Development of Hydrogel Films Consisting of Thermal Responsive Amine-Functionalized Microgel Particles and Linear Polymers as CO2 Absorbent in Wet Environment

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論 文 名　：Development of Hydrogel Films Consisting of Thermal Responsive Amine-Functionalized Microgel Particles and Linear Polymers as CO_2 Absorbent in Wet Environment

（高湿度環境における CO_2 吸収材としてのアミンで機能化された温度応対性のマイクロゲル粒子や長鎖高分子からなるハイドロゲルフィルムの開発）

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論 文 内 容 の 要 旨

The accumulation of CO_2 in atmosphere caused by the burning of fossil fuels has caused serious climate change. Thus the sorption of CO_2 from the main emission sources such as fire power plants is essential to mitigate the greenhouse effect and to generate the carbon based energy.

Currently the most commercialized CO_2 recovery method from the humid exhaust gases of fire power plants is absorption by using aqueous solution of small molecule amines. In this process, CO_2 in exhaust gas is selectively absorbed at low temperature, and desorbed by heating the solution to a high temperature, typically above 140 °C. Though the aqueous amine solution showed large CO_2 capture capacity, the high energy consumption make them less attractive. As an alternative for the aqueous amine solution, the porous solid materials were developed. The CO_2 can be released in a relatively mild condition, however the intrinsic property of porous materials make them negatively affected by the water gases, because the water gases will compete with the CO_2 to be adsorbed on the pore surface, and the liquefied water will block the small pores and the capillaries.

Thus it is of great importance to develop a CO_2 sorbent that is capable of working in wet environment and being regenerated at a relatively lower temperature (< 100 °C). Hydrogel films comprising temperature responsive GPs were developed as CO_2 absorbents from wet environment using cooling and heating cycles in a narrow temperature range (30-75 °C). The GP films reversibly absorbed CO_2 with a large absorption capacity in a wet environment (about 1.7 mmol/g).The amount of CO_2 absorbed by the GP films was proportional to their thickness up to 200-300 μm, and was not affect by added water amount when above 1 mL/g.

The design rationale of amine-functionalized thermo-responsive GP films that reversibly capture and release large amounts of CO_2 efficiently from a model of the exhaust gas of fire power plants over a narrow temperature range (30-75 °C) was revealed, inspired by the efficient CO_2 transport mechanism of hemoglobin, known as the Bohr effect. Appropriate pK_a values of the GPs at the CO_2

capture and release temperatures (30 °C and 75 °C, respectively) are essential for the reversible CO_2 capture stoichiometry of the GPs films. At 30 °C, a high pK_a value, above the pK_{a1} of H_2CO_3, is required for efficient CO_2 capture. Simultaneously, a low pK_a value at 75 °C, below the pK_{a1} of H_2CO_3, is required for the efficient release of CO_2. The pK_a 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 pK_a transition over a wide temperature range above the VPTT. (2) Controlling the size of the GPs–smaller GPs show higher pK_a values. (3) Controlling the swelling ratio, which influences ΔpK_a, and consequently the pK_a 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 pK_a values. The GP, D55B2T43, which exhibited a large reversible CO_2 capture capacity (68 mL CO_2/g GPs, 3.0 mmol CO_2/g GPs) as well as a high reversible CO_2 capture stoichiometry (0.93 mol CO_2/mol amine) was successfully designed and acquired, by optimizing the pK_a value of GPs containing a maximum amount of amine-monomer.

The polyvinylamine (PVAm) modified by Me, i-Pr and t-Bu with different modification ratio were used as CO_2 capture absorbents. The CO_2 capture stoichiometry of the copolymers can be improved by the "spacing effect" of the modification groups, the larger modification groups usually show stronger "spacing effect". Phase separation behavior of the copolymers can also facilitate the CO_2 capture stoichiometry if the LCST is above and close to 30 °C. However excessively modified copolymer with LCST below 30 °C show significantly low CO_2 capture stoichiometry. LCST of the copolymers can be decreased by increasing the hydrophobic modification ratio or by using more hydrophobic modification groups. Besides, the copolymers showed larger CO_2 capture stoichiometry than the polymer blends at the same modification ratio, indicating the intra-polymer interaction between amine groups and hydrophobic modification groups are essential for the CO_2 capture.

The effect of inner gel structure on the CO_2 capture and release kinetics of the films were studied. Briefly, the large inter-GP pores and the fast responsibility of GPs promoted the CO_2 release rate of GP films. Then large inner pores also facilitated the CO_2 capture rate.