FOCUS REVIEW

Hydrogel particles for CO_2 capture

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Abstract

Capturing CO_2 from various sources, such as postcombustion exhaust gases and the atmosphere, is essential for a sustainable human society. Effective CO_2 separation materials such as adsorbents and membranes are of utmost importance in efficient CO_2 capture. This short review is focused on CO_2 separation materials consisting of hydrogel particles. The first chapter introduces stimuli-responsive micro- and nanogel particles that reversibly absorb CO_2 in response to thermal stimuli. The development of temperature-responsive hydrogel films comprising gel particles for reversible CO_2 capture is introduced. The importance of choosing amines with optimal pK_a values for efficient CO_2 capture from various sources is explained in detail. The assembly of CO_2 separation membranes consisting of amine-containing hydrogel particles is introduced in the final chapter. The paper highlights the promise of separation materials consisting of hydrogel particles for efficient CO_2 capture from postcombustion gases and air and the prospects for further advances in this area.

Introduction

The development of efficient CO_2 capture processes is crucial for rebalancing the global carbon cycle [1–3]. Chemical absorption processes using aqueous amine solutions to absorb CO_2 have been the standard industrial processes for CO_2 capture. However, high temperatures and large amounts of energy are needed to regenerate the solutions that absorb CO_2, which limits the use of this process for carbon capture from sources with low concentrations of CO_2, such as postcombustion gases (~10 vol% CO_2) and air (400 ppm CO_2), for economic reasons. Thus, the development of materials and processes that do not require high temperatures and large energy input is of great importance.

Several porous solid sorbents, such as activated carbon [4], metal-organic frameworks (MOFs) [4, 5], zeolites [4, 5], and physically or chemically supported amine polymers [4–9] that can be regenerated under relatively mild conditions, have been proposed to address the aforementioned problems. These sorbents show large absorption/adsorption capacities of up to ~3 mmol CO_2 g^{-1} [4–9] due to the large surface areas of the pores in the sorbents. However, most porous sorbents cannot be used without drying the gases before CO_2 capture because water adsorption competes with CO_2 and/or capillary condensed water to prevent gas diffusion in the pores [4–9]. Thus, the development of solid sorbents that work in wet conditions and can be regenerated under mild conditions is of great interest.

The membrane separation process has been developed as an alternative approach for CO_2 capture [10–12]. Ideal membranes showing highly selective permeation of CO_2 enable CO_2 capture without heat. To realize the ideal membrane, ultrathin membranes without defects must be prepared that allow rapid sorption, diffusion, and desorption of CO_2 and minimal sorption of competing gases [10]. Defect-free thin membranes consisting of graphene oxide [13], metal–organic frameworks [14], polymers [15–17], zeolites [18], organic/inorganic interpenetrating networks [19], and liquid water [20] have been reported. However, further improvements in their CO_2 permeabilities and selectivities are needed [21].

This short review is focused on the development of hydrogel particles for CO_2 capture. Hydrogels are aqueous materials solidified by polymer networks. Diffusion of the solutes in the gels is much faster than it is in other solids and comparable to those of liquids [22–24], so it is attractive for CO_2 absorption and CO_2 separation membranes [25]. The chemical properties of gels, such as the equilibrium and kinetics for CO_2 absorption, can be tuned by introducing

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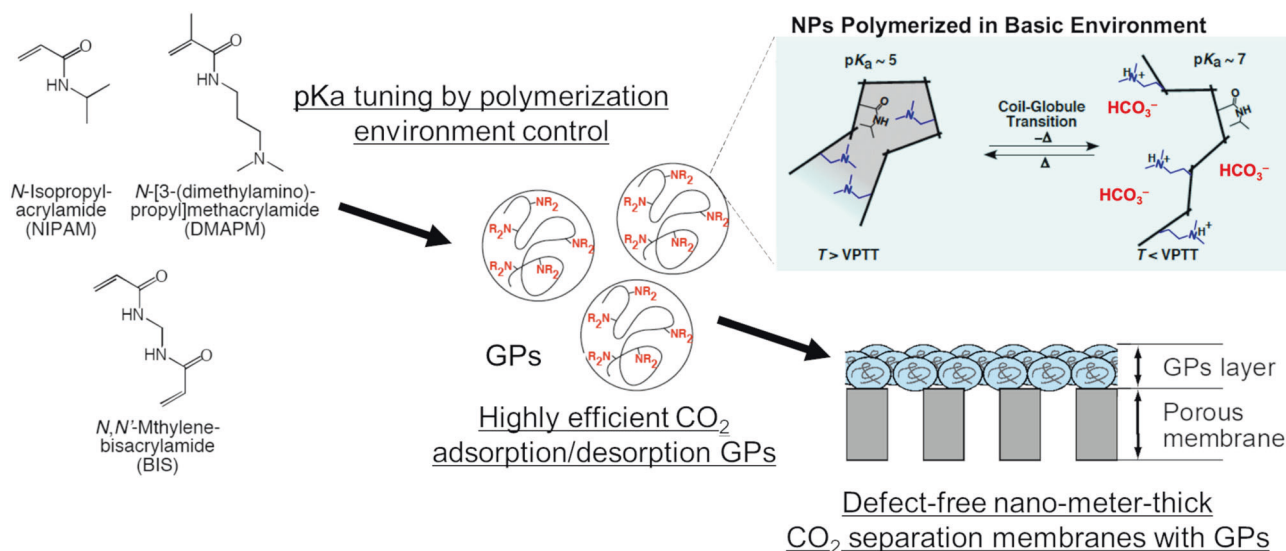   Motooka, Nishi-ku, Fukuoka 819-0395, Japan

Fig. 1 Overview of this review

appropriate functional groups into the hydrogels and designing the structures of the polymers [26–28]. The physical properties of gels, such as the viscoelasticity, flexibility, adaptability, deformability, and diffusivity, can also be tailored by selecting the properties and structures of the polymers [26–28].

Temperature-responsive hydrogels with various functions have been designed with poly-N-isopropyl acrylamide (pNIPAm) as the network polymer. pNIPAm is highly hydrated at low temperatures, but above the lower critical solution temperature (LCST), the nonpolar side chains dehydrate and aggregate, which causes precipitation of the polymer [29–44]. Hydrogels composed of pNIPAm swell at temperatures below the LCST but shrink due to dehydration when the temperature is raised above the LCST. Various stimulus-responsive gels have been proposed that use these volume phase transitions (VPTs). In volume phase transitions of bulk gels, dense polymer layers, named the skin layers, formed on the surface of the gel during VPT restricts mass transfer of water from inside to outside the gels. Thus, the VPT of the entire gel takes a long time [45]. On the other hand, hydrogel particles with particle sizes ranging from tens of nanometers to micrometers have very large surface areas relative to the volume of each gel, so they show rapid VPTs [46].

CO$_2$ absorbents that reversibly absorb CO$_2$ in response to small temperature changes have been developed to take advantage of the quick temperature-responsive changes of nano- to micrometer-sized hydrogel particles [26, 27, 47, 48]. The flexibilities and shape adaptabilities of the gel particles enabled the formation of temperature-responsive hydrogel films on the surfaces of various substrates for reversible CO$_2$ capture [26, 49, 50]. It has also

been reported that polymerization as well as the combinations and populations of functional monomers in particles can be engineered to optimize adsorption for efficient CO$_2$ capture from various CO$_2$ sources [26, 27, 51]. The deformabilities of the particles enabled assembly of defect-free nanometer-thick CO$_2$ separation membranes consisting of the particles. The development of each material is reviewed in this manuscript (Fig. 1) [21].

Stimuli-responsive micro- and nanogel particles that reversibly adsorb CO$_2$ in response to thermal stimuli

Aqueous amine solutions (such as ethanol amine) have been tested for CO$_2$ capture from point sources such as fossil fuel power plants [52, 53]. The amine solutions absorbed CO$_2$ at low temperatures (~40 °C) via an exothermic reaction and desorbed the CO$_2$ upon heating (>120 °C) [54–57]. Although this amine process, called a chemical absorption process, exhibits a high capacity for CO$_2$ capture, a high energy consumption equivalent to 20–40% of that for a typical power plant output prevented sustainable use of this process [55–60]. Furthermore, amines are easily oxidized and volatilized during high-temperature regeneration and need must recovered to avoid air pollution [61]. Thus, nonvolatile sorbents that desorb CO$_2$ at low temperatures (<100 °C) must be developed [54, 62].

In the bloodstreams of living animals, a protein called hemoglobin plays a key role in efficient CO$_2$ transport in an ambient environment. The dynamic and reversible shifts of the pK_a values of Brønsted acids and bases in hemoglobin are crucial for energy-efficient CO$_2$ transport (Bohr effect)

Fig. 2 Illustration of reversible CO₂ absorption triggered by phase transitions of amine-containing micro- and nanogel particles [26, 47]
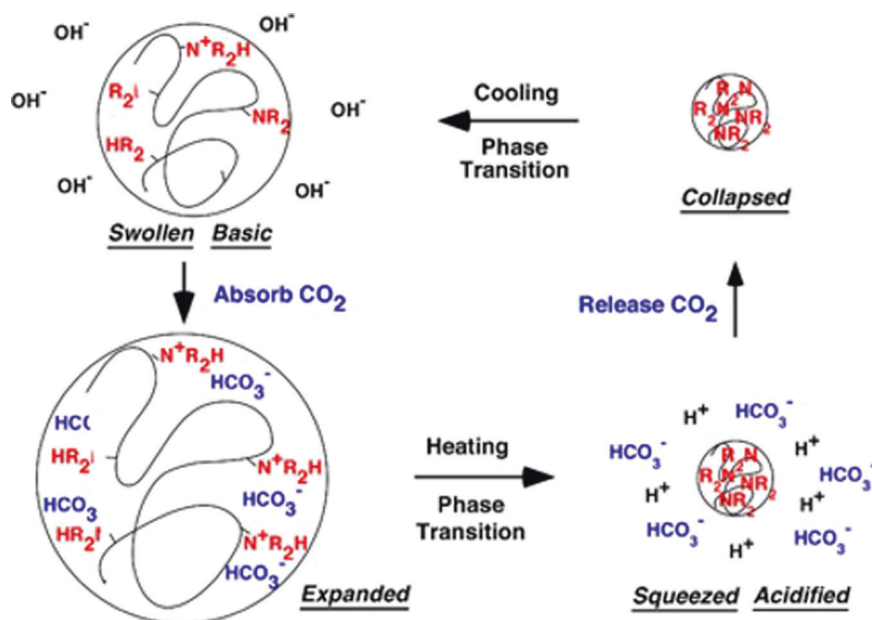
[63, 64]. In the lungs, the pK_a of the ammonium and imidazolium ions in/on hemoglobin decrease due to drastic conformational changes of the polypeptides caused by oxygen binding to heme. The pK_a shift triggers the release of protons into the blood, lowers the pH of the blood, and drives efficient CO₂ release from the lungs without heating the system. When hemoglobin reaches a capillary blood vessel where the concentration of oxygen is low, dissociation of oxygen from the heme triggers a change in the conformation back to the original structure. Subsequently, the pK_a values of the ammonium and imidazolium ions in/on the hemoglobin increase back to their original values. The high pK_a of the ammonium ions on the hemoglobin enables efficient CO₂ capture from the tissues around the capillaries in the form of ammonium and imidazolium bicarbonates.

Motivated by the process of reversible ion capture instigated by the structural transitions in proteins, the research conducted by Shinkai and his team is of significance [65, 66]. It has also been reported that temperature-responsive pNIPAm hydrogel films, nanoparticles (GPs), and fibers comprising functional groups reversibly captured targets such as ionic dyes [67, 68], drugs [40, 69], peptides [33], proteins [70, 71], nucleotides [30], and cells [72] during heating and cooling cycles. The ability of pNIPAm GPs to capture target ions [37], peptides [33], and proteins [35] can be enhanced by polymerizing the GPs in the presence of target molecules that serve as templates. During molecular/ion imprinting polymerization, the three-dimensional structure of the target molecule is imprinted into the polymer matrix to generate complementary binding sites within the network after extraction [37, 73, 74]. The imprinted GPs showed greater affinity

shifts in response to phase transitions than the nonimprinted GPs [26].

Recently, it was reported that the pK_a values of Brønsted acids and bases incorporated in pNIPAm shifted reversibly in response to phase transitions of the polymers, which were induced by cooling-heating cycles [30, 33, 70–72, 75]. pNIPAm-based GPs that show large and reversible pK_a shifts can be prepared by the "proton imprinting" [37] and "microenvironment imprinting" [31] strategies. When acidic monomers such as acrylic acids are protonated during the polymerization process, the protonated acids are incorporated into the hydrophobic domains of the growing dehydrated-pNIPAm GPs and are subsequently stabilized with cross-linkers. As a result, acids with high pK_as were imprinted in the GPs. When the degree of cross-linking was not too high, the structures of the high-pK_a acidic sites were reversibly denatured by temperature-induced conformational changes of the polymer chains, resulting in large, reversible pK_a shifts. The greatest pK_a variation range observed in proton-imprinted GPs was significantly larger than that of the non-imprinted particles (the particles polymerized with deprotonated acrylic acids) and enzymes that transport protons in the blood [64]. The pK_a shift enabled reversible capture and release of the target ions [31, 37, 47, 76, 77].

Taking advantage of the reversible pK_a shifts of the pNIPAm GPs, materials that reversibly absorb and desorb CO₂ via phase transitions induced by small temperature changes were synthesized (Fig. 2) [47, 76, 77]. Amine-containing monomers, such as N-[3-(dimethylamino)propyl]methacrylamide (DMAPM), were incorporated into the GPs as functional units to capture CO₂ at 30 °C, which is below the volume phase transition temperature (VPTT). Most amines present in the swollen GPs undergo

Fig. 3 Fabrication methods for energy-efficient temperature-responsive GP films with high absorption capacities and reversible CO_2 absorption-desorption characteristics in response to temperature [50]
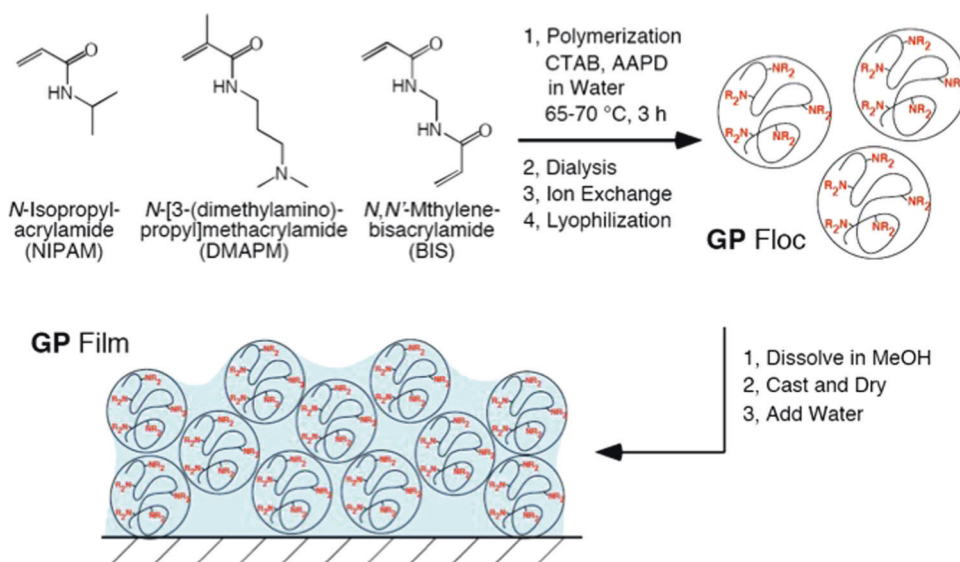
protonation and create ion pairs with the absorbed bicarbonate ions. However, at 75 °C, above the VPTT, shrinkage of the GPs lowers the pK_as of the protonated amines (ammonium ions), thereby resulting in almost complete desorption of CO_2. The amines in the GPs undergoing VPTs reversibly absorb more CO_2 than the DMAPM monomer and polymer without VPTs. This indicates the importance of polymer temperature-responsive phase transitions in determining the degree of absorption.

Development of temperature-responsive hydrogel films comprising microgel particles for reversible CO_2 capture

The amount of CO_2 reversibly absorbed by amines in the GPs during a small temperature change was greater than those of traditional CO_2 absorbents such as ethanolamine [47]. However, the absorption capacity per weight of the absorbent solution was very small because the concentration of GPs in the solution (~0.1 wt%) was much lower than those of traditional amines (20–30 wt%) [47]. As a result, the energy consumed by the GP solution in separating CO_2 was significantly larger than those of amine solutions, despite the use of a low temperature for the regeneration process. To improve the energy efficiency, the amount of water had to be dramatically reduced.

Hydrogel films consisting of temperature-responsive GPs (GP films) were developed to prepare energy-efficient CO_2 absorbents with high absorption capacities per weight [26, 50]. The films were prepared by simply casting a solution of the temperature-responsive GPs onto the surface of a solid substrate. The films combined the best of the high stoichiometric absorption efficiencies of the GP solutions

with the large absorption capacities per weight of the solid sorbents. Furthermore, it was revealed that the GP films responded much faster to external stimuli than monolithic hydrogel films (Fig. 3) [26, 50].

Tuning the pK_as of amines in the particles to design thermally responsive particle films that reversibly absorb large amounts of CO_2 from postcombustion gases

The capacity for reversible absorption by a GP film can be enhanced with the use of more DMAPM. However, GPs with larger amounts of DMAPM do not always release CO_2 completely during heating [26]. In the fabrication of thermally responsive GP films capable of capturing and liberating substantial quantities of CO_2 within a confined temperature range (30–75 °C), meticulous optimization of the pK_a values for the ammonium ions in the GPs at both the CO_2 absorption (30 °C) and release (75 °C) temperatures is required [26]. At 30 °C, a sufficiently high pK_a value of the ammonium ion is needed to drive the reaction between the amine and CO_2 to form ammonium bicarbonate for efficient CO_2 capture. Conversely, a sufficiently low pK_a is needed to protonate bicarbonate at 75 °C for efficient release of the CO_2.

Yue et al. reported that the pK_a values of GPs containing DMAPM were readily adjusted to the desired level via four methods [26]. These were: (1) Controlling the VPTT of the GPs above and close to the absorbing temperature (30 °C) so the phase transition induced a large pK_a shift over a wide temperature range above the VPTT. The VPTT is increased by incorporating larger amounts of amines in the particles but decreased by replacing the NIPAm with more hydrophobic monomers such as *N-tert*-butylacrylamide (TBAm). (2)

Controlling the sizes of the GPs, since smaller GPs show higher pK_a values because the proportion of amines incorporated in the polar microenvironment on the exterior of the gel particles increases for smaller GPs. (3) Regulating the swelling ratio, which impacts the extent of the pK_a fluctuations and, in turn, directly affects the pK_a of the GPs. The particles with larger amounts of cross-linker showed less swelling during the cooling process, which limited the pK_a increase for the of ammonium ions in the GPs. (4) Controlling the imprinted microenvironments of amines in the GPs. Amines in the GPs that were synthesized in acidic environments showed relatively high pK_a values because the amines were protonated and thus incorporated into the hydrophilic microenvironment. On the other hand, amines in the GPs synthesized in a basic environment showed relatively high pK_as because the amines were protonated and thus incorporated into the hydrophilic microenvironment.

The optimal GPs comprising the designed proportions of 55 mol% DMAPM, 43 mol% TBAm, and 2% N,N'-methylenebis(acrylamide) (BIS), showed a high capture capacity (68 mL CO_2/g dry GPs, 3.0 mmol CO_2/g dry GPs) for simulated postcombustion gases (10% CO_2, water-saturated gas), although the regeneration temperature was as low as 75 °C. The GP film comprising these GPs is expected to become a new CO_2 absorbent used to separate CO_2 from large point sources such as fire power plants with low energy costs.

Importance of optimizing the pK_a values of amines in the particles for efficient CO₂ capture from various CO₂ sources

Honda et al. reported the design principles for temperature-responsive hydrogels used with various CO_2 concentrations [27]. Computational predictions and experimental observations indicated that the pK_as of the ammonium ions in the hydrogel particles must be tuned based on the concentration of CO_2. It was shown that a pK_a of approximately 8 was sufficient to absorb relatively concentrated CO_2 (~10%), such as that in postcombustion exhaust gas, whereas a pK_a of 10 or more was needed to absorb dilute CO_2 efficiently, such as that in the atmosphere (400 ppm).

Tuning the structures, combinations, and populations of functional groups in the hydrogels

Hydrogels with various functional groups have been proposed for use as CO_2 absorbents. Early studies reported the effects of the polymerization conditions and the comonomer compositions on CO_2 absorption by hydrogel particles

using DMAPM, a commercially available tertiary amine-containing monomer [47]. NIPAm and TBAm were used as comonomers to achieve ideal VPTs [26]. A small amount of BIS, a water-soluble cross-linker, was added to adjust the degree of swelling of the gel particles [26].

Rieger et al. proposed a microgel-based CO_2 absorbent in which acrylamide with 2,2,6,6-tetramethyl-piperidine, which is a cyclic secondary amine, was copolymerized with NIPAm and BIS [78]. The particles showed a VPTT with a large shift in pK_a from 8.6 (at room temperature) to 6.7 (at 85 °C) with increased temperature. An aqueous solution of the gel particles reversibly and quickly released CO_2. Rieger et al. also proposed a temperature-responsive CO_2 absorbent consisting of polyethylenimine functionalized with a hydrophobic functional group [79]. Polyethylenimine that was partially acylated with butyric anhydride (b-PEI) showed an LCST together with a reversible pH shift in water. The solution showed improved CO_2 release associated with the LCST behavior of the polymer.
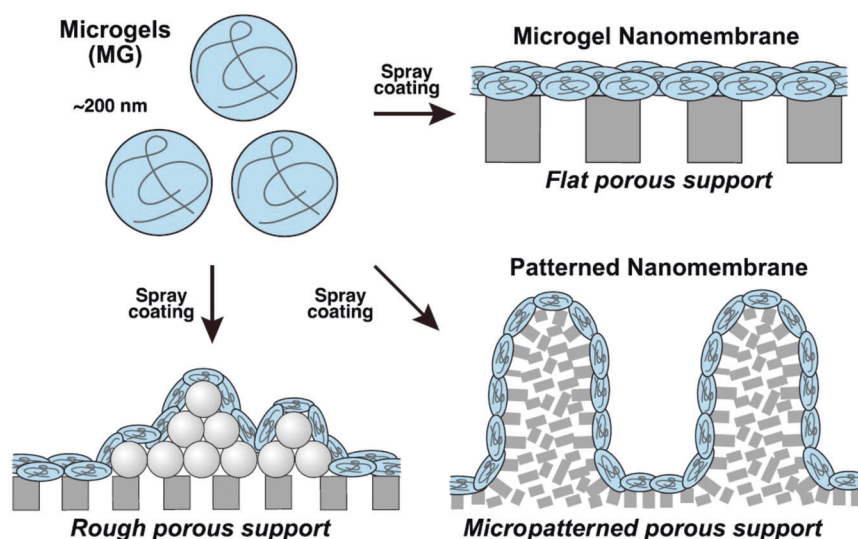
Yue et al. proposed a temperature-responsive hydrogel-based CO_2 absorbent composed of polyvinylamine, which is a typical primary polyamine [48]. Microgels with poly-vinyl amine (PVAm) were synthesized by copolymerizing N-vinylformamide with pNIPAm and BIS followed by hydrolysis of formamide with strong acids. Temperature-responsive gel particles with high colloidal stabilities and a large amounts of primary amine (3.2 mmol/g) were synthesized by increasing the amount of BIS introduced along with the increased content of the vinylamine.

The design principle for a temperature-responsive hydro-gel film consisting of linear polymers was reported by Yue et al. [51]. Reversible CO_2 capture by hydrogel films consisting of acylated PVAm copolymers, as well as blended films with the homopolymer of PVAm and 100% acylated PVAm, were compared in detail. The findings indicated that simply by combining with temperature-responsive polymers, the efficiency of reversible CO_2 capture by the polyamine films was enhanced. While the homopolymer films prepared through blending demonstrated marginally lower capacities for reversible CO_2 absorption compared to their partially acylated copolymer counterparts, the strategy of polymer blending remains appealing due to the ease of creating high-performance films merely by combining readily available and/or inexpensive materials.

Assembly of CO₂ separation membranes consisting of amine-containing hydrogel particles

CO_2-separation membranes are of great interest for energy-efficient CO_2 capture because they enable complete CO_2 separation without heat consumption [10, 11, 80]. To

achieve ideal membranes, materials that allow fast CO_2 absorption, diffusion, and release should be developed. Hydrogels are attractive options for separating CO_2 due to their high solute diffusivities, which are comparable to those of liquids [22–25].

Taniguchi and colleagues found that hydrated amine-containing membranes made of poly(vinyl alcohol) (PVA) and 3-(1-piperazinyl)-1,2-propanediol (PzPD) exhibited highly selective permeation of CO_2 against hydrogen [81]. Amine-containing PVA membranes with thicknesses of 3–10 μm were fabricated by casting an aqueous solution of PVA and the amine on a flat surface followed by drying. The high concentration and diffusivity of the bicarbonate ions in the membrane enabled selective CO_2 permeation.

Hoshino et al. proposed that ultrathin defect-free hydrogel membranes (hydrogel nanomembranes) for CO_2 separation could be prepared by coating an aqueous suspension of amine-containing colloidal hydrogel particles (GPs) onto a porous support [21]. Given that the pores are hydrophilic and the pore dimensions are smaller than the microgel hydrodynamic diameter, planar, coarse, and microstructured porous membranes can be used as substrates. The deformable characteristics of the GPs facilitated autonomous assembly of defect-free CO_2 separation layers with thicknesses of 30 to 50 nm, which originated from deformed discoidal entities approximately 15 nm thick. (Fig. 4)

Dried films with tertiary amine groups did not exhibit significant CO_2 permeance. However, when the membranes were adequately hydrated to form a hydrogel, the CO_2 permeance dramatically increased, indicating that free water in the membranes enabled quick bicarbonate ion diffusion. Selective CO_2 permeance (850 GPU, $\alpha CO_2/N_2 = 25$) against simulated postcombustion gases (10% CO_2, water-saturated gas) was observed for the hydrogel nanomembranes contained in amine (DMAPM)-containing gel particles. In addition, acid-containing microgel membranes, when doped with amines, displayed exceptional CO_2 selectivity against simulated postcombustion gases (1010 GPU, $\alpha CO_2/N_2 = 216$) as well as in direct air capture (1270 GPU, $\alpha CO_2/N_2 = 2380$). The versatile route of fabricating hydrogel nanomembranes via autonomous assembly of deformable GPs will enable large-scale manufacturing of high-performance separation membranes and low-cost carbon capture from postcombustion gases and air.

Prospective

In this paper, we briefly reviewed the recent developments in CO_2 separation materials consisting of hydrogel particles. By taking advantage of temperature-responsive shifts in the pK_a values of ammonium ions in the amine-containing micro- and nanogel particles induced by quick and reversible volume phase transitions of the particles, CO_2 absorbents that reversibly absorb CO_2 in response to small temperature stimuli have been developed. The flexibilities and shape adaptabilities of the gel particles enabled the formation of temperature-responsive hydrogel films on the surfaces of various substrates for reversible CO_2 capture. The polymerization conditions as well as the combinations and feed ratios of the functional monomers in the particles were optimized for efficient CO_2 capture from various sources. The deformability of the gel particles allowed the assembly of defect-free nanometer-thick CO_2 separation membranes consisting of amine-containing hydrogel particles. Although durability tests and the development of separation processes are needed, the excellent mass production capability of hydrogel particles in addition to their high functionalities will provide low-cost CO_2 separation from postcombustion gases and air.

Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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