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Adsorption of CO_2 by hierarchical structures of f-MWCNTs@Zn/Co-ZIF and N-MWCNTs@Zn/Co-ZIF prepared through in situ growth of ZIFs in CNTs

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ABSTRACT

Zeolitic Imidazolate Frameworks (ZIFs) are one of the best porous materials for the selective adsorption of CO_2. Hierarchical porous hybrid materials of Zn/Co-ZIFs (ZIF-8/ZIF-67) with carboxylate functionalized MWCNTs (f-MWCNTs) or nitrogen doped MWCNTs (N-MWCNTs) have been synthesized through in-situ insertion of MWCNTs in ZIFs. Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Thermogravemetric analysis (TGA), Powder X-Ray diffraction and Brunauer–Emmett–Teller (BET) techniques have been used to examine the morphology, texture, phase and surface area of as prepared hybrids. These hybrids adsorb 2.07–2.48 wt% of CO_2 at 298 K and 1.0 bar pressure. f-MWCNTs@Zn/Co-ZIF adsorbed more CO_2 compared to f-MWCNTs@ZIF-8 or f-MWCNTs@ZIF-67. A marginal increase in CO_2 uptake was observed by hybrids composed with N-MWCNTs.

1. Introduction

The combustion of fossil fuels contributes 85% of the global energy consumption, which results in the emission of massive amounts of CO_2 to the atmosphere [1,2]. Carbon Capture and Storage (CCS) is a promising technology that can trap upto 90% of the carbon dioxide (CO_2) emissions mainly from power stations and industrial sites to avoid the climate change [3,4]. The CCS technology consists of three parts i.e., capturing, transporting and storing of CO_2. To make CCS viable, which apparently in very expensive for practical applications, scientists are working to develop new solid adsorbents with lower heat capacity than water [5]. Therefore, there is a growing interest in developing technologies for the efficient adsorption or storage of large quantities of carbon dioxide. Physical adsorption is considered to be one of the promising technologies available for capturing CO_2 due to its low energy requirement and operating cost [6,7]. Several types of adsorbents have been used for CO_2 adsorption, including zeolites [8,9], mesoporous silica [10], carbon nanotubes [11,12], porous carbons [13–15], metal organic frameworks (MOFs) [16,17] and zeolitic imidazole frameworks (ZIFs) [18].

Among the physical adsorbents, carbon based porous materials hold the greatest potential for commercial use, due to their high surface areas, good thermal/chemical stabilities, easy-to-control pore structures, and regeneration [19,20]. As per recent reports, pristine-MWCNTs, HNO_3 treated and H_2SO_4/HNO_3 treated MWCNTs had shown adsorption of 1.74, 2.28 and 2.53 mmol/g of CO_2, respectively at 273 K and relative pressure 0.95 [21]. MWCNTs prepared through catalytic chemical vapour deposition adsorbed 25.36 g/g of CO_2 at 298 K and 15 bar [22]. Many researchers have demonstrated that introducing nitrogen (N) on carbon surface can enhances the uptake capacity of CO_2 [23,24]. Further, another class of porous materials, Metal-organic Framework (MOFs) have also been employed in recent decade for emerging applications such as gas storage and catalysis. Zeolitic imidazolate frameworks (ZIFs) based on imidazole bridging with metallic nodes (e.g. Zn, Co) are a sub-family of MOFs with a sodalite-type cage similar to zeolites. Their properties such as permanent porosity and unexpected thermal (> 550 °C under N_2) and chemical stability make them attractive as unique potential candidates for several applications e.g. gas adsorption/storage, separation and catalysis, etc [25,26]. Some very recent reports appeared in the literature had shown that the nano and micron sized MOF (UiO-66-NH_2) material prepared using microwave synthesis adsorbed abut 1.8 mmol/g of CO_2 at 298 K and 1 bar [27]. ZIF-8 prepared through thermally annealing post-synthesis had shown the adsorption of about 1.5 mmol/g of CO_2 at 25 °C and 1 bar [28]. On the other hand, nanoparticles of ZIF-8 prepared in MeOH, DMF and DMSO adsorbed 1.11, 1.27 and 1.48 mmol/g of CO_2, respectively, at 298 K and 1 bar [29]. Another nanoparticle ZIF(ZIF-67) prepared hydrothermally adsorbed 0.71 mmol/g of CO_2 at 25 °C and 1.16 bar [30].

In order to improve the high CO_2 selectivity/adsorption on π-conjugated surface of the CNTs, many researchers have inserted inorganic materials such as MOF/ZIF. On earlier report on CNT@ZIF-8 prepared

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through in situ synthesis, had shown 0.65 wt% adsorption of CO_2 at 25 °C [31]. A similar observation was made in case of ZIF-8/CNT composite prepared in situ synthesis which had exhibiting adsorption of 2.1 mmol/g of CO_2 at 273 K and 1.2 bar [32]. In addition, hierarchical structures of ZIF (JUC-160) and nitrogen doped carbons derived through in situ synthesis adsorbed CO_2 upto 3.50 mmol/g at 298 K and 1 bar [33]. In this context, several strategies such as mixed metal, bi-metallic and core-shell ZIFs as well as composites with carbon nanostructures have been extensively explored to develop the solid adsorbents to enhanced CO_2 uptake. Herein, we report the reversible adsorption/desorption of CO_2 by hierarchical structures of f-MWCNTs@Zn/Co-ZIF and N-MWCNTs@Zn/Co-ZIF synthesized through co-precipitation of Zn or Co or Zn/Co and 2-methylimidazolate in presence of f-MWCNTs or N-MWCNTs.

2. Material and methods

2.1. Materials and synthesis

All chemicals were obtained commercially and used without further purification. $Zn(NO_3)2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ and Poly vinyl pyrrolidine (PVP) were purchased from Sigma-Aldrich, 2-methylimidazole was purchased from Alfa-Aesar, Multi-Walled Carbon Nanotubes (MWCNTs) from Spectro chem. Acids and solvents were purchased from Merck, India. The raw MWCNTs were placed in a silica crucible and calcined in the furnace for 2 h at 500–520 °C followed by the treatment with 6.0 M HCl for 6 h at 95 °C. After heating, the MWCNTs were washed several times with deionized water until the pH of the solution was neutral. It was then dried overnight at 40 °C to get the Pristine-MWCNT (p-MWCNT). 0.3 g of the p-MWCNTs and 150 ml of nitration mixture (1:3 HNO_3 and H_2SO_4) was refluxed for 6 h under magnetic stirring. The resulting solid was filtered and washed up to neutral pH. The sample was dried overnight in vacuum at 40 °C to get COOH-MWCNTs (f-MWCNTs) [34–37]. 1.0 g of p-MWCNTs was dispersed in 30 mL deionized water, and then 5.0 mL of NH_4OH was added slowly. The mixture was stirred at 25 °C for 20 min and transferred into an autoclave with a volume of 50.0 mL. Then the mixture was hydrothermally treated at 180 °C for 12 h and the solid products were separated by centrifugation and washed with distilled water. Then, the nitrogen doped MWCNTs (N-MWCNTs) were obtained by freeze drying [38].

Hierarchical structures were prepared according to the procedure reported by Huang et.al [39]. 350 mg of f-MWCNTs or N-MWCNTs and 1.75 g of PVP were dissolved in 150 mL of methanol solution and was ultasonicated for 30 min for uniform dispersion. This solution was mixed with 5.13 g of $Zn(NO_3)_2{\cdot}6H_2O$ (for ZIF-8) or 4.98 g of $Co(NO_3)_2$ $6H_2O$ (for ZIF-67). The resultant black solution, obtained after 60 min stirring at room temperature, was mixed with a solution of 150 mL of methanol containing 7.65 g of 2-methylimidazole. The solution was stirred vigorously for 24 h. The precipitated product thus obtained was separated by centrifugation and washed thoroughly with methanol several times to remove the impurities. It was finally dried at 70 °C to get the f-MWCNTs@ZIF-8, f-MWCNTs@ZIF-67, N-MWCNTs@ZIF-8, N-MWCNTs@ZIF-67. To prepare the mixed metal composite of f-MWCNTs@Zn/Co-ZIF or N-MWCNTs@Zn/Co-ZIF, 5.13 g of Zn $(NO_3)_2{\cdot}6H_2O$ and 4.98 g of $Co(NO_3)_2$ $6H_2O$ were used in place of single metal precursor.

2.2. Characterization

The morphology of the prepared samples was examined using Philips CM200 Transmission Electron Microscope (TEM) and Zeiss Ultra plus Field Emission Scanning Electron Microscope (SEM) equipped with an EDS. Thermogravimetry Analysis (TG-DTA) was conducted using Shimadzu DTG-60 A at a heating rate of 5 °C min^{-1} from 30 °C to 600 °C under nitrogen flow. Bruker D8 Powder X-ray diffractometer with Ni filtered Cu Kα radiation (λ = 1.5406 A°) was used to identify the phase and composition of hierarchical structures. Specific surface area was determined according to Brunauer–Emmett–Teller (BET) method using Quantachrome NOVA 1200e.

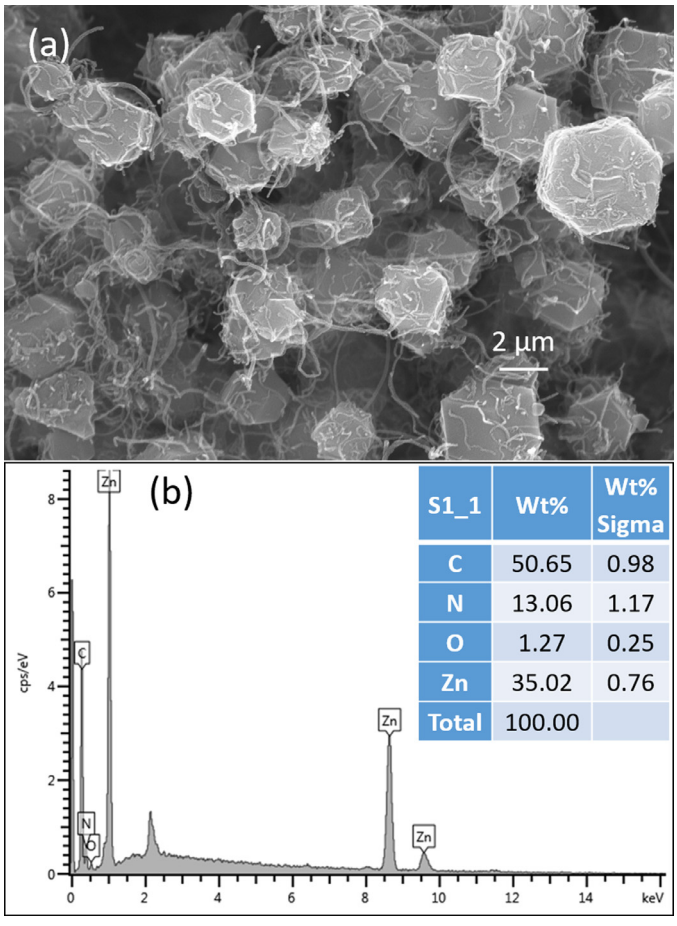
2.3. CO_2 adsorption

Volumetric CO_2 uptake measurements were performed at 298 K over the pressure range of 0–1 bar with BELSORP-HP (BEL, Japan). Ultra-pure helium and CO_2 gases (99.9999%) were used for the measurements to get accurate results. Before measuring the CO_2 adsorption/desorption isotherms, all the samples were degassed under vacuum at 200 °C.

3. Results and discussion

3.1. Morphology

Hierarchical structures of f-MWCNTs@Co/Zn-ZIF and N-MWCNTs@Co/Zn-ZIF have been synthesized along with f-MWCNTs@ZIF-8, N-MWCNTs@ZIF-8, f-MWCNTs@ZIF-67 and N-MWCNTs@ZIF-67 through in situ synthesis. Multi-walled carbon nanotubes (MWCNTs) were acid functionalized via treatment with HNO_3/H_2SO_4 to get COOH-MWCNTs and hydrothermally treated at 180 °C in presence of NH_4OH to get the nitrogen doped MWCNTs (N-MWCNTs) serving as nucleation centres for loading ZIFs. During in situ synthesis, after mixing the metal source and 2-methylimadazole to f-MWCNTs or N-MWCNTs, CNTs are embedded within the ZIF-8 or ZIF-67 or Zn/Co-ZIF matrix. In situ growth of f-MWCNTs@ZIF-8 is shown in Fig. 1. Micro and nano-sized rhombic dodecahedron shape of ZIF-8 crystals of about 200–500 nm are grown through intertwined with f-MWCNTs. EDAX analysis shows the



S1_1	Wt%	Wt% Sigma
C	50.65	0.98
N	13.06	1.17
O	1.27	0.25
Zn	35.02	0.76
Total	100.00	

Fig. 1. SEM image (a) and EDAX analysis (b) of f-MWCNTs@ZIF-8.