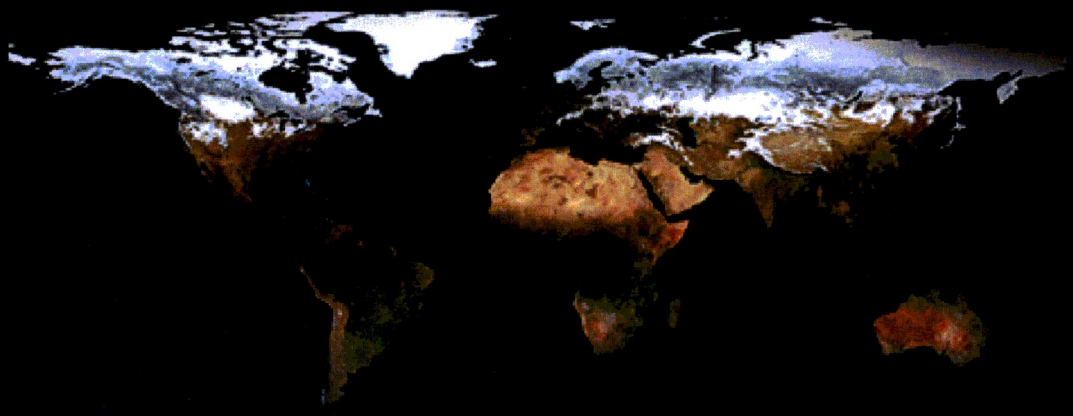

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Chapter 4

DEVELOPMENT AND EVALUATION OF FIBROUS ADSORBENTS FOR CARBON DIOXIDE REMOVAL

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ABSTRACT

The mitigation of carbon dioxide (CO_2) emissions has attracted worldwide attention because of the environmental and economic threats posed by possible global climate changes. Considering that the utilization of fossil energy carriers will continue and may even increase over the coming decades, advanced CO_2 capture materials and technologies are of the utmost importance. Micro/nanofibers have unique porous structure, high surface area, and good mechanical properties and thereby are

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attractive candidates as advanced sorbents for CO_2 removal. Fibrous sorbents may have high CO_2 capture capacity and little resistance to bulk gas flow and thereby have fast kinetics. In this chapter, we have summarized the recent progress in the development of fibrous sorbents (e.g. amine-modified fibers, carbon fibers, hollow fiber membranes, etc.) for CO_2 removal, described the types of fiber materials that have been studied, and discussed their fabrication variables and CO_2 adsorption performance in details. This review may pave the way for developing advanced fibrous adsorbents for CO_2 removal from power plants and even from the atmosphere.

Keywords: CO_2 removal, fibrous adsorbent, fiber, nanofiber, membrane

1. INTRODUCTION

Global carbon dioxide (CO_2) emission caused by escalating energy use may have resulted in a series of environmental problems such as anomalous climate change and rising of sea levels [1-3]. Studies have revealed that the concentration of CO_2 in the atmosphere has increased by ~ 23% to a value of 380 ppm during the last half century and it is projected to continue to rise if anthropogenic sources remain unchecked [4]. In the U.S., over 94% of the CO_2 emission comes from the combustion of carbon-based fossil fuels and thus the U.S. Department of Energy (DOE) issued a carbon sequestration roadmap in 2009 aiming to achieve 90% CO_2 capture at an increased cost of electricity of no more than 35% for the post-combustion process by 2020 [4-6]. Technologies for CO_2 capture and storage (CCS) present some of the most promising and effective options for large-scale reductions in CO_2 emissions [1]. As a means to remove CO_2 from flue gases on a large-scale, there are four main methods to separate CO_2 from other gases: solid sorbents, cryogenic distillation, solvent, and membrane [7]. It is evident that the progress and achievement of most of these technologies depends heavily on the development of materials.

Carbon fibers and their composites as well as hollow fiber membranes have been developed for gas separation [8, 9]. Benefiting from the unique properties (e.g. high porosity, high surface area, and good mechanical properties) of fibrous structures [10, 11], fibrous adsorbent has emerged in the past decade as a new class of adsorption materials; considerable efforts have been applied on their adsorbent design and optimization [12-14]. In this

chapter, the recent progress of fibrous sorbents used for CO_2 capture and separation has been reviewed.

2. FIBROUS ADSORBENTS FOR CO_2 CAPTURE

2.1. Amine-modified Fibrous Adsorbents

Recently, modification with amine groups on the surfaces of adsorption materials has attracted much attention due to the potential low energy requirement, low cost, and ease of applicability over a wide range of temperatures and pressures [15]. Up to now, amine-modified particle adsorbents such as amine-modified MCM-41, SBA-15, polymethyl-methacrylate, fly ash, zeolite, and activated carbon have been extensively investigated for CO_2 capture [16-18]. All of the supports mentioned above are microporous or mesoporous particles with a high surface area and a large pore volume. The supports can be amine-treated by coating their surfaces with amine-rich polymers or compounds, for example, polyethylenimine (PEI), allylamine, and aminosilanes [19]. In this section, we have focused on the recent progress of some amine-modified fibrous adsorbents.

2.1.1. Glass Fibrous Adsorbent

In 1991, Andreopoulos and coworkers [20] demonstrated that fibrous adsorbents based on PEI coated polypropylene fibers had high adsorption capacities to acidic gases (e.g. SO_x). More recently, glass fiber has received much attention due to its high surface area, low price, and convenience to be used as a matrix (Figure 1a). Inspired by Andreopoulos' work, Li et al. [21] developed a novel fibrous adsorbent for CO_2 capture by coating PEI on a glass fiber matrix using epoxy resin as a crosslinking agent. They systematically investigated the fabrication variables (e.g. crosslinking agent dosage, coating weight, moisture, adsorption temperature, and CO_2 concentration of the simulated flue gas) that may affect the adsorption capacity of their fibrous adsorbents and found that a maximum adsorption capacity of 276.96 mg of CO_2/(g of PEI) was obtained at a PEI/epoxy resin ratio of 10:1. Moisture was observed to enhance the adsorption of CO_2; the CO_2 adsorption capacity of the fibrous adsorbent in the presence of moisture could be 19 times higher than that in the absence of moisture. It is worthy noting that higher molecular weight and larger steric obstruction of the cross- linking agent used (i.e. epoxy resin) led to poorer diffusion of CO_2 in the fibrous adsorbent and thus poorer

kinetics. Therefore, it is of interest to identify better cross-linking agents with lower molecular weight to replace the epoxy resin in order to achieve better performance. Li et al. replaced epoxy resin (MW=370) with epichlorohydrin (ECH, MW=92.5) and developed adsorbents of PEI modified glass fibers [23]. As expected, the PEI modified glass fibers improved adsorption performance (e.g. higher CO_2 capacity, faster kinetics, and better regenerability) [22]. As shown in Figure 1b, PEI was deposited as a porous layer on the surfaces of glass fibers, and this process might have contributed to the more efficient contact with CO_2 thereby leading to a higher adsorption rate and capacity.

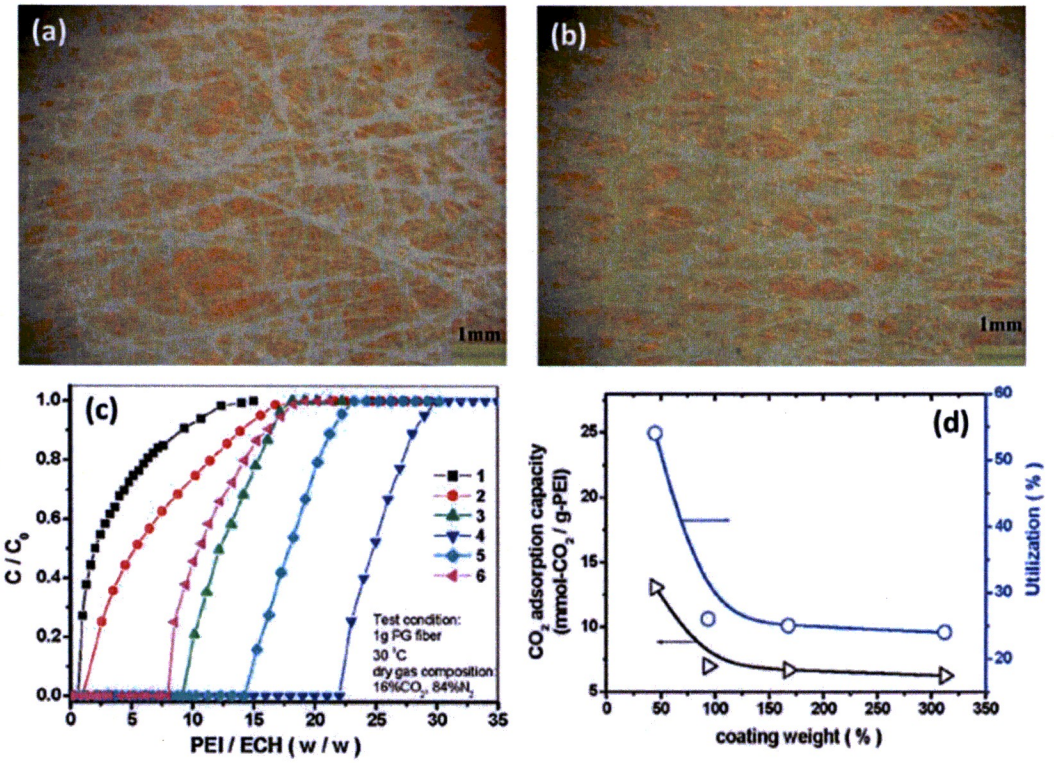

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Figure 1. Micrograph images of (a) glass fiber and (b) PEI modified glass fibers; (c) Breakthrough curves of CO_2 adsorption on PEI modified glass fibers with different PEI/ECH ratios: (1) 5:1; (2) 10:1; (3) 15:1; (4) 20:1; (5) 25:1; and (6) 30:1. (d) CO_2 adsorption capacity *vs.* coating weight of PEI modified glass fibers.

The CO_2 adsorption capacities of the PEI modified glass fiber adsorbents with different coating weights are shown in Figure 1c. The maximum CO_2 adsorption capacity of 13.08 mmol CO_2/(g of PEI) was achieved at the lowest coating weight of 45 wt.%. The adsorption rate was rapid in the beginning

phase, leading to a nearly zero concentration of CO_2 in effluent gas for several minutes. It is obvious that the CO_2 adsorption capacity does not increase with increasing coating weight (Figure 1d).

2.1.2. Fibrous Polyacrylonitrile (PAN) Adsorbent

Polymer supports for amines have attracted considerable attention since they are light in weight, flexible, and easy to handle [7]. Solid amine adsorbents using synthetic polymer fibers as matrix may offer advantages for CO_2 adsorption because of the high external surface area, potential low pressure drops, and flexibility of the matrix fibers [23].

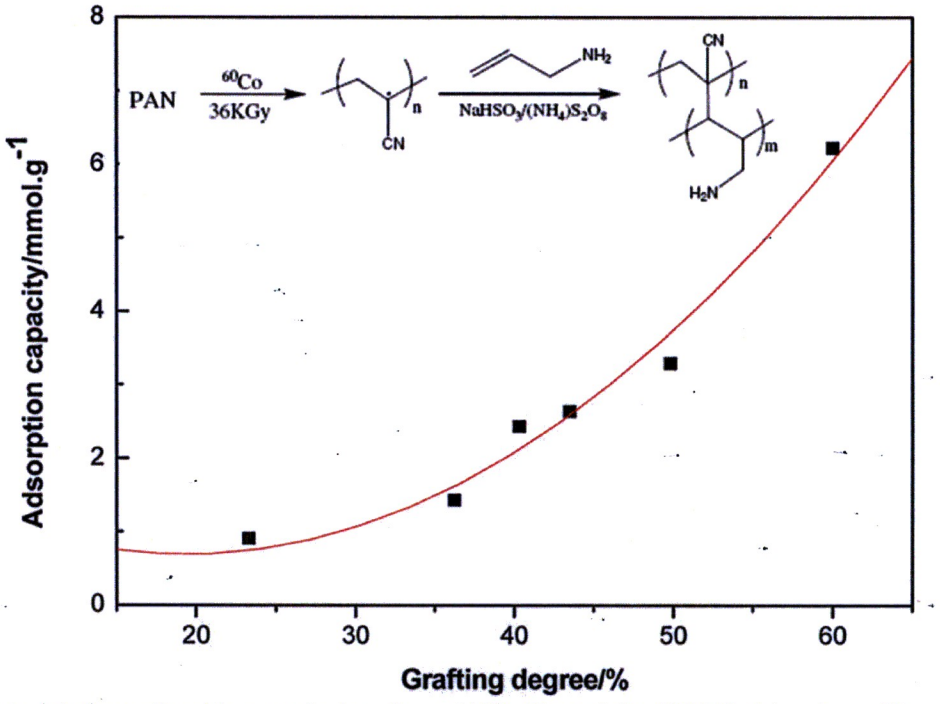

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Figure 2. Effect of grafting degree on adsorption capacity (adsorption temperature: 22 °C; concentration of CO_2: 15.2%). Inset shows the preparation procedure of irradiation grafting of allylamine onto PAN fiber.

For amine-impregnated sorbents, CO_2 molecules could easily be adsorbed on the surface of the amines especially at low temperature, but the diffusion of CO_2 molecules into the interior of the amines is difficult [13]. Additionally, poor adhesion between amine and the support would lead to easy leakage from the support thus spoiling the regeneration performance. To enhance the adhesion between amines and the support, the grafting copolymerization

method was introduced. For example, Yang et al. [19] demonstrated that solid amine-containing fibrous adsorbent could be prepared by pre-irradiation grafting copolymerization of allylamine onto PAN fiber (PAN-AF), using the redox system of $(NH_4)_2S_2O_8/NaHSO_3$ as an initiator (Figure 2, inset). They found that the reaction conditions such as reaction time, temperature, monomer concentration, and amount of the initiator had great effects on CO_2 adsorption performance. As presented in Figure 2, higher grafting degree resulted in higher CO_2 uptake and the adsorption capacity of PAN-AF reached 6.22 mmol CO_2/(g of PAN-AF) at the grafting degree of 60.0 wt.%. They attributed the good performance of this fibrous adsorbent to the fibrous structure, which might have reduced the resistance to gas flow thereby maximizing sorbent performance while minimizing energy consumption, and the highly stable interface (i.e. grafting copolymerization of amines onto fibers) between amines and the support [19].

2.1.3. Nanofibrillated Cellulose (NFC) Adsorbent

NFC is an abundant natural material composed of cellulose fibril aggregates (10~100 nm in diameter and several micrometers in length) [14]. NFC is rich in surface hydroxyl groups, which can be used to covalently anchor chemical functionalities to its cellulose backbone [24, 25]. Amine functionality has been introduced on NFC through grafting of aminosilanes [26]. However, the hydrolysis and self-condensation of aminosilanes with three alkoxy groups may lead to the build-up of three-dimensional siloxane networks, which is unfavorable for CO_2 capture; the siloxane networks may block the functional amine sites and the pores in the support [27].

To avoid the undesired blocking of functional amine sites, Gebald and coworkers [12] developed a new adsorbent based on aminosilanes with two alkoxy functions (N-(2-aminoethyl)-3 aminopropylmethyldimethoxysilane or AEAPDMS. The adsorbent was synthesized through freeze-drying (FD) of an aqueous suspension of NFC and AEAPDMS. Before FD, the NFC hydrogel morphology was composed of entangled cellulose nanofibrils of submicrometer diameter (Figure 3a). After FD, the NFC-FD morphology exhibited cellulose sheet structures with single irregularly distributed cellulose nanofibrils attached to the cellulose sheets (Figure 3b). The presence of AEAPDMS in the NFC suspension (i.e. AEAPDMS-NFC-FD) further increased the sheet-forming tendency and eliminated single cellulose nanofibrils (Figure 3c). The adsorption rate of AEAPDMS-NFC-FD was comparable to those of hyperbranched aminosilica, PEI/silica, 3-aminopropyltrimethoxysilane modified PEI/silica (A-PEI/silica), and tetraethyl

orthotitanate modified PEI/silica (T-PEI/silica) in their powder forms (Figure 3d). The favorable CO_2 uptake rate could be explained by the highly porous structure of AEAPDMS-NFC-FD, which is composed of cellulose sheets separated by pores in the micrometer range. During 2 h of CO_2 adsorption and 1 h of CO_2 desorption in Ar, the average cyclic CO_2 capacity was 0.695 mmol CO_2/g. The AEAPDMS-NFC-FD adsorbent was found to be stable for at least 20 adsorption/desorption cycles (Figure 3e) [12].

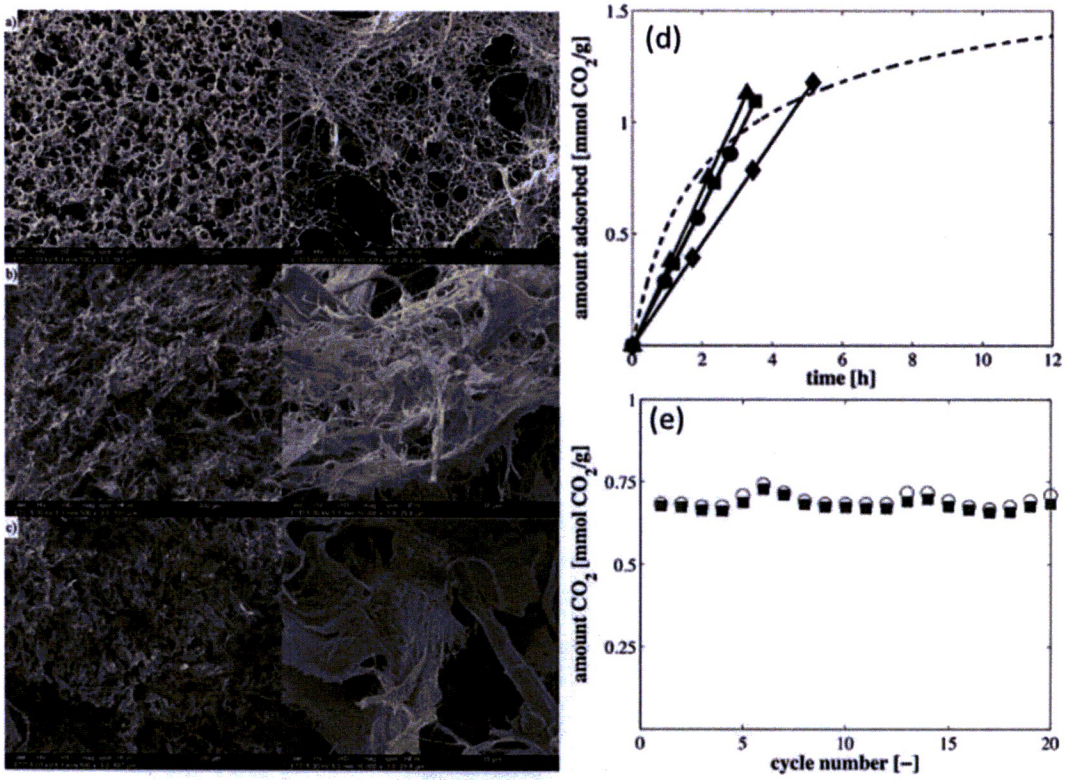

Figure 3. (a) Scanning electron microscopy images of NFC hydrogel, (b) NFC-FD, (c) AEAPDMS-NFC-FD. (d) Comparison of CO_2 capacity as a function of time of AEAPDMS-NFC-FD (dashed line), hyperbranched aminosilica (spheres), PEI/silica (rhombuses), A-PEI/silica (triangles), and T-PEI/silica (squares). (e) Multicycle adsorption (squares) and desorption (spheres) experiments with AEAPDMS-NFC-FD. Reprinted (adapted) with permission from [12].

2.1.4. Mesoporous Silica/Cotton Fibrous Adsorbent

Ordered mesoporous silica materials have evoked much interest in the past ten years due to their potential applications in catalysis, sorbents, drug delivery, optical devices, and nanostructure templates [28, 29]. Recently, one interesting research orientation is the utilization of the as-synthesized

mesoporous silica as a crucial template component for functional materials [30]. The template is utilized to disperse amines, and thus enhances the adsorption capacity of this system by modifying the interaction between CO_2 and the amines. However, the industrial application of these mesoporous materials remains a challenge, i.e. fine powder can be dissipated with carrier gas due to the small size of the particles. Recently, Ma et al. [31] developed a method to shape the mesoporous silica (i.e. SBA-3) by *in situ* synthesis on the surfaces of cotton fibers. These shaped composite materials were subsequently modified with tetraethylenepentamine (TEPA) to form composite fibrous adsorbents, as shown in Figure 4. During the synthesis of mesoporous silica, the strong bibulous ability of cotton fiber enables it to absorb the whole reaction solution. Cross-linked cotton fibers were used to construct a flexible three-dimensional (3D) netlike matrix to disperse and support mesoporous silica particles thus preventing over-packing of the particles. The reported SBA-3/cotton (S/Cot) fiber composite materials exhibited considerable CO_2 adsorption capacity [106 mg/(g of S/Cot composites)] and stable cyclic adsorption/desorption performances. This approach may produce inexpensive shaped composite materials with high-performance, and the composite fibrous adsorbents may have advantages over CO_2 powder adsorbents.

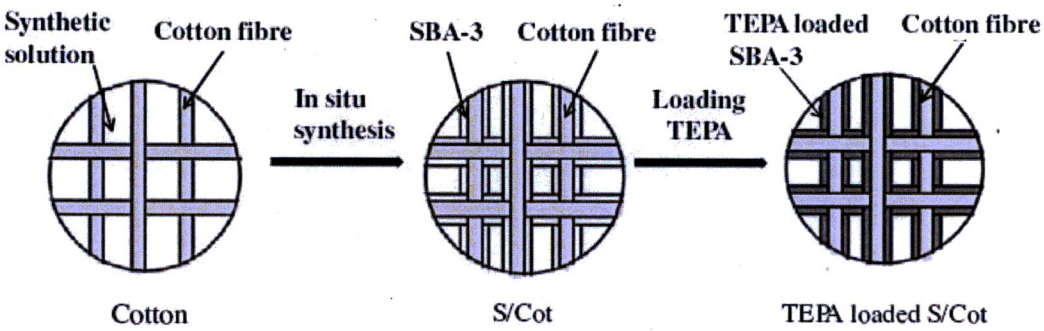

Figure 4. Schematic diagrams for the formation of S/Cot and TEPA loaded S/Cot fibrous adsorbents. Reprinted with permission from [31].

2.2. Carbon Fiber Adsorbents

Porous carbon materials are well-known CO_2 adsorbents due to their highly developed porosity, extended surface area, flexible surface chemistry, and high thermal stability. Recently, some new classes of carbon materials (e.g. carbon fiber, carbon molecular sieves) have emerged as adsorbents for

gas separation and storage. Carbon fiber refers to fibers which are at least 90 wt.% carbon in composition obtained by the controlled pyrolysis of an appropriate precursor material (e.g. pitch, PAN, rayon, nonheterocyclic aromatic polymers) [32]. The structures of fibers can be crystalline or amorphous, and the crystalline form of carbon is graphite. When the proportion of graphite is high, the fiber is called graphite fiber.

2.2.1. Carbon Fiber Composite Molecular Sieve (CFCMS)

The CFCMS is a monolithic activated carbon that is composed of petroleum pitch-derived carbon fiber and a phenolic resin-derived binder. The U.S. Oak Ridge National Laboratory has investigated CFCMS applications in a variety of gas separation and gas storage [33]. Activation of the CFCMS creates microporosity in the carbon fibers, yielding high micropore volumes (>0.5 cm^3/g) and BET surface areas (>1000 m^2/g). Moreover, the CFCMS material is a rigid, strong monolith with an open structure that allows the free-flow of fluid/gas through the material. This combination of properties provides an adsorbent material that has several distinct advantages over granular adsorbents in gas separation systems such as pressure swing adsorption units. The room temperature CO_2 adsorption capacity of CFCMS is about 120 mg/(g of CFCMS), and the CFCMS exhibited rapid adsorption and desorption compared to zeolites and conventional granular activated carbons [33].

2.2.2. PAN-based Activated Carbon Fiber (PAN-ACF)

PAN-ACFs with high surface areas and nitrogen contents can be made from PAN fibers through a partial gasification reaction. Much research has been devoted to the preparation of PAN-ACFs from modified PAN, and some attention has been paid to the use of PAN-ACFs for CO_2 removal. Hierarchical porous PAN-ACFs with a large BET surface area (2231 m^2/g) and a high pore volume (1.16 cm^3/g) were made from PAN fibers through pre-oxidation and chemical activation. This type of material contains a large number of nitrogen-containing groups (N content > 8.1 wt.%) and thereby basic sites, leading to a faster adsorption rate and a higher CO_2 adsorption capacity (2.4 mmol/g). Moreover, PAN-ACF adsorbents had stable CO_2 adsorption/desorption performance under multiple cycle conditions [34].

2.2.3. Graphite Nanofiber (GNF)

As one of the most important carbon materials, graphite fibers have great potential for applications in gas storage, electrodes, filler, and catalyst supports [35-37]. However, graphite fibers have relatively lower specific surface area

compared to other carbon materials, and effort therefore has diverted into engineering graphite fibers into nanosize or porous structures in order to increase their surface area and ultimately enhance their CO_2 adsorption capacity. For instance, Meng et al. [35] found that porous GNFs (Figure 5) could be fabricated using a KOH etching method at temperatures

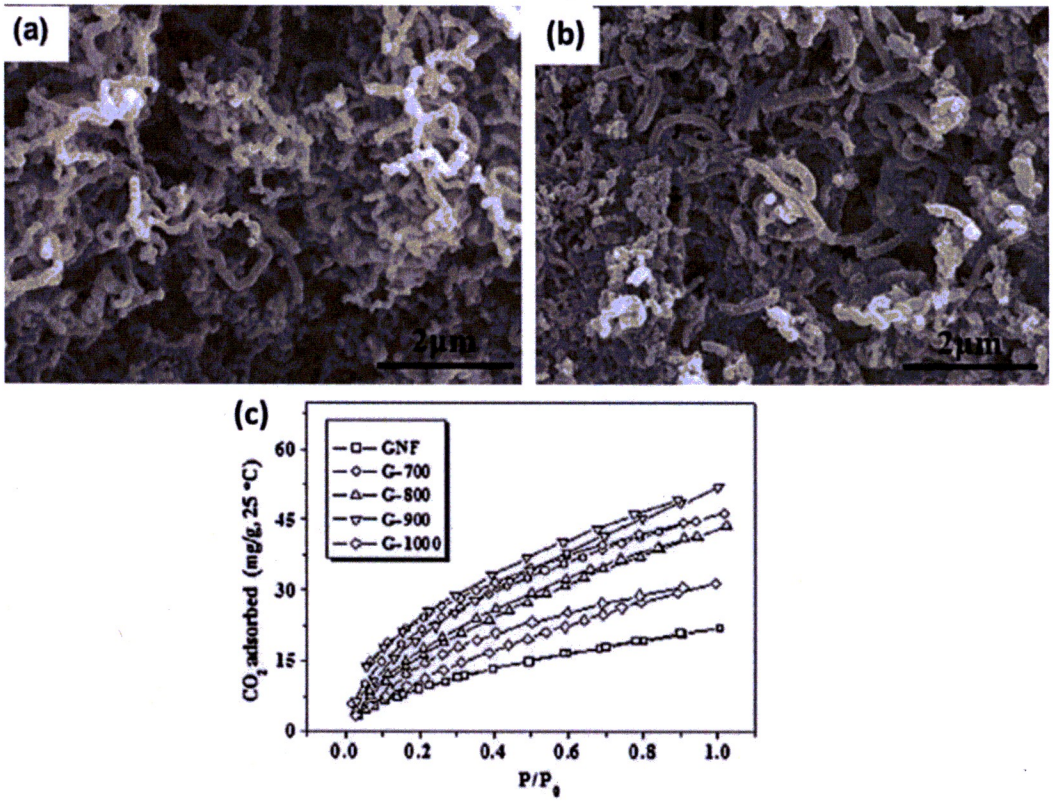

Figure 5. Typical field emission scanning electron microscopy images (a) pristine and (b) chemical-treated GNFs. (c) CO_2 isotherms of the pristine and chemical-treated GNFs [35]. Reprinted with permission from [35].

in the 700-1000°C range. Chemical activation of GNFs (Figure 5) with KOH begins with a chemical reduction of the hydroxide, followed by intercalation of the metal into the graphene layers, leading to increased microporosity. Typical adsorption/desorption isotherms of N_2 on the pristine and chemical-treated GNFs showed that KOH activation promoted the development of pores in the samples. The CO_2 adsorption isotherms revealed that GNFs treated under 900°C had the highest BET surface area (567 m^2/g) and the best CO_2 adsorption capacity (59.2 mg/g) (Figure 5c).

2.3. Hollow Fiber Membranes for CO_2 Removal

Membranes have been studied to separate CO_2 from flue gas [38-42]. Benefiting from the high ratio of membrane area per volume, hollow fiber membrane geometry is expected to have the potential to overcome the disadvantages (e.g. phase dispersion, limited mass transfer areas) of conventional membranes and lead CO_2 capture technology to a new level when integrated with chemical absorption [43]. The compact modular structure of membrane contactors also provides much larger gas-liquid interfaces and the flexibility to scale up or down. Up to now, hollow fiber membranes have been constructed using a number of different polymeric materials, including polysulfones, polyethersulfones, polyphenylene oxide, polyetherimide, and polyimides [44-46]. Because of the potential advantages offered by hollow fiber membranes, considerable academic research has been conducted [47, 48]. For instance, Karoor et al. [47] carried out comprehensive experiments and simulated the gas-liquid absorption in a microporous hydrophobic hollow fiber device using CO_2, SO_2, CO_2-N_2, and SO_2-air mixtures as feed gases and water as an absorbent. To solve the gas absorption performance deterioration of membranes caused by membrane wetting, Lv et al. [39] developed superhydrophobic polypropylene hollow fiber membranes by depositing a rough hydrophobic layer on membrane surfaces. The membrane-absorbent interaction results demonstrated that the modification treatment effectively enhanced the stability and maintained the superhydrophobicity of fibers contacting with the absorbent.

PERSPECTIVE AND CONCLUSION

CO_2 removal has been attracting broad attention from both science and technology. In this chapter, we have reviewed the recent progress in developing fibrous sorbents (e.g. amine-modified fibers, carbon fibers, graphite nanofibers, hollow fibers, etc.) with potential applications for CO_2 removal. Clearly, the selection of capture materials is essential for any technologies in CO_2 removal. In general, fibrous materials have advantages such as ease of design and synthesis, high porosity, tailored pore properties, high surface area, and good mechanical properties. These properties make them highly attractive for the development of adsorbents with high CO_2 capture capacity and fast kinetics. However, further exploration is needed on

several important issues, which may hamper their practical application, as discussed below.

The gas flows treated in practical CO_2 removal always contain water and it is not economically feasible to dry the flue gas by an additional process before separation. Therefore, adsorption materials require a high tolerance to water or to be superhydrophobic. However, only a few evaluations of the effect of water on the separation performances of fibrous adsorbents have been reported. Addressing this issue should include research on both the physical co-adsorption of water in the fibrous materials and the material structure and functional design.

Some fibrous materials do not have CO_2 adsorption ability until they are modified with amine groups as described in this chapter. However, the undesired blocking of fiber surfaces with thick amines will lower the CO_2 capture performance of the adsorbents. Further research should focus on the achievement of effective surface modification strategies. For example, surface modifying fibrous materials using layer-by-layer nano-assembly technology [49, 50] via depositing CO_2-adsorbing amine polymer would be a potential method to solve this problem.

As demonstrated in this chapter, nanostructured fibrous adsorbents (e.g. NFC, GNF) exhibited improved CO_2 adsorption performance due to their large specific surface areas. Therefore, the design of nanofibrous adsorbents for CO_2 capture and the exploitation of new nanofiber fabrication methods (e.g. electrospinning [10]) will be of interest. Additionally, paralleling experimental studies and molecular simulation of fibrous adsorbents must be further developed.

Despite the numerous challenges surrounding CO_2 removal, the ease and low cost of the synthesis of fibrous adsorbents in large scale will be extremely important in determining their potential for industrial applications.

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CONFLICT OF INTEREST

None.

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