Design rationale of thermally responsive microgel particle films that reversibly absorb large amounts of CO$_2$: fine tuning the pK$_a$ of ammonium ions in the particles†

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Herein we revealed the design rationale of thermally responsive gel particle (GP) films that reversibly capture and release large amounts of CO$_2$ over a narrow temperature range (30–75 °C). The pK$_a$ value of ammonium ions in the GPs at both the CO$_2$ capture temperature (30 °C) and release temperature (75 °C) is found to be the primary factor responsible for the stoichiometry of reversible CO$_2$ capture by the amines in the GP films. The pK$_a$ values can be tuned by the properties of GPs such as volume phase transition temperature (VPTT), size, swelling ratio, and the imprinted microenvironment surrounding the amines. The optimal GP obtained according to the design rationale showed high capture capacity (68 mL CO$_2$ per g dry GPs, 3.0 mmol CO$_2$ per g dry GPs), although the regeneration temperature was as low as 75 °C. We anticipate that GP films that reversibly capture other acidic and basic gases in large amounts can also be achieved by the pK$_a$ tuning procedures.

Introduction

The accumulation of CO$_2$ in the atmosphere due to burning of fossil fuels is considered the main cause of global climate change.3 Meanwhile, CO$_2$ is expected to be a carbon source for the production of liquid fuels, such as methanol and dimethyl ether, through the use of regenerative energy.2 Thus, the development of energy-efficient CO$_2$ separation and recovery processes for point sources, such as fossil fuel power plants, is essential not only for minimizing climate change but also for the future use of carbon-based energy.

Conventional processes that recover CO$_2$ from the high humidity exhaust gases of power plants use aqueous solutions of ethanalamine as a CO$_2$ absorbent. CO$_2$ in the exhaust gases is selectively captured by the absorbent at a low temperature (≈40 °C) and then recovered by heating the solution, typically above 140 °C.2–5 Although the amine solution exhibits a high CO$_2$ absorption capacity, the high-energy consumption of the heating process limits its use in the environmentally friendly process.4–8

Porous solid sorbents that can be regenerated under relatively mild conditions, such as metal–organic frameworks (MOFs),9,10 zeolites,9,10 and silica with physically or chemically supported amine polymers,9–12 have recently been developed as alternatives to the aqueous amine solution. However, solid CO$_2$ sorbents are rarely capable of efficiently capturing CO$_2$ from highly humid gases because the adsorption of water molecules competes with that of CO$_2$ on the pore surfaces. Furthermore, the capillaries and pores of the sorbents are easily blocked by the liquefied water, preventing CO$_2$ from diffusing into the pores.8–12 Thus, the development of sorbents that absorb/adsorb large amount of CO$_2$, even in humid environments, and desorb CO$_2$ at low temperatures (<100 °C) is of great importance.

It has been reported that poly-N-isopropylacrylamide (pNIPAm) undergoes a reversible volume phase transition from a hydrophilic swollen state to a hydrophobic collapsed state at temperatures below and above, respectively, the volume phase transition temperature (VPTT) of ≈32 °C.14 The phase transition is induced by the entropy-driven dissociation of water from pNIPAm chains after heating above the VPTT.14 The temperature responsive pNIPAm-based functional hydrogels have been widely used as materials to reversibly capture targets, such as dyes,15,16 drugs,17,18 peptides,19 proteins,20,21 nucleotides,22 cells,23 and protons,24 in aqueous media via the volume phase transition. The multipoint interactions are reversibly switched on/off by varying the volume density of hydrophobic functional groups,25,26 the number of charged functional groups,22,27 and/or the rigidity of the polymer chains28 at temperatures above and below the VPTT.

Recently, we reported that hydrogel films composed of temperature-responsive microgel particles (GPs) consisting of NIPAm and N-[3-(dimethylamino)propyl]methacrylamide (DMAPM) reversibly absorbed and released CO$_2$ via a volume phase transition during cooling (30 °C) and heating (75 °C) cycles, respectively.29 Below the VPTT, amines in the swollen...
GPs were capable of forming ion pairs with absorbed bicarbonate ions. Above the VPTT, shrinkage of the GPs triggered CO$_2$ desorption.$^{27}$ The GP films showed faster CO$_2$ capture and release rate$^{29}$ than the conventional bulk hydrogel films due to the fast thermal responsibility of the GPs.$^{30}$

However, guidelines to design GP films that reversibly absorb CO$_2$ with high capacity and stoichiometry have not been revealed.

In the case of reversible CO$_2$ absorption by the blood of animals, the pK$_a$ value of the Brønsted acid and base in the hemoglobin plays a crucial role for the control of CO$_2$ solution equilibrium: The pK$_a$ value of the ammonium and imidazolium cations decreases due to the drastic conformational change of the hemoglobin caused by oxygen binding to the heme. The shift of the pK$_a$ triggers the release of H$^+$ into the blood, leading to the release of CO$_2$ efficiently from lungs (Bohr effect).$^{31,32}$

Inspired by the Bohr effect of hemoglobin, we hypothesized that the pK$_a$ value of the protonated amines (ammonium ions) within GPs (pK$_a$ value of GPs) at the CO$_2$ capture temperature (30 °C) and release temperature (75 °C) would contribute to the reversible capture efficiency of CO$_2$.

In this study, in order to clarify the design rationale, we prepared a series of GPs with a variety of compositions using different polymerization conditions. The effects of the physical and chemical properties of GPs, such as VPTT, size, swelling ratio, on pK$_a$ values and the reversible CO$_2$ capture stoichiometry against amines were systematically investigated. pK$_a$ values of the ammonium ions in the GPs were also tuned by the “microenvironment-imprinting strategy” as we described in the recent report.$^{24}$ The reversible CO$_2$ capture capacity was maximized based on the design rational revealed in this study. Humidified gas (60 °C) consisting of 10% CO$_2$ and 90% N$_2$, which is comparable to the post-combustion gas of fire power plants after wet desulfurization process, was used as feed gas.$^{6,23}$ The CO$_2$ was captured at 30 °C and released at 75 °C under the same atmosphere (10% CO$_2$, 90% N$_2$, 60 °C water moisture).

### Experimental

#### Preparation of GPs

A series of GPs containing NIPAm, a functional tertiary amine monomer DMPAM, and a crosslinker N,N$'$-methylenbisacrylamide (Bis) were synthesized by precipitation polymerization as reported (Scheme 1).$^{29}$ The amount of Bis was varied to prepare GPs with different degrees of crosslinking and swelling ratios. GPs with the same composition but different pK$_a$ values were synthesized via a “microenvironment-imprinting” strategy by adding HCl or NaOH into the monomer solution.$^{24}$ Larger GPs were obtained by decreasing the concentration of surfactant, while smaller GPs were prepared from solutions with a lower total monomer concentration. To decrease the VPTT of GPs, a more hydrophobic monomer, N-tert-butyl acrylamide (TBAm), was incorporated into the GPs. Details of the polymerization conditions of the GPs are summarized in Table 1. Polymerization process is described in ESI.$^\dagger$

#### Quantification of hydrodynamic diameters, VPTTs, and swelling ratios of GPs

The hydrodynamic diameters and VPTT of GPs were measured by dynamic light scattering (DLS) as described.$^{27,29}$ The swelling ratio is defined as the ratio of the diameters at 30 °C ($D_{30}$) and 75 °C ($D_{75}$).

#### Quantification of amine content and pK$_a$ of ammonium ions in GPs

The amine content and pK$_a$ of amines in GPs was quantified by acid–base titration under N$_2$ purging as described.$^{27,29}$

#### Measurement of pK$_a$ shift curve during heating process

Since the apparent pK$_a$ can be approximated as the pH value at the half-neutralization point, the temperature dependent pK$_a$ shift of the GP solution was measured with the pH probe as follows. The half-neutralized GP solution was prepared by
adding 0.5 eq. of HCl to the GP solution. Then, under a N₂ atmosphere with stirring the pH value and temperature of the solution were recorded by the pH meter every 3 s during the heating process.

Preparation of GP films

The lyophilized GPs were dissolved in methanol. The hydrogel films were then prepared by casting the methanol solutions containing 120 mg of GPs on the inner bottom surface of a stainless steel container with a surface area of 120 cm². After completely evaporating the methanol, 4 mL of water was added per gram of GPs.

Measurement of CO₂ absorption capacity of GP films

The CO₂ absorption capacities of the GP films are quantified as illustrated in Scheme S1. † 10% CO₂ (90% N₂, 10 mL min⁻¹) gas was passed through 60 °C water to generate saturated water vapor. The resulting 60 °C water-saturated gas mixture was channeled into a stainless steel container with the GP film on the inner surface, and then to a gas chromatograph after condensing the water moisture at 5 °C.

More detailed information about materials and experimental process are shown in ESI. †

Results and discussion

Effect of pKₐ values of GPs on the reversible CO₂ capture stoichiometry of GP films

The dynamic and reversible transition of the pKₐ values of Bronsted acid and base groups in proteins plays an important role in their functions, such as molecule/ion transfer, enzymatic reactions, and molecular recognition.32,34 The pKₐ values are significantly influenced by the microenvironment around the functional groups, such as hydrophobicity, hydrogen bonding, and distance to the neighboring charges.32,34-38 Thus, the pKₐ value can be further dynamically shifted by the conformational change of polypeptides around the functional groups, which induces a microenvironment change.

In the case of CO₂ transfer through the bloodstream of animals, the pKₐ value of the ammonium and imidazolium cations in/on the hemoglobin decreases due to the drastic conformational change of the polypeptides caused by oxygen binding to the heme. The shift of the pKₐ value triggers the release of H⁺ into the blood, lowers the pH of the blood, and drives the CO₂ efficiently from the lungs (Bohr effect).32,38

Inspired by the function of hemoglobin, we expected that the pKₐ value of the protonated amines (ammonium ions) within GPs (pKₐ value of GPs) at the CO₂ capture temperature (30 °C) and release temperature (75 °C) would contribute to the reversible capture efficiency of CO₂.

To clarify the effect of the pKₐ value of GPs on the reversible CO₂ capture stoichiometry of GP films in the temperature swing process from 30 °C to 75 °C, a series of GPs with the same composition but different pKₐ values were prepared by the “microenvironment-imprinting” strategy.34,39 Imprinting is a method to create polymers with specific microstructures that show strong affinity to target molecules and ions by cross-linking the polymer networks in the presence of targets.40,41 It has been reported that pNIPAm-based acrylic acids (AAc) containing GPs with different pKₐ values can be prepared by the “proton-imprinted” strategy.24 The GPs polymerized at a pH below the pKₐ of AAc showed a much higher pKₐ value at the collapsed state than those prepared at a high pH because stronger proton-affinity sites were incorporated into the relatively hydrophobic microenvironment around the protonated AAc. Note that the GPs were polymerized at the collapsed state in the temperature above the VPTT.

We anticipated that amine-containing GPs with different pKₐ values could also be prepared via the “microenvironment-
imprinting” strategy. Thus, the GPs were polymerized in the presence of acid (1 or 1/2 eq. of HCl against the amine monomer DMAPM) or base (1/2 eq. of NaOH). All GPs were polymerized in the aqueous monomer solution consisting of 5 mol% DMAPM, 2 mol% Bis and 93 mol% NIPAm at the temperature above the VPTT of the growing GPs (70 °C).

The VPTTs of the GPs were determined by monitoring the scattering intensity of the GP solutions during the heating process (Fig. S1a in ESI†). Despite the different polymerization conditions, all four GPs, D5B2-1/1HCl (1 eq. HCl), D5B2-1/2HCl (1/2 eq. HCl), D5B2-1/2NaOH, (1 eq. NaOH), and D5B2 (without HCl or NaOH), show similar VPTTs at about 38 °C. Similar swelling ratios in the range of 2.3–2.7 are also observed (Fig. S1b in ESI†), indicating the VPTTs and swelling ratios of GPs are independent of the polymerization conditions.

The apparent pHₐ values of the GPs at 30 °C and 75 °C were determined by acid–base titration of the GP solutions and are plotted as the top and bottom, respectively, of the gray bars in Fig. 1a. All GPs show lower pHₐ values than the amine monomer DMAPM, at both temperatures, indicating the relatively low dielectric constant and high steric hindrance around the amine groups in the GPs, as well as the high electrostatic repulsion between neighboring charges.41,42 Moreover, in accordance with our expectation, the pHₐ values of D5B2-1/1HCl and D5B2-1/2HCl at 75 °C (7.4 and 7.0, respectively) were significantly higher than those of D5B2 and D5B2-1/2NaOH (5.3 and 4.9, respectively).

The large difference in pHₐ values can be explained by the “microenvironment-imprinting” effect. When the GPs are polymerized in a proton-rich solution (in the presence of HCl), the protonated DMAPM is imprinted in the polar and hydrophilic microenvironment of the GPs (D5B2-1/1HCl and D5B2-1/2HCl), resulting in higher pHₐ values than those of the GPs polymerized in the proton-poor solution (D5B2 and D5B2-1/2NaOH). Although there is variation in the GP diameters (Fig. S1b in ESI†), the large difference in the pHₐ values (>2) at 75 °C cannot be a result of the size differences because the smallest GP, D5B2 (74 nm), and the largest GP, D5B2-1/2NaOH (136 nm), show a pHₐ difference of only 0.4 (5.3–4.9).

Fig. 1a also shows that the pHₐ difference between 30 °C and 75 °C (ΔpKₐ) of all GPs (1.5–2.5) is larger than that of the monomer (0.9). For better understanding of the temperature dependent pHₐ difference, the apparent pHₐ values of D5B2 and the monomer DMAPM, were recorded during the heating process. Fig. 1b shows that a sharp pHₐ transition of D5B2 occurs at a temperature around its VPTT, and a steep pHₐ decrease continues over a wide temperature range above the VPTT. However, this sharp pHₐ transition is not observed in the case of the monomer, indicating that the sharp pHₐ decrease was induced by a volume phase transition of GPs, during which the increased hydrophobicity and steric hindrance, and the decreased dielectric constant at high temperature make the amine groups more difficult to be protonated.42

In Fig. 1a, the ΔpKₐ values between 75 °C and 30 °C of the GPs polymerized with HCl, D5B2-1/1HCl (1.5) and D5B2-1/2HCl (1.6), are significantly lower than those of D5B2-1/2NaOH (2.3), although the swelling ratios are similar (2.3–2.7). We hypothesize that in comparison with D5B2 and D5B2-1/2NaOH, which were polymerized with 0 and 0.5 eq. of NaOH, respectively, the protonated DMAPM groups (ammoniums) within D5B2-1/1HCl and D5B2-1/2HCl are relatively distant from the hydrophobic pNIPAm moieties and backbones in the collapsed GPs. This is because the protonated amine groups are relatively polar and hydrophilic. In other words, the amine groups of the GPs prepared with HCl are located in a pseudo-swollen microenvironment analogous to the swollen state even at the collapsed state. After the volume phase transition from the collapsed to the swollen state, swelling has less effect on the amines within the “pseudo-swollen” GPs. As a result, the ΔpKₐ values of the GPs prepared with HCl are less than those of the GPs prepared without HCl.

The reversible CO₂ capture stoichiometries of the GP films are presented as red plots in Fig. 1a. D5B2-1/1HCl and D5B2-1/2HCl show very low reversible CO₂ capture stoichiometries (0.18 and 0.27 mol CO₂ per mol amine, respectively), while the values for D5B2 and D5B2-1/2NaOH are both ~0.97 mol CO₂ per mol amine.
The difference in the stoichiometry can be interpreted by the acid–base theory as follows. It has been reported that the tertiary amines in GPs and CO2 form ammonium ions (RN₃H⁺) and bicarbonate ions (HCO₃⁻) via base-catalyzed reactions.⁴⁴,⁴⁵ In aqueous media containing RN₃H⁺ and HCO₃⁻, there is always an equilibrium between their corresponding conjugated base–acid, as described in Scheme 2.

When the pKₐ of NR₃H⁺ is above the pKₐ of H₂CO₃, which indicates that NR₃H⁺ holds a proton more tightly than H₂CO₃ does, the proton will move from the stronger acid, H₂CO₃, to the stronger base, NR₃. As a result, more RN₃ will be consumed and more CO₂ will be captured, as presented by the blue arrows in Scheme 2. In contrast, when the pKₐ of NR₃H⁺ is below the pKₐ of H₂CO₃, more CO₂ will be released, as indicated by the red arrows in Scheme 2.⁴⁶

The pKₐ value of carboxylic acid (H₂CO₃) is in the range of 6.35 ± 0.05 at both 30 °C and 75 °C, as determined by Harned and Davis,⁴⁷ however, the pKₐ values of the amine-containing thermal responsive GPs dramatically depend on the temperature, as presented in Fig. 1. The high pKₐ values of DSB2-1/1HCl and DSB2-1/2HCl at 75 °C (7.4 and 7.0, respectively) are higher than the pKₐ of H₂CO₃ (6.35) and inhibit the release of CO₂. As a result, the reversible CO₂ capture stoichiometries of DSB2-1/1HCl and DSB2-1/2HCl are low (0.18 and 0.27 mol CO₂ per mol amine, respectively), although the pKₐ values at 30 °C (8.9 and 8.6, respectively) are high enough to capture CO₂ efficiently. For DSB2 and DSB2-1/2NaOH, the high reversible CO₂ capture stoichiometries (0.97 mol CO₂ per mol amine for both) are achieved due to the low pKₐ values at 75 °C (5.3 and 4.9, respectively), which are below the pKₐ of H₂CO₃, and meanwhile, the high pKₐ values at 30 °C (7.8 and 7.2, respectively), which are above the pKₐ of H₂CO₃.

Effect of ΔpKₐ values of GPs on the reversible CO₂ capture stoichiometry of GP films

Despite the low pKₐ values of DSB2 and DSB2-1/2NaOH at 75 °C (Fig. 1a), their larger ΔpKₐ values between 30 °C and 75 °C (2.5 and 2.3, respectively) than those of DSB2-1/1HCl and DSB2-1/2HCl (1.5 and 1.6, respectively) may also be responsible for their high reversible CO₂ capture stoichiometries.

In order to distinguish the effects of the pKₐ value and the ΔpKₐ on the reversible CO₂ capture stoichiometry of the GP films, a GP with a smaller ΔpKₐ than DSB2 was prepared by increasing the Bis cross-linker to 10 mol% into the GP that contains 5 mol% DMAPM (DSB10), since it has been reported that the crosslink degree influences the ΔpKₐ of the GPs.⁴⁴

The pKₐ values of DSB2 and DSB10 at 30 °C and 75 °C are plotted as the top and bottom of the gray bars in Fig. 2. The ΔpKₐ of DSB10 (1.4) is apparently less than that of DSB2 (2.5). However, the pKₐ value of DSB10 (5.9) at 30 °C is below the pKₐ of H₂CO₃, Thus the possible reason for the lower reversible CO₂ capture stoichiometry of DSB10 than DSB2 (0.74 and 0.97 mol CO₂ per mol amine, respectively), the smaller ΔpKₐ of DSB10 than DSB2 and/or the low pKₐ value of DSB10 at 30 °C which is below the pKₐ of H₂CO₃, still cannot be distinguished.

To identify the main factor that governs the reversible CO₂ capture stoichiometry, we designed another GP with a greater pKₐ value than DSB10 and a lower ΔpKₐ than DSB2, using the “microenvironment-imprinting” strategy described above. The GPs were prepared by polymerizing DSB10 in the presence of an appropriate amount of HCl (DSB10-1/4HCl).

Fig. 2 shows the pKₐ values and ΔpKₐ of DSB10-1/4HCl. The pKₐ values at 30 °C and 75 °C of DSB10-1/4HCl (6.8 and 5.3, respectively) are higher than those of DSB10 (5.9 and 4.5, respectively), but the ΔpKₐ of DSB10-1/4HCl (1.5) is comparable to that of DSB10 (1.4). DSB10-1/4HCl shows a much higher CO₂ capture stoichiometry (0.97 mol CO₂ per mol amine) than DSB10 (0.74 mol CO₂ per mol amine), despite the similar ΔpKₐ values.

On the other hand, as displayed in Fig. 2, the pKₐ value of DSB10-1/4HCl at 75 °C (5.3) is similar to that of DSB2 (5.3), while the ΔpKₐ of DSB10-1/4HCl (1.5) is much less than that of DSB2 (2.5). However, both GPs exhibit comparably high reversible CO₂ capture stoichiometries (0.97 mol CO₂ per mol amine), even though the ΔpKₐ values are much different.

We conclude from these results that the ΔpKₐ has a minor influence on the reversible CO₂ capture stoichiometry, and a high reversible CO₂ capture stoichiometry is possible for GPs that exhibit reduced ΔpKₐ values as long as the pKₐ values lie within the appropriate range. The pKₐ value of the GPs must be tuned above the pKₐ of H₂CO₃ (6.35) at the CO₂ capture temperature (30 °C) and below the pKₐ of H₂CO₃ (6.35) at the CO₂ release temperature (75 °C) in order to achieve a high reversible CO₂ capture stoichiometry.

Effect of VPTT of GPs on the reversible CO₂ capture stoichiometry of GP films

As shown in Fig. 1b, the thermal responsive volume phase transition of the GPs leads to a sharp pKₐ transition. In
addition, the pK_a value of the GPs has been revealed essential for the reversible CO_2 capture stoichiometry. Therefore, it is interesting to observe the effect of the VPTT of GPs on the reversible CO_2 capture stoichiometry of the GP films.

A GP with a lower VPTT than D_5B_2 was synthesized by polymerizing 40 mol% of TBAm, which is more hydrophobic than NIPAm, together with 5 mol% DMAPM and 2 mol% Bis (D_5B_2T_40). The relative scattering intensity of the GP solutions is shown in Fig. 3a. Compared with D_5B_2 (VPTT = 38 °C), the VPTT of D_5B_2T_40 is only 12 °C. The higher intra-particle hydrophobic interaction of the GPs containing 40 mol% TBAm causes the entropy-driven collapse of D_5B_2T_40 to occur at a lower temperature.

Fig. 3b shows the temperature dependent pK_a values of D_5B_2 and D_5B_2T_40. Similar to D_5B_2, D_5B_2T_40 shows a sharp pK_a transition at a temperature around its VPTT (12 °C) and a steep pK_a decrease continues over a wide temperature range above the VPTT. As a result, the pK_a values of D_5B_2T_40 at 30 °C and 75 °C (6.0 and 4.8, respectively) are both low. The lower reversible CO_2 capture stoichiometry of D_5B_2T_40 (0.60 mol CO_2 per mol amine) than that of D_5B_2 (0.97 mol CO_2 per mol amine), can be explained by the low pK_a value of D_5B_2T_40 at 30 °C (6.0), which is below the pK_a1 of H_2CO_3.

Besides D_5B_2 and D_5B_2T_40, another pair of GPs with different VPTTs were prepared by increasing the feed ratio of DMAPM to 30 mol% (D_30B_2 and D_30B_2T_40). Fig. 3c shows that the VPTT of D_30B_2 is above 60 °C. To lower the VPTT, 40 mol% of TBAm was incorporated into the 30 mol% DMAPM-containing GP (D_30B_2T_40). In comparison, the VPTT of D_30B_2T_40 is only 40 °C (Fig. 3c).

Fig. 3  (a) Relative scattering intensity as a function of temperature for D_5B_2 (green) and D_5B_2T_40 (purple). (b) pK_a shift of D_5B_2 (green) and D_5B_2T_40 (purple) during the heating process. (c) Relative scattering intensity as a function of temperature for D_30B_2 (blue) and D_30B_2T_40 (red). (d) pK_a shift of D_30B_2 (blue) and D_30B_2T_40 (red) during heating process. (e) pK_a values (left Y-axis) at 75 °C (bottom of bar) and 30 °C (top of bar) of the GPs, and reversible CO_2 capture stoichiometries (right Y-axis, red dot) of the GP films in the temperature range 30–75 °C.
In Fig. 3d, the pKₐ values of D30B2 are linearly dependent on temperature, and no obvious sharp transition is observed in the temperature range due to the high VPTT. However, the pKₐ value of D30B2T40 exhibits a transition from the temperature around its VPTT (40 °C), and a steeper pKₐ decrease than that of D30B2 is observed at the temperatures above the VPTT. As a result, D30B2T40 has lower pKₐ values at higher temperatures (>10 °C) and a larger ΔpKₐ between 30 °C and 75 °C than D30B2 (Fig. 3e).

The degree of pKₐ transition of D30B2T40 (Fig. 3d) induced by the phase transition is less significant than D5B2 and D5B2T40 (Fig. 3b). This may be a result of the increased intra-GP charge repulsion within D30B2T40 caused by the smaller amine–amine distance.

The pKₐ values at 30 °C and 75 °C of D30B2 (7.8 and 6.8, respectively) and D30B2T40 (7.7 and 6.3, respectively) are shown in Fig. 3e. The reversible CO₂ capture stoichiometry (0.72 mol CO₂ per mol amine) of D30B2 is quite low; however, that of D30B2T40 is much higher at 0.97 mol CO₂ per mol amine. The improved stoichiometric efficiency can be explained by the relatively low pKₐ value of D30B2T40 at 75 °C (6.3), which is below the pKₐ of H₂CO₃. The VPTT of D30B2T40, which is close to 30 °C, induces a sharp pKₐ transition and a steep pKₐ decrease over a wide temperature range above the VPTT, lowers the pKₐ value at 75 °C, and consequently improves the reversible CO₂ capture stoichiometry.

In summary, the results in Fig. 3 lead to a comparable conclusion to those of Fig. 1 and 2: the pKₐ values of the GPs at 30 °C and 75 °C govern the reversible CO₂ capture stoichiometry. However, the VPTT of the GPs also plays a crucial role. The GPs with a much lower VPTT than the CO₂ capture temperature (30 °C) show low reversible CO₂ capture stoichiometries due to the low pKₐ value. Meanwhile, to achieve a high reversible CO₂ capture stoichiometry, the VPTT should be above and as close to 30 °C as possible to generate a large pKₐ transition over a wide temperature range above the VPTT.

However, a VPTT above and close to 30 °C is not enough for a high CO₂ capture stoichiometry if the pKₐ values at 30 °C and 75 °C lie at an improper level. For example, in Fig. 1, though the VPTTs of D5B2-1/1HCl and D5B2-1/2HCl are both 38 °C, the high pKₐ values at 75 °C (7.4 and 7.0, respectively) considerably restrict efficient CO₂ release (0.18 and 0.27 mol CO₂ per mol amine, respectively).

### Effect of GP size on the reversible CO₂ capture stoichiometry of GP films

We have reported that the GP films exhibited larger CO₂ capture capacities than conventional bulk hydrogel films due to the small dimensions of GPs, which lead to a fast response and fast ion diffusion. Herein, the effect of GP size on the reversible CO₂ capture stoichiometry is discussed.

Larger GPs can be prepared by increasing the concentration of monomer or by decreasing the concentration of surfactant. In this study, GPs with the same composition (5 mol% DMAPM and 2 mol% Bis) but different size were designed. A GP with a larger hydrodynamic diameter (D5B2-L) than D5B2 was prepared by decreasing the concentration of surfactant, while a smaller GP (D5B2-S) was synthesized using a monomer solution with a lower total concentration.

The diameters of the GPs at 30 °C and 75 °C are shown in Fig. 4a. As expected, D5B2-L (638 nm at 30 °C and 322 nm at 75 °C) has a larger diameter than D5B2 (196 nm at 30 °C and 74 nm at 75 °C), and D5B2-S has the smallest diameter (115 nm at 30 °C and 49 nm at 75 °C). The pKₐ values of the GPs at 30 °C and 75 °C are presented as the top and bottom, respectively, of the bars in Fig. 4b. It can be seen clearly that the pKₐ values of the GPs at both temperatures increase with the decreasing diameter.

The amine groups located at the exterior of the GPs are expected to show higher pKₐ values than those of the interior groups because of the high dielectric constant of water, as well as the reduced steric hindrance. In the meantime, the amine groups of the exterior of the smaller GP account for a much larger percentage than those of the larger GPs. Therefore, smaller GPs show higher pKₐ values than the larger GPs.

Fig. 4b also shows that the three GPs exhibit similar, high reversible CO₂ capture stoichiometries (0.96–1.0 mol CO₂ per mol amine), despite the difference in GP diameters and pKₐ values.

Another pair of GPs showing different pKₐ ranges from those of the GPs in Fig. 4a and b was polymerized using the “micro-environment-imprinting” strategy by adding 0.5 eq. of NaOH to the monomer solution [D5B2-1/2NaOH and D5B2-1/2NaOH-S]. D5B2-1/2NaOH-S, having a smaller diameter than D5B2-1/2NaOH, was prepared by lowering the total monomer concentration.

Fig. 4c and d show the diameters and pKₐ values, respectively, of the GPs at 30 °C and 75 °C. In good agreement with the results in Fig. 4a, the diameters of D5B2-1/2NaOH-S (83 nm at 30 °C and 57 nm at 75 °C) are much smaller than the diameters of D5B2-1/2NaOH (715 nm at 30 °C and 349 nm at 75 °C). The pKₐ values of the smaller GP are also higher than those of the larger GP. However, the reversible CO₂ capture stoichiometry of D5B2-1/2NaOH-S (0.74 mol CO₂ per mol amine) is lower than that of D5B2-1/2NaOH (0.98 mol CO₂ per mol amine), as shown in Fig. 4d.

The different results from Fig. 4b and d could also be ascribed to the different pKₐ values of the GPs. The high pKₐ values of D5B2-L, D5B2, D5B2-S, and D5B2-1/2NaOH at 30 °C (7.0, 7.8, 8.5, and 7.2, respectively), which are above the pKₐ of H₂CO₃ (6.33), and the low pKₐ values at 75 °C (4.8, 5.3, 6.1, and 4.9, respectively), which are below the pKₐ of H₂CO₃, result in high reversible CO₂ capture stoichiometries. However, the pKₐ values of D5B2-1/2NaOH-S at 30 °C and 75 °C are 8.4 and 6.6, respectively. Its high pKₐ value at 75 °C (6.6), which is above the pKₐ of H₂CO₃, restricts the efficient release of CO₂, resulting in a low reversible CO₂ capture stoichiometry (0.74 mol CO₂ per mol amine).

In general, the results of Fig. 4 lead to the conclusion that the reversible CO₂ capture stoichiometry of GPs can be improved by regulating their pKₐ values at both 30 °C and 75 °C through varying their diameter. The smaller diameter leads to a higher pKₐ value.
Effect of swelling ratio of GP on the reversible CO₂ capture stoichiometry of GP films

The swelling ratio of thermal responsive GPs plays an important role in their function such as the reversible target binding. The swelling ratio of GPs is typically controlled by the crosslink degree. Herein, we prepared a series of GPs containing 5 mol% of DMAPM with 0, 2, 5, and 10 mol% Bis crosslinker (D5B0, D5B2, D5B5, and D5B10, respectively) to investigate the effect of the swelling ratio on the reversible CO₂ capture stoichiometry of GPs.

The diameters at 30 °C and 75 °C, and the swelling ratios of the GPs are plotted in Fig. 5a. It is noteworthy that GP can be obtained without Bis crosslinker (D5B0), possibly due to the slight self-crosslinking. As expected, the swelling ratios of D5B2 (2.7), D5B5 (2.0), and D5B10 (1.6) decrease with the increasing crosslink degree. The diameters of the GPs at 75 °C increase slightly with the increasing amount of Bis crosslinker, indicating that Bis influences the nucleation process during polymerization, as observed by Pelton’s group.

Fig. 5b shows the pKₐ values of the GPs at 30 °C and 75 °C, and the ΔpKₐ values. The ΔpKₐ values of D5B2 (2.5), D5B5 (2.1), and D5B10 (1.3) between 30 °C and 75 °C show a positive correlation with the swelling ratios of the GPs (2.7, 2.0, and 1.6, respectively). This suggests that from 30 °C to 75 °C the microenvironmental changes, such as the change of dielectric constant and polymer density, around the less cross-linked amines are greater than those of the highly cross-linked amines in the GPs. At 30 °C, the pKₐ values of the swollen GPs, D5B2 (7.8), D5B5 (6.7), and D5B10 (5.9), decrease with the reduction in the swelling ratio, indicating the GP with a smaller swelling ratio is in a relatively collapsed state at 30 °C compared to those with higher swelling ratios, because swelling of the GP is inhibited by the high crosslink degree. The pKₐ value of D5B2 at 30 °C (7.8) is similar to that of D5B0 (7.7), although D5B0 exhibits a much larger swelling ratio, indicating that D5B2 is also fully swollen at 30 °C.

In Fig. 5b, D5B0, D5B2, and D5B5 exhibit similar reversible CO₂ capture stoichiometries (0.97–1.0 mol CO₂ per mol amine), while that of D5B10 (0.74 mol CO₂ per mol amine) is much lower. The difference in the reversible CO₂ capture stoichiometries can also be explained by their pKₐ values. The higher pKₐ values of D5B0, D5B2, and D5B5 at 30 °C (7.7, 7.8, and 6.7, respectively), which are above the pKₐ1 of H₂CO₃, and the lower pKₐ values at 75 °C (5.2, 5.3, and 4.4, respectively), which are below the pKₐ1 of H₂CO₃, lead to high reversible CO₂ capture stoichiometries. However, the pKₐ value of D5B10 at 30 °C (5.9) is too low and the basicity is too weak to capture CO₂ efficiently.

Conclusively, the swelling ratio (D₃₀/D₇₅), which can be controlled by crosslink degree, is an important factor to tune the ΔpKₐ and consequently the pKₐ values of GPs to improve the reversible CO₂ capture stoichiometry.

Design rationale of GP film with large reversible CO₂ capture stoichiometry

The above discussion has revealed the design rationale of GPs that show large reversible CO₂ capture stoichiometry within a...
narrow temperature range of 30 °C to 75 °C. The \( pK_a \) values of the GPs at 30 °C and 75 °C are the principal factors that govern the reversible CO\(_2\) capture stoichiometry. Higher \( pK_a \) values at 30 °C, above the \( pK_{a1} \) of H\(_2\)CO\(_3\) (6.35), and lower \( pK_a \) values at 75 °C, below the \( pK_{a1} \) of H\(_2\)CO\(_3\), enable high reversible CO\(_2\) capture stoichiometries of GP films. This is because the GPs are capable of capturing CO\(_2\) efficiently at 30 °C due to the stronger basicity of the amine than HCO\(_3^-\), and then releasing CO\(_2\) sufficiently at 75 °C because of the weaker basicity. High reversible CO\(_2\) capture stoichiometry can be achieved for GPs that exhibit a smaller \( \Delta pK_a \) as long as the \( pK_a \) values lie within the appropriate range.

The \( pK_a \) value of the GPs can be readily adjusted to the desired level by varying the VPTT of the GPs above and close to the CO\(_2\) capture temperature (30 °C in this study), because the volume phase transition of GPs always brings out a large \( pK_a \) transition throughout a wide temperature range above the VPTT. The \( pK_a \) value of the GPs can also be tuned by controlling the size of the GPs since smaller GPs show higher \( pK_a \) values. Another method is to regulate the GP swelling ratio, which influences \( \Delta pK_a \) and consequently the \( pK_a \) value of GPs. Finally, the imprinted microenvironment around the amine groups in the GPs can also influence the \( pK_a \) values of the GPs because the GPs synthesized in the presence of a large amount of protons exhibit higher \( pK_a \) values. The inter-relationship between these factors is illustrated by Scheme 3.

**Optimization of GPs to maximize reversible CO\(_2\) capture capacity**

In order to improve the CO\(_2\) capture capacity by GP films, the ratio of functional amine monomer, DMAPM, was maximized to 55 mol% (GPs with a higher DMAPM concentration precipitated during polymerization process). However, D55B2 exhibited a low CO\(_2\) capture stoichiometry (0.73 mol CO\(_2\) per mol amine) due to its high \( pK_a \) value at 75 °C (6.8) (Fig. 6a). According to the design rationale described above, highly efficient CO\(_2\) capture cycles could be achieved if the \( pK_a \) value of the 55 mol% DMAPM-containing GP at 75 °C is below the \( pK_{a1} \) of H\(_2\)CO\(_3\) (6.35).

Since the VPTT of D55B2 is greater than 75 °C, one approach to reducing the \( pK_a \) value of the 55 mol% DMAPM-containing GP at 75 °C is to lower its VPTT. Thus, 43 mol% TBAm was incorporated into the 55 mol% DMAPM-containing GP (D55B2T43).

In accordance with the design rationale, the \( pK_a \) value of D55B2T43 at 75 °C decreases to about 6.35 (Fig. 6a) due to the reduced VPTT via the incorporation of TBAm. Consequently, a high reversible CO\(_2\) capture stoichiometry (0.93 mol CO\(_2\) per mol amine) is obtained. As a result of the high amine content and the high stoichiometric efficiency, as shown in Fig. 6b, D55B2T43 shows the largest reversible CO\(_2\) capture capacity (68 mL CO\(_2\) per g dry GPs, 3.0 mmol CO\(_2\) per g dry GPs) in this study.

Though the GP D55B2T43 showed high CO\(_2\) capture capacity (68 mL CO\(_2\) per g dry GPs, 3.0 mmol CO\(_2\) per g dry GPs), taking into account of water and support that are necessary for the GP films, the CO\(_2\) capture capacity of the GP film is lower than the

![Scheme 3](image318x79to538x311)
However the GP films can be used directly to capture CO₂ from desulfurized post-combustion exhausted gas, without pre-treatment of the exhausted gas to remove water vapor inside, nor to decrease the temperature of the water vapor. Furthermore, the low regeneration temperature of the GP films (75 °C) enables the utilization of abundant and low cost waste heat (<100 °C) of factories as an energy source. Consequently the energy consumption of the GP films might be lowered.

Fig. 6a summarizes the pKₐ values and the reversible CO₂ capture stoichiometries of the GPs studied in this paper. Over-all, it can be concluded that the GPs with pKₐ values at 30 °C above the pKₐ1 of H₂CO₃, and pKₐ values at 75 °C below the pKₐ1 of H₂CO₃ (red) generally show larger reversible CO₂ capture stoichiometries than other GPs (blue).

**Reversibility of the optimized GPs as CO₂ absorbent in wet environment**

In order to show the cycle stability of the GP film, the reversible CO₂ capture-release by D55B2T43 film was carried out for 10 cycles. The result is shown in Fig. 7 red plots. The reversible CO₂ capture capacity decreased gradually from 0.93 mol CO₂ per mol amine of the 1st cycle to 0.71 mol CO₂ per mol amine of the 10th cycle. The reason is that the GP film partly dried out, as can be

![Fig. 7 CO₂ capture/release stoichiometry (right Y axis) and CO₂ capture/release capacity (left Y axis) of GP D55B2T43 film with 4 mL water per g GPs. Red: first 10 cycles of CO₂ release/capture by the GP film. After the first 10 cycles, 4 mL water per g GPs was supplied to the dried part of the GP film. Blue: the CO₂ release-capture by the GP film after supplying 4 mL water per g GPs to the dried part of the GP film.](image-url)
seen in Fig. 2a in ESIF However, by supplying 4 mL water per g GPs to the dried part of the GP film after 10 CO2 release/capture cycles, the reversible CO2 capture capacity can be completely recovered (Fig. 7 blue plots).

We believe the problem of cycle stability can be solved by tuning mass balance of water carefully by engineering the CO2 capture processes, such as reactor shape and operation condition optimization.

Conclusions

Inspired by the efficient CO2 transport mechanism of hemoglobin, known as the Bohr effect, here we revealed the design rationale of amine-functionalized thermo-responsive gel particle (GP) films that reversibly capture and release large amounts of CO2 efficiently from a model of the exhaust gas of fire power plants over a narrow temperature range (30–75 °C). Appropriate pKav values of the GPs at the CO2 capture and release temperatures (30 °C and 75 °C, respectively) are essential for the reversible CO2 capture stoichiometry of the GPs films. At 30 °C, a high pKav value, above the pKav of H2CO3, is required for efficient CO2 capture. Simultaneously, a low pKav value at 75 °C, below the pKaw of H2CO3, is required for the efficient release of CO2.

The pKav value of the GPs can be readily adjusted to the desired level via four methods. (1) Controlling the VPTT of the GPs above and close to 30 °C – the phase transition induces a large pKav transition over a wide temperature range above the VPTT. (2) Controlling the size of the GPs – smaller GPs show higher pKav values. (3) Controlling the swelling ratio, which influences ΔpKaw, and consequently the pKav value of the GPs. (4) Controlling the imprinted microenvironment of the GPs – the GPs synthesized in the presence of a large amount of protons exhibit higher pKaw values.

We successfully designed and acquired the GP, D55B2T43, which exhibited a large reversible CO2 capture capacity (68 mL CO2 per g dry GPs, 3.0 mmol CO2 per g dry GPs) as well as a high reversible CO2 capture stoichiometry (0.93 mol CO2 per mol amine), by optimizing the pKav value of GPs containing a maximum amount of amine-monomer. We believe GPs with an even larger CO2 capture capacity could be designed by incorporating co-monomers that are more hydrophobic than TBAm into the tertiary amine-containing GPs, and/or by using more hydrophobic tertiary amine monomers such as N-[3-(diethylamino) propyl] methacrylamide. The advantages of amine functionalized GP films, such as the large capture capacity, the low regeneration temperature (75 °C), and the unique ability to work in wet environments, would enable the use of GP films as energy efficient CO2 absorbers for the exhaust gas of fire power plants. We anticipate that GP films that can reversibly capture other acidic and basic gases with a large capacity can also be achieved by the same strategy inspired by the Bohr effect of hemoglobin.

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