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Supporting Information should be included here (for submission only; for publication, please provide Supporting Information as a separate PDF file).

Supporting Information

Free-standing HKUST-1 Membranes Converted from Copper Hydroxide Nanostrands Thin Films at Room Temperature

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1. **Experimental Section:**

Preparation of CHNs: CHNs were synthesized by quickly mixing a base solution into a copper-salt solution using a magnetic stirrer and by aging at room temperature. The nanostrand prepared from 2 mM copper nitrate (Across Chemicals) and 0.7 mM aminoethanol (Across Chemicals) was stable at room temperature for at least 1 month.

Preparation of free-standing HKUST-1 membrane: Firstly, a free-standing mesoporous CHNs layer was prepared by filtering certain CHNs on a PC membrane and then peeled off from the PC by immersing into the ethanol solution. Then the ethanol was removed by pipette. After that 10 ml, 10 mM 1,3,5-benzenetricarboxylic acid (Sigma-Aldrich) ethanol/water solution with volume ratio of 1:1 was added and kept reacting at room temperature. The color turned out from light blue of the CHNs layer to dark blue after a few minutes. Typically, after two hours, a free-standing HKUST-1 membrane was obtained and used for gas separation. The parameters, including reaction time, solvent and concentration, were investigated in detail (see supporting information).

Characterization: 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 SEM (Hitachi S-4800), and SEM observation was conducted after coating a thin platinum layer by using a Hitachi e-1030 ion sputter at the pressure of 10 Pa and the current density of 10 mA. The thermogravimetric measurements were carried out in Simultaneous DSC-TGA Instrument (SDT Q600) under a flow of air (40 cm3/min) and a heating rate of 10℃/min. The BET measurements were carried out in Micromeritics instrument (ASAP 2020) by activating 12 hours at 120°C. The gas permeation was carried out by using dead-end separation system with stainless steel filter holders (Millipore XX4502500, 25 mm, max inlet pressure 345 bar) and mass flow meters (Seven-star D07-19BM). The free-standing HKUST-1 membrane was transferred onto an anodic alumina oxide (AAO) membrane with pore size of 200 nm and diameter of 2.5 cm. Then the preloaded AAO membrane was sealed into the above separation system. Before gas permeation measurements, the separation system was heated from room temperature to 100 ^{o}C at a rate of 20 °C·h^{-1} and held for 0.5 h, then cooled to room temperature at the same rate. After that, the activated HKUST-1 membrane was tested by gas permeation experiments. The separations of binary gases with mole ration of (50:50) were measured by on-line gas chromatograph (GC 9790, Zhejiang Fuli Analysis Equipment Company).

2. Photographs and UV-vis spectra:

Figure S1 shows a 3.2 cm freestanding copper hydroxide nanostrands (CHNs) film changes its color with reaction time, which transformed from slight blue to deep turquoise clearly. Accordingly, the conversion was further monitored by UV-vis spectroscopy and the peak appearred at about 729 nm (Figure S2) which indicated that the HKUST-1 is formed. The peak intensity increased with time and reaches the maximium at about 2 hours.

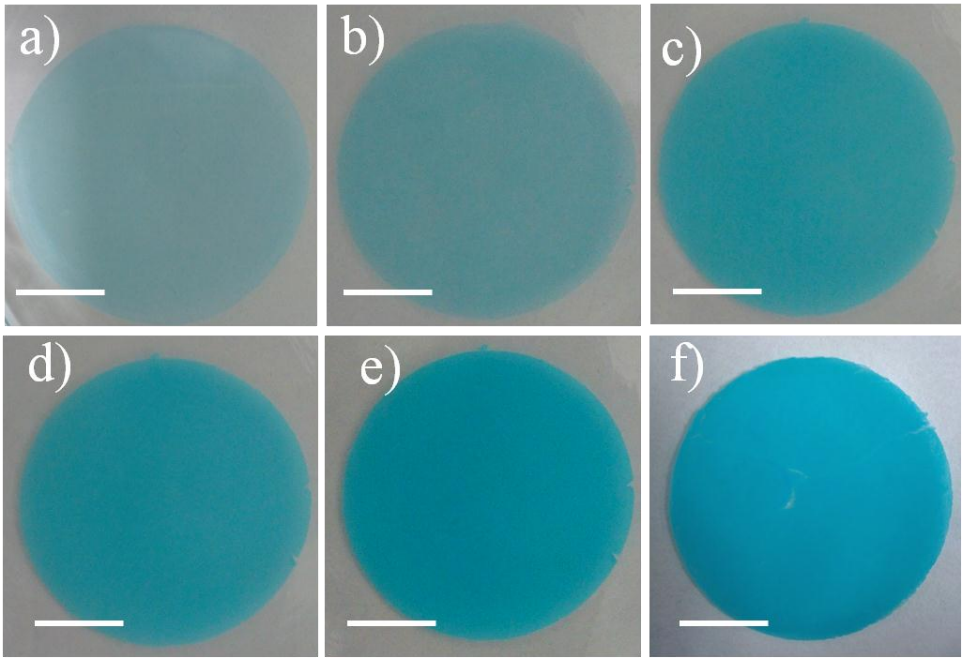

Figure S1. Photographs of the free-standing CHNs thin films with diameter of 3.2 cm filtered from 170 ml CHNs solution, reacted with 30 ml, 10 mM H_3BTC water/ethanol (vol 1:1) solution for (a) 0, (b) 5, (c) 10, (d) 15 min, (e) 30 min and (f) 60 min, respectively. The scale bar is 1 cm.

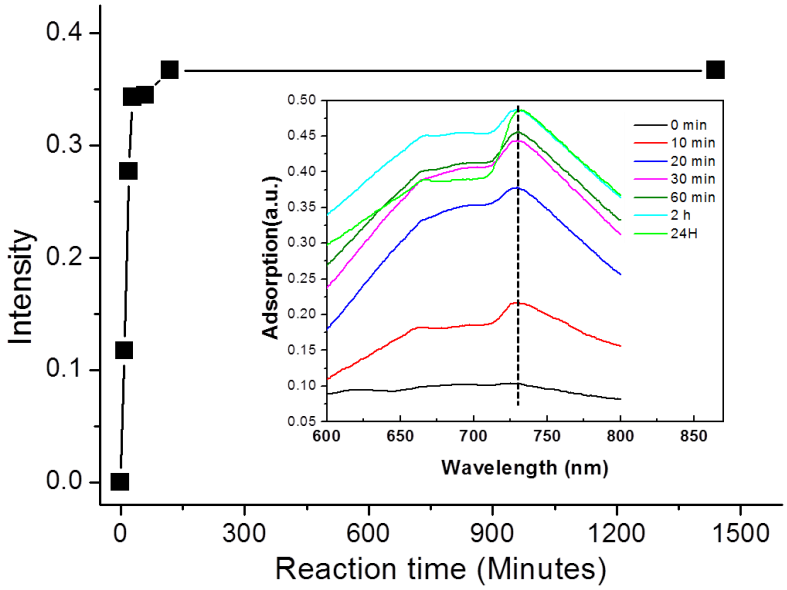

Figure S2. The intensities of the peak at 729 nm plot along reaction times. The inset is UV-vis spectra recorded from the samples after reacted for different time as shown in Figure S1.

3. **SEM images of CHNs thin films**:

Figure S3 shows the linear fibrous structure of CHNs. The thickness of the CHNs thin films could be easily controlled by the filtration volumes, such as 30 ml resulted in 1380 nm and 60 ml resulted in 2810 nm thick CHNs film, with effective diameter of 1.9 cm, respectively.

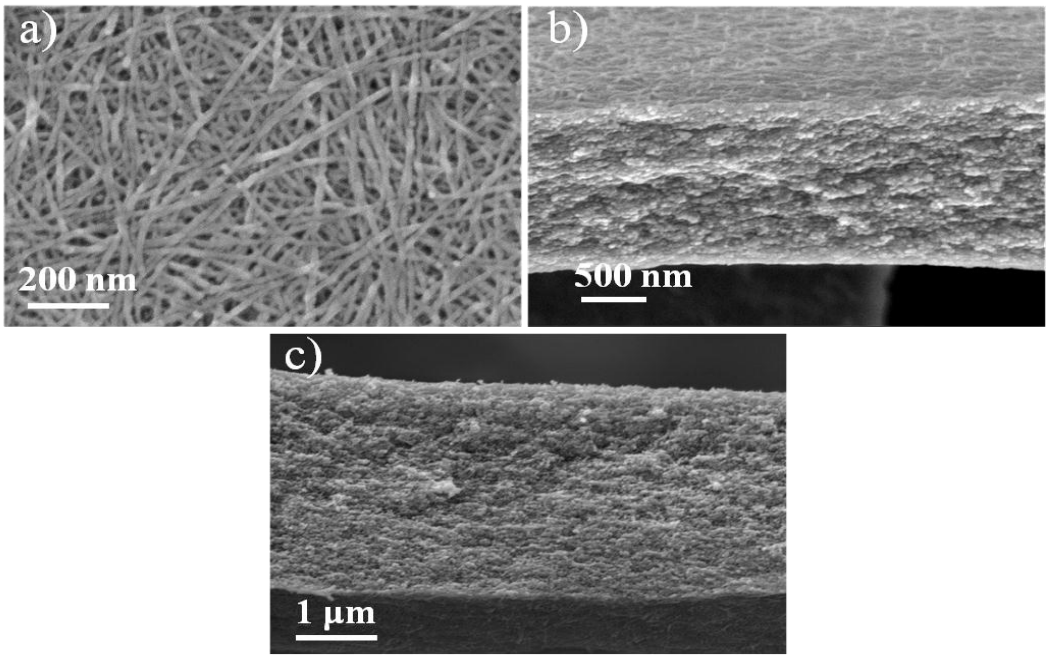

Figure S3. SEM image of the CHNs thin films (a) surface; (b) and (c) are the cross-section of the films prepared by filtering 30 ml and (c) 60 ml CHNs on PC membrane with effective diameter of 1.9 cm, respectively.

4. **Additional SEM and photo images of the HKUST-1 membrane:**

Figure S4 shows the surface of the robust free-standing HKUST-1 membrane which was densely intergrown uniformly. The membrane was transferable by a tweezers. Besides, the membrane is also relatively transparent to see the characters under it.

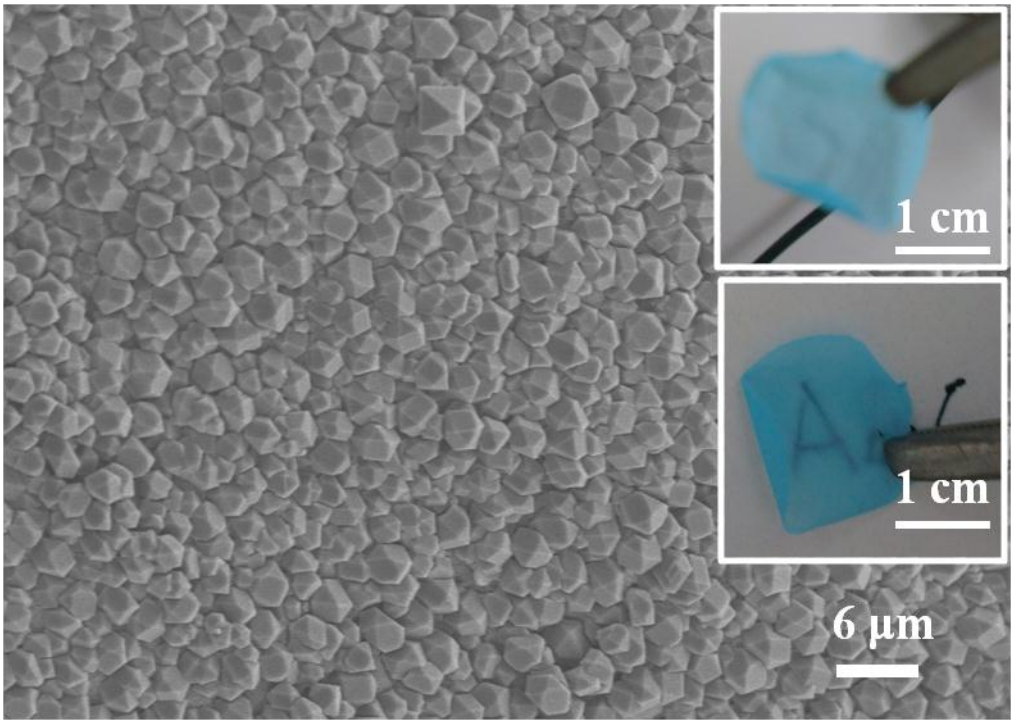

Figure S4. Low magnification SEM image of the HKUST-1 membrane prepared by reacting 1.9 cm diameter 2810 nm thick CHNs film with 10 ml, 10 mM H_3BTC water/ethanol (vol 1:1) solution for 2 hours. The Insets show the membrane is transferable to another substrate and relatively transparent.

5. **XRD patterns of the samples prepared for different time:**

Figure S5 shows the XRD patterns of samples with different reaction time. The peaks became stronger and sharper as time went on and indicate more and more HKUST-1 is formed with maximum intensity at 2 hours. This is consistent with the SEM observation (Figure 1) and Uv-vis results (Figure S2).

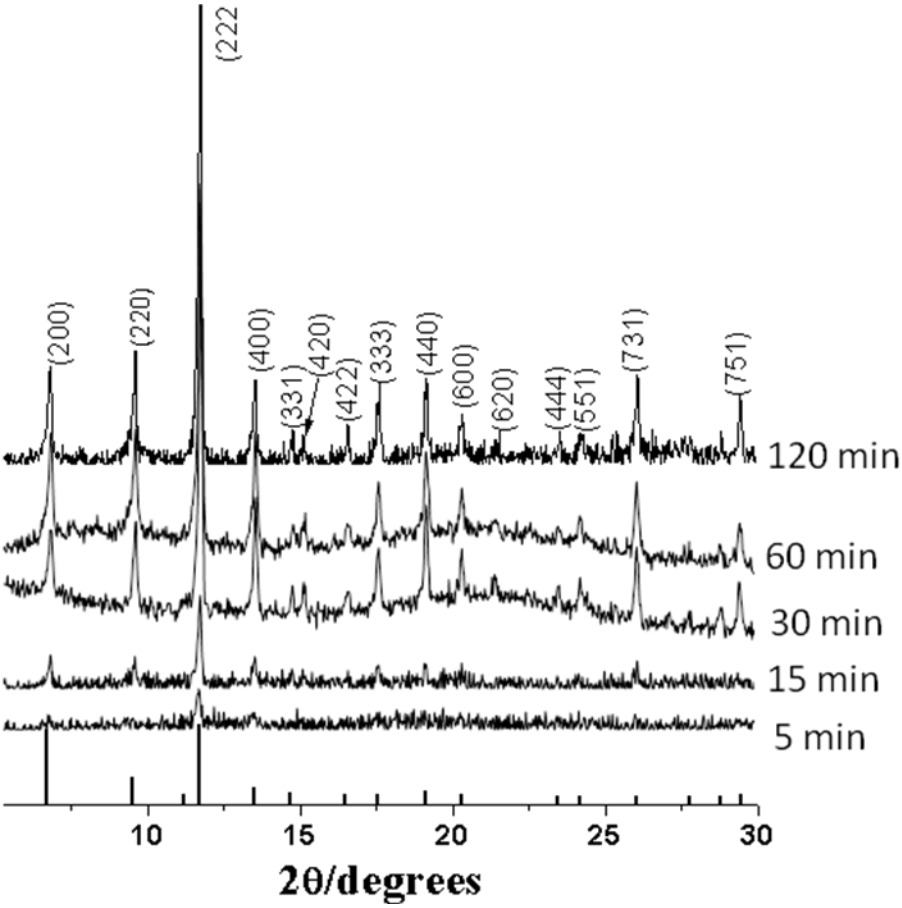

Figure S5. XRD patterns of the samples prepared prepared by by reacting 1.9 cm diameter 2810 nm thick CHNs film with 10 ml, 10 mM H_3BTC water/ethanol (vol 1:1) solution for different time.

6. **TGA and DCS results:**

Figure S6 shows the TGA and DSC curves of the free-standing HKUST-1 membrane after reacting 2 hours. It is clearly see that the decomposed temperature is 330℃.

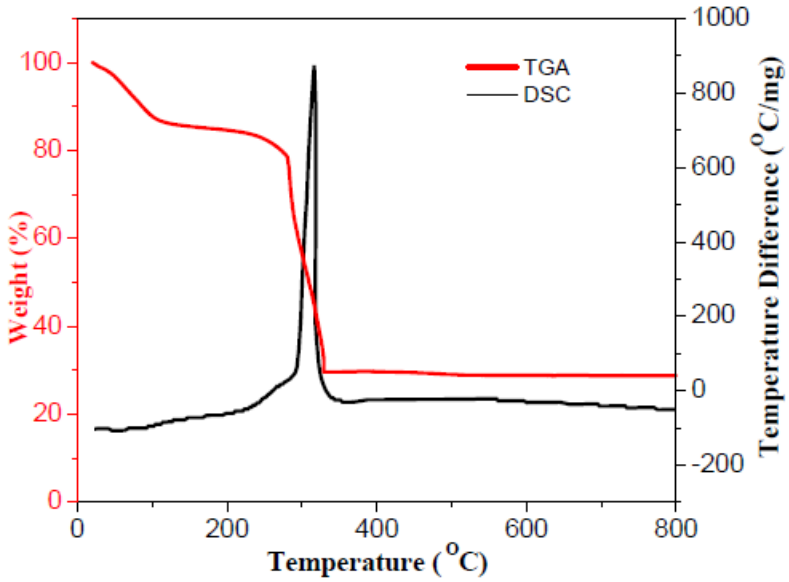

Figure S6. The TGA and DSC curves of the free-standing HKUST-1 membrane prepared by reacting 1.9 cm diameter 2810 nm thick CHNs film with 10 ml, 10 mM H_3BTC water/ethanol (vol 1:1) solution for 2 hours.

7. **Effects of solvents, concentration and nanostrands amounts**

We further found that the solvent and the concentration of H_3BTC also took significant effect on the morphology and growth speed of the HKUST-1 crystals. By using H_3BTC (10 ml, 10 mM) pure ethanol solution, very nice 400 nm octahedrons HKUST-1 crystals loosely packed after reaction for one hour (Figure S7a-c). However, much smaller HKUST-1 nanoparticles were formed after 1 hour when DMF was used as the solvent (Figure S7d). In addition, very small irregular HKUST-1 particles were formed when 1 mM H_3BTC water/ethanol solution with volume ratio of 1:1 for 1 hour (Figure S8a). But

when the reaction was performed in 5 mM H_3BTC water/ethanol (vol 1:1) solution after 1 hour, the result turned out to be not well intergrown 1.5 μm HKUST-1 cuboctahedrons (Figure S8b). Of course, the amount of CHNs is also very important to form continuous intergrown HKUST-1 membrane. For example 15 ml CHNs layer and 30 ml CHNs layer react with 10 ml, 10 mM H_3BTC water/ethanol (vol 1:1) solution could not produce densely intergrown HKUST-1 membranes (Figure S9).

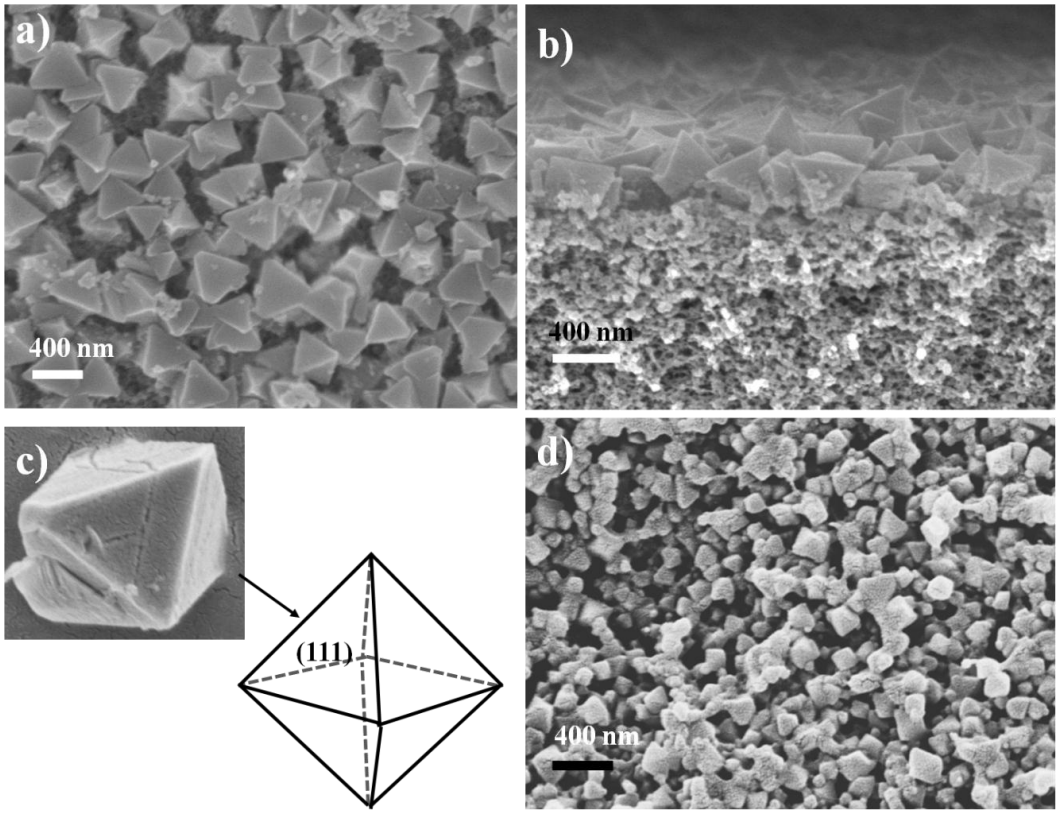

Figure S7. SEM images of the samples prepared by reacting 1.9 cm diameter 2810 nm thick CHNs free-standing films with 10 ml, 10 mM H_3BTC (a) to (c) ethanol solution and (d) DMF solution, respectively, for 1 hour.

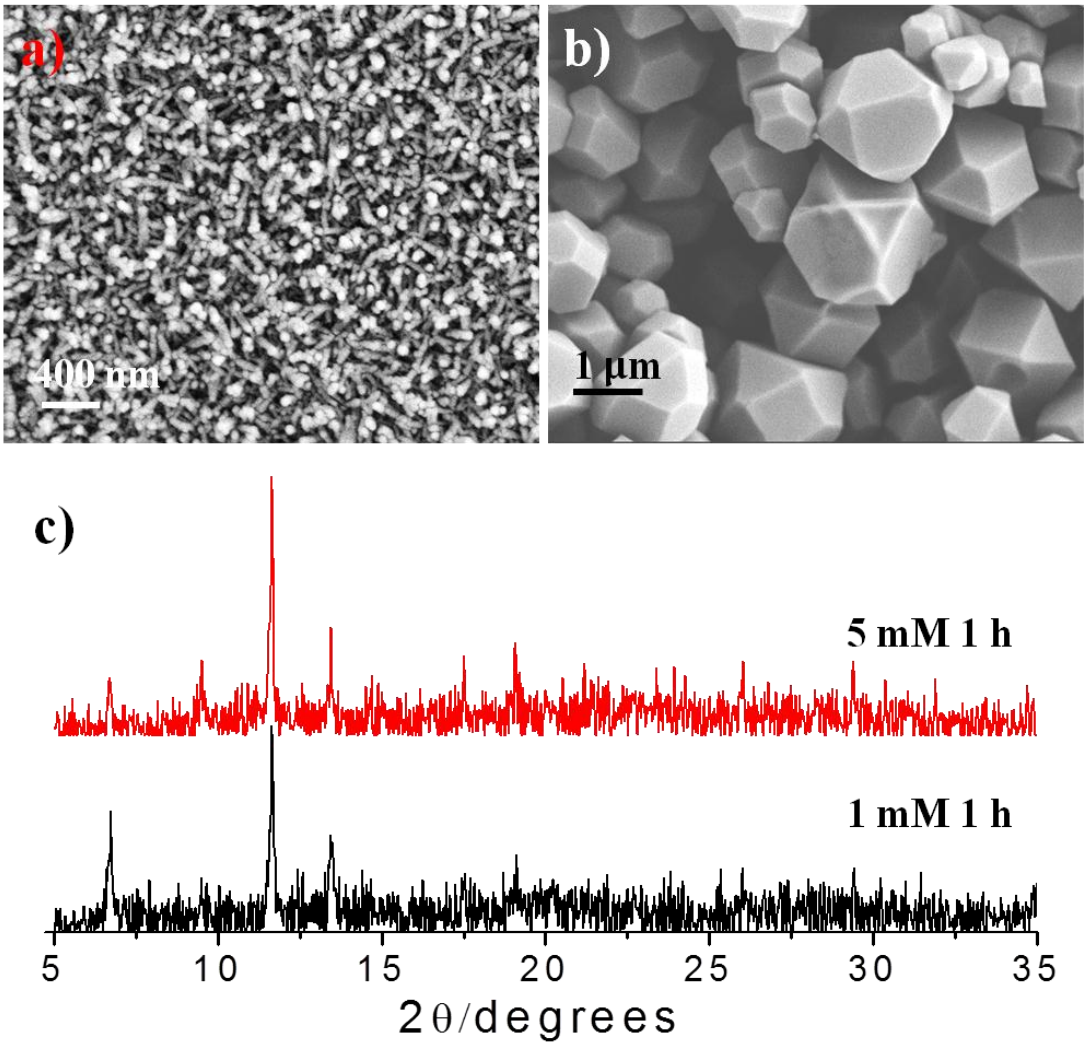

Figure S8. (a) and (b) the SEM images of the samples prepared by by reacting 1.9 cm diameter 2810 nm thick CHNs film with 10 ml (a) 1 mM and (b) 2 mM H_3BTC water/ethanol solution (vol 1:1) for 1 hour, respectively. (c) The XRD patterns recorded from (a) and (b).

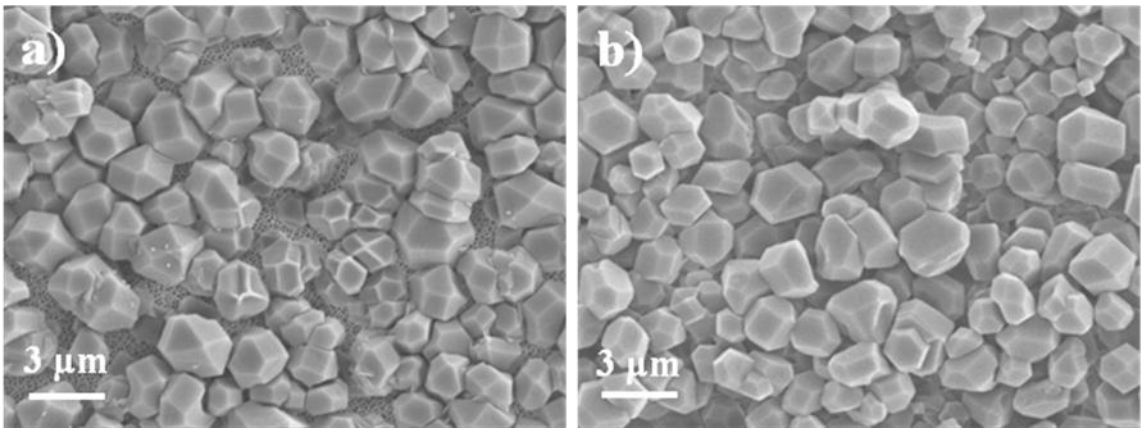

Figure S9. SEM images of the samples prepared by CHNs thin films (diameter of 1.9 cm) from (a) 15 ml CHNs and (b) 30 ml CHNs solution, reacted with 10 ml, 10 mM H_3BTC water/ethanol solution (vol 1:1) for 1 hour.