Supporting Information

Hetero-Metal Hydroxide Nanostrand Assisted Synthesis of MIL-110 Nanorod Arrays on Porous Substrate

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1.Experimental Section:

Materials: Copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$), zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$), cadmium nitrate ($Cd(NO_3)_2 \cdot 4H_2O$), aluminium nitrate ($Al(NO_3)_3 \cdot 9H_2O$), 2-aminoethanol (NH_2-CH_2CH_2OH), were purchased from Acros Chemicals. 1,3,5-benzenetricarboxylic acid (trimesic acid, H_3BTC) was purchased from Sigma-Aldrich. The supports were porous Anopore alumina membranes (Whatman) with an average pore size of ca.200 nm. Ultrapure water of 18.2 MΩ produced by a Millipore direct-Q system was used throughout the experiments.

MIL-110 nanorod arrays synthesis: Typically, the MIL-110 nanorod arrays were prepared including the formation of CHNs mesoporous thin films by filtering 15, 30 and 60 ml CHNs solution on a porous alumina membrane surface with effective area of 2.83 cm^2, respectively. The obtained CHNs thin films were then placed face-up on the bottom of an autoclave with 30 ml, 1 mM H_3BTC deionized water solution and heated at 120℃for 3, 6, 9 and 24 h. After that, the autoclave was cooled to room temperature with a cooling rate of 10℃h^{-1}. The obtained samples were washed with abundant deionized water for several times and then treated at 40℃in an oven to prevent the appearance of cracks caused by the release of interface stress.[1]

Charaterization: The phases of the as-prepared products were characterized by XRD at room temperature using an X'Pert PRO (PANalytical, Netherlands) instrument with

Cu Kα radiation. The morphologies and structures were characterized by using scanning electronic microscopy (SEM) (Hitachi S-4800), and TEM (Tecnai G2 F20 S-TWIN). SEM observation was conducted after coating a 2 nm thick platinum 30 layer by using a Hitachi e-1030 ion sputter at the pressure of 10 Pa and the current density of 10 mA. The metal ion concentration was determined by an ICP-AES (IRIS INTREPID II XSP, American). XPS spectra were recorded by using VG ESCALAB MARK II with Mg Ka: 1253.6 eV and Step of 0.2 eV.

2.CHNs thin films

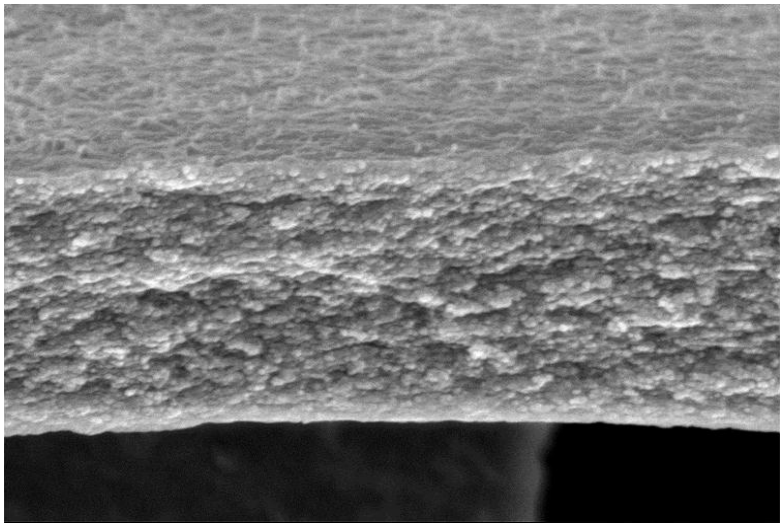

Figure S1. Cross-section SEM image of the CHNs thin films filtered from 30 ml CHNs soltuion on PC membrane with effective diameter of 1.9 cm.

3.XPS spectrum of MIL-110 nanorod arrays

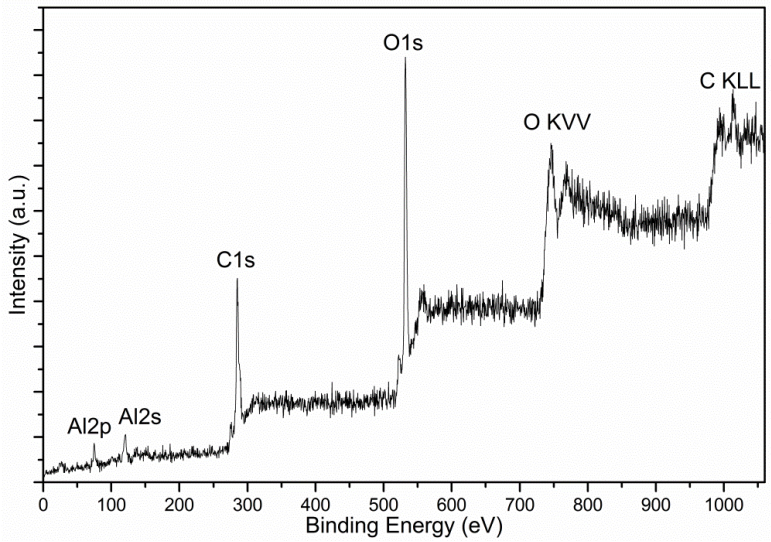

Figure S2. XPS spectrum of MIL-110 nanorod arrays as shown in Figure 1b.

4. X-ray Energy dispersive analysis spectra (EDS) of the samples reacting with different time

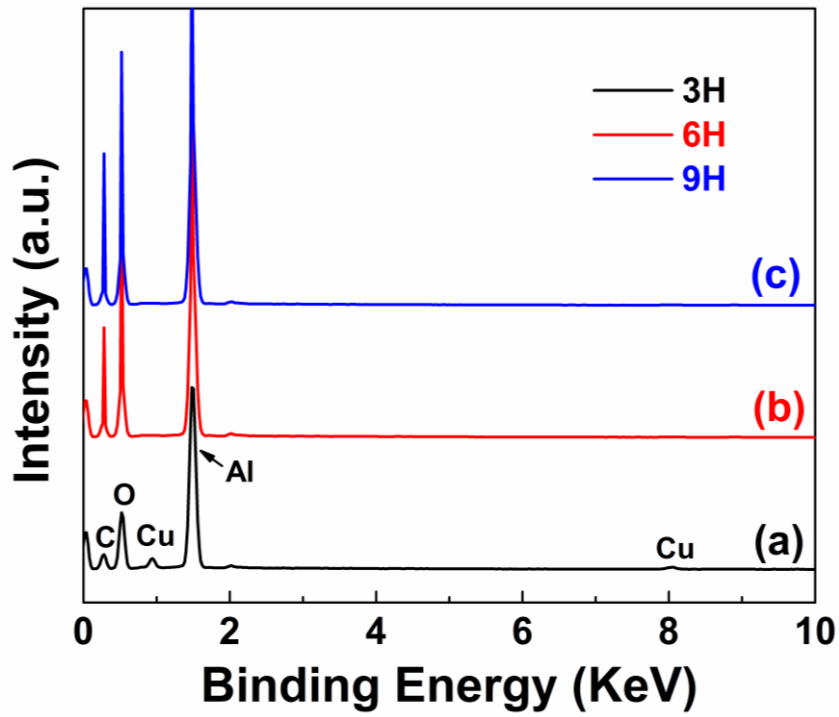

Figure S3. X-ray Energy dispersive analysis spectra of the samples prepared by putting CHNs thin films filtered from 30ml CHNs solution in 30 ml, 1mM H_3BTC aqueous solution at 120℃ for (a) 3 h, (b) 6 h, (c) 9 h, respectively.

5.The samples prepared in different solvents

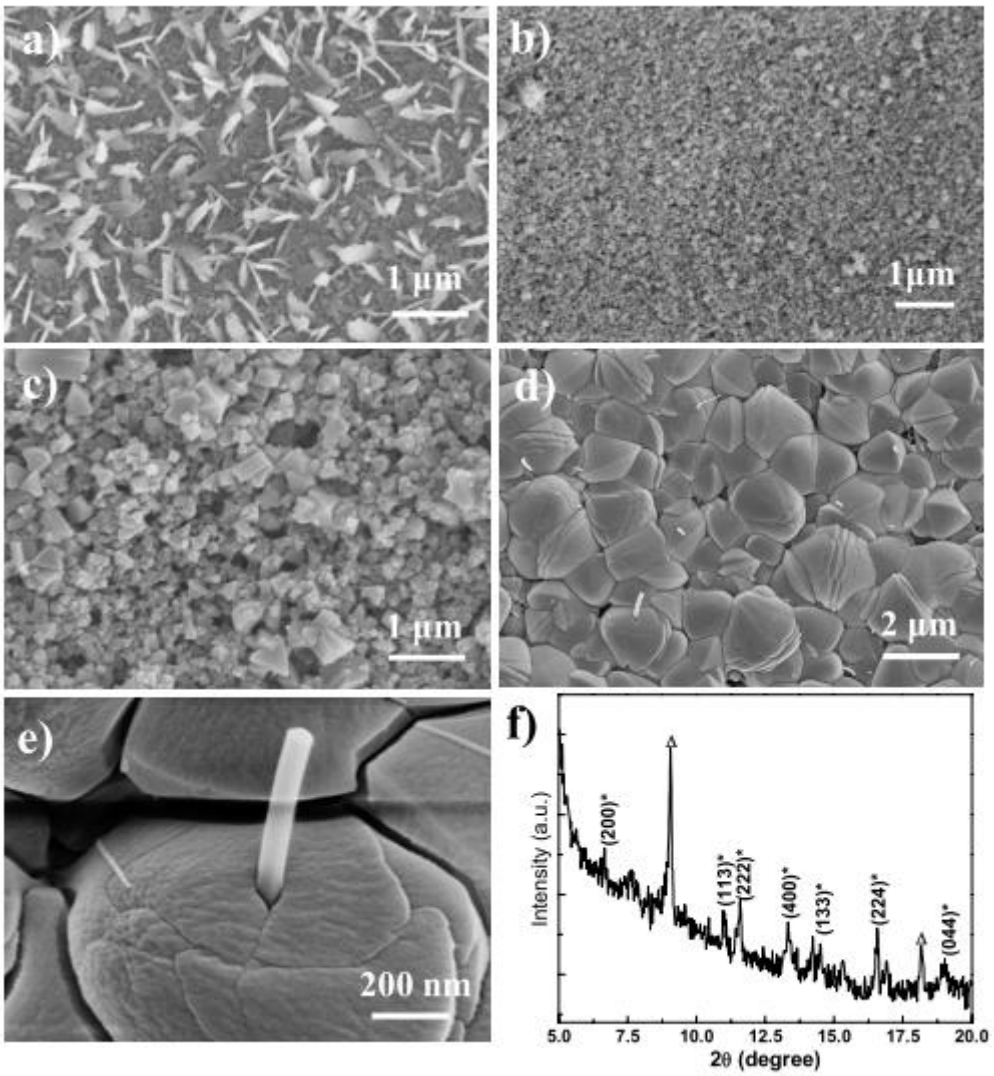

Figure S4. the SEM images of the samples prepared in 30 ml, 1mM H_3BTC (a) octanol, (b) DMF, (c) ethanol solutions; (d-e) 8 mM H_3BTC water/ethanol (volume ratio of 1:1) solution, respectively. CHNs filtred from 30 ml CHNs soltuion were used and kept at 120 ^oC for 24 hours for all the samples. (f) XRD recorded from (d) the peaks marked as star (*) are belonged to HKUST-1 phase. Thepeaks marked as trangle (Δ) are assigned to $[Cu_2(OH)(BTC)(H_2O)]\cdot 2nH_2O$. Due to the very less amount of the MIL-110 nanorods, no obvisouly XRD peaks of MIL-110 phase are observed.

6.EDS and XRD of the samples prepared by using zinc and cadmium hydroxide nanostrands

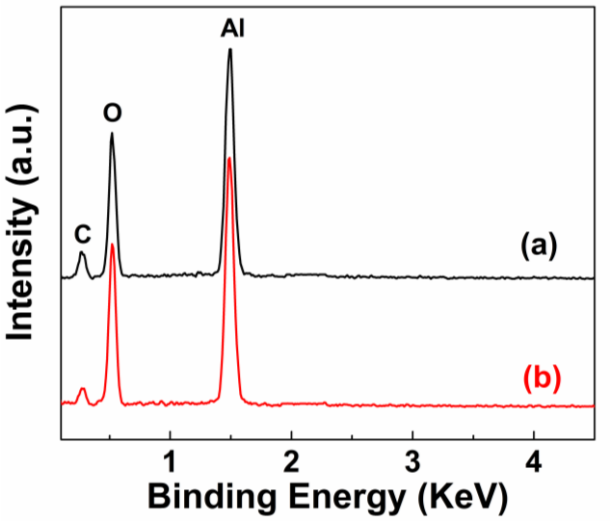

Figure S5. EDS of the samples prepared by putting thin films filtered from (a) 30ml cadmium hydroxide nanostrands , (b) 30ml zinc hydroxide in 30 ml, 1mM H_3BTC aqueous solution at 120℃ for 24h, respectively.

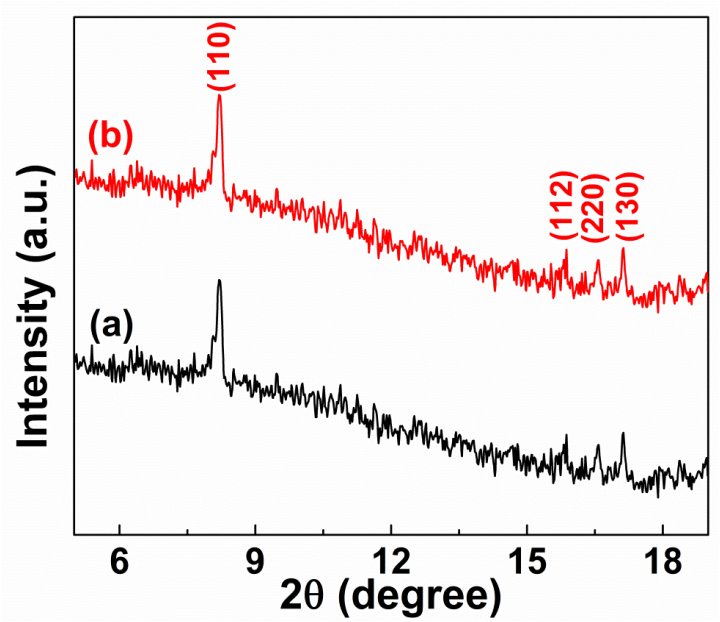

Figure S6. XRD of the samples prepared by putting thin films filtered from (a) 30ml cadmium hydroxide nanostrands , (b) 30ml zinc hydroxide in 30 ml, 1mM H_3BTC aqueous solution at 120℃ for 24h, respectively.

Reference:

1 J. Nan, X. Dong, W. Wang, W. Jin and N. Xu, *Langmuir* **2011**, *27*, 4309-4312.