template effect of Supercritical CO_2 in Ionic Liquid to Fabricate Highly Mesoporous Cobalt Metal-Organic Framework

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1. Experimental part

Materials: The surfactant N-ethyl perfluorooctylsulfonamide ($C_2H_5NHSO_2C_8F_{17}$; N-EtFOSA) (>95%) was purchased from Shanghai Aladdin industrial Corporation. 1, 1, 3, 3-tetramethylguanidinium ($[(CH_3)_2N]_2C{=}NH_2^+$ acetate; TMGA) was synthesized by direct neutralization of 1, 1, 3, 3-tetramethylguanidine with the acetic acid.[1] CO_2 (purity>99.9%) was provided by Zhengzhou Analysis Instrument Factory. $Co(NO_3)_2{\cdot}6\ H_2O$ (A. R. grade) and ethanol (A. R. grade) were purchased from Zhengzhou Chemical Reagents Company. Potassium acid phthalate (KHBDC) (purity 98%) was purchased from Aladdin.

Preparation of Co-MOFs: In a typical synthesis, $Co(NO_3)_2{\cdot}6\ H_2O$ (0.116 g, 0.4 mmol), Potassium acid phthalate (KHBDC, 0.061 g, 0.3 mmol), N-ethylperfluorooctylsulfonamide (N-EtFOSA, 0.4 g), and 1, 1, 3, 3-tetramethylguanidinium (TMGA, 0.6 g) were added into a 50 mL high-pressure cell with a magnetic stirrer. The temperature of the cell was controlled to 80 ˚C. Then, CO_2 was charged into the cell until 16 MPa. After reaction for 24 h and 48 h, CO_2 was released. Finally, the precipitate was collected and washed with ethanol four times. For comparison, the Co-MOF was synthesized in 12 MPa, 8 MPa, pure IL without SC CO_2 and pure SC CO_2 with ethanol, respectively. All the other experimental parameters are the same as those above.

2. Characterization: The morphology of the sample was characterized by a field-emission scanning electron microscope (FE-SEM, JEOR JSM-6700F) equipped with EDX, and a transmission electron microscope TEM (FEI Tecnai G2 20) operated at 100 kV. The porosity of the obtained Co-MOF was determined using a Brunauer–Emmett-Teller (BET) surface analyzer (ASAP 2010, Micromeritics, USA). The mesopore size of the Co-MOF was calculated from the adsorption branch by using BJH model. Thermal gravimetric analysis (TGA) was conducted on a SMP/PF7548/MET/600W instrument from 50 ˚C to 800 ˚C with a heating rate of 10 ˚C/min in nitrogen atmosphere. Fourier transform infrared spectra (FTIR) were recorded on a TENSOR 27 FTIR spectrometer (Bruker) in the absorption mode with resolution of 2 cm^{-1}. Power X-ray diffraction (XRD) data was collected on a Y-2000 X-ray Diffrctometer using copper Kα radiation (λ =1.5406 Å) at a scanning speed of 10º (2θ)/min. The elemental analysis of C, O, and Co was performed on FLASH EA1112 elemental analysis instrument. X-rayphotoelectron spectroscopy (XPS) measurements were made on an ESCALABMK spectrometer using electrostatic lens mode with the pass energy of 100 eV. Al Kα radiation was used as the excitation source.

3. Electrochemical measurements: A three-electrode configuration was used to measure the electrochemical behaviors of the electrode materials. Cyclic voltammetry (CV) and galvanostatic charge/discharge were performed on a CHI 660D electrochemical workstation at room temperature. The working electrode was prepared by mixing 80 wt% Co-MOF material, 10 wt% polytetrafluoroethylene (PTFE) used as a binder, and 10 wt% carbon black. The mixture was spread and pressed onto nickel foam (1 × 1 cm^2). After the electrode materials were loaded, the working electrode was pressed and dried in vacuum at 80 ˚C for 12 h. The auxiliary and reference electrode were Pt wire and Ag/AgCl, respectively. The electrolyte used in all of the measurements was a 1.0 M LiOH solution. The potential range for CV tests was 0 to 0.6 V, and the scan rate was 10, 25, 50, 75, 100, 150 and 200 mV s^{-1}. Galvanostatic charge/discharge measurements were done from 0 to 0.6 V with different current densities at 0.5, 1, 2, 4, 6, 8 and 10 A g^{-1}. The specific capacitance of

Co-MOF electrode at different current densities could be calculated according to the equation $C=It/\Delta Vm$, where C is the specific capacitance, t is the total discharge time, I is the discharge current, ΔV is the potential drop during discharge and m is the mass of Co-MOF within the composite electrodes.

4. Supporting Figures

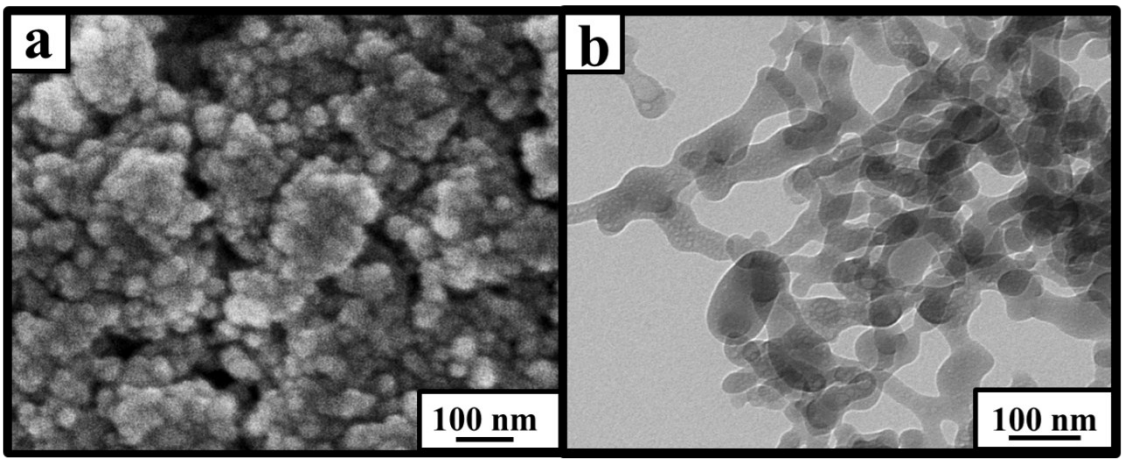

Fig. S1 SEM image (a) and TEM image (b) of the Co-MOF synthesized at 16 MPa and 80 ˚C for 48 h.

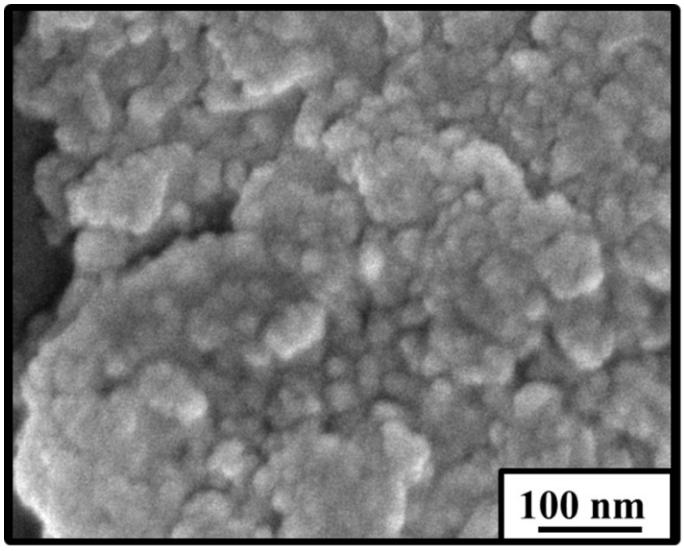

Fig. S2 SEM image of the Co-MOF synthesized at 16 MPa and 80 ˚C for 24 h.

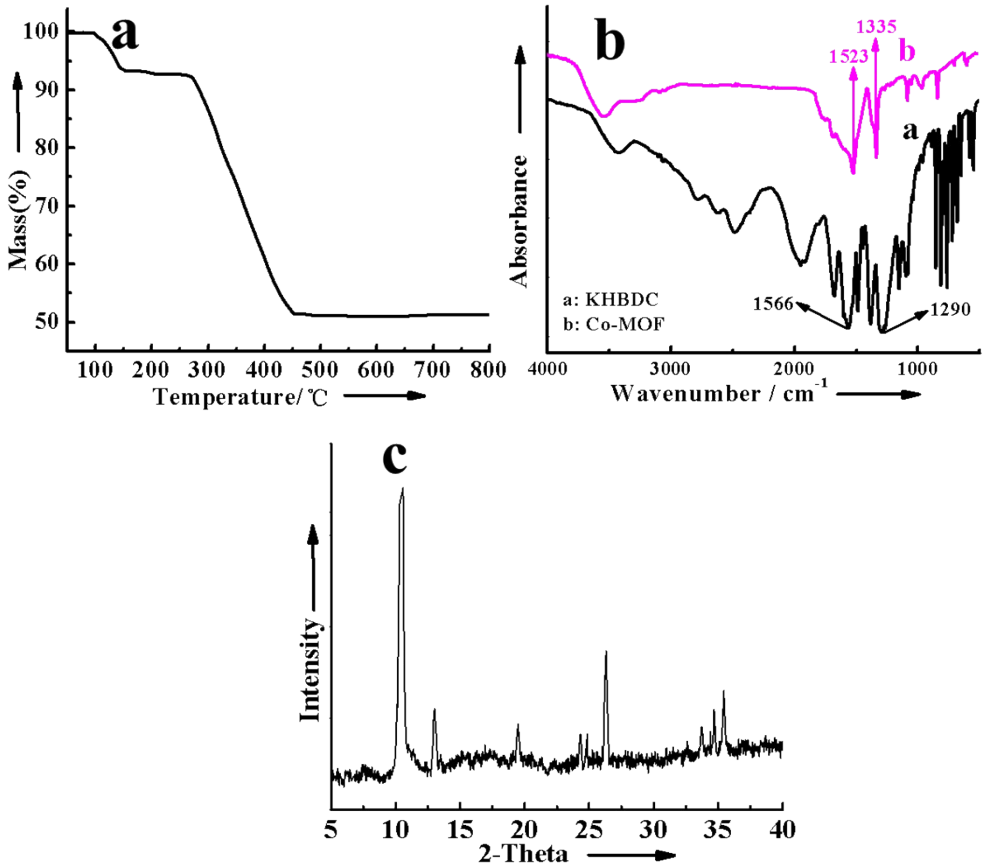

Fig. S3 (a) Thermogravimetric analysis curve of Co-MOF. (b) Fourier transform infrared spectra of the ligand KHBDC and Co-MOF. (c) XRD pattern of Co-MOF. All samples were synthesized at 16 MPa and 80 ℃ for 48 h.

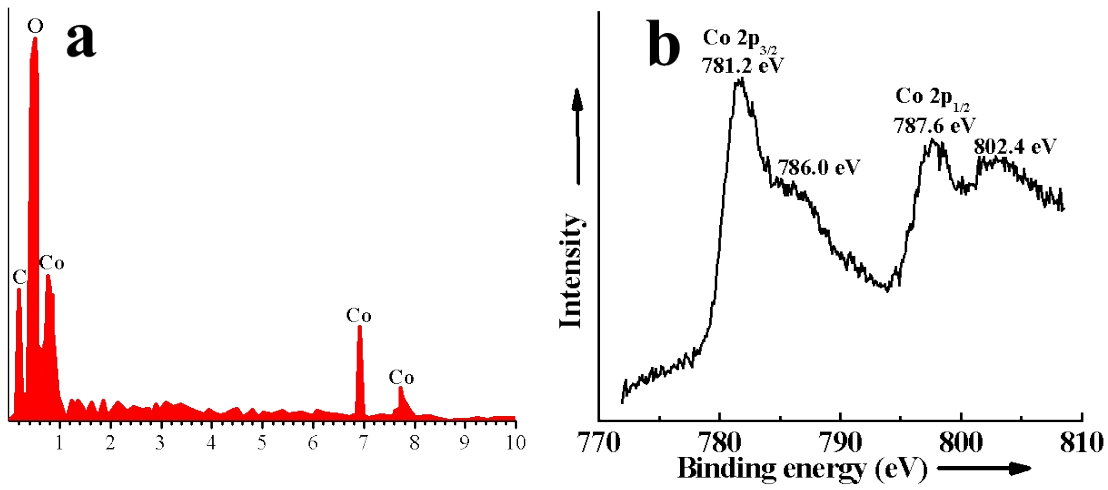

Fig. S4 EDX spectrum (a) and Co 2p XPS (b) of Co-MOF synthesized at 16 MPa and 80 ℃ for 48 h.

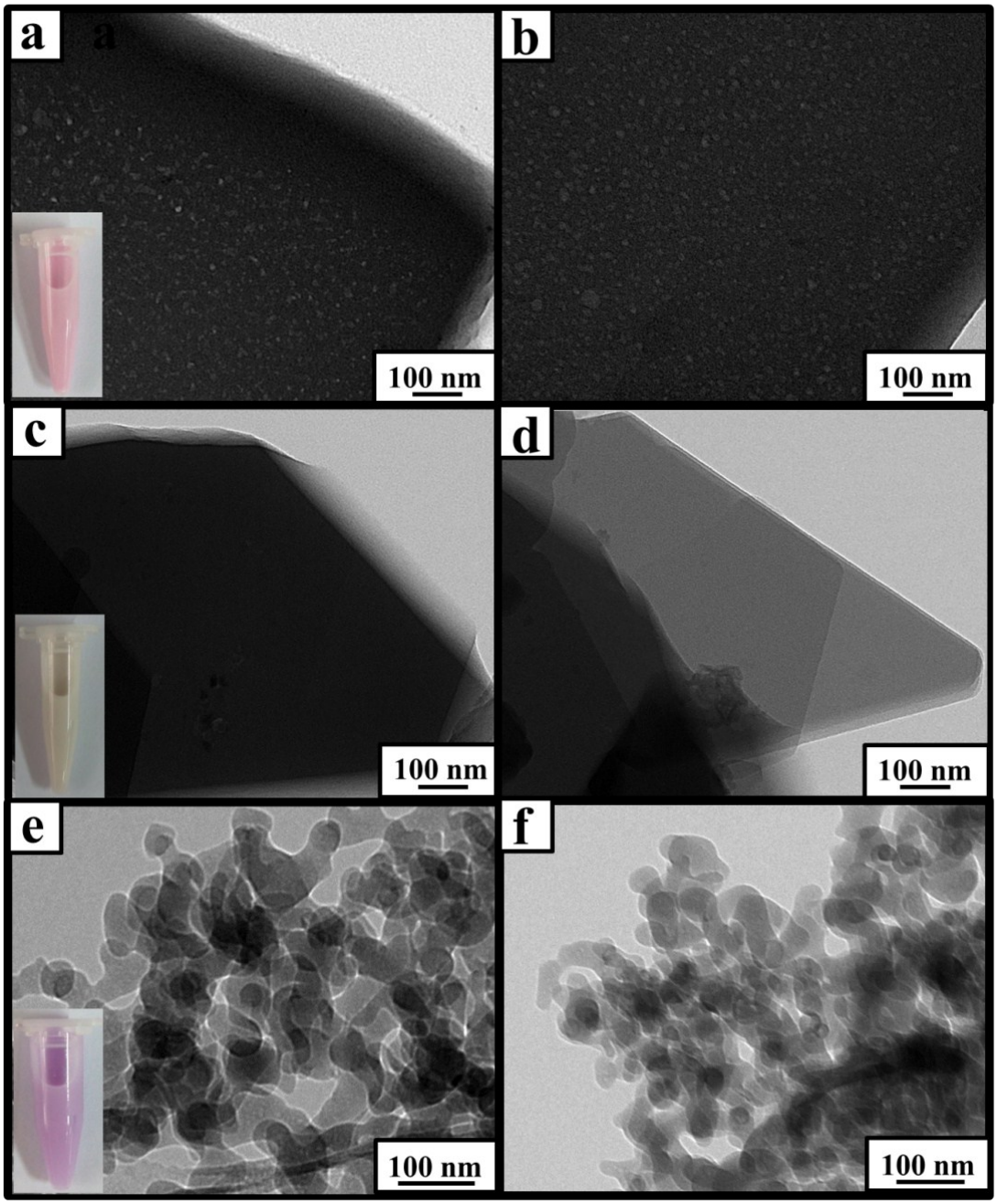

Fig. S5 TEM images of Co-MOFs synthesized for 48 h at different conditions. (a, b) without IL at 16 MPa and 80 ˚C. (c, d) without SC CO_2 at 80 ˚C. (e, f) with both IL and SC CO_2 at 16 MPa and 80 ˚C. The inset in (a, c, e) shows the color change of Co-MOF synthesized at various conditions.

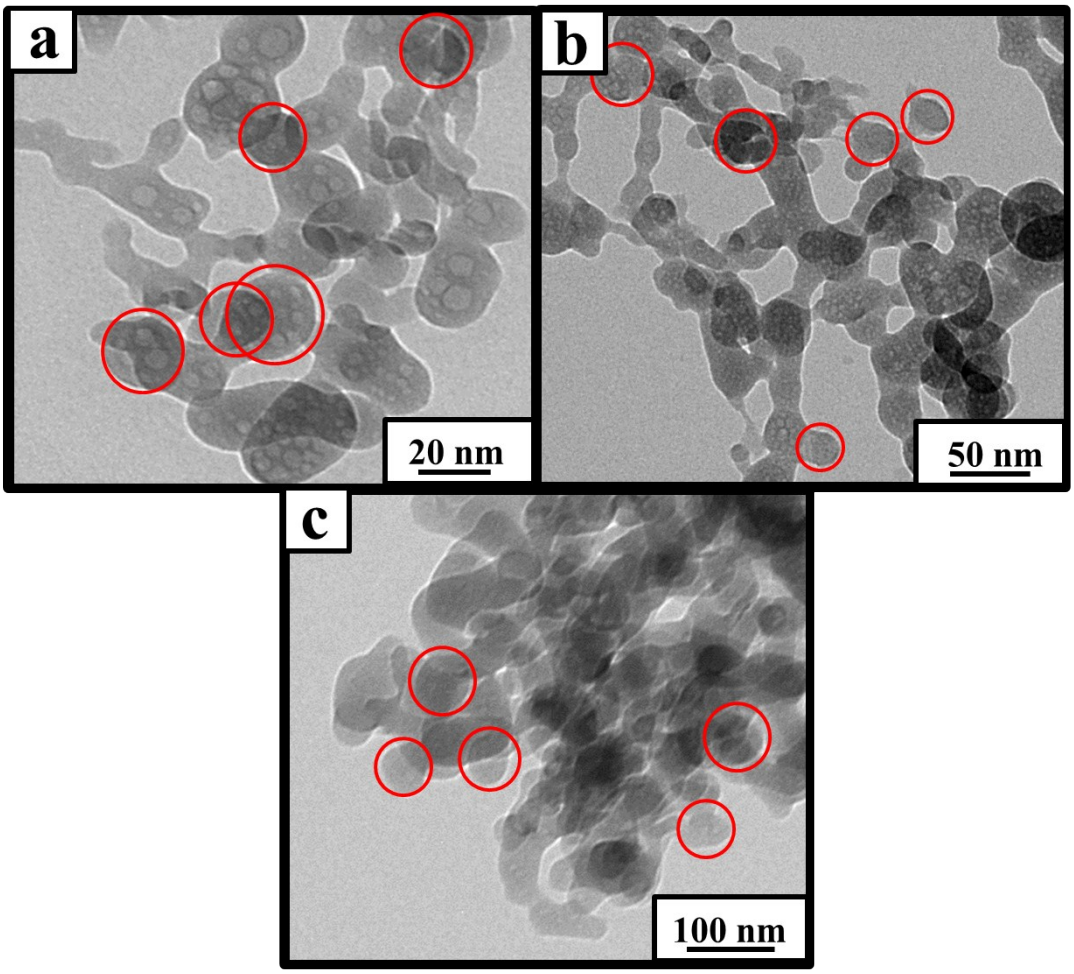

Fig. S6 TEM images of Co-MOFs synthesized at 80 ˚C for 48 h with different pressure. (a) 8 MPa. (b) 12 MPa. (c) 16 MPa. The average diameter of nanospheres for (a-c) was about 18 nm, 32 nm and 50 nm, respectively. Obviously, the higher pressure favors the formation of larger nanospheres.

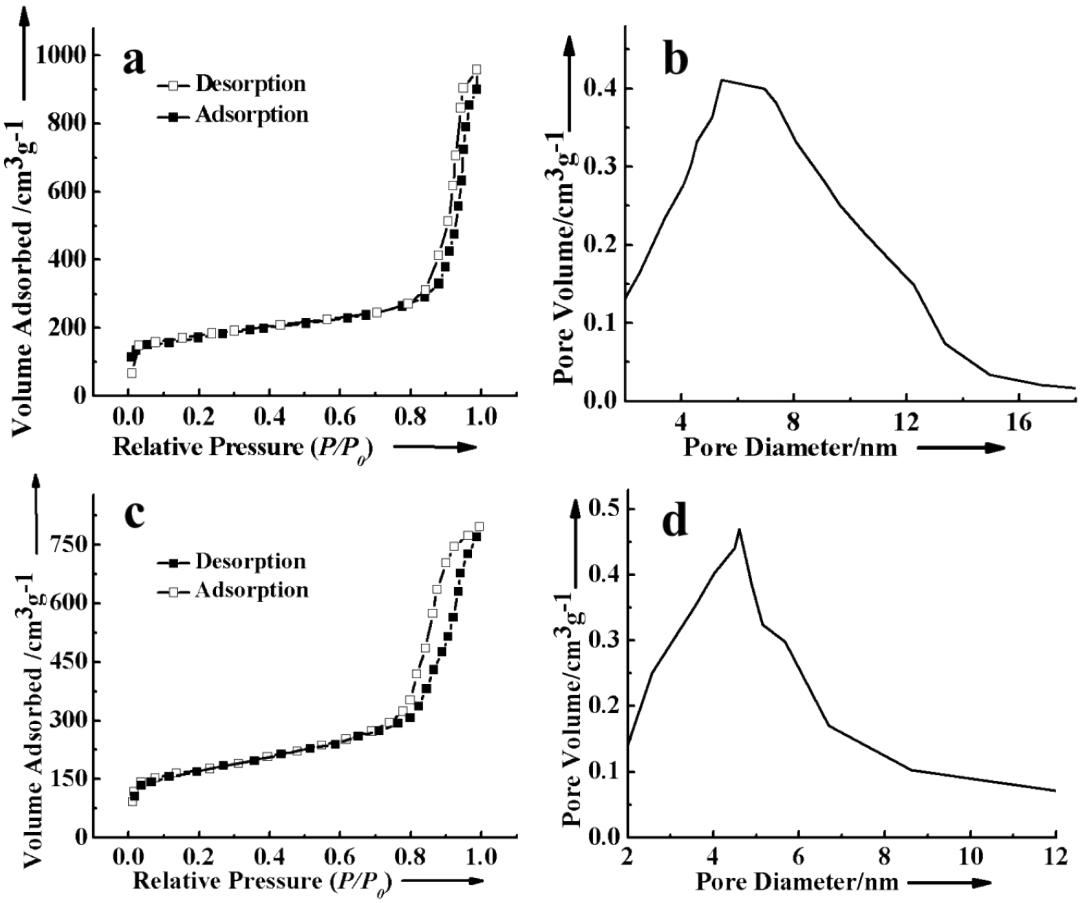

Fig. S7 (a) N_2 adsorption-desorption isotherms and (b) mesopore size distribution curve of Co-MOF synthesized at 8 MPa. (c) N_2 adsorption-desorption isotherms and (d) mesopore size distribution curve of Co-MOF synthesized at 12 MPa. Both samples were synthesized at 80 ˚C for 48 h.

Pressure (MPa)	$D_{spheres}$ (nm)	D_{meso} (nm)
8	18	6
12	35	4.9
16	50	3.2

$D_{spheres}$ is the average diameter of nanospheres.
D_{meso} is the average diameter of mesopores.

Table S1 Physicochemical properties of Co-MOF synthesized at different pressure. All samples were synthesized at 80 ˚C for 48 h.

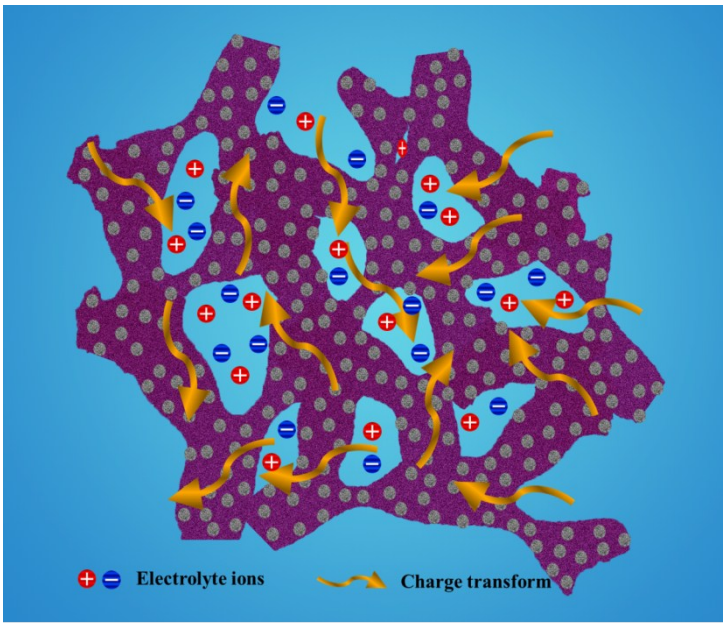

Fig. S8 Schematic illustration for the diffusion of charge and electrolyte when Co-MOF (synthesized at 16 MPa and 80 °C for 48 h) are used as electrode material for supercapacitor.

Reference

1 H. X. Gao, B. X. Han, J. C. Li, T. Jiang, Z. M. Liu, W. Z. Wu, Y. H. Chang and J. M. Zhang, *Synth. Commun.*, 2004, **34**, 3083.