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HIGHLY STRUCTURED ZEOLITIC IMIDAZOLATE FRAMEWORKS-8 (ZIF-8) ON ELECTROSPUN NANOFIBER SCAFFOLD FOR GAS STORAGE

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ABSTRACT

An increasing demand for sustainable gaseous fuels, such as biomethane and hydrogen, stimulated intensive efforts for developing new technologies and novel materials for gas separation and storage. Herein, a feasible strategy is developed for fabricating metal-organic frameworks (MOFs) nanofiber via combining electrospinning and in-situ growth method for high performance of biogas upgrading and storage. This approach rends the highly porous MOF materials highly distributed on the surface of the PAN nanfiber, which affords the resultant hierarchical porous structures without sacrificing their extraordinary properties such as ultra high surface area, thus contributing to the excellent gas storage capacities. The approach thus providing an promising strategy for structuring MOFs for gas storage applications.

Keywords: MOFs, Electrospinning, ZIF-8, Gas storage, nanofiber

NONMENCLATURE

Abbreviations	
APEN	Applied Energy
Symbols	
n	Year

1. INTRODUCTION

In recent decades, great concerns on dramatically increasing greenhouse emissions and climate change have driven an increasing efforts for the development of gas storage and separation technologies. The European Climate Foundation just published the report of NET ZERO 2050 recently, which point out that we need build up a long-term clean as well as high thermal efficiency fossil-free energy systems to achieve zero carbon demands [1]. Correspondingly, several different strategies have be explored to achieve the targets, such as membrane [2], cryogenic distillation [3], gas hydrate [4], chemical absorption [5]. Despite of great efforts, the significant improvements to achieve the industrial requirements for specific applications is still facing challenge, especially for small scale applications in vehicle transportation, due to problems with large energy dissipation/demand footprint, volume or high weight. Among various strategy, adsorbed natural gas/ biomethane storage (ANG) or efficient storage of hydrogen in high-pressure adsorption devices is regarded as a promising alternative, in which the stable, high performing and efficient adsorbents is very important.

Metal-Organic Frameworks (MOFs) are a relatively new class of adsorbent materials which are interesting gas adsorption materials for attract worldwide attention due to its porosity [6]. In general, MOFs are new porous materials assembled by the metal ions/clusters and organic linkers. This kind of materials prepared by the choice of a variety of chemical compositions with rich porous structures and tailorable pore size afford rich adsorption sites , leading to properties such as large internal surface areas with specific surface properties (charges, hydrophilicity/ hydrophobicity,…), ultralow densities and uniform size of cavities of MOFs structure [7]. Owing to these properties, this class of materials has large potential for the application in gas storage [8] or separation applications [9].

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Ma et al. [10] has synthesized a molecular sieve called MAMS-1, and then they modified the pore size of MAMS-1 to be used for separating H_2/CO and N_2/CH_4. Besides, Yaghi et al. [11] reported the pore size of another MOFs material (IRMOF) can be adjusted by "reticular synthesis". Although great effort have been devoted on the synthesis of new MOFs and investigation on their properties, there are still facing various requirement of pore sizes depending on different applications. While the structure of most pure MOF materials are fixed and stable, hence their pore size are difficult to be modified, it is better to find a strategy to fabricate the pore size of MOFs structure to match the different industrial requirement. Küsgens et al. [12] achieved to make the pore size of HKUST-1 to be adjustable by growing the MOFs crystal on the surface of fiber structure. So the pore size of MOFs probably achieved to be controlled by spinning into fiber structure. Then the electrospinning method is occurred as a more efficient approach to fabricate material into fiber structure [13]. Therefore, this work is focusing on reconstructing the pore size of MOFs materials with the help of electrospinning method.

In this work, we choose zeolitic imidazolate frameworks (ZIF) as adsorbents, due to it is easily to be synthesized and un-patent-protected. Moreover, the ZIF are reported to have the advantages on thermal [14], hydrothermal [15] and chemical [16] stabilities when compared with the other types of MOFs materials, which will provide a persistent and stable performance for the further gas storage application. Therefore, the ZIF-8 will be synthesized and then be fabricated into fiber structure with the help of electrospinning process from PAN/DMF polymer-solvent system, then the final product will be used as adsorbent for gas storage.

2. EXPERIMENTAL SECTION

2.1 Materials

In this work, the $Zn(OH)_2$ and 2-methylimidazole with purity of ≥99.0% were purchased from Sigma-Aldrich. The Polyacrylonitrile (PAN, average molecular weight of 150000) and Dimethylformamide (DMF) were purchased from Parchem fine & specialty chemicals Co., Ltd. What else, the deionized water (D.I.) was produced in laboratory by an ultrapure water system with a resistivity over 18.0 ≥ mΩ cm^{-1}.

2.2 Procedures

In this work, the experiments are separated into two steps: the $Zn(OH)_2$/PAN fiber was firstly prepared by the electrospinning method. And then the ZIF-8/ PAN fibers are synthesized based on the $Zn(OH)_2$/PAN fiber.

Normally, as shown in Fig.1, 0.8 g of $Zn(OH)_2$ and 1 g of PAN dissolved in the 10 g DMF solvent was used for the electrospinning (Linari Nanotech). The flow rate is 0.8 mL h^{-1} in a syringe (10 ml), the voltage is 35 kV, and the distance between the collector and spinneret is 12 cm. The obtained $Zn(OH)_2$/PAN fibers were collected on the aluminum foil. As for the synthesis of ZIF-8/ PAN fibers, typically, 2 g of 2-methylimidazole was dissolved in to the 50 Ml methanol. Then, the $Zn(OH)_2$/PAN fibers were immersed into above solution for 1 day. After that, the $Zn(OH)_2$/PAN fibers were converted into the ZIF-8/ PAN fibers. The resultant ZIF-8/ PAN fibers were washed with ethanol and dried at the room temperature. Moreover, the morphology of samples was measured by scanning electron microscopy (SEM, Zeiss Merlin), and the microcosmic structure are determined by x-ray diffraction (XRD, Bruker D8), as well as the porosity is measured by Specific Surface area and porosity measurement (BET, Nova 4000e).

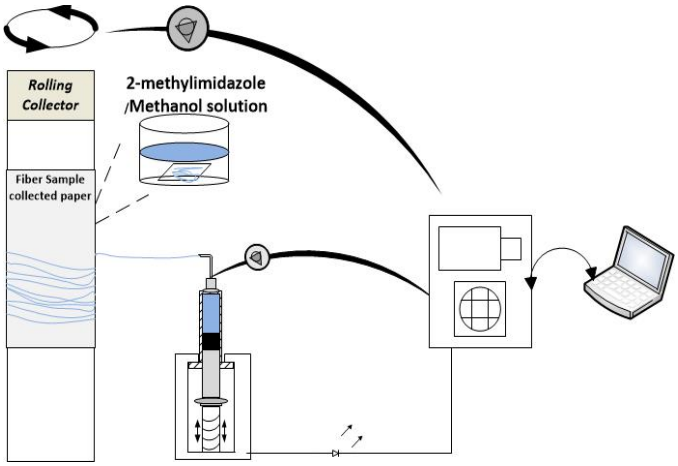

Fig 1 Schematic diagram of electrospinning process

3. RESULT AND DISCUSSION

3.1 Morphology

In order to visualize the morphology the ZIF-8 powder and ZIF-8/PAN composite nanofiber, we carried out SEM analysis on two samples. As shown in Fig.2 (a), the average diameter of ZIF-8 particles is in the range of 1.2-2.0 μm, which means the size of ZIF-8 particles is relatively homogeneous. Besides, according to the Fig.2 (b), the fibrous structures are observed, and the fibers are consist of series of spheroidal particles. It means the

ZIF-8 particles are in-situ growth on the surface of the fiber structure. We can speculate that the heat and mass transfer process of gas adsorption process can be enhanced due to the open porous structure and the high surface area of ZIF-8 anchored on nanofiber scaffold.

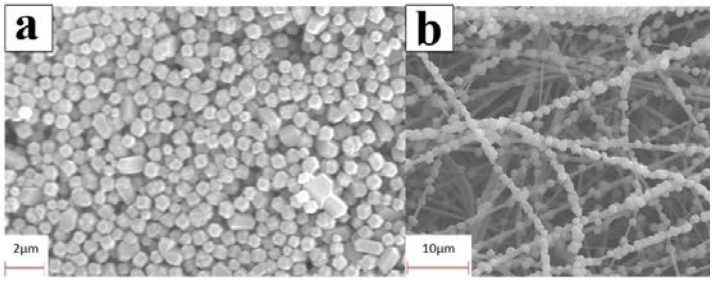

Fig 2 SEM images of: (a) ZIF-8 powder; (b) ZIF-8/PAN nanofiber

3.2 *Surface area analysis*

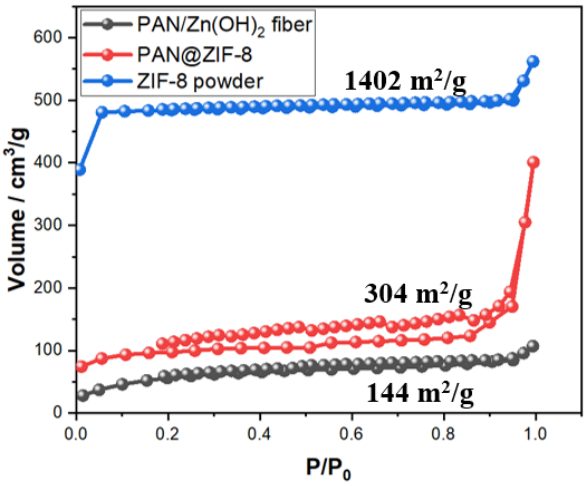

Fig 3 N_2 adsorption isotherms of ZIF-8 powder, ZIF-8 fiber and $Zn(OH)_2$ fiber

In order to determine the influence of the electrospinning process for the porosity of the material of ZIF-8, we collected the N_2 adsorption isotherms for ZIF-8 powder, ZIF-8 fiber and $Zn(OH)_2$ fiber, respectively. As shown in Fig. 3, the poorest BET surface area are obtained from $Zn(OH)_2$ fiber (144 m^2/g), while the ZIF-8 fiber structure has a better performance than it (304 m^2/g). It means the electrospinning process provides a performance boost when the ZIF MOFs structure have been synthesized. However, the optimum results are obtained from ZIF-8 powder (1402 m^2/g), which is even higher than the ZIF-8 fiber sample. This phenomenon maybe caused by the follow reason: during the electrospinning process, parts of pore structures are blocked by the polymer or some other materials. It will undoubtedly to affect the gas storage ability with the ZIF-8 fiber, and we should pay more attention to solve this problem in the next step.

3.3 *Microcosmic structure analysis*

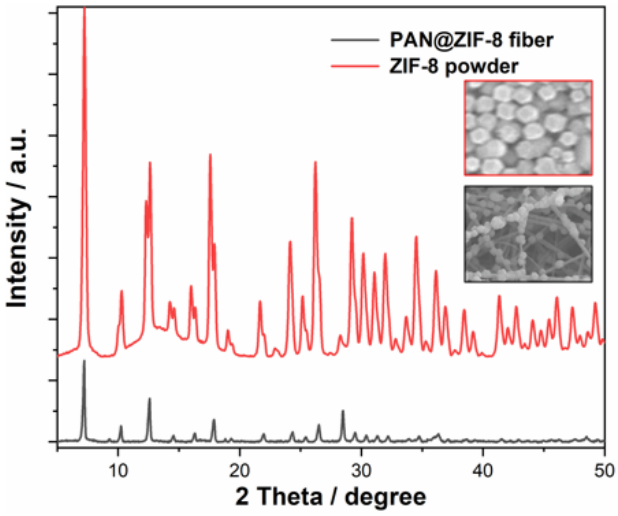

Fig 4 XRD patterns of the ZIF powder and fiber

In order to further reveal the influence of electrospinning process in microcosmic structure scale, Fig.4 shows the X-ray diffraction (XRD) patterns with ZIF-8 powder and fiber samples. On the one hand, peak broadening could be observed obviously from both patterns, indicating there have been formatted regular nanosizee crystal. On the other hand, the comparison of the patterns of the two different samples indicates the electrospinning process has a pretty low (or none) influence in the microcosmic structure scale. Moreover, the lower signal-to-noise ratio of the ZIF-8 fiber structure can be attribute to the amorphous polymer (binder between the MOF particles).

4. CONCLUSION

In summary, a novel strategy for fabrication of ZIF-8 nanofiber is developed by the electrospinning process. This approach tends the high exposed ZIF-8 powders are grown on the surface of fiber, resulting in the porous structure of ZIF-8 are well remained. The comparison of the BET data of fiber structure of ZIF-8 and $Zn(OH)_2$ nanofiber indicates the porosity has an obviously enhancement when compared with the raw material, we can expect that the gas capacity and separation

efficiency will be improved remarkably in the further application.

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