

# Chapter 10

## Electrospun Nanofibrous Sorbents and Membranes for Carbon Dioxide Capture

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**Abstract** CO<sub>2</sub> emission resulting from combustion of fossil fuel is a major anthropogenic factor for global warming. Current commercial CO<sub>2</sub> capture approaches using aqueous amine scrubbing require high energy consumption for regeneration which leads to significantly decreased efficiency. Therefore, novel CO<sub>2</sub> capture materials and technologies for economical CO<sub>2</sub> capture are of the utmost importance. Nanofibers, mainly fabricated by electrospinning, have unique porous structure, high surface area, and good mechanical properties thereby exhibit potential as advanced sorbents for CO<sub>2</sub> capture and storage. More significantly, nanofiber-based sorbents are expected to have extremely low resistance for gas transport and extremely fast kinetics due to the unique structure of nanofibers. In this chapter, we summarize recent progress in the development of electrospun nanofibrous sorbents or membranes (e.g., nanofiber-supported metal-organic frameworks, carbon nanofibers, ionic liquid-based nanofibrous membranes, metal oxide nanofibers, etc.) for CO<sub>2</sub> capture, describe the types of nanofibrous materials that have been developed, and discuss their fabrication variables and CO<sub>2</sub> adsorption performance in detail. This chapter may pave the way for developing advanced nanofibrous sorbents for CO<sub>2</sub> capture from power plants and even the atmosphere.

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## 10.1 Introduction

The global climate change phenomenon, which is mainly caused by CO<sub>2</sub> emission into the atmosphere, has attracted more and more attention [1–3]. It is reported that the concentration of CO<sub>2</sub> in the atmosphere has increased from about 310 to 394 ppm during the last half century and it is projected to continue to rise if anthropogenic sources remain unchecked [4, 5]. Technologies for CO<sub>2</sub> capture and storage (CCS) present some of the most promising and effective options for large-scale reduction in CO<sub>2</sub> emissions [1]. The CCS strategies embody a group of technologies for the capture of CO<sub>2</sub> from power plants, followed by compression, transport, and permanent storage. Capturing CO<sub>2</sub> from the mixed-gas streams produced during power generation is a first and critical step for CCS. Three strategies for incorporating capture into power generation scenarios are of primary focus today: precombustion, post-combustion, and oxyfuel processes.

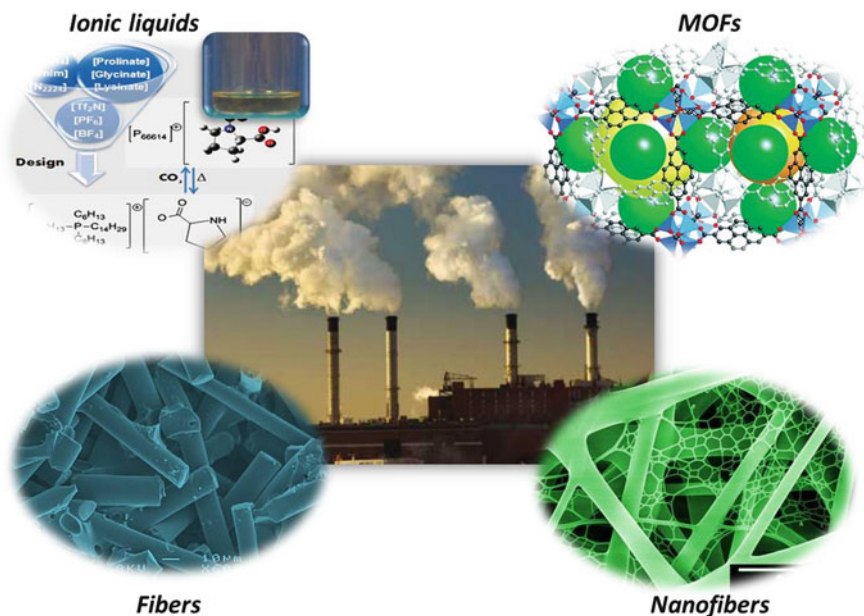
To reduce the amount of CO<sub>2</sub> released into the atmosphere, four main methods are being developed for CCS: solution absorption, adsorption, membrane diffusion, and cryogenic distillation [6, 7]. It is evident that the achievement of most of these technologies depends heavily on the development of materials. Among them, adsorption or sorbent is of great interest because of its low energy consumption, low equipment cost, and ease of application. A number of materials have been used for CO<sub>2</sub> adsorption, and materials with large surface area (e.g., zeolites, activated carbon) have been widely investigated. Nanomaterials have shown potential in CO<sub>2</sub> capture due to their high surface area and adjustable properties and characteristics. Higher surface areas provide more sites of reaction and hence boost the adsorption or absorption capacity [8]. For instance, CaO nanopods with higher surface area (16.92 m<sup>2</sup>/g) showed higher CO<sub>2</sub> capture capacity [17.5 mmol CO<sub>2</sub>/(g sorbent)] than that [12.1 mmol CO<sub>2</sub>/(g sorbent)] of commercial CaO sorbents with surface area of 0.40 m<sup>2</sup>/g [9].

Nanomaterials also offer an advantage in that their structure can be tailor-made to improve the properties and characteristics of a compound or element. For example, carbon nanotubes are able to be produced in different dimensions and diameters. Nanofibers, as one of the most important one-dimensional (1D) nanomaterials, are expected to have extremely low resistance for gas transport and extremely fast kinetics; therefore, they have great potential for CO<sub>2</sub> capture and storage. As a nanofabrication technique, electrospinning has been established as a robust and versatile method for fabricating fibers with diameters down to the nanometer by applying a high voltage to a polymer solution [10, 11]. A variety of materials such as polymers, ceramics, and even metals have been electrospun into fibers with well-controlled sizes, compositions, and structures [12]. It has been shown that the outstanding properties of such nanofibers are highly attractive to numerous applications including biotechnology, textiles, filters, sorbents, sensors, and so on [13]. Benefitting from the unique properties (e.g., high porosity, high surface area, and good mechanical properties) of nanofibrous structures [14], nanofibrous adsorbent has emerged as a new class of adsorption materials, and considerable

effort has been applied to their adsorbent design and optimization [15, 16]. In this chapter, currently emerging new materials for CO<sub>2</sub> capture are briefly introduced and then the recent advances of nanofibrous sorbents used in CO<sub>2</sub> capture and separation are highlighted. We conclude with a summary of current and future research efforts and opportunities in the development of electrospun nanofibers for CO<sub>2</sub> capture applications.

## 10.2 New Materials for CO<sub>2</sub> Capture

A number of promising new materials exist for CO<sub>2</sub> capture from precombustion, post-combustion, and oxyfuel processes [17]. Examples of new materials include ionic liquids (ILs), metal-organic frameworks (MOFs), membranes, and fibrous and nanofibrous sorbents (Fig. 10.1).



**Fig. 10.1** Schematic of new materials for CO<sub>2</sub> capture. Permissions for individual pictures were obtained (Reprinted with the permission from Brennecke and Gurkan [18]. Copyright 2010 American Chemical Society. Reprinted with the permission from Rowsell and Yaghi [22]. Copyright 2006 American Chemical Society. Reprinted from Thiruvengatachari et al. [27]. Copyright 2009, with permission from Elsevier. Reprinted with permission from Wang et al. [30]. Copyright 2010 IOP Publishing Ltd.)

### **10.2.1 Ionic Liquids (ILs)**

ILs are low-melting salts that are attractive for a number of applications as they are relatively nonvolatile, nonflammable, environmentally benign, and exceptionally thermally stable [18]. In addition, there are numerous combinations of cations and anions that can be used to produce ILs, and thus chemical and physical properties of ILs can be tuned, which is needed to design an energy-efficient liquid absorbent for CO<sub>2</sub> capture. The mechanism for CO<sub>2</sub> capture in ILs is often based on physisorption and involves a weak association between the IL and CO<sub>2</sub> molecules [19]. Once the CO<sub>2</sub> has been removed from the gas mixture, it can be released from the ILs (which would be reused) by either a decrease in pressure or an increase in temperature [18]. While the viscosity of ILs minimizes solvent loss from the gas stream, this attribute also limits mass transfers, and they often suffer from low rates of absorption. To overcome these shortcomings and increase the capacity of simple ILs, amine-functionalized ILs have been developed, which allow higher rates of sorption to be achieved at pressures relevant to flue streams [19, 20]. A number of reports have also demonstrated high CO<sub>2</sub>/N<sub>2</sub> selectivity in polymerized ILs, which exhibit enhanced CO<sub>2</sub> solubility relative to the monomeric ILs [21].

### **10.2.2 Metal-Organic Frameworks (MOFs)**

MOFs are novel materials constructed by coordinate bonds between multidentate ligands and metal atoms or small metal-containing clusters [4], which have recently attracted intense research interest because of their permanent porous structures, large surface areas, and potential applications as novel adsorbents [22]. Most of the MOF materials have three-dimensional (3D) structures with uniform pores and a network of channels. The integrity of these pores and channels can be retained after careful removal of the guest species. The remaining voids within the 3D structures can then adsorb other guest molecules. Several reviews have summarized the research efforts in gas adsorption applications for MOFs, such as hydrogen and methane storage, and CO<sub>2</sub> capture [4, 19]. Recently, Liu and co-workers contributed a review on the progress and challenges in using MOFs for adsorption-based CO<sub>2</sub> capture including both experimental and simulation studies [4].

### **10.2.3 Membranes**

A gas separation membrane typically consists of multiple layers with different functions. A dense ultrathin selective layer (~100 nm in thickness) performs the molecular separation, while a microporous support structure provides mechanical strength and minimal transport resistance [23]. The constituent materials of

membranes are typically classified as inorganic (e.g., ceramic, metal oxide, metallic, molecular sieves, and MOFs) or organic (e.g., cellulose acetate, polysulfone, polyamide, and polyimide) [19].

A membrane separates species by selectively permeating certain components of a mixture faster than others through a thin barrier in response to an external driving force, such as a concentration, partial pressure, or, more generally, a chemical potential gradient. A variety of mechanisms influence the separation of gases by a membrane, with the most important being solution diffusion and molecular sieving. Membranes offer a number of inherent advantages over other technologies for separating gases, including (1) simple, passive operation with no moving parts; (2) environmentally benign separation without the use of hazardous chemicals; (3) small footprint, which is critically important in some applications (e.g., aboard aircraft, spacecraft, or on offshore natural gas platforms); and (4) lower energy use because they can separate species without a phase change.

Clearly, membranes represent a promising technology for gas separation; however, they suffer a number of drawbacks, particularly with regard to CO<sub>2</sub> capture from flue gas. In this case, the low CO<sub>2</sub> partial pressure provides a minimal driving force for gas separation, which creates an energy penalty due to the need for compression of the feed gas. Membrane materials also suffer from a decrease in permeability over time due to particulate deposition on the surface [19].

#### 10.2.4 *Fibrous Sorbents*

Solid amine adsorbents using a fibrous structure instead of particles as the matrix are expected to offer amazing benefits (e.g., fast kinetics and high CO<sub>2</sub> capture capacity) for the adsorption of CO<sub>2</sub> because of their high external surface area and porosity, low pressure drops, and flexibility of the matrix fibers. Recently, Li et al. [24] developed a novel fibrous adsorbent for CO<sub>2</sub> capture by coating polyethylenimine (PEI) on a glass fiber matrix using epoxy resin as a cross-linking agent. They found that a maximum adsorption capacity of 6.3 mmol CO<sub>2</sub>/(g of PEI) was obtained at a PEI/epoxy resin ratio of 10:1. Then, they replaced epoxy resin ( $M_w = 370$ ) with a lower molecular weight cross-linking agent (i.e., epichlorohydrin,  $M_w = 92.5$ ) and developed adsorbents of PEI modified glass fibers [23]. The resultant fibrous sorbent improved adsorption performance (e.g., higher CO<sub>2</sub> capacity, faster kinetics, and better regenerability) [25]. The maximum CO<sub>2</sub> adsorption capacity of 13.08 mmol CO<sub>2</sub>/(g of PEI) was achieved at a coating weight of 45 wt%. Polymer supports for amines have attracted considerable attention since they are light in weight, flexible, and easy to handle [6]. Yang et al. [26] demonstrated that solid amine-containing fibrous adsorbent could be prepared by pre-irradiation grafting copolymerization of allylamine onto polyacrylonitrile fiber (PAN-AF). The higher grafting degree resulted in higher CO<sub>2</sub> uptake, and the adsorption capacity of PAN-AF reached 6.22 mmol CO<sub>2</sub>/(g of PAN-AF) at the grafting degree of 60 wt%. They attributed the good performance of this fibrous adsorbent to the fibrous structure, which might

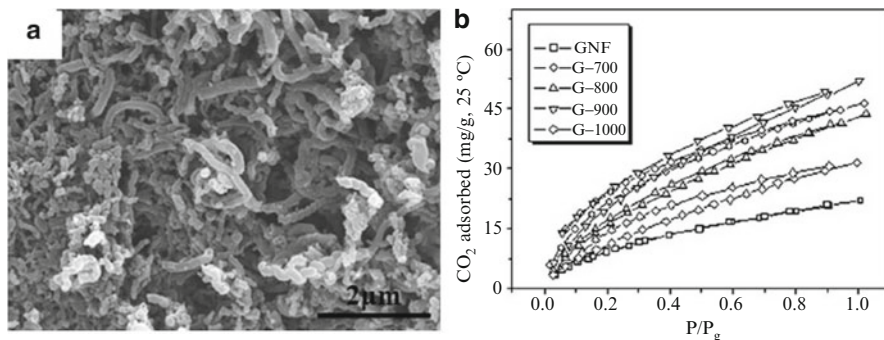
have reduced the resistance to gas flow, thereby maximizing sorbent performance while minimizing energy consumption, and the highly stable interface (i.e., grafting copolymerization of amines onto fibers) between amines and the support [26].

Apart from the amine-modified fibrous adsorbents, porous carbon materials are well-known adsorbents for CO<sub>2</sub> adsorption 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) [27]. Much research has been devoted to the preparation of PAN-based activated carbon fiber (PAN-ACF) from modified PAN, and some attention has been paid to the use of PAN-ACFs for CO<sub>2</sub> removal. Hierarchical porous PAN-ACFs with a large Brunauer-Emmett-Teller (BET) surface area 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 consequently basic sites, leading to a faster adsorption rate and a higher CO<sub>2</sub> adsorption capacity (2.4 mmol/g). Moreover, PAN-ACF adsorbents had stable CO<sub>2</sub> adsorption/desorption performance under multiple cycling conditions [28].

### 10.3 Why Electrospun Nanofibers?

Due to the unique structure and mechanical properties of nanofibers, nanofiber-based sorbents are expected to have extremely low resistance for gas transport and thereby extremely fast kinetics. Due to the high surface area and low density of nanofibers, the developed nanofibrous sorbents are also expected to have high CO<sub>2</sub> capture capacity. Various nanofibrous sorbents (e.g., nanofibrillated cellulose and graphite nanofibers or GNFs) have been developed for CO<sub>2</sub> capture. For instance, Meng et al. [16] found that porous GNFs could be fabricated using a KOH etching method at temperatures in the 700–1,000 °C range (Fig. 10.2a). The CO<sub>2</sub> adsorption isotherms revealed that GNFs treated under 900 °C had the highest BET surface area (567 m<sup>2</sup>/g) and the best CO<sub>2</sub> adsorption capacity of 59.2 mg/g (Fig. 10.2b).

Electrospinning is a simple and versatile technique to produce continuous nanofibers with a diameter down to nanometers. Due to the combination of a high fiber production rate and the simplicity of the setup, the electrospinning approach has the unique ability to produce nanofibers with most materials (organic, inorganic, or hybrid), easily providing various fibers with the desired composition and surface properties [15]. Their high surface-to-volume ratio, large porosity (up to over 80 %), and adjustable functionality make electrospun fibrous membranes useful for numerous applications in particulate gas separation [29, 30].



**Fig. 10.2** (a) SEM image of chemical-treated GNFs. (b) CO<sub>2</sub> isotherms of the pristine and chemical-treated GNFs (Reprinted from Meng and Park [16]. Copyright 2010, with permission from Elsevier)

## 10.4 Electrospun Nanofibers for CO<sub>2</sub> Capture

### 10.4.1 Electrospun Nanofiber-Supported MOF for CO<sub>2</sub> Capture

Great attention has been paid to preparing MOF particles with novel structures and desired properties. Recently, new focus has been placed on the fabrication of supported MOF thin films and membranes [31], particularly given their utility in engineering-related applications such as membrane-based molecular separators, reactors, and chemical sensors [15]. The use of compact substrates and surface modification with organic functional groups are the most commonly used approaches for fabricating MOF thin films [32]. More recently, several attempts have been made to generate more useful MOF membranes by growing continuous MOF crystals on porous organic polymer substrates [33, 34]. Nevertheless, well-intergrown, free-standing, and high MOF-loading films were difficult to achieve. Therefore, a new class of porous substrates with easily tunable structural parameters (e.g., composition, porosity, thickness, and size), in particular, surface properties, or with seed crystals tightly embedded on the surface, is highly desirable.

Nanofibrous membranes produced by electrospinning are ideal porous substrates for developing chemical systems due to their high specific surface area, large porosity, and enormous structural and chemical tenability [15]. Recently, Ostermann et al. [35] reported the fabrication of MOF-containing polymer nanofibers via electrospinning. However, since the MOF particles were embedded in the electrospun polymer nanofibers, an additional diffusion barrier formed around the MOF particles and thus resulted in reduced gas uptake and access into MOFs. In order to overcome this drawback, Wu et al. [15] reported a new strategy to produce free-standing MOF membranes using electrospun nanofibrous membranes as skeletons. A two-step procedure was developed, namely, the preparation of MOF nanocrystal

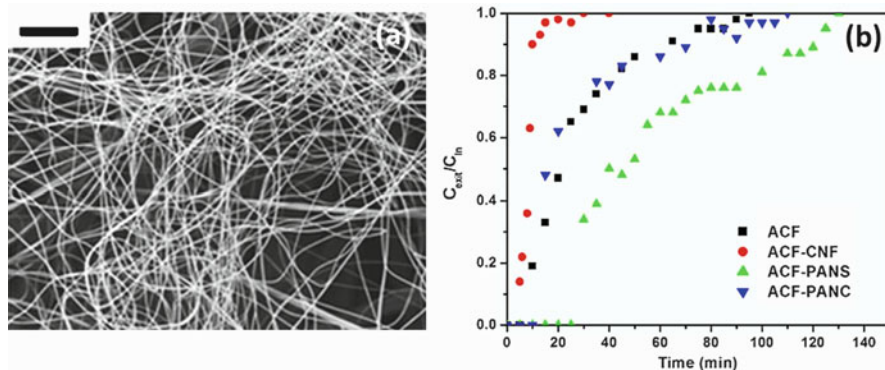
(e.g., zeolite-imidazolate framework-8 or ZIF-8) doped electrospun fibers followed by a second growth. By using a second-growth approach with MOF crystal embedded electrospun fibrous mats as the seeding layer and skeleton, an MOF membrane mostly consisting of MOF crystals was obtained. Compared with the MOF crystal embedded electrospun fibers, the second-growth MOF membranes exhibit a much higher gas adsorption capacity. Gas separation experiments of the prepared free-standing ZIF-8 membrane were tested in custom-made analytical equipment. In the case of the 1:1 mixture of  $N_2/CO_2$ , due to the preferred affinity of ZIF-8 for  $CO_2$  and its high specific surface area, the membrane exhibited capture of the  $CO_2$  component from the mixture. After the “capture” by the ZIF membranes, the proportion of  $CO_2$  (50 %) in the effluent was reduced to less than 30 %, and for  $N_2$ , it increased to more than 70 %. The separation factor of  $N_2/CO_2$  reached 2.4 on average.

### 10.4.2 *Electrospun Carbon Nanofibers for $CO_2$ Capture*

Porous carbon materials have been preferred for  $CO_2$  adsorption due to their highly developed porosity, extended surface area, surface chemistry, and thermal stability. Various carbon materials such as activated carbons, activated carbon fibers (ACF), carbon molecular sieves, and carbon nanotubes have been used as adsorbents for  $CO_2$  [36, 37]. Recently, Bai et al. [38] reported the fabrication of oxyfluorinated activated electrospun carbon nanofibers (OFACFs) for  $CO_2$  capture. Electrospun CFs were prepared from a PAN/*N,N*-dimethylformamide (DMF) solution via electrospinning and heat treatment. The electrospun CFs were chemically activated in order to generate the pore structure, and then oxyfluorination was used to modify the surface. Through the  $N_2$  adsorption isotherm, the specific surface area and pore volume decreased slightly as a result of oxyfluorination treatment. Nevertheless, the  $CO_2$  uptake of OFACFs increased up to 16.2 wt% due to the highly developed microporous structure and semi-ionic interaction effect of oxyfluorination. The mechanism of the improved effects of oxyfluorinated activated carbon nanofibers was proposed. The nonpolar  $CO_2$  molecules near the carbon pores are affected by the semi-ionic interaction of oxygen groups, which has the lone-pair electron, causing the electron attraction in the  $CO_2$  molecules. This reaction might play an important role as a guide for enhancing the  $CO_2$  storage capacity. Eventually, the  $CO_2$  gas can be stored in the silt pores of carbon. Some of the residual  $CO_2$  molecules in the carbon silt pores can also be affected by oxygen group effects, such as the grabbing effects due to semi-ionic interaction, resulting in the high efficiency of  $CO_2$  storage [38].

Recently, Katepalli et al. [39] reported the synthesis of a carbon polymer micro-/nanocomposite by electrospinning PAN nanofibers directly onto ACF substrates to prepare hierarchical fabric structures (ACF-PANS) (Fig. 10.3a). The composite materials were subsequently pyrolyzed, followed by steam activation, to yield the hierarchical activated carbon fabrics consisting of PAN-derived carbon nanofiber (CNF) on ACF (ACF-PANC). These multi-scale fabrics (ACF-PANS



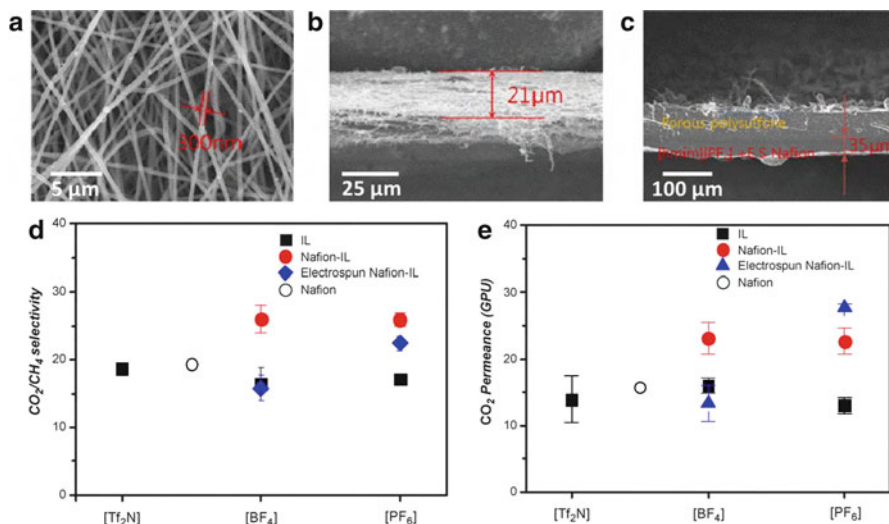


**Fig. 10.3** (a) SEM image of ACF-PANS (scale bar equals to 20  $\mu\text{m}$ ) and (b) breakthrough profiles of  $\text{SO}_2$  over different materials (ACF, ACF-CNF, ACF-PANS, and ACF-PANC) (Reprinted from Katepalli et al. [39]. Copyright 2011, with permission from Elsevier)

and ACF-PANC) were tested for their adsorption properties toward common atmospheric pollutants (e.g.,  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{NO}$ , and toluene), and the performance was compared to ACF and another hierarchical carbon fabric fabricated by growing carbon nanofibers on metal-impregnated ACF (ACF-CNF) by chemical vapor deposition. Interestingly, the performance of the ACF-PANS was found to be superior to that of ACF, ACF-PANC, and ACF-CNF fabrics (Fig. 10.3b). The superior adsorptive performance of ACF-PANS may be attributed to the large number of nitrogen-based surface functional groups, which favored the adsorption and catalytic oxidation of  $\text{SO}_2$  or  $\text{CO}_2$ .

### 10.4.3 Ionic Liquid-Based Nanofibrous Membranes for $\text{CO}_2$ Separation

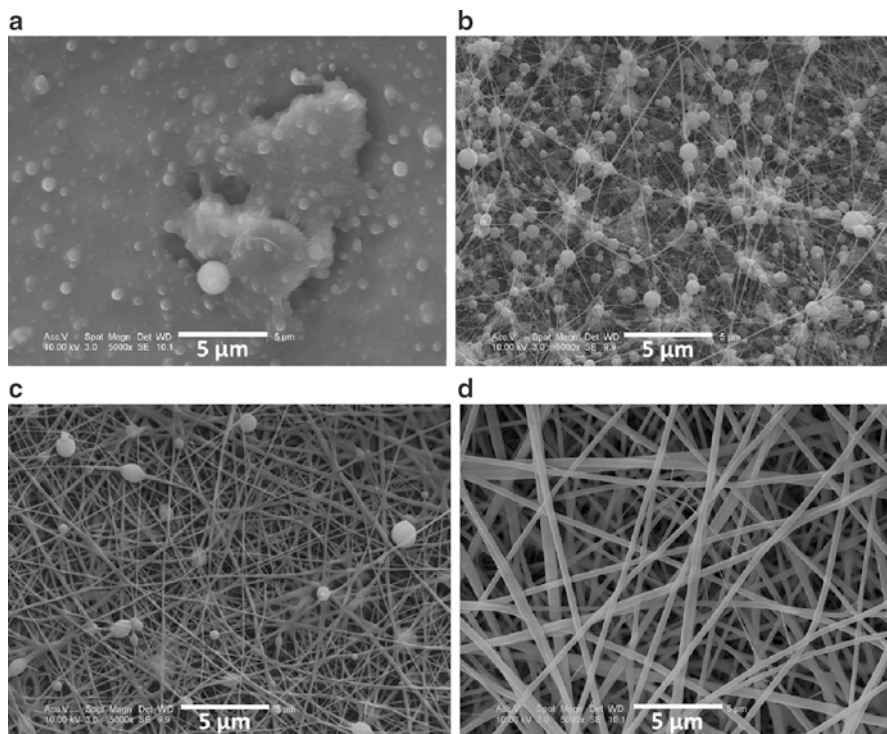
To date, many kinds of  $\text{CO}_2$  separation membranes have been reported, including polymeric membranes, composite membranes, and facilitated transport membranes. Further improvements in membrane performance depend on effective  $\text{CO}_2$  separation materials, and one candidate is ILs. It has been reported that ILs have good  $\text{CO}_2$  selectivity, suggesting that they may be a possibility for the development of new  $\text{CO}_2$  separation materials. Since ILs are liquid at room temperature, it is necessary to affix ILs to appropriate support materials. Supported IL membranes have been prepared by impregnation of commercial porous polymer films with 1-*n*-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([hmim][Tf<sub>2</sub>N]) and have obtained good  $\text{CO}_2/\text{He}$  separation properties [40]. Recently, electrospun Nafion/polyethylene oxide (PEO)-supported IL membranes were fabricated for  $\text{CO}_2$  separation [41]. In this composite membrane, the electrospun Nafion/PEO material acted as a gutter layer for ILs and PEO was added to form clean nanofibrous



**Fig. 10.4** SEM images of the (a) surface and (b) cross-section of an electrospun Nafion/PEO composite membrane. (c) Cross-sectional image of an electrospun Nafion/PEO composite membrane containing [hmim][PF<sub>6</sub>]. (d) Ideal selectivity and (e) CO<sub>2</sub> permeance of the membrane prepared with IL, electrospun Nafion-IL, and Nafion-IL membranes (Reprinted from Yoo et al. [41]. Copyright 2010, with permission from Elsevier)

membranes via electrospinning. Figure 10.4 shows the representative scanning electron microscopy (SEM) images of the Nafion/PEO electrospun structures. It can be seen that dry membranes are composed of numerous randomly oriented fibers with diameters of about 300 nm (Fig. 10.4a). The SEM image of IL-swollen Nafion membranes showed that almost all the voids among fibers were filled (Fig. 10.4c). Figure 10.4d and e presents the CO<sub>2</sub> separation parameters of IL, Nafion-IL dense membranes, and electrospun Nafion/PEO supported IL membranes. The gas permeance and selectivity of electrospun Nafion/PEO/[hmim][BF<sub>4</sub>] maintained the characteristics of supported IL membranes containing [hmim][BF<sub>4</sub>], while the CO<sub>2</sub> permeance through the electrospun Nafion/PEO/[hmim][PF<sub>6</sub>] increased from 20 to 28 GPU. The selectivity of CO<sub>2</sub>/CH<sub>4</sub> slightly increased from 17.1 to 22.4, implying that the high adsorption of [hmim][PF<sub>6</sub>] into Nafion made a definite contribution in CO<sub>2</sub> separation.

Recently, Tang et al. [21] reported that poly(ionic liquids) showed significantly enhanced and fast CO<sub>2</sub> absorption compared to ILs. Especially, the polymers of tetraalkylammonium-based ILs have CO<sub>2</sub> sorption capacities 6.0–7.6 times of those of room temperature ILs. Electrospinning of the poly(ionic liquid) solution was first demonstrated by Chen and co-workers [42]. Figure 10.5 shows the electrospun fibers from various concentrations of poly(1-[(2-methacryloyloxy)ethyl]-3-butylimidazolium tetrafluoroborate or MEBIm-BF<sub>4</sub>) in cosolvent 3/1 acetonitrile/DMF. At 2.5 wt%, a concentration below the entanglement concentration, only droplets were obtained (Fig. 10.5a). Beaded fibers were observed at 5 and

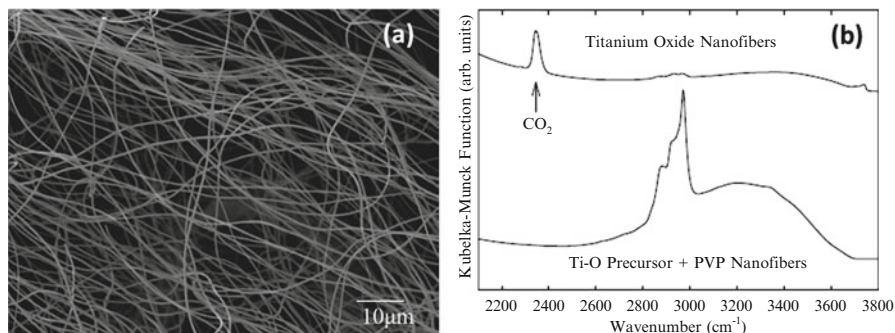


**Fig. 10.5** Concentration effect on the electrospinning of poly(MEBIm-BF<sub>4</sub>) in 3/1 acetonitrile/DMF. Polymer concentrations: (a) 2.5, (b) 5, (c) 6, and (d) 8 wt% (Reprinted with the permission from Chen and Elabd [42]. Copyright 2009 American Chemical Society)

6 wt% (Fig. 10.5b, c) and defect-free fibers were formed at 8 wt% (Fig. 10.5d). Due to high solution conductivities, electrospinning produces fibers approximately an order of magnitude smaller than neutral polymers at equivalent normalized solution concentrations. Although the CO<sub>2</sub> capture performance of poly(ionic liquid) nanofibers has not been reported, we can expect that these novel nanofibrous materials will be very prospective as sorbent and membrane for CO<sub>2</sub> separation.

#### 10.4.4 CO<sub>2</sub> Sequestered in Electrospun Metal Oxide Nanofibers

Most of the electrospinning procedures that yield metal oxide nanofibers involve pyrolysis of a guide polymer as a final processing step. Bender and co-workers demonstrated, using diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS), that CO<sub>2</sub> is sequestered in electrospun metal oxide nanofibers upon



**Fig. 10.6** (a) SEM image of TiO<sub>2</sub> nanofibers and (b) DRIFTS spectra of TiO<sub>2</sub> nanofibers before and after pyrolysis (Reprinted from Bender et al. [43]. Copyright 2006, with permission from Elsevier)

removal of the guide polymers by pyrolysis [43]. CO<sub>2</sub> is not present before pyrolysis and is formed during combustion of the polymer. Figure 10.6 shows a representative SEM image of titania (TiO<sub>2</sub>) nanofibers after 700 °C pyrolysis. When the composite nanofibers are heated to 700 °C, it shows a DRIFTS feature around 2,340–2,350 cm<sup>-1</sup> from CO<sub>2</sub> (Fig. 10.6b). They propose that CO<sub>2</sub> is trapped within the fibers as opposed to being adsorbed on the surface and the nature of the metal oxide nanofiber structure is responsible for the CO<sub>2</sub> entrapment.

## 10.5 Concluding Remarks and Outlook

CO<sub>2</sub> removal from post-combustion flue gas at large point sources has been spotlighted in recent years as a potential way to reduce greenhouse gas emissions. Among a range of separation technologies, adsorption with nanomaterial-based sorbents is emerging to be one of the most promising CO<sub>2</sub> capture strategies. In this chapter, we reviewed recent progress in developing electrospun nanofibrous sorbents with potential applications for CO<sub>2</sub> removal. Clearly, the selection of capture materials is essential for any technologies in CO<sub>2</sub> removal. In general, nanofibrous materials have advantages such as ease of design and synthesis, high porosity, tailored pore properties, high surface area, and good mechanical properties, which make them highly attractive for the development of sorbents with high CO<sub>2</sub> capture capacity and fast kinetics.

Despite recent advances toward the development of nanofibrous sorbents for CO<sub>2</sub> capture applications, several challenges still remain. (1) Some nanofibrous materials do not have CO<sub>2</sub> adsorption ability until they are modified with amine groups or ILs as described in this chapter. However, the undesired blocking of fiber surfaces/interior with amines or ILs will reduce CO<sub>2</sub> capacity and kinetics of the adsorbents. Further research should focus on the achievement of effective surface

modification strategies. For example, surface modifying nanofibrous materials using layer-by-layer nano-assembly technology [44, 45] by depositing a CO<sub>2</sub>-adsorbing amine polymer will be a potential method to solve this problem. (2) The gas flows treated in practical CO<sub>2</sub> capture always involve 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 superhydrophobicity. However, quite few investigations of the effect of water on the capture performances of nanofibrous adsorbents have been reported. Addressing this issue should include research on both the physical co-adsorption of water in the nanofibrous materials and the material structure and functional design. (3) In parallel with experimental studies, computational modeling methods must be further developed as a tool to predict the performance of nanofibrous sorbents which are proposed for a given separation process. Despite the numerous challenges surrounding CO<sub>2</sub> removal, further understanding of fibrous sorbent structure-property relationships and the subsequent improvement of sorbent performance under realistic operating conditions will likely allow for the realization of nanofibrous sorbents in practical CO<sub>2</sub> capture processes in the near future.

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