Supporting Information

A New Kind CO_2/CH_4 Separation Material: Open Ended Nitrogen Doped Carbon Nanotubes Formed by Direct Pyrolysis of Metal Organic Frameworks

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Contents:

Experimental

The synthesis of $[Co(HTTG)(H_2O)_2]_n$ used for pyrolysis has been described elsewhere.[1] In a typical synthesis, 0.7g Co-MOFs was placed in two ceramic boats. The ceramic boats were insert into the center of a one end closed quartz tube (with inside diameter of 3 cm and length of 50 cm), which was placed inside a tube furnace. Subsequently, the furnace was heated to 600 °C at a rate of 10 °C·min^{-1} and kept at the temperature for 1 h. After cooling to room temperature naturally, black product was found in the ceramic boats. For catalyst elimination, black product was added into diluted hydrochloric acid (~10 %) with vigorous stir. The system was heated to 80 °C and kept at the temperature for 10 h until cooled to room temperature naturally. After centrifugal separation, black precipitate was obtained and washed with deionized water and absolute ethanol.

The morphology of the product was performed by FE-SEM using a Hitachi S4800 operating at 10 kV. XRD patterns were collected in a Shimadzu XRD-6000 operating at 40 kV and 30 mA with graphite-monochromatized Cu *K*α radiation (wavelength λ = 1.5147 Å). TEM was performed with Philips Tecnai 12 at an accelerating voltage of 120 kV. HR-TEM (JEOL-2010) was performed to characterize the microstructure of the products. Nitrogen concentration and bond properties were studied by XPS (Thermo ESCALAB 250) with Al Kα radiation. Nitrogen cryo-adsorption isotherm was performanced with Micromeritics ASAP-2020. CO_2 and CH_4 adsorption isotherms of products were measured with Intelligent Gravimetric Analyzer (IGA-100, Hiden).

Figure S1. Thermogravimetric analysis (TGA) result of Co-MOF under air flow at a heating rate of 10 ℃ min^{-1}.

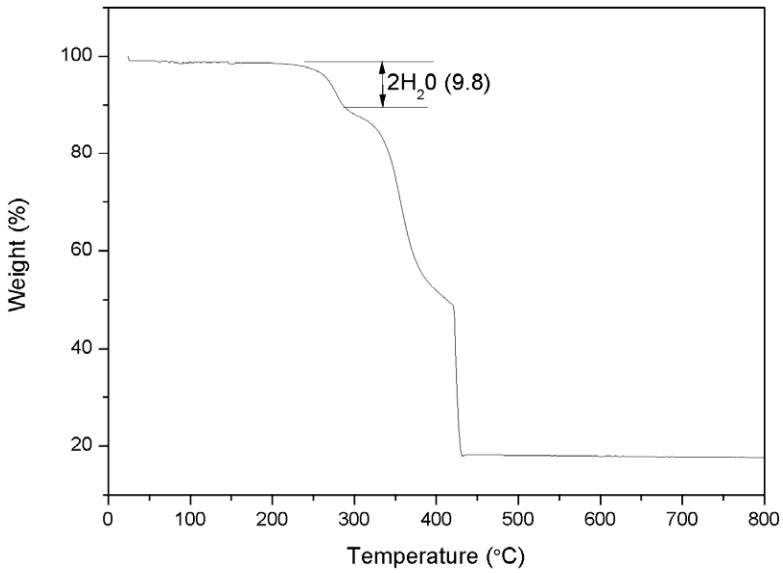


Figure S2. TEM images of as prepared CN_x before HCl treatment. Most of ends are just enclosed with cobalt particles (a), some have little amorphous carbon around tip (b).

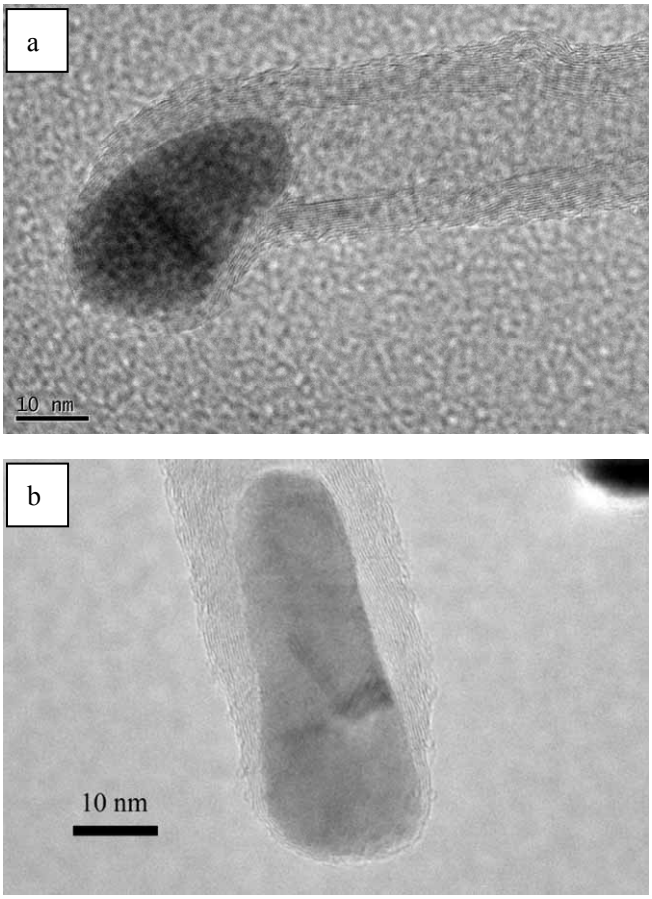


Figure S3. Schematic illustration of proposed growth model. Grey, amorphous carbon; black, cobalt particles.

1) As the temperature increases, bulk precursor first in-situ decomposes to cobalt nanoparticles surrounded by amorphous carbon.

2) When it further increases to a higher temperature, carbon starts to dissolve in cobalt nanoparticle on the surface and precipitates around the particle in the form of graphitic tubular structure. During the precipitation, the cobalt nanoparticle will be lift up by carbon nanotube and elongated to fit the small 1D carbon channel. Meanwhile, amorphous carbon starts to decompose to hydrocarbon species. Following a "tip-growth" mechanism, the hydrocarbon species dissolve in cobalt nanoparticle and precipitates thereafter, leading to the growth of CN_x.

3) Since amorphous carbon is consumed during CN_x growth process, the cobalt nanopaticles under the surface which suppose to be protected by amorphous carbon start to aggregate.

4) The growth will be accomplished when amorphous carbon was exhausted, leaving carbon nanotubes anchored on bulk cobalt substrate.

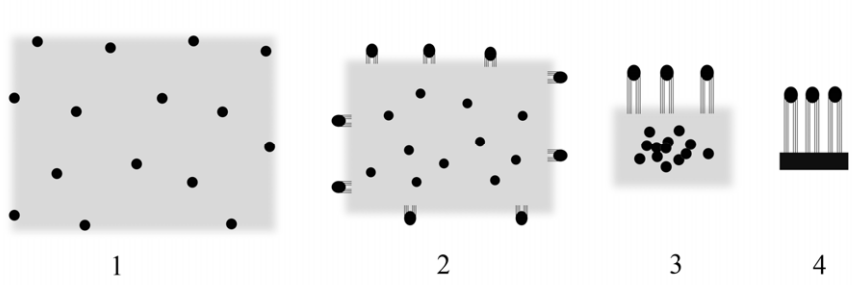


Figure S4. XRD patterns of a) raw and b) HCl purified CN-1. Co^{2+} in Co-MOFs was reduced to face centered cubic lattice of Co (PDF, card no. 15-0806) during the reaction. After careful removal of cobalt by diluted hydrochloric acid, strong diffraction peaks for carbon nanotubes can be observed.

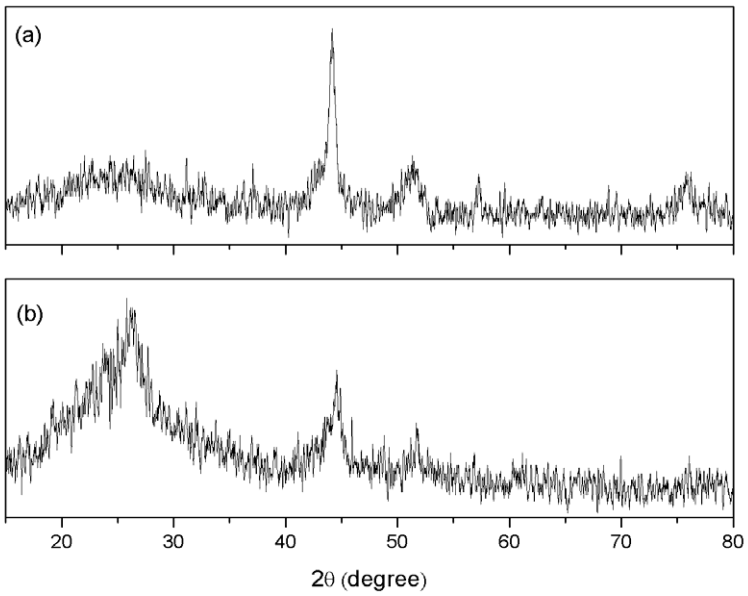


Figure S5. Representive HR-TEM images of CNx. (The graphene layers are unparallel to aixal, but the oblique layers do not interlink to form bamboo-like compartments.)

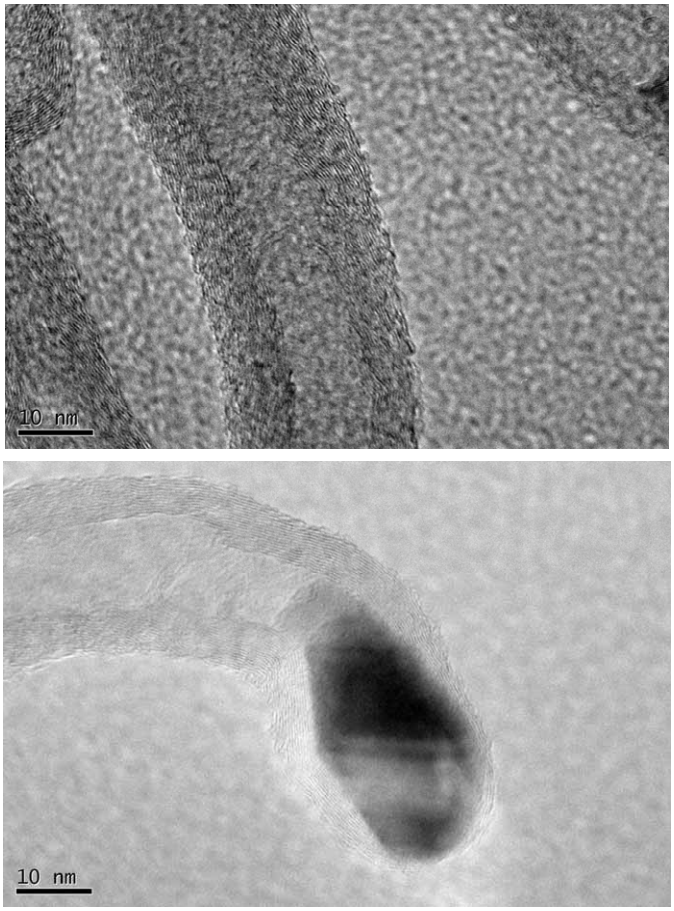


Figure S6. XPS N 1s-spectum of CN-1. The spectrum is fitted to two Gaussian-type components.

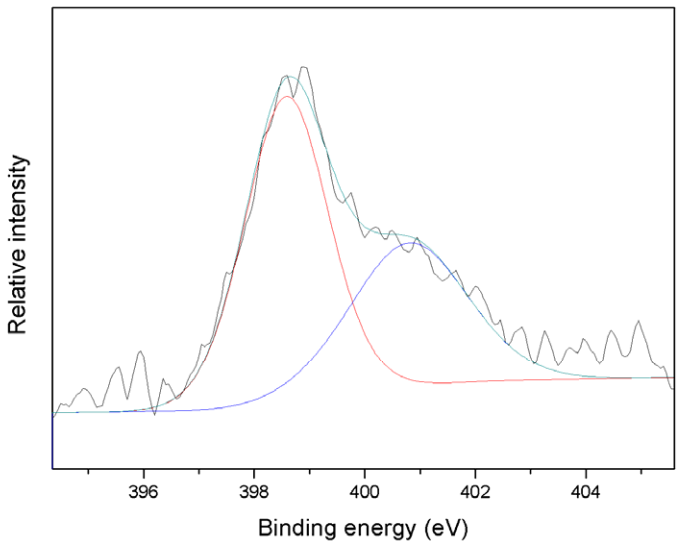


Figure S7. a) Nitrogen adsorption isotherm of CN-2 at 77 K, b) pore size distribution of CN-2.

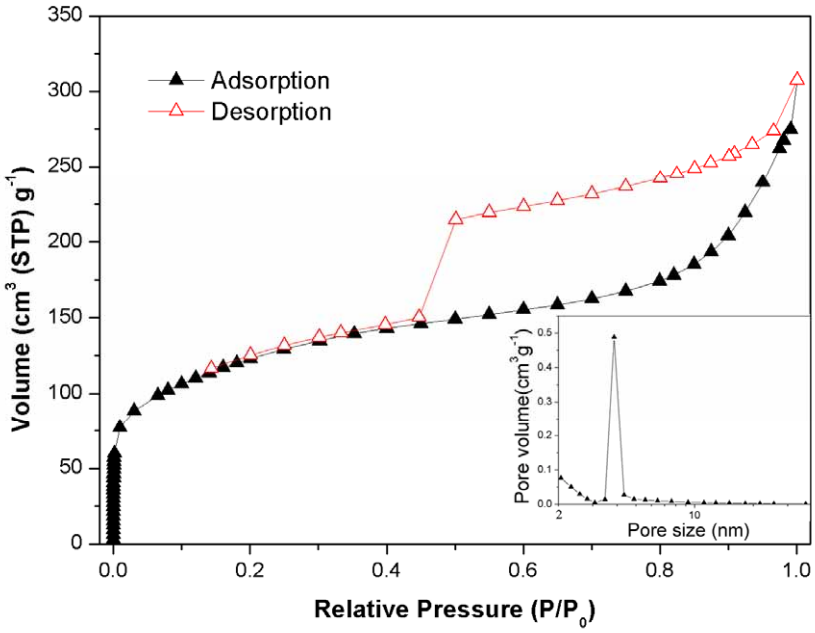
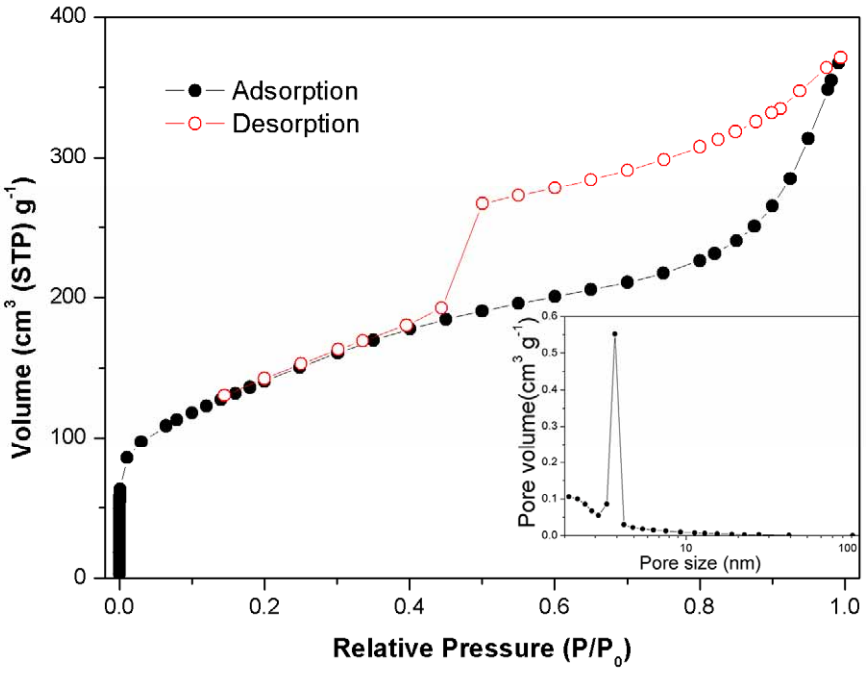


Figure S8. a) Nitrogen adsorption isotherm of CN-3 at 77 K, b) pore size distribution of CN-3.



Reference

1. S. Wang, J. Bai, H. Xing, Y. Z. Li, Y. Song, Y. Pan, M. Scheer and X. Z. You, *Cryst. Growth Des.*, 2007, **7**, 747-754.