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Temperature-Responsive Microgel Films as Reversible Carbon Dioxide Absorbents in Wet Environment**

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Abstract: *Hydrogel films composed of temperature-responsive microgel particles (GPs) containing amine groups work as stimuli-responsive carbon dioxide absorbent with a high capacity of approximately 1.7 mmol g^{-1}. Although the dried films did not show significant absorption, the reversible absorption capacity dramatically increased by adding a small amount of water (1 mL g^{-1}). The absorption capacity was independent of the amount of added water beyond 1 mL g^{-1}, demonstrating that the GP films can readily be used under wet conditions. The amount of CO_2 absorbed by the GP films was proportional to their thickness up to 200–300 μm (maximum capacity of about 2 L m^{-2}). Furthermore, the films consisting of GPs showed faster and greater absorption and desorption of CO_2 than that of monolithic hydrogel films. These results indicated the importance of a fast stimulus response rate of the films that are composed of GPs in order to achieve long-range and fast diffusion of bicarbonate ions. Our study revealed the potential of stimuli-responsive GP films as energy-efficient absorbents to sequester CO_2 from high-humidity exhaust gases.*

The worldwide use of fossil fuels has led to the accumulation of CO_2, a primary greenhouse gas, which has contributed to the global climate change.[1] At the same time, CO_2 can be a potential carbon source for the production of liquid fuels such as methanol and dimethyl ether by using regenerative energy.[2] Thus, the development of energy-efficient and scalable CO_2-capture processes from high-humidity exhaust gases of point sources such as fossil fuel power plants is essential for the future use of carbon-based energy.

The capture of CO_2 from high-humidity exhaust gases of power plants using aqueous solutions of amines such as ethanol amine and sterically hindered amines as absorbents has been considered to be the most implementable process.[3] The amine solutions absorbed CO_2 at a low temperature (about 40 °C) by an exothermic reaction and desorbed CO_2 upon heating (>140 °C).[4] Though these conventional methods exhibited a high capacity for CO_2 capture, they have drawbacks as well, such as reactor corrosion and high-energy consumption—equivalent to 20–40 % of a typical power plant output because of the high regeneration temperature.[4,5] Furthermore, amines and their reaction products in the solution that are easily volatilized during the regeneration process need to be recovered in order to avoid air pollution.[6] Thus, the development of nonvolatile sorbents that desorb CO_2 at low temperatures (<100 °C) has been required.[5]

The use of porous solid sorbents is one of the available remedies to circumvent the aforementioned problems. In recent years, a number of porous sorbents such as activated carbon,[7] metal–organic frameworks (MOF),[7,8] zeolites,[7,8] and physically or chemically supported amine polymers[7–9] that can be regenerated under relatively mild conditions have been reported.[7–9] The porous solid sorbents showed an enormous binding capacity of up to 3 mmol CO_2 per gram[7–9] because of the large surface area of the pores. However, only a few studies have been conducted on solid CO_2 sorbents capable of capturing CO_2 under wet conditions, because the adsorption of water vapor competes with that of CO_2 on the pore surface and/or liquefied water blocks the capillaries and pores of the sorbents to prevent CO_2 from diffusing into or out of the pores.[7–9] Thus, nonvolatile sorbents capable of working reversibly under wet conditions by a low-temperature regeneration process are required.

We have reported that aqueous solutions of temperature-responsive microgel particles (GPs) consisting of *N*-isopropyl acrylamide (NIPAM) and *N*-[3-(dimethylamino)propyl]methacrylamide (DMAPM) reversibly absorbed CO_2 by volume phase transition (VPT).[10] Poly(NIPAM) hydrogels underwent VPT from a swollen to a shrunken state at the volume phase transition temperature (VPTT).[10] The GPs were highly hydrated below the VPTT while above it, the water dissociated from the GPs, thereby allowing the shrinkage of the hydrogel structure.

It has been reported that poly(NIPAM) hydrogels comprising functional groups reversibly captured targets such as CO_2,[10,11] dyes,[12] cancer drugs,[13] peptides,[14] proteins,[15] enzymes,[16] nucleotides,[17] and cells[18] through electrostatic, hydrophobic and/or hydrogen-bonding interactions at heating–cooling cycles across the VPTT. The interactions were switched off by either lowering the volume density of the functional groups in the hydrogel below the VPTT,[12,13,16] suppressing the flexibility of polymer chains above the VPTT,[19] or lowering the number of the charged functional groups[10,17] by decreasing the dielectric constant around the functional groups above the VPTT. In the case of reversible CO_2 absorption by the amine-containing GPs, most amines in the swollen GPs were capable of forming ion pairs with the absorbed bicarbonate ions below the VPTT (30 °C). However, above the VPTT (75 °C), the shrinkage of the GPs

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lowered the pK_a value of these amines, resulting in efficient desorption of CO_2.[10]

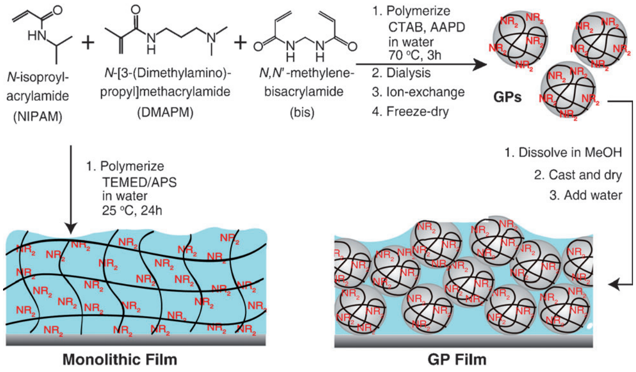
The capacity for CO_2 absorption per amine in the GPs in solution was either comparable or superior to the commercially available CO_2 absorbents consisting of ethanolamine.[10] However, the absorption capacity per weight of the solution was much smaller than that of the aqueous solution of ethanol amines because the concentration of GPs in solution (about 0.1 wt %) was much lower than that of the amine solution (20–30 wt %).[10] As a result, the energy consumed by the solution of GPs to sequester CO_2 was significantly larger than the amine solution in spite of using low temperature for the regeneration process. In order to improve the energy efficiency, the concentration of GPs had to be dramatically increased.[10]

We report herein a new class of solid sorbent films that consist of temperature-responsive GPs. The films were expected to bring together the best of high stoichiometric absorption efficiency of GP solutions and large absorption capacity per weight of solid sorbents, even under wet conditions. Furthermore, it was expected that the temperature-responsive hydrogel films consisting of GPs would respond much faster to external stimuli compared to the monolithic hydrogel films.[20,21]

Lyon and co-workers prepared microgel-based films using the layer-by-layer (LbL) method.[22] Dawson and Lynch made composite microgel films in the form of “plum-pudding” gels, wherein pNIPAM-based microgels were immobilized in a hydrogel matrix.[20] In spite of the large and monolithic appearance, these films retained the rapid response rate of the microgel building blocks.[20]

In this study, the GP films were prepared simply by casting a GP solution onto the surface of a solid substrate[23] (Scheme 1) without further immobilization of the GPs with either polyelectrolyte (LbL gel film)[22] or cross-linked matrix polymers (plum-pudding gel film).[20] We expected that the as-cast GP films would be stable enough for gas-phase applications and respond fast enough to thermal stimuli.

A series of pNIPAM GPs containing 0, 5, and 30 mol % DMAPM and 2 mol % cross-linker (*N*,*N*′-methylenebis(acrylamide) = bis) (GP0, GP5, GP30, respectively) were prepared as reported (see Scheme 1, the Supporting Information, and Table S1).[10] For the fluorescent-labeled GPs, an acrylamide derivative containing fluorescein in the side chain (Fluorescein monomer) was synthesized as reported previously[22] and copolymerized (0.01 mol %) in GP30 (GP30F; see the Supporting Information). The methanol solution of the lyophilized GPs was casted onto the surface of a flat stainless steel container and then dried. The hydrated films of GPs were eventually made by adding water to the dry films. To observe the inner structure of the casted film, the GP30 film was casted with 1 wt % GP30F (10^{-4} mol % Fluorescein monomer) on a glass bottom dish (GP30F film). Then, a three-dimensional fluorescent image was taken using a confocal laser-scanning microscope (LSM 700, Carl Zeiss).



Scheme 1. Preparation of temperature-responsible microgel films and analogous monolithic films (TEMED = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine and APS = ammonium persulfate).

Monolithic film containing 30 mol % DMAPM and 2 mol % bis was prepared as a control (M30 film; see the Supporting Information). The polymerization was carried out in deionized water at room temperature (25 °C) for 24 h using ammonium persulfate (APS) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) as radical initiators. The same film with 10^{-4} mol % Fluorescein monomer was also prepared for confocal microscopy to investigate the inner structure of the monolithic gel film (M30F film).

The two- and three-dimensional fluorescent images of the GP30F film and the M30F film are shown in Figure 1. Figure 1 a and 1 c indicate that the submicron-sized granulous structure of GPs were not degraded and were homogeneously dispersed without forming aggregates in the GP30F film, although the GPs were lyophilized from water and then dissolved in methanol prior to casting. The average film thickness could also be obtained from the image. Figure 1 b and 1 d suggest that the M30F film has a very homogeneous structure.

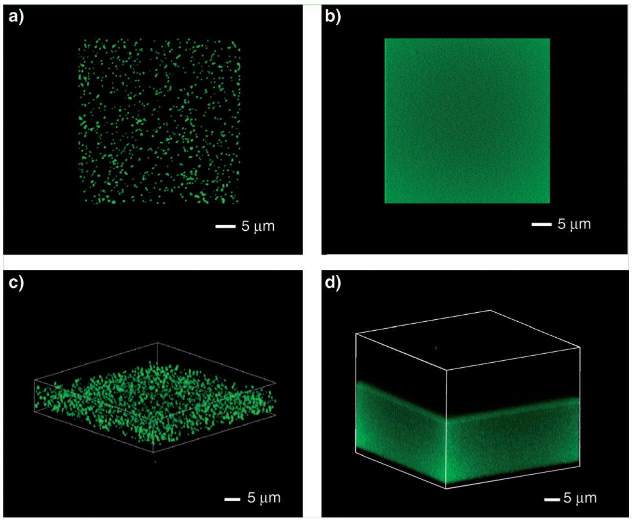


Figure 1. Confocal fluorescence images of a) a GP film comprising 99 wt % GP30 and 1 wt % GP30F and b) a monolithic gel film M30F, and 3D images of c) a GP film comprising 99 wt % GP30 and 1 wt % GP30F and d) a monolithic gel film M30F.

Water-saturated gas containing CO_2 (10 % CO_2, 90 % N_2, 25 °C, 10 mL min^{-1}) was passed continuously on the surface of the GP films in the stainless steel container to quantify the capacity for reversible CO_2 absorption. After saturating the films with CO_2 at 30 °C for 2 h, the amount of CO_2 desorbed from the films at 75 °C was quantified by integrating the CO_2 level in the downstream gas every 1.7 minutes using a gas chromatograph (GC; see the Supporting Information and Scheme S1). As shown in Figure 2a, the dried films, with or without amine (GP30 and GP0, respectively), did not show obvious CO_2 desorption. In addition, meager release of CO_2 was observed by the wet films consisting of GP0. However, a significant amount of CO_2 was desorbed from the hydrated films consisting of amine-containing gel particles (GP30). The volume of desorbed CO_2 increased dramatically on increasing the amount of added water up to 1 mL g^{-1}. Then the capacity for CO_2 desorption was not further affected by the volume of water added when the film was hydrated with more than 1 mL g^{-1} (Figure 2b). This result clearly demonstrates that the amine-containing GP films can readily be used under wet conditions.

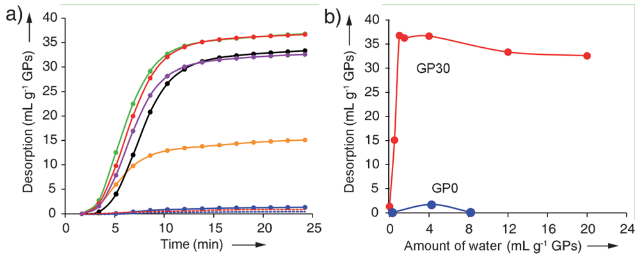


Figure 2. a) Time course of CO_2 absorption by a GP30 film hydrated with 0 (blue), 0.5 (orange), 1 (green), 4 (red), 12 (black), and 20 (purple) milliliters of water per gram of GPs and a GP0 film with 0 (blue dotted line) and 4 (red dotted line) milliliters of water per gram of GPs monitored by GC. b) Dependence of volume of water on CO_2 absorption capacity of GP30 (red) and GP0 (blue) films. A water-saturated gas containing CO_2 (10% CO_2, 90% N_2, 25 °C, 10 mL min^{-1}) was passed continuously on the surface of the GP films.

It has been reported that the reaction of CO_2 with tertiary amines occurred in one equivalent water to form bicarbonate anions and ammonium cations.[10] However, more than 55 mmol (about 1 mL) of water, which was 27 times greater than the number of tertiary amines in the film was required to achieve maximum desorption capacity (Figure 2b). This result suggests that the films have to be hydrated with water not only to react with CO_2 to form ammonium bicarbonate but also for the bicarbonate ions to diffuse into and out of the films.

The effect of the film thickness on the amount of CO_2 desorbed was investigated using hydrated (4 mL g^{-1}) GP films (Figure 3). Surprisingly, the volume of the desorbed CO_2 increased linearly with increasing film thickness up to 200–300 μm (R^2 for GP5 and GP30 are 0.9973 and 0.9985, respectively), indicating that most of the amine groups inside the hydrogel films could be used to capture and release CO_2 by an efficiency analogous to that on the surface of the films. This result also suggests that diffusion of bicarbonate ions into and out of the GP films will not limit CO_2 capture/release when the films are thinner than 200–300 μm.

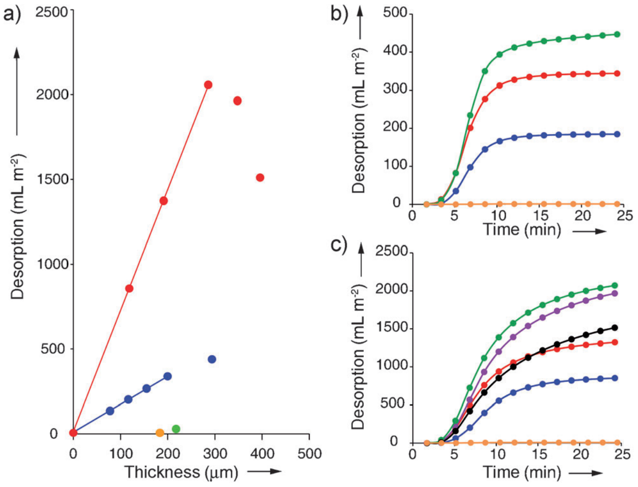


Figure 3. a) Amount of CO_2 released from a GP30 film (red), a GP5 film (blue), a GP0 film (green), and a dry GP5 film (orange) as a function of the film thickness. b) Time course of CO_2 desorption from the GP5 films with thickness of 0 (orange), 120 (blue), 200 (red), and 300 (green) micrometers. c) Time course of CO_2 desorption from GP30 films with thickness of 0 (orange), 120 (blue), 190 (red), 280 (green), 350 (purple), and 400 (black) micrometers. All the films contained 4 mL of water per gram of GPs except for the dry GP5 film. A water-saturated gas containing CO_2 (10% CO_2, 90% N_2, 25 °C, 10 mL min^{-1}) was passed continuously on the surface of the films.

To investigate the reversibility of CO_2 capture in an environment similar to that of the exhaust gases of power plants, high-temperature wet gas containing CO_2 (10% CO_2, 90% N_2, 60 °C, 10 mL min^{-1}) was passed continuously on the surface of the hydrated films. Then, the film was repeatedly heated (75 °C, 25 minutes) and cooled (30 °C, 46 minutes) to release and capture CO_2.

Figure 4 shows that the GP30 film reversibly absorbed and desorbed CO_2 without showing an obvious decrease in the performance. Although the temperature interval was only 45 °C and the surfaces of the films were flat (Figure S1), the capacity for reversible CO_2 absorption (about 38 mL g^{-1} GPs,

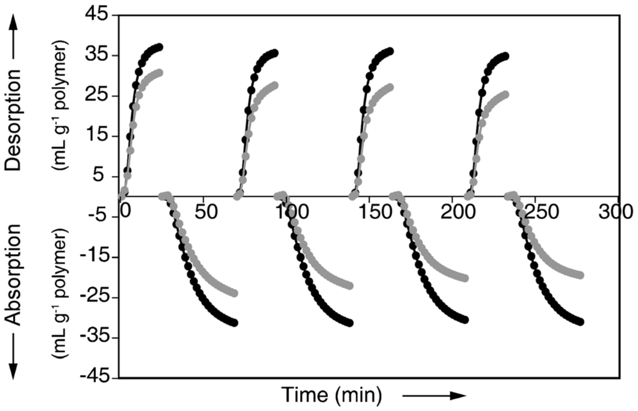


Figure 4. Temperature-responsive absorption (30 °C) and desorption (75 °C) of CO_2 by a GP30 film (black) and a M30 film (gray) over four cycles. A water-saturated gas containing CO_2 (10% CO_2, 90% N_2, 60 °C, 10 mL min^{-1}) was passed continuously on the surface of the films containing 4 mL of water per gram of polymer.

about 1.7 mmol g^{-1} GPs) was comparable to that of a highly porous solid adsorbent.[7–9] Furthermore, the GP30 film shows a faster absorption–desorption rate, a larger absorption–desorption capacity, and a better repeatability than the M30 film.

It has been reported that molecules and ions significantly smaller than the size of the polymer network in hydrogels are capable of diffusing into hydrogels as fast as in water.[24] Furthermore, the molecules diffuse faster into temperature-responsive hydrogels consisting of GPs than into monolithic hydrogels,[20–25] because small GPs have a much larger surface-area-to-volume ratio than the large monolithic gels, the transfer of water into and out of the hydrogel does not limit the shrinkage kinetics.[26] Furthermore, a dense surface layer will be formed on the large monolithic gel surface because the surface layer of the hydrogels shrunk faster than the internal gel.[20,21] The dense layers prevent the release of internal water, limiting the shrinking kinetics of large gels. For the same reasons, stimuli-responsive capture and release of target molecules into and out of the monolithic hydrogels would be limited.[20,21] Results in Figures 3 and 4 indicate the importance of a fast stimulus response rate of the films that are composed of GPs in order to achieve the long-range and fast diffusion of bicarbonate ions as suggested by previous studies.[20–26]

The mechanism of CO_2 absorption and diffusion into the temperature-responsive GP film is different from surface adsorption by porous solid adsorbents assisted by rapid gas-phase diffusion of CO_2 and chemical absorption by aqueous amine solution assisted by rapid liquid-phase diffusion and convection, and provides a new strategy to prepare hydrogel-based CO_2 absorbents.

In summary, hydrogel films comprising temperature-responsive GPs were successfully prepared by simply casting the GP solution onto the surface of a solid substrate. The amount of CO_2 absorbed by the GP films was proportional to their thickness up to 200–300 μm (maximum capacity of about 2 L m^{-2}). The GP films reversibly absorbed CO_2 with a large absorption capacity in a wet environment (about 1.7 mmol g^{-1}) using cooling and heating cycles (30–75 °C). The GP films showed faster and greater absorption and desorption of CO_2 than that of monolithic gel films. Our results revealed the potential of the stimuli-responsive GP films as energy-efficient absorbents to sequester CO_2 from high-humidity exhaust gases. We anticipate that the molecular mechanism proposed in this work provides a novel strategy for the development of stimuli-responsive gas absorbent.

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