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Hybrid metal-organic framework nanomaterials with enhanced carbon dioxide and methane adsorption enthalpy by incorporation of carbon nanotubes

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ABSTRACT

Two hybrid materials composed of metal-organic framework (JUC-32) nanoparticles and carboxyl-modified multi-wall carbon nanotubes (MWCNTs) were synthesised successfully in situ and characterized by TEM, PXRD, and TGA. The gas adsorption properties of these two hybrid materials were compared with the original JUC-32 material and a physical mixture of JUC-32 and MWCNTs. The results indicated that the composite materials absorbed larger amounts of CO_2 and CH_4 per specific surface area than the original materials, and that the adsorption enthalpies of CO_2 and CH_4 had significantly increased.

As the issue of global climate change becomes more and more serious, it is attracting worldwide attention [1]. Many researchers have focused on the investigation of new porous materials, such as metal-organic frameworks (MOFs) [2–8], covalent organic frameworks (COFs) [9], carbon-based materials [10–12] and membrane materials [13], which can capture CO_2 or store clean energy, similar to natural gas. To achieve this target, novel materials with larger and larger surface areas are being developed and many synthesis methods have been suggested to enhance the gas loading per specific surface area (SSA) [14–16]. Materials with high gas loading per SSA usually possess high sorption enthalpy, which offers effective adsorption of gas molecules.

MOFs are a class of microporous materials structured by assembling inorganic metal ions or metal clusters with organic ligands in appropriate solvents [17,18]. With the advantages of the porosity, the large surface areas and the uniform pore characteristics, these MOF materials have great potential for a variety of applications, such as gas storage, chemical separation, catalysis, sensing and drug delivery [19–22]. Furthermore, owing to the diversity of metal centres and functional ligands, MOF materials offer the opportunity of developing new types of composite materials that may show enhanced gas storage properties or new behaviour compared with the original MOFs [15,23–31].

In our previous work, we synthesised a kind of MOF material, $Dy(BTC)(H_2O)\cdot DMF$ (named JUC-32, JUC = Jilin University, China) [32], which exhibits excellent thermal stability and high carbon dioxide storage capability. We then successfully used JUC-32-Y (replacing the metal Dy with Y) as the host for a hybrid material, by assembling guest molecules of ammonia borane (AB) materials, which exhibited a dramatic improvement in the hydrogen release kinetics, the lower operational temperature and the purity of the released hydrogen [33]. The interaction between the framework and the AB compound led to an ideal result, indicating the great potential of hybrid materials based on the JUC-32 MOF material.

Many studies have been carried out to try to improve CO_2 adsorption by MOFs and can be summarised into three main categories, catenation and interpenetration, chemical bonding enhancement and electrostatic force involvement [34]. Herein, we suggest a strategy to promote the adsorption enthalpy of the original material by incorporating another species. We have explored a new class of gas absorption material, formed using a combination of multi-wall carbon nanotubes (MWCNTs) and nano-sized JUC-32-Y. Carbon nanotubes (CNTs), used as composite fillers, have been investigated for various applications and enhanced composite performance has been achieved [35,36]. In particular, CNTs can be an effective additive to improve the kinetics of other gas storage materials [14,37,38]. In this study, we prepared two hybrid composites (named MWCNTs@JUC32-1 and MWCNTs@JUC32-2) by incorporating MWCNTs into JUC-32-Y, enhancing the adsorption enthalpy for CO_2 and CH_4.

In a typical preparation process (Scheme 1), MWCNTs was firstly dispersed in the Dimethylformamide (DMF) by sonication. Different volumes (2 ml and 10 ml) of this suspension were added into the synthesis system of JUC-32 to replace part of the solvent DMF, obtaining

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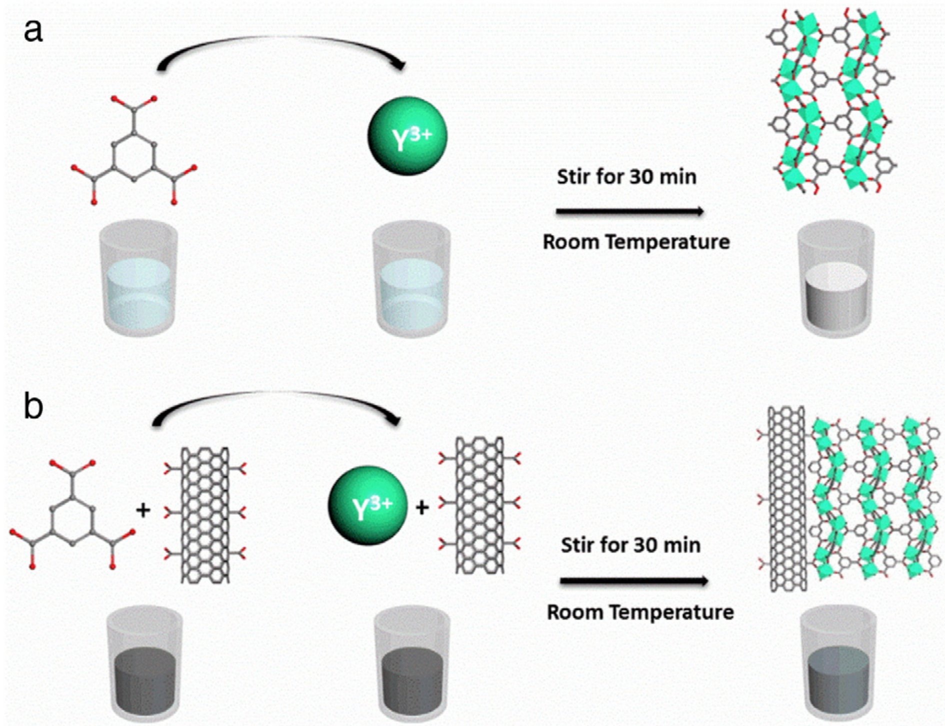

Scheme 1. Schematic diagram of preparation of (a) nano-sized JUC-32(Y) and (b) MWCNTs@JUC32 hybrid composite.

two grey powders as MWCNTs@JUC32-1 and MWCNTs@JUC32-2, respectively. Specific details of the experiments and characterization can be found in the supporting information. The presence of carboxyls decorated on the MWCNTs promoted the nuclearity and growth of JUC-32 nanocrystals on their surfaces, due to the coordination between the metal ions and the –COOH groups. Fig. 1 shows the TEM images of

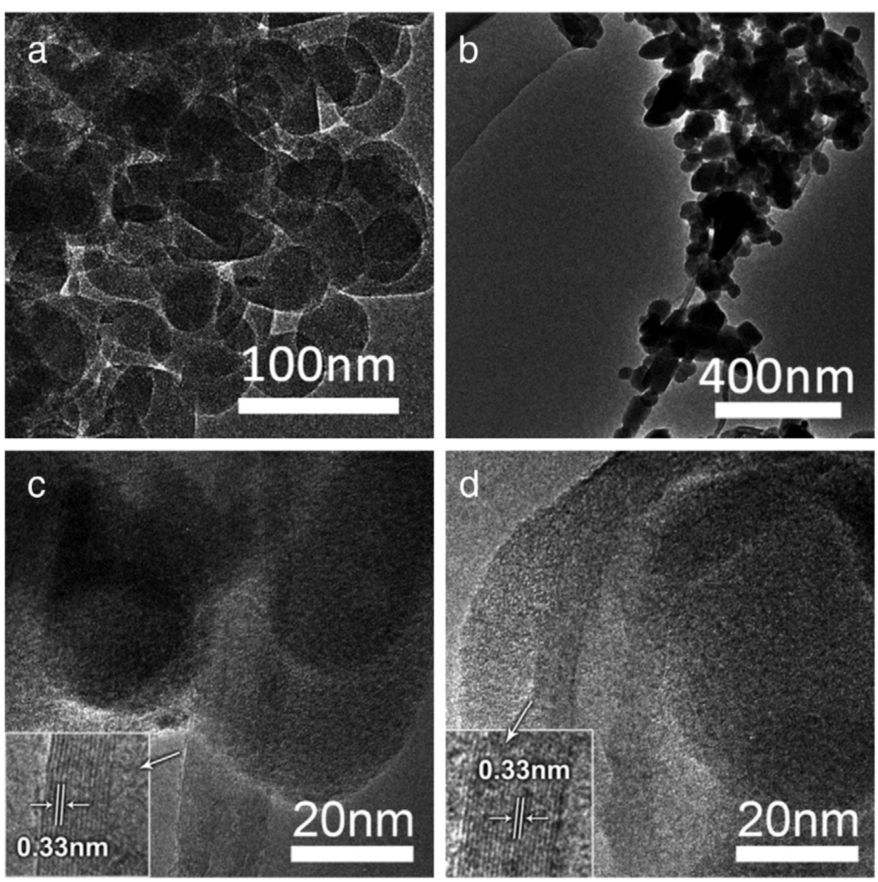

Fig. 1. Low magnification TEM images of (a) pure JUC-32 and (b) MWCNTs@JUC32-1. High magnification TEM images of (c) MWCNTs@JUC32-1 and (d) MWCNTs@JUC32-2.