

In-situ synthesis of carbon nanotubes doped metal-organic frame work for CO₂ capture.

Nousheen Iqbal,^{ab} Xianfeng Wang,^{*abcd} Jianyong Yu,^d Naila Jabeen,^e Hameed-ullah Wazir,^{*f} and Bin Ding^{*abcd}

^a Key Laboratory of High Performance Fibers & Products, Ministry of Education, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China. Email wxf@dhu.edu.cn; binding@dhu.edu.cn

^b State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China.

^c Key Laboratory of Textile Science & Technology, Ministry of Education, College of Textiles, Donghua University, Shanghai 201620, China

^d Nanomaterial's Research Center, Modern Textile Institute, Donghua University, Shanghai 200051, China.

^e National center for Physics, Quaid-e-azam University, Islamabad 44000 Pakistan.

^f Hazara University, Department of Chemistry, Mansehra 21300, Pakistan. Email hameedwazir@yahoo.co.uk

***Corresponding author at:** Key Laboratory of High Performance Fibers & Products, Ministry of Education, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China. Key Laboratory of Textile Science & Technology, Ministry of Education, College of Textiles, Donghua University, Shanghai 201620, China. Tel: +86-21-62378202.

Supporting Information

Characterization

The morphology of the MOFs was examined by a field emission scanning electron microscope (FE-SEM) (S-4800, Hitachi Ltd. Japan). Powder X-Ray Diffraction (XRD) patterns were obtained by a Philips XPERT PRO using CuK α ($\lambda = 1,542 \text{ \AA}$) radiation. In order to avoid the effects of preferred crystal orientation, crystals were grounded. Mica sample was used as an internal standard to calculate the displacement error of the instrument. N₂ adsorption isotherms were measured on an ASAP (surface area and porosity analyzer) at 77 K using an ASAP 2020 physisorption analyzer (Micromeritics Co., USA). The micropore surface area values were calculated by the Brunauer-Emmett-Teller (BET) and Langmuir methods.

CO₂ adsorption measurements

CO₂ adsorption measurements were performed on a Micromeritics ASAP 2050 for the adsorption analysis. First, the CO₂ adsorption capacities of the doped MOFs samples (around 0.5639 g) were measured under different parameters. CO₂ adsorption capacity was determined by placing a sample in the ASAP 2050 while evacuating and heating thoroughly in order to outgas the sample. The chamber was then back-filled with CO₂ and the temperature swung from 22 °C while recording the mass lost, and subsequently gained upon cooling to 22°C. Our second study utilized the doped MOFs sample with the largest CO₂ capacity. The sample was outgassed in vacuum and allowed to come to equilibrium at 22°C in flowing N₂. Then sample was purged with CO₂ and the specimen mass gain was recorded. Finally, the CO₂ adsorption as a function of CO₂ partial pressure at 22°C was determined by controlling the flow rates of both N₂ and CO₂.

S1. Methodology

Materials and Synthesis

2,5-Dihydroxyterephthalic acid and Benzene-1,3,5-tricarboxylic acid was purchased by (Sigma Aldrich (Germany)), Zn(OAc)₂·2H₂O and Cu(NO₃)₂·2.5H₂O was purchased by (Merck Germany), *N,N*-Dimethylformamide (DMF) (RDH Germany), Methanol, 4-aminobenzoic acid, Phosphorous penta oxide, Hydrochloric acid, Sulphuric acid, Nitric acid and Ethanol was purchased by (RDH Germany).

All chemicals were used without further purification.

S1. Chemical Synthesis of doped MOFs

Synthesis of MWCNTs-MOFs

1.1 Amine Functionalized MWCNTs Zn MOF-74

In 20 mL of DMF, 2,5-Dihydroxyterephthalic acid (1.43 g) and Zn(OAc)₂·2H₂O (4.1 g) were dissolved. The di-acid solution was added to the stirring solution of zinc salt and the mixture was stirred at room temperature for 18 hours. Then 0.05 g of NH₂ functionalized CNTs, were added. The product was centrifuged and the mother liquor was decanted. The product was washed with 60 mL of DMF. It was then washed with 40 mL of methanol and immersed in methanol (20 mL) overnight. This methanol wash-immersion procedure was repeated twice more. The methanol was decanted and the MOF-74 was evacuated for 7 hours at ambient temperature. Under vacuum, it was heated to 110 °C for 10 hours, then to 260 °C for 12 hours, after which it was cooled to room temperature over 1 hours.

1.2 Cu-BTC Amine Functionalized MWCNTs

About 1.126 g (4.84 mmol) of Cu (NO₃)₂·2.5H₂O was dissolved in 25 ml of distilled water, and 0.491 g of benzene-1,3,5-tricarboxylic acid (H₃BTC; 2.33 mmol) was dissolved in 25 ml of DMF. Then adding of 0.05 g of NH₂ functionalized CNTs. The solutions were mixed in a 100 ml round-bottom flask that was put in a pre-heated oil bath at a temperature of 100 °C for 4 hours. The blue precipitate was then filtered off, washed thoroughly with DMF and water to remove residual precursor species, and dried at 200 °C in order to remove the DMF solvent..

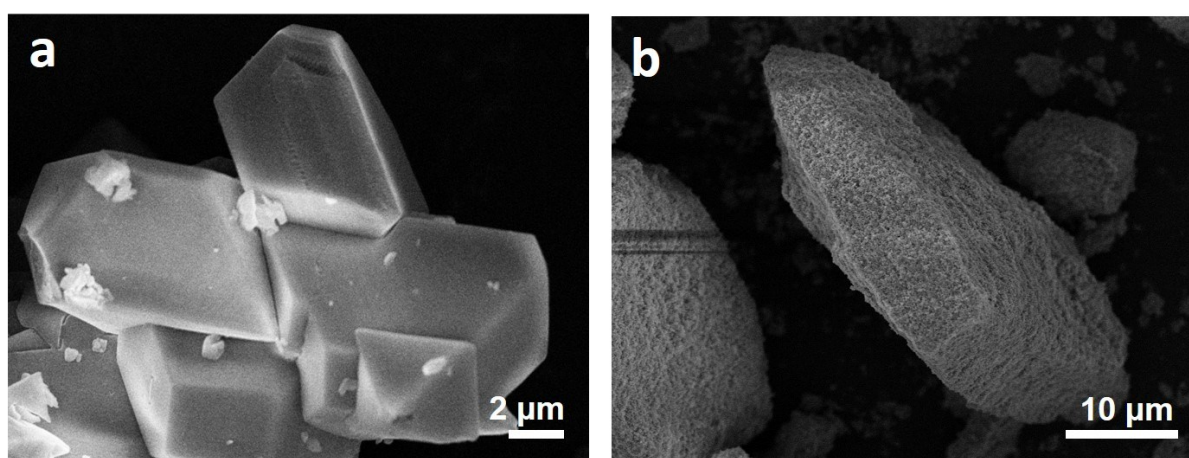
1.3 Zn MOF-74 Acid Functionalized MWCNTs

2-5-Dihydroxyterephthalic acid (1.43 g) and Zn (OAc)₂·2H₂O (4.1 g) were dissolved in 20 mL of DMF and stirred solution over 10 minutes, at room temperature for 18 hours then adding 0.05 g acid functionalized CNTs. The product was

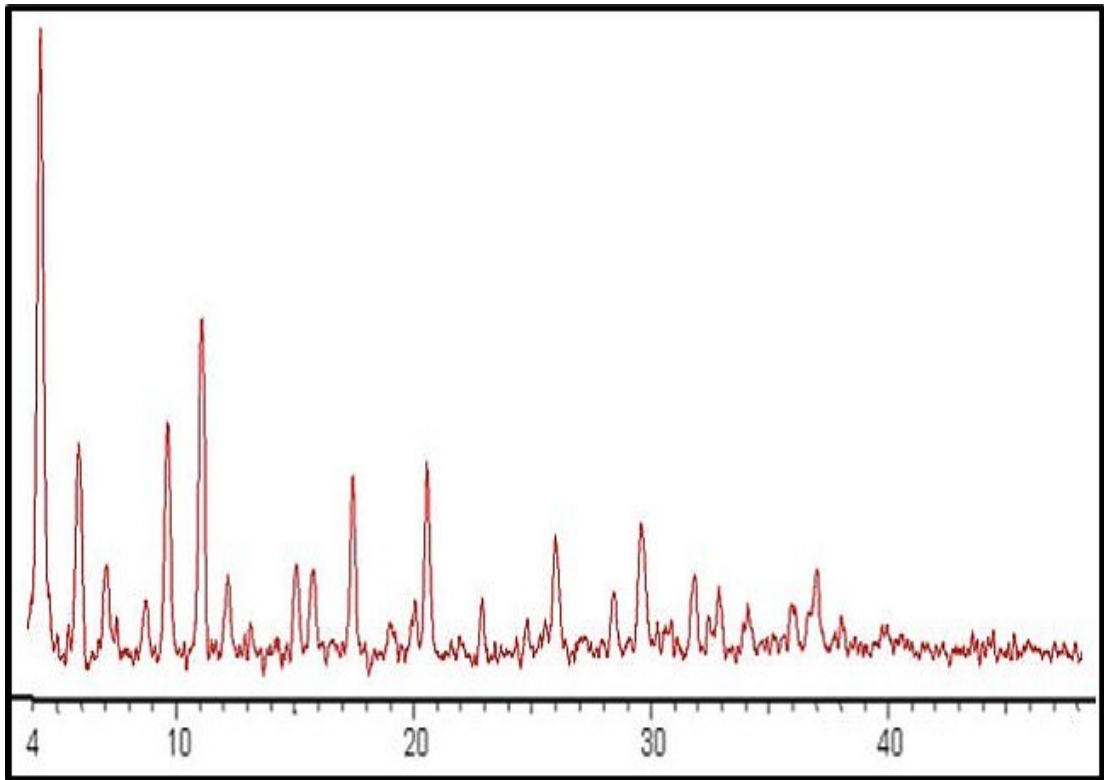
centrifuged and the mother liquor was decanted. The product was washed with 60 mL of DMF and 40 mL of methanol and immersed in methanol (20 mL) overnight. This methanol wash-immersion procedure was repeated twice more. The methanol was decanted and the MOF-74 was evacuated for 7 hours at ambient temperature. Under vacuum, it was heated to 110 °C for 10 hours, then to 260 °C for 12 hours, after which cooled to room temperature.

1.4 Cu-BTC Acid Functionalized MWCNTs

In 25 ml of DMF 0.491 g of benzene-1-3-5-tricarboxylic acid (H_3BTC ; 2.33 mmol) was dissolved and about 1.126 g (4.84 mmol) of $Cu(NO_3)_2 \cdot 2.5H_2O$ was dissolved in 25 ml of distilled water. Then 0.05g of acid functionalized CNTs were added. The required solutions were mixed in a 100 ml round-bottom flask that was put in a pre-heated oil bath at a temperature of 100 °C for 4 hours. At the end the blue precipitate was then filtered off and washed thoroughly with DMF and water to remove residual materials, and dried at 200 °C in order to remove the DMF solvent.



S2 (a) FE-SEM image of crystalline structure of Cu-BTC, and (b) FE-SEM image of crystalline structure of Zn MOF-74.



S3. XRD pattern of Pure Zn-MOF-74.