# Experimental

## Chemicals and Materials.

All chemicals were at least AR grade, kept at 4 °C in the dark until used without further treatment, which were purchased from Aladdin Reagents Co. Ltd. (Shanghai, China) or Kelong Chemical Reagent Co. Ltd. (Chengdu, China). Ultrapure water (18.25 MΩ·cm) used for all experiments was obtained from a water purification system (PCWJ-10, Pure Technology Co. Ltd, Chengdu, China).

## Instrumental

The powder X-ray diffraction (PXRD) patterns were carried out with an EMPYREAN (Panalytical Inc., Netherlands) with a Cu sealed tube. For the TG analysis, the obtained MOFs crystals were heated using a thermogravimetric analyzer (EXSTAR 6000, Seiko Instrument Inc., Japan). The morphology of the obtained MOFs crystals was characterized by scanning electron microscope (SEM) (Hitachi, Japan). GC-MS data were obtained from a GCMS-QP2010 Plus (Shimadzu Instrument Inc., Japan). The NMR data were collected from a nuclear magnetic resonance spectrometer (Bruker AV II-600 MHz). The electron paramagnetic resonance (EPR) spectra of the generated radicals spin-trapped by 5,5-dimethyl-1-pyrroline N-oxide (DMPO) were collected at room temperature by using a BRUKER spectrometer (EXM, Germany). The EDS spectra were obtained by using an energy dispersive spectrometer (AXIS Ultra DLD 800 X, Kratos, UK).

## EPR Data Analysis

The EPR results were obtained from the supernant in the reactor after the synthesis process of MOF-5 by the proposed strategy. It was shown in Figure 4 that the combined signal of hydrogen radical with hyperfine of $a_N$=14.7 G, $a_{H\alpha}$=$a_{H\beta}$=19.2 G and dimethylaminoformyl radical (•DMF) with hyperfine of $a_N$=14.3 G, $a_{H\beta}$=17.4 G, in accordance with the previously reported, respectively (J. Magn. Reson., 1973, 9, 510; J. Catal., 2016, 339, 292).

# Tables

**Table S1 Parameters for the exhibitive synthesis of MOFs using the proposed strategy**

| MOFs | Metal ions (M) | Ligands (M) | Solvent | Voltage (V) | Current (A) | Reaction time (min) | Yield (%) |
|---|---|---|---|---|---|---|---|
| MOF-5 | $Zn(NO_3)_2•6H_2O$<br>0.144 | Terephthalic acid (BDC) 0.065 | DMF | 32 | 1.20 | 30 | 50 |
| HKUST-1 | $Cu(NO_3)_2•3H_2O$<br>0.106 | Benzenetricarboxylic acid (BTC) 0.061 | DMF | 40 | 1.32 | 1 | 50 |
| ZIF-8 | $Zn(NO_3)_2•6H_2O$<br>0.118 | N-methyl Imidazole<br>0.853 | DMF | 40 | 1.28 | 1 | 70 |
| UiO-66 | $ZrCl_4•6H_2O$<br>0.150 | BDC<br>0.104 | DMF | 40 | 1.27 | 10 | 80 |
| $Mn_2(BDC)_3(DMF)_3$ | $MnCl_2•4H_2O$<br>0.059 | BDC<br>0.125 | DMF | 40 | 1.24 | 30 | 80 |
| Tb(BTC)(DMF) | $Tb(NO_3)_3$<br>0.010 | BTC<br>0.010 | DMF | 40 | 1.23 | 1 | 70 |
| UiO-66-$NH_2$ | $ZrCl_4•6H_2O$<br>0.150 | $NH_2$-BDC<br>0.104 | DMF | 40 | 1.27 | 10 | 78 |

Note: for the preparation of Au@ZIF-8 or Ag@ZIF-8: 0.118 M $Zn(NO_3)_2•6H_2O$ and 0.853 M N-methyl imidazole as precursors, reacting at 40 V and 1.28 A for 1 min, followed by the addition of 0.1 mL concentrated $HAuCl_4$ in $H_2O$ or 25 mg•mL$^{-1}$ $AgNO_3$, and reaction for another 10 min.

**Table S2 BET values of the obtained MOFs crystals and those reported previously**

| MOF | Measured BET ($m^2 \cdot g^{-1}$) | Reported BET ($m^2 \cdot g^{-1}$) | Reference |
|---|---|---|---|
| ZIF-8 | 1832 | 1470/1630 | [1]/[2] |
| MOF-5 | 1680 | ~1300/1263 | [3]/[4] |
| HKUST-1 | 1400 | 1880 | [5] |
| UiO-66 | 966 | 855 | [6] |

References:

[1] Shi, Q.; Chen, Z.; Song, Z.; Li, J.; Dong, J. *Angew. Chem. Int. Ed.*, **2011**, *50*(3), 672-675.

[2] Park, K. S.; Ni, Z.; Cote, A. P.; Choi, J. Y.; Huang, R.; Uribe-Remo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. *PNAS*, **2006**, *103*(27), 10186-10191.

[3] Yoo, Y.; Lai, Z.; Jeong, H. K., *Micropor. Mesopor. Mat.,* **2009**, *123*(1-3), 100-106.

[4] Lu, C. M.; Liu, J.; Xiao, K.; Harris, A. T., *Chem. Eng. J.*, **2010**, *156*(2), 465-470.

[5] DeCoste, J. B.; Weston, M. H.; Fuller, P. E.; Tovar, T. M.; Peterson, G. W.; LeVan, D. M.; Farha, O. K. *Angew. Chem. Int. Ed.*, **2014**, *53*, 14092-14095.

[6] Kandiah, M.; Nilsen, M. H.; Usseglio, S.; Jakobsen, S.; Olsbye, U.; Tilset, M.; Lillerud, K. P. *Chem. Mater.*, **2010,** *22*, 6632–6640.

**Table S3 Morphology and size of MOF-5 crystals obtained by using varied parameters**

| $Zn^{2+}$[M] | Solvent | Voltage (V) | Current (A) | Reaction time (min) | Size (μm) | Morphology |
|---|---|---|---|---|---|---|
| 0.144 | DMF | 10 | 0.36 | 60 | - | - |
| 0.144 | DMF | 20 | 0.82 | 60 | - | - |
| 0.144 | DMF | 22 | 1.02 | 60 | 8±5 | Cube with rough surface |
| 0.144 | DMF | 24 | 1.08 | 60 | 10±5 | Concave cube |
| 0.144 | DMF | 26 | 1.12 | 60 | 13±5 | Cube |
| 0.144 | DMF | 30 | 1.16 | 30 | 20±5 | Cube |
| 0.144 | DMF | 32 | 1.20 | 30 | 25±5 | Cube |
| 0.144 | DMF | 38 | 1.25 | 30 | 30±5 | Cube |
| 0.144 | DMF | 40 | 1.29 | 30 | 30±5 | Cube |
| 0.144 | DMF | 32 | 1.20 | 10 | 5±2 | Cube |
| 0.144 | DMF | 32 | 1.20 | 60 | 35±10 | Cube |
| 0.072 | DMF | 32 | 1.18 | 30 | 20±5 | Hexagonal plates |

Note: -, no MOF-5 crystals obtained.

**Table S4 Yield of ZIF-8 crystals obtained with varied synthetic parameters**

| $Zn^{2+}$[M] | Solvent | Voltage (V) | Current (A) | Reaction time (min) | Yield (%) |
|---|---|---|---|---|---|
| 0.118 | DMF | 30 | 1.12 | 1 | - |
| 0.118 | DMF | 42 | 1.32 | 1 | 72 |
| 0.118 | DMF | 40 | 1.28 | 1 | 70 |
| 0.118 | DMF | 40 | 1.28 | 3 | 78 |
| 0.118 | DMF | 40 | 1.28 | 10 | 88 |
| 1.18 | DMF | 40 | 1.28 | 1 | 80 |
| 11. 8 | DMF | 40 | 1.28 | 1 | 76 |
| 0.118 | Alcohol | 42 | 1.44 | 1 | 75 |
| 0.118 | Alcohol | 40 | 1.40 | 1 | 70 |
| 0.118 | Alcohol | 30 | 1.32 | 1 | 62 |
| 0.118 | Alcohol | 30 | 1.32 | 3 | 70 |
| 0.118 | Alcohol | 30 | 1.32 | 10 | 86 |

Note: -, none ZIF-8 crystals observed.

**Table S5 Size and yield of HKUST-1 crystals obtained with varied parameters**

| $Cu^{2+}$[M] | Solvent | Voltage (V) | Current (A) | Reaction time (min) | Size (μm) | Yield (%) |
|---|---|---|---|---|---|---|
| 0.106 | DMF | 40 | 1.32 | 1 | 1±0.5 | 50 |
| 0.106 | DMF | 40 | 1.32 | 5 | 2±1 | 61 |
| 0.106 | DMF | 40 | 1.32 | 10 | 3±1 | 72 |
| 0.106 | DMF | 40 | 1.32 | 30 | 4±1 | 90 |
| 0.106 | Alcohol | 40 | 1.40 | 1 | 1±0.5 | 72 |
| 0.106 | Alcohol | 40 | 1.40 | 5 | 3±1 | 90 |
| 0.106 | Alcohol | 40 | 1.40 | 10 | 4±1 | 90 |
| 0.106 | Alcohol | 40 | 1.40 | 30 | 6±1 | 92 |
| 0.106 | DMSO | 40 | 1.42 | 5 | 2±0.5 | 85 |
| 0.106 | Methanol | 40 | 1.42 | 5 | 2±0.5 | 86 |
| 0.106 | Propanol | 40 | 1.44 | 5 | 2±0.5 | 90 |
| 0.106 | Ethylene glycol | 40 | 1.38 | 5 | 1±0.5 | 82 |
| 0.106 | Tetrachloromethane | 40 | 1.32 | 5 | no crystals | - |

**Table S6 Verification of $H_2$ generation during MOFs synthesis with specific conditions**

| MOFs | Concentration* | Solvent | Voltage (V) | Reaction time (min) | $H_2$ |
|---|---|---|---|---|---|
| MOF-5 | 5-fold | DMF | 40 | 15 | less |
| HKUST-1 | 5-fold | DMF | 40 | 15 | less |
| ZIF-8 | 5-fold | DMF | 40 | 15 | less |
| HKUST-1 | 5-fold | Alcohol | 36 | 15 | Plenty |
| ZIF-8 | 5-fold | Alcohol | 36 | 15 | Plenty |
| Blank | | Alcohol | 36 | 15 | No |
| Blank | | DMF | 36 | 15 | less |

* 5-fold concentrations of metal ions and organic linkers for the plasma-induced synthesis described in this work.

**Table S7 The threshold value of DBD input voltage for the synthesis of MOFs**

| MOFs | Threshold value (V) |
|---|---|
| ZIF-8 | 40 |
| MOF-5 | 24 |
| HKUST-1 | 20 |
| UiO-66 | 30 |

# Figures

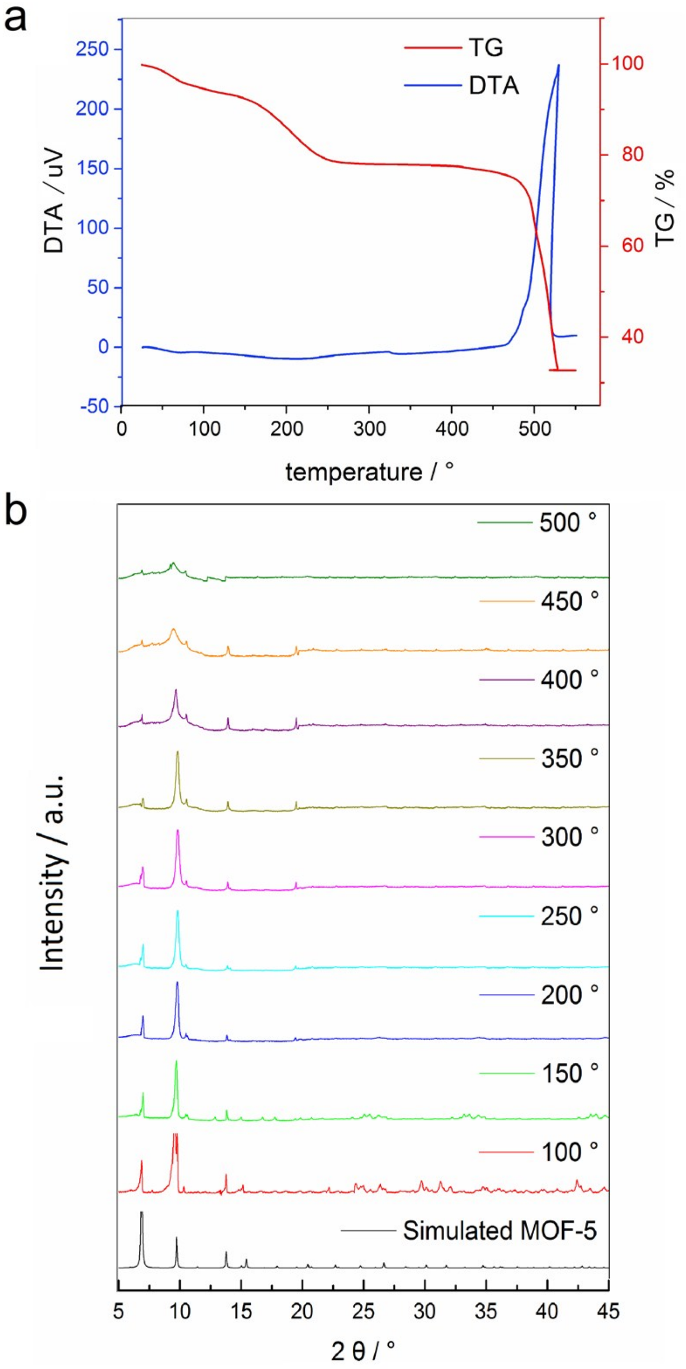

**Figure S1** (a) thermal gravity analysis (TGA) of MOF-5; (b) powder X-ray diffraction (PXRD) patterns of MOF-5 heated at varied temperature.

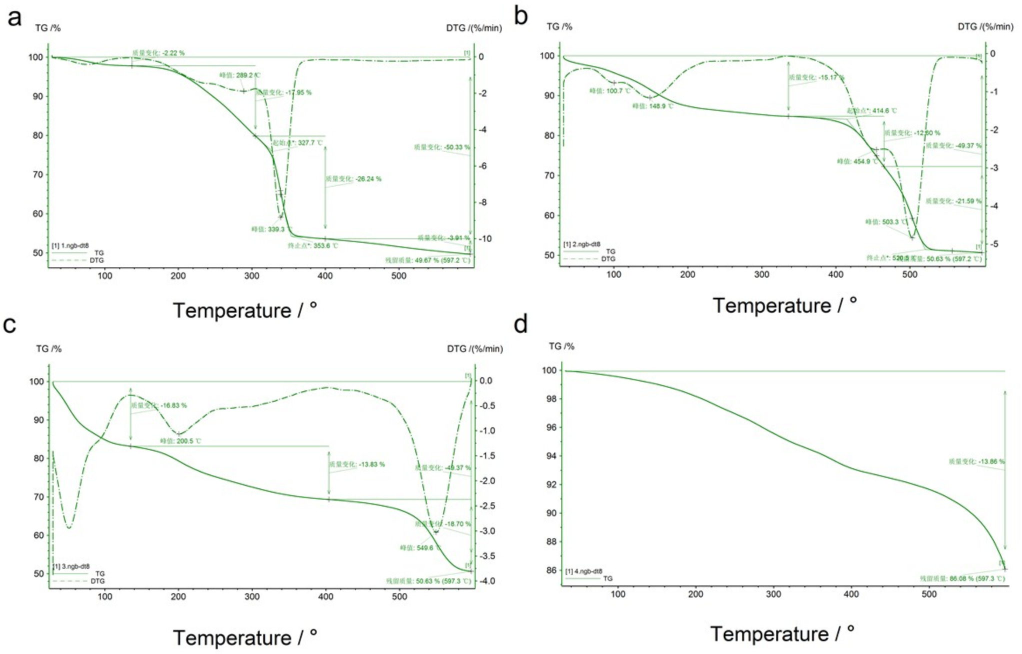

**Figure S2** TGA of HKUST-1 (a), ZIF-8 (b), UiO-66 (c), and $Mn_2(BDC)_3(DMF)_3$ (d).

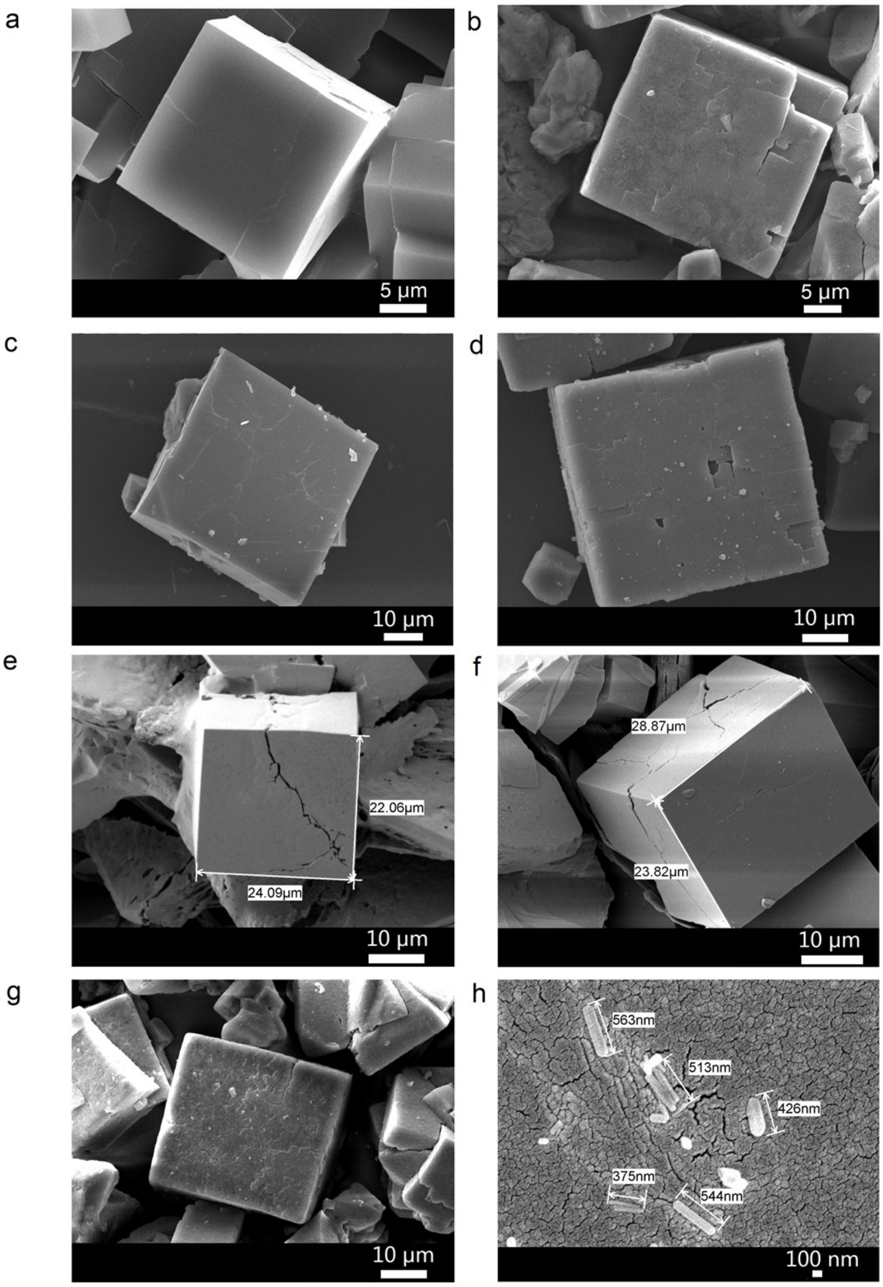

**Figure S3** FESEM images of MOF-5 synthesized with different conditions: (a) V: 30 V; I: 1.16 A; P: 34.8 W; and t: 30 min; (b) V: 38 V; I: 1.25 A; P: 37.5 W; and t: 30 min; (c) V: 38 V; I: 1.25 A; P: 37.5 W; and t: 40 min; (d) V: 38 V; I: 1.25 A; P: 37.5 W; and t: 80 min; (e) V: 30 V; I: 1.16 A; P: 34.8 W; and t: 60 min; (f) V: 34 V; I: 1.02 A; P: 34.8 W; and t: 60 min; (g) V: 32 V; I: 1.16 A; P: 37.1 W; and t: 60 min; (h) V: 32 V; I: 0.5 A; P: 16 W; and t: 60 min.

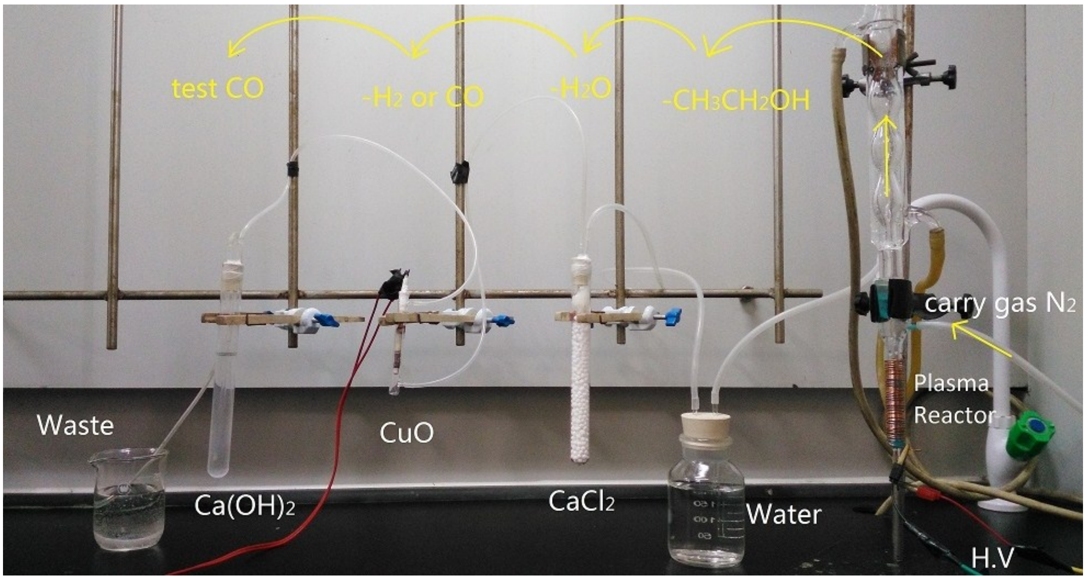

**Figure S4** Photograph of a self-designed system to verify the gaseous by-product.

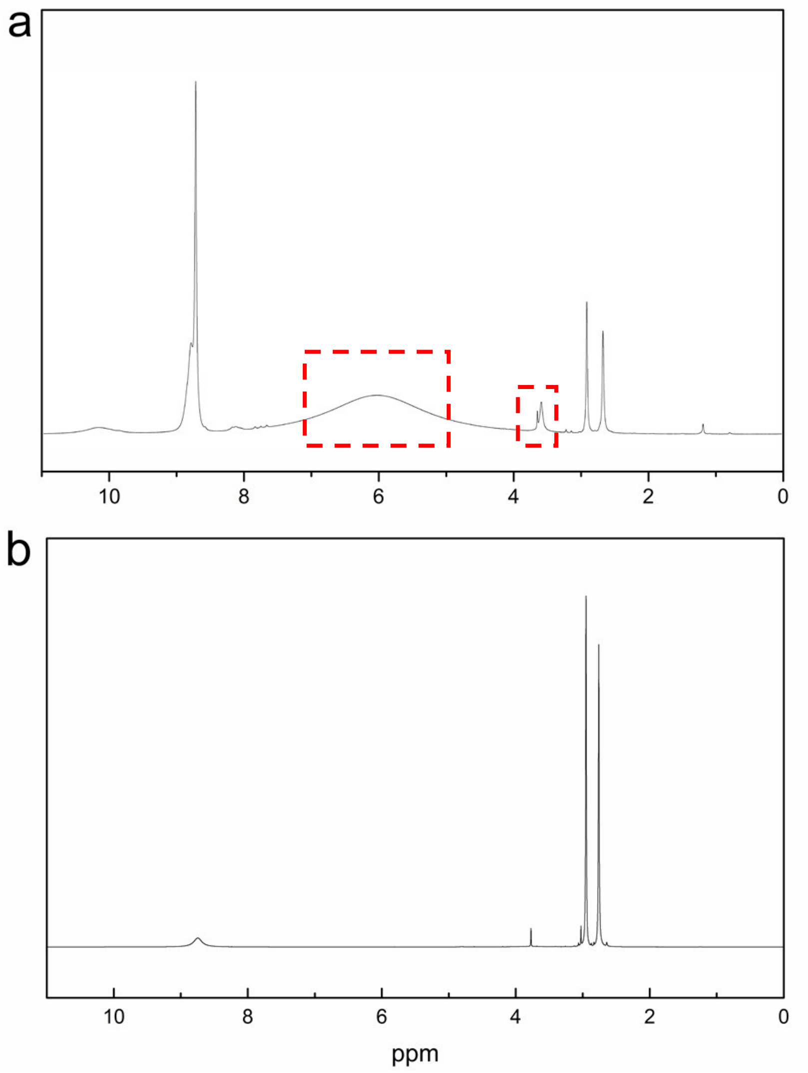

**Figure S5** NMR spectra obtained from the supernate in the reactor after (a) and before (b) the MOFs synthesis procedure using the proposed strategy.

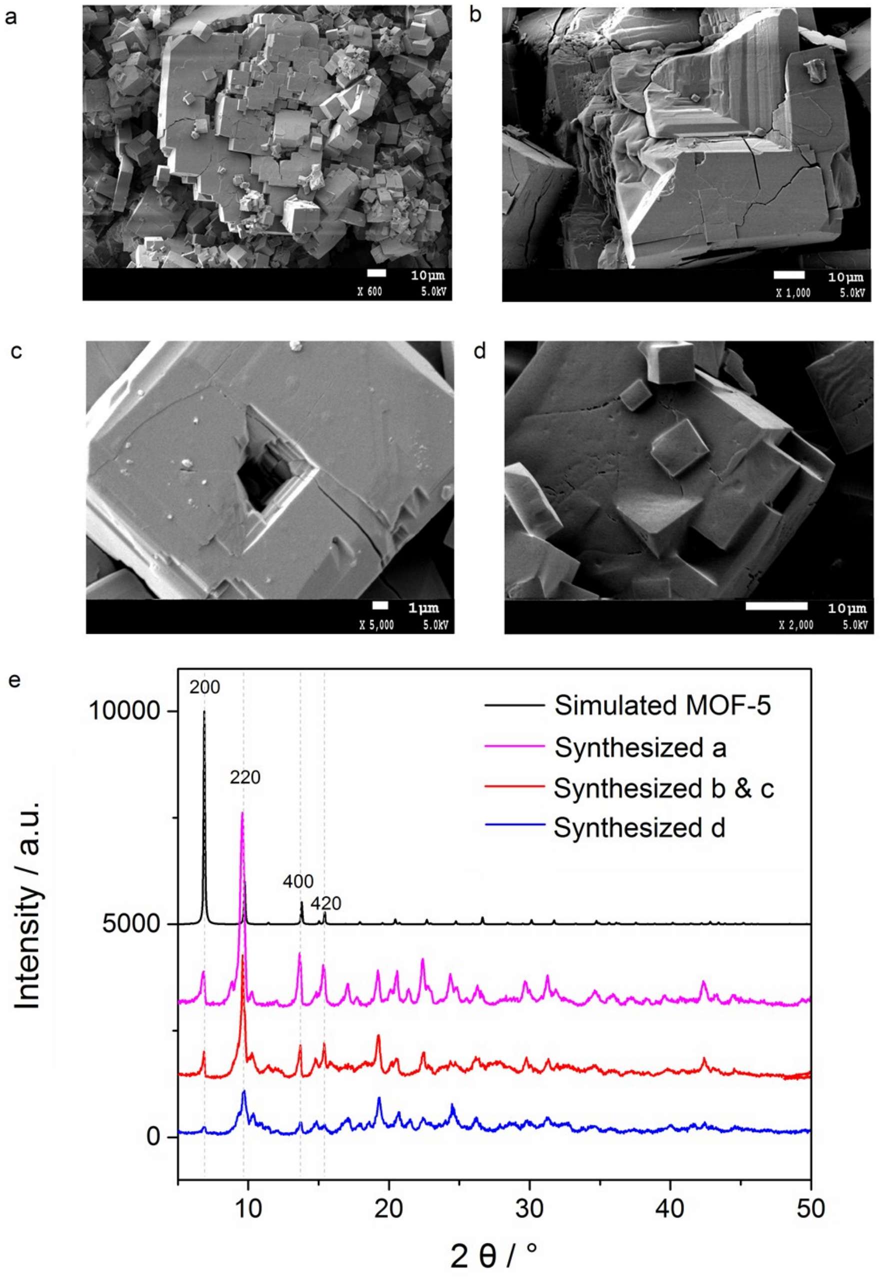

**Figure S6** FESEM images (a-d) and PXRD spectra (e) of the obtained MOF-5 crystals with the morphology in a layer-by-layer deposition manner (synthetic conditions: 38 V, 30 min).

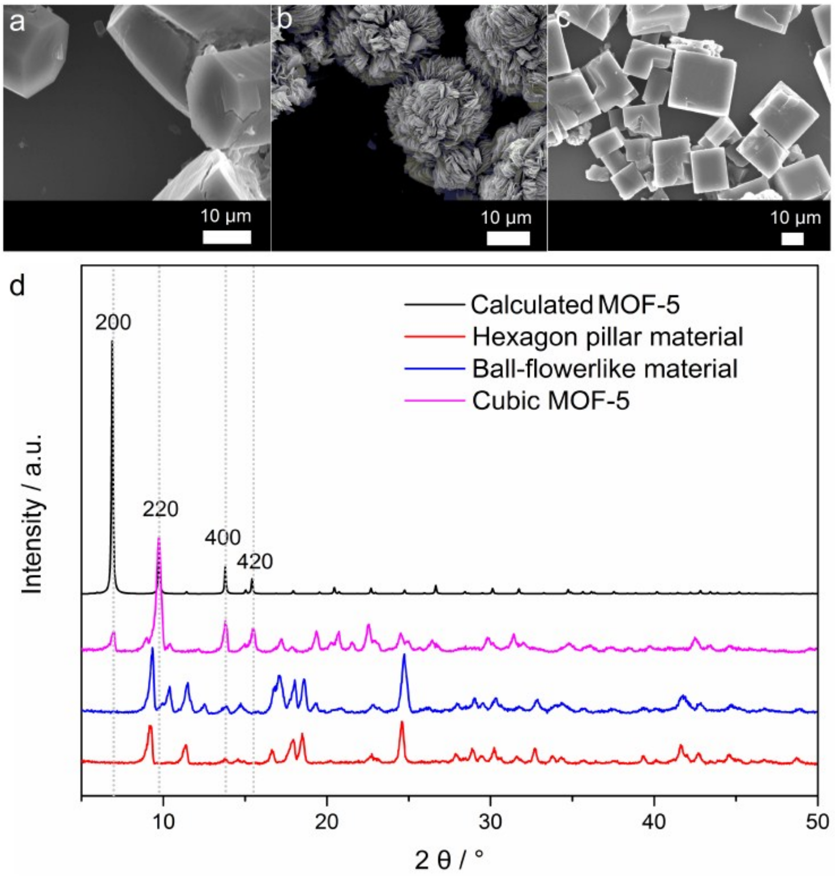

**Figure S7** SEM images of the product collected after MOF-5 precursors reacted for 10 min (a), 20 min (b) and 30 min (c) under the synthetic conditions: 28 V, 1.13 A.

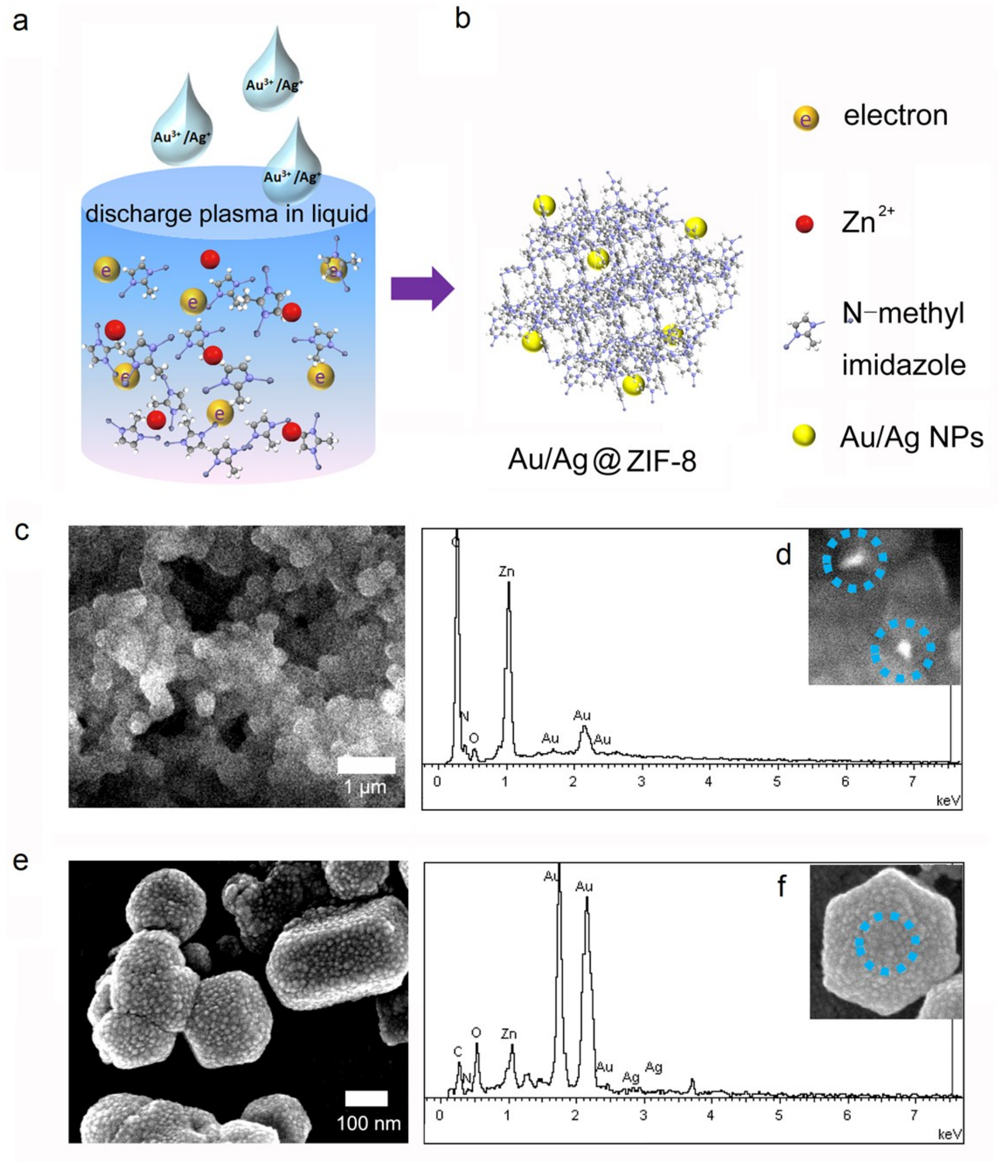

**Figure S8** Scheme about the incorporation of Au or Ag nanoparticles into nanoZIF-8 crystals (a)&(b); FESEM images Au@ZIF-8 (c) and Ag@ZIF-8 (e), along with the according EDS spectra (d&f).

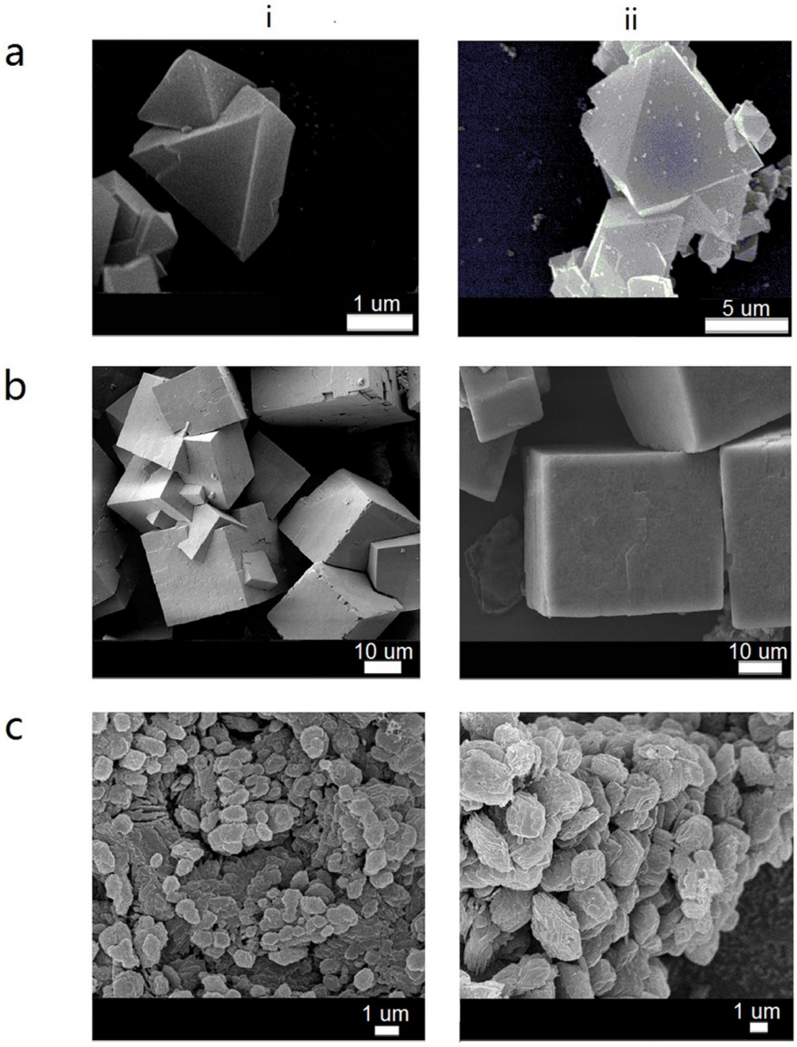

**Figure S9** FESEM images of (a) HKUST-1, (b) MOF-5 and (c) $Mn_2(BDC)_3(DMF)_3$ synthesized in non-flow (i) and continuous flow (ii) manner, respectively.