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Advanced CO$_2$/H$_2$ separation materials incorporating active functional agents

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1. **Research Subject**

   Advanced CO_2/H_2 separation materials incorporating active functional agents

2. **Abstract**

   The basic concept for a novel supercritical CO_2 (SC-CO_2) directing method was invented for preparation of an innovative CO_2/H_2 separation membrane possessing a CO_2 molecular gate function. Poly(amidoamine) (PAMAM) dendrimer was selected as the CO_2 molecular gating material, held within a rigid matrix of cellulose acetate. A nascent membrane containing PAMAM, cellulose acetate and *N*-methylpyrrolidone (NMP) as a solvent was treated under an SC-CO_2 atmosphere to remove the solvent and form a membrane with a CO_2 molecular gate function. SC-CO_2 may work as a structure directing agent for creating the CO_2 molecular gate channel. Additionally, with the removal of NMP, CO_2 molecules would form carbamate ion pairs with the amino moieties of the PAMAM dendrimer under the SC-CO_2 atmosphere to regulate PAMAM dendrimer morphology for ideal CO_2 molecular gating channels. The resulting membrane had dense, uniform morphology and showed CO_2/H_2 selectivity.

3. **Introduction**

   CO_2 capture and storage (CCS) is an important option for mitigating global warming. However, CCS in terms of present-day technology consumes a large amount of energy and is costly, especially in CO_2 capture. Several CO_2 capture technologies such as chemical and physical absorption, adsorption and membranes are under research and development. Among these, membranes are the least energy intensive method.

   We have been developing advanced composite materials possessing molecular interaction forces with specific molecules using nanoscale control technologies in polymeric and inorganic materials. For example, such forces can selectively extract CO_2 from CO_2 and H_2 mixed gas. The materials consist of active functional agents in the nanopores of a porous substrate or polymeric matrix. We control the configurations, surface atoms/molecules and the compositions of the pore/matrix and functional compounds to create the desired molecular interaction forces. Our research is expected to provide detailed insight into molecular dynamics in nanoscale structures and result in the future production of superior separation materials.

   One objective of this research is to realize the development of an improved CO_2 separation membrane for CCS. Such an innovative material will greatly reduce energy consumption and costs in the separation process.

Basic concept of CO₂ molecular gate membrane

Figure 1 shows the basic outline of the CO_2 molecular gate membrane. In Figure 1 (b), the pathway for gas molecules is occupied solely by CO_2, which acts as a gate to block the passage of other gases. Consequently, the amount of H_2 permeating to the other side of the membrane is greatly limited and high concentrations of CO_2 can be obtained. The molecular gate membrane can achieve reverse size separation of CO_2 and H_2. Figure 1 (c) shows further detail of the amine compounds, such as polyamidoamine (PAMAM) dendrimers. In the figure, one CO_2 molecule is shown to form a carbamate ion pair with two amine moieties from the membrane material. The carbamate ion pair works as a quasi cross-linkage that restricts H_2 permeation through the membrane. On the other hand, because carbamate ion pairs are in equilibrium with free CO_2 and amine moieties, CO_2 can release from the original carbamate ion pair and jump down to the next pair of amine moieties via the CO_2 concentration gradient in the membrane. As a result, only CO_2 molecules permeate the membrane.

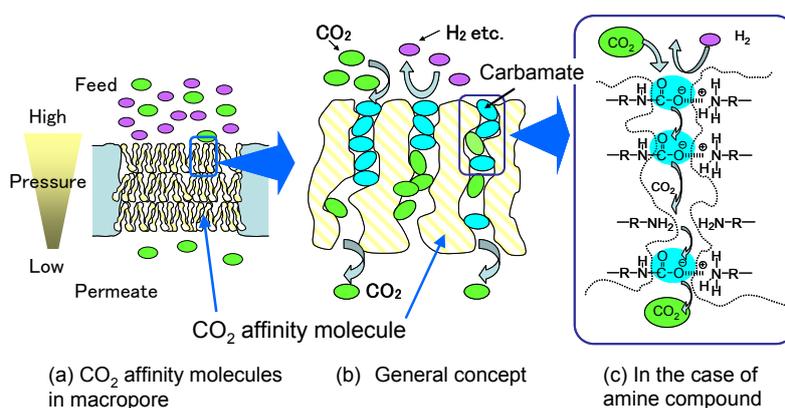(a) CO₂ affinity molecules in macropore   (b) General concept   (c) In the case of amine compound

Figure 1: Concept of the CO₂ molecular gate membrane

The CO_2 molecular gate requires strict morphological arrangement. In Figure 1 (c), a strict morphological control of the distance between two amine moieties is required for the perfect CO_2 molecular gate. If the distance is too small and allows strong hydrogen bonding of the amine moieties, the membrane will not have sufficient CO_2 permeability (Figure 2(a)). On the other hand, if the distance is too large, there will not be enough carbamate ion pairs for the gate to function. It is critical that this is avoided for better CO_2 selectivity (Figure 2(b)).
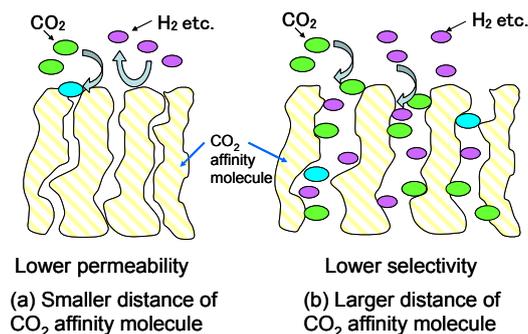
Figure 2: Morphological deformation and the molecular gate function

Excess water absorbed in an existing PAMAM dendrimer membrane has been observed to lead to a sharp decrease in CO_2 selectivity. A large excess of water absorbed into the membrane seems to enlarge the molecule distance of the dendrimer membrane, resulting in insufficient formation of carbamate ion pairs. Excess CO_2 molecules absorbed physically in the membrane at an elevated pressure will also enlarge the molecule distance.

A promising way of maintaining the best morphology for the gate is the incorporation of a CO_2 affinity agent into rigid nanoscale spaces. The rigid nanoscale space works as a hoop that restricts the expansion of the CO_2 affinity agent induced by physically absorbed H_2O and CO_2 (Figure 3). As a result, the hoop of rigid nanoscale space is effective for maintaining materials in the best morphology for the CO_2 molecular gate function. The rigid nanoscale space can be provided by a nanoporous substrate or polymeric matrix.
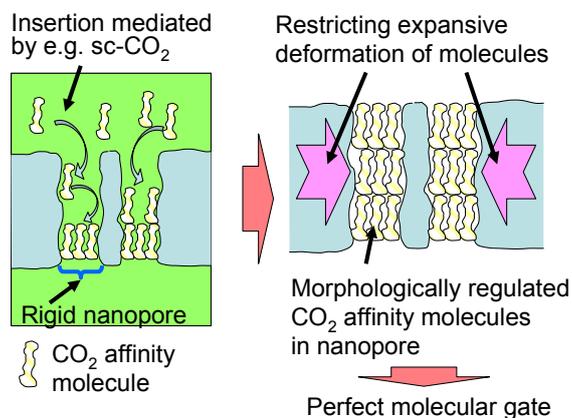

Figure 3: Insertion of CO_2 affinity molecule into rigid nanoscale space and resulting restricted deformation of the molecules

To include a CO_2 affinity molecule in the nanoscale space of a nanoporous substrate or polymeric matrix, proper selection of the medium carrying the CO_2 affinity agent into the spaces is critically important. The medium should be able to penetrate the nanopores freely and possess sufficient solubility for the CO_2 affinity molecules. From this viewpoint, supercritical CO_2 (SC-CO_2) and subcritical CO_2 (Sub-CO_2) are selected as the medium, as shown in Figure 3, because of their having near-zero surface tension. Additionally, Sub- and SC-CO_2 would help to form a quasi cross-linkage for improved morphology of the CO_2 molecular gate in nanopores during membrane preparation, as in shown in Fig. 1-C. In this case, Sub- or SC-CO_2 molecules work as a structure directing agent.

4. Background

Creation of a CO_2/H_2 separation membrane is a very hot topic in gas separation membrane research. RITE is a leading research institute on CO_2 separation technologies and has studied PAMAM dendrimer membranes for CO_2 separation (Figure 4). A PAMAM dendrimer membrane was first reported by Professor Sirkar's group at the New Jersey Institute of Technology as an immobilized liquid membrane for CO_2/N_2 separation [1]. A liquid state dendrimer has been successfully and stably fixed in a polymeric matrix as a composite hollow fiber membrane at RITE [2]. RITE's membrane holds the world record for CO_2/H_2 separation properties (CO_2/H_2 selectivity: 30) at an elevated CO_2 pressure. In this membrane, PAMAM dendrimer was incorporated into a cross-linked polymeric matrix, whereby a continuous channel of PAMAM dendrimer through membrane was formed. Further improvement of the dendrimer membrane and morphologic regulation of the dendrimer channel is required.
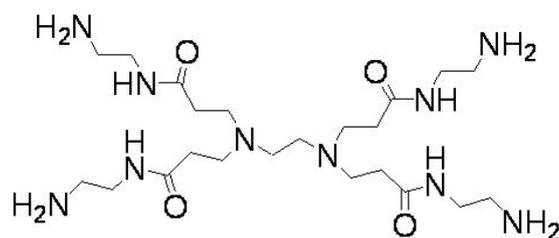

Figure 4: Chemical structure of PAMAM dendrimer (conventional).

Professor Freeman's group at the University of Texas at Austin also attains very good CO_2/H_2 separation membranes of cross-linked poly(ethylene glycol) (PEG) network, which show a selectivity of 10 at 30 °C and an elevated CO_2 pressure, as well

as a good CO_2 permeability [3]. Professor Ho's group at Ohio State University has reported a cross-linked poly(vinyl alcohol) membrane containing amine compounds [4]. Professor Matsuyama's group at Kobe University in Japan has also reported a gel membrane, which consists of poly(vinyl alcohol)/poly(acrylic acid) co-polymer and an amine as CO_2 carrier [5]. Both membranes exhibit very good CO_2/H_2 selectivity at an elevated temperature and a low CO_2 partial pressure.

The word "molecular gate" is sometimes used in the field of separation membranes. The term is also used by Sirkar's group but its concept in their paper was not clear [1]. The concept of a CO_2 molecular gate mentioned above was developed at RITE and the concept is now being confirmed.

Structure directing agents are commonly applied for preparing a desired molecular structure in inorganic materials such as zeolite. Specific amine compounds are preferably selected here as structure directing agents for regulating the molecular structure when creating an ideal CO_2 molecular gate channel. SC-CO_2 has been selected, for the first time, as the structure directing agent in this GCEP study for the reasons given above.

5. Results

We have developed CO_2 molecular gate membranes using poly(amidoamine) (PAMAM) dendrimer immobilized in a polymer matrix network. Conventional dendrimer membranes for CO_2 molecular gates have phase-separated, bicontinuous structures of PAMAM dendrimer and polymer matrix phases, which indicated the presence of PAMAM dendrimer channels throughout the polymeric membrane. Figure 5 shows an image of a typical structure of the dendrimer membranes obtained by a laser scanning confocal microscope. In the image, bright green and dark sections represent the polymeric matrix of the poly(ethylene glycol) (PEG) network and the PAMAM dendrimer, respectively. An average PAMAM dendrimer domain size was calculated by summation of a series of 2D sliced fluorescent images and about 2-4 μm in proportion to the PAMAM dendrimer concentration in the polymeric membrane. This phase-separated structure, which has a channel throughout the membrane, would be crucial to enable preferential CO_2 permeation through the polymeric membrane. Control of the channel structure on the nanometric scale would also be critically important to obtain a better CO_2 molecular gating function.

PAMAM dendrimer- in PEG network

PEG dimethacrylate

+

PAMAM dendrimer

+

PEG-FITC*

*Fluoresceinisothiocyanate isomer

UV →

20 x 20x 20 μm
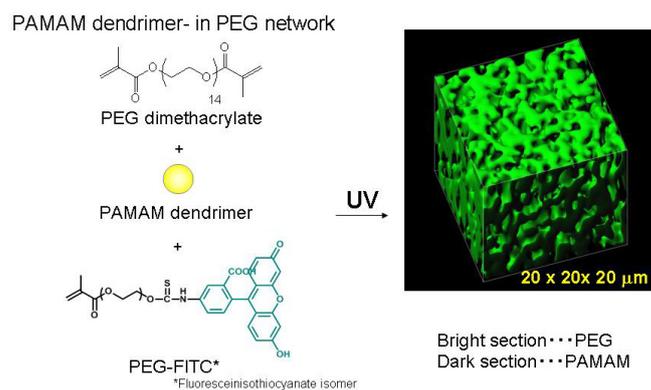
Bright section···PEG
Dark section···PAMAM

Figure 5: LSCM image of PAMAM dendrimer membrane incorporated in a PEG network.

Structural control on a nanometric scale is successfully attained with a specific amine compound acting as the structure-directing agent for preparing a tailor-made nano-porous material. In our new research in GCEP, CO_2 itself will be used as the structure-directing agent for producing an ideal CO_2 molecular gating structure. Figure 6 shows the basic concept of SC-CO_2 directing method for preparing the ideal CO_2 transporting channel with a CO_2 molecular gating function. To obtain the most effective molecular gating function, accurate control of the dimensions of the CO_2 transporting channel, surrounded by CO_2 affinity materials such as the PAMAM dendrimer, seems to be crucial. In the figure, SC-CO_2 would work as a structure-directing agent for controlling the dimensional accuracy of the diameter of the CO_2 transporting channel due to the formation of a carbamate ion pair that bridges two amino compounds in a nascent membrane. SC-CO_2 will also work as a solvent remover to maintain the carbamate formation. SC-CO_2 causes negligible deformation of the structure during solvent removal, due to its near-zero surface tension. As a result, the SC-CO_2 directing method will offer an ideal channel structure for the CO_2 molecular gate.
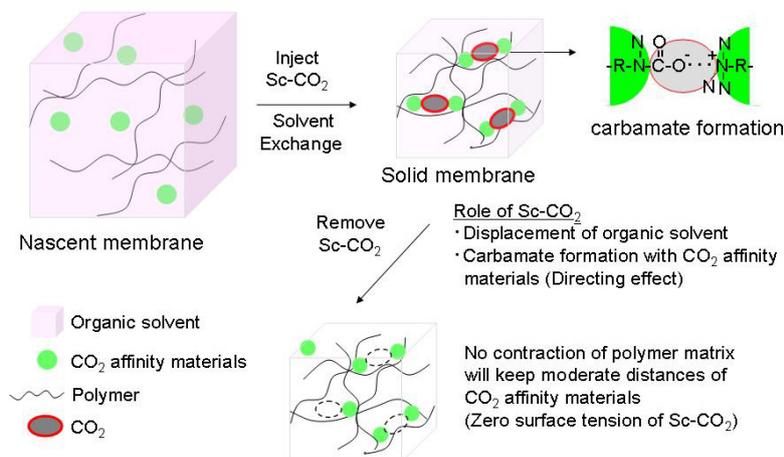

Inject Sc-CO_2
Solvent Exchange

carbamate formation

Solid membrane

Nascent membrane

Remove Sc-CO_2

Role of Sc-CO_2
· Displacement of organic solvent
· Carbamate formation with CO_2 affinity materials (Directing effect)

Organic solvent
CO_2 affinity materials
Polymer
CO_2

No contraction of polymer matrix will keep moderate distances of CO_2 affinity materials (Zero surface tension of Sc-CO_2)

Figure 6: Basic concept of the SC-CO2 directing method.

Figure 7 shows the setup for the SC-CO$_2$ directing method. The setup consists of a syringe pump, high pressure view cell with a sapphire window, a back pressure regulator and a monitoring camera. A nascent membrane containing solvent was formed on a glass plate, followed by curing in a high-pressure cell. CO$_2$ was injected gradually into the cell with a high pressure pump to produce a supercritical condition at 40 °C. Pressure was maintained for a while at 10 MPa and then decreased at a rate of 0.1MPa/min to create channels with the CO$_2$ molecular gate functionality.
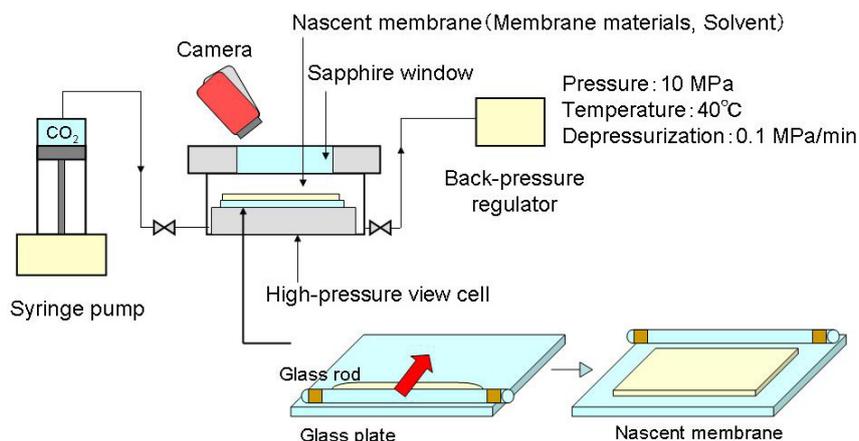

Figure 7: Setup for the SC-CO2 directing method.

In preliminary experiments, the effect of SC-CO$_2$ induced phase separation was compared with that of conventional non-solvent induced phase separation. Non-solvent induced phase separation is a very popular method for preparing asymmetric membrane structures in the field of water treatment and gas separation. Nascent membranes containing cardo polyamide of membrane material and N-methylpyrrolidone (NMP) solvent were placed in SC-CO$_2$ and the non-solvent, water. Neither SC-CO$_2$ nor water will dissolve the polymer but they are miscible with NMP. As a result, NMP was removed from the nascent membrane to produce cardo polyamide membranes. Structures of the resulting membranes were observed by scanning electron microscope (SEM). Figure 8 shows SEM images of membranes prepared by SC-CO$_2$ and non-solvent induced phase separation methods. In the image of the non-solvent induced phase separation, large elongated voids were observed, as seen in conventional asymmetric membranes. On the other hand, the SC-CO$_2$ induced phase separation method creates a sponge-like void structure with a smaller size. This indicates that SC-CO$_2$-induced phase separation might have potential for creating a unique membrane structure. To attain this GCEP's purpose, a uniform structure without voids will be necessary. SC-CO$_2$-induced phase separation will be extended to

a SC-CO$_2$ directing method for creating CO$_2$ channels with molecular gate functionality.

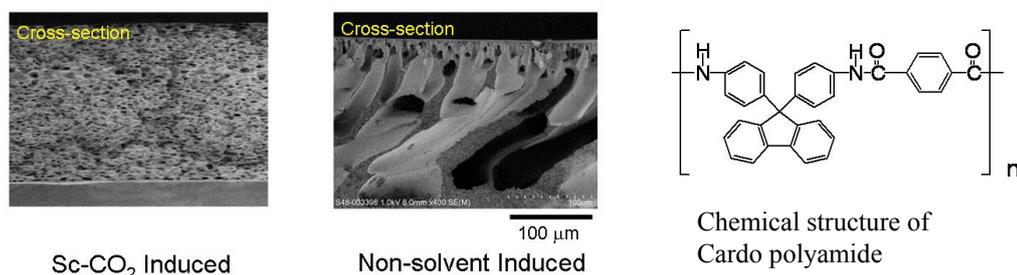Sc-CO$_2$ Induced   Non-solvent Induced   Chemical structure of Cardo polyamide

Figure 8: SEM image of cardo polyamide membrane prepared by SC-CO2 and non-solvent induced phase separation method.

For producing an ideal CO$_2$ channel with molecular gate functionality, the SC-CO$_2$ directing method will produce a dense uniform membrane structure incorporating CO$_2$ affinity materials such as a PAMAM dendrimer. To obtain a dense, uniform membrane structure, selection of polymeric materials and optimization of the conditions for the SC-CO$_2$ directing method will be important. As a result of the preliminary screening process, cellulose acetate was selected as one of the candidate polymeric materials for incorporating PAMAM dendrimer. A nascent membrane containing PAMAM dendrimer, cellulose acetate and NMP was placed in a high-pressure cell, followed by gradually increasing the CO$_2$ pressure to 10 MPa at 40 °C to reach the SC-CO$_2$ condition. For removal of NMP, CO$_2$ was replaced at a rate of 2 mL (STP)/min for 240 min under SC-CO$_2$ conditions. CO$_2$ pressure was then decreased gradually to obtain the desired membrane. The thickness of the resulting membrane was about 70 μm.

Time course of solvent removal and membrane formation in Sc-CO$_2$ condition (1→4)   SEM image
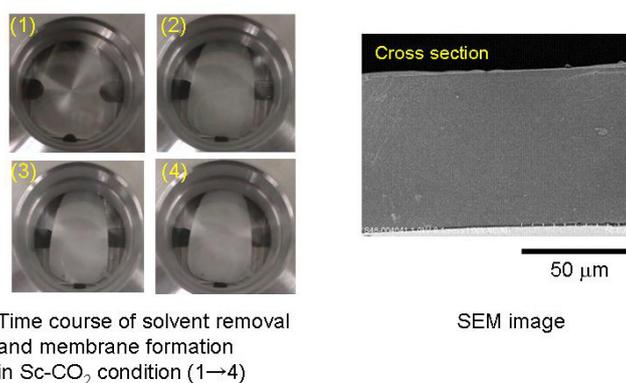
Figure 9: Photo images during membrane formation and SEM image of the resulting membrane.

Figure 9 shows a series of photographic images taken during membrane formation under SC-CO_2 conditions and a SEM image of the resulting membrane. In the series of photos, the transparent nascent membrane (upper left) became opaque over the course of time due to the removal of NMP under SC-CO_2 conditions. In the SEM image, the resulting membrane was observed to have a dense, uniform structure.

CO_2/H_2 separation properties of the resulting membrane (thickness: 70 μm) were obtained, as shown in Figure 10. In the figure, the left and right axes of the ordinate represent permeability and CO_2/H_2 selectivity (α), respectively. The axis of the abscissa represents the PAMAM dendrimer concentration (wt%) in the total solid content of the nascent membrane. The CO_2/H_2 selectivity (α) for a 35 wt% of PAMAM dendrimer concentration was 4, which was slightly larger than that of the original cellulose acetate membrane. This may mean that a continuous PAMAM dendrimer channel could not be formed at a PAMAM dendrimer concentration of 35 wt%. At 52 wt%, CO_2/H_2 selectivity (α) was increased to about 16. This result is the first accomplishment of a reasonably high CO_2/H_2 selectivity by the novel SC-CO_2 directing method, even though the value of CO_2/H_2 selectivity was not large enough for an ideal CO_2 molecular gate. However, this accomplishment is encouraging that the SC-CO_2 directing method will provide a new method for creating CO_2 molecular gate membranes. Improvement of the SC-CO_2 directing method, as well as the other trials mentioned in the Introduction section, is now on-going.
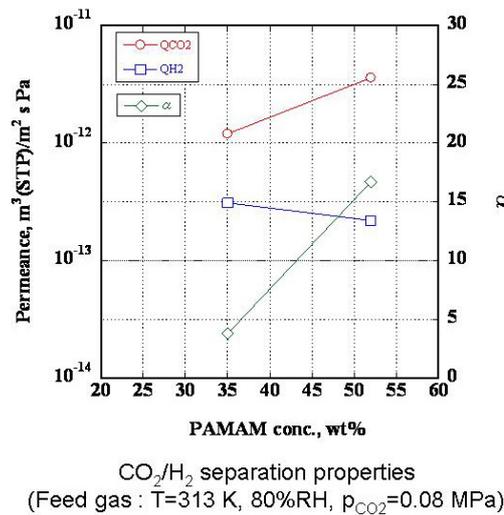

CO$_2$/H$_2$ separation properties
(Feed gas : T=313 K, 80%RH, p$_{CO2}$=0.08 MPa)

Figure 10: CO_2/H_2 separation properties of a membrane prepared by the SC-CO_2 directing method (thickness: 70 μm).

6. Progress

CO_2 separation membranes will be preferably employed for CO_2 capture from a pressurized gas stream such as the Integrated Coal Gasification Combined Cycle (IGCC) as a means of CO_2 capture and storage (CCS). An IGCC power plant of 300 MW would emit roughly one million metric tons of CO_2 a year. Assuming 90% CO_2 recovery in the membrane system, the GCEP outcome will potentially contribute to a CO_2 reduction of 0.9 million metric tons per 300 MW power plant. When 100 IGCC plants employ the membrane system, the contribution to CO_2 reduction is counted as 90 million metric tons per year. Additionally, the GCEP outcomes in CO_2 membrane research might be applicable to existing power plants such as coal-fired thermal power plants. A 1000 MW coal-fired power plant emits roughly five million metric tons of CO_2 a year. Significant improvement of CO_2 permeability is required for effective CO_2 membrane separation from existing power plants but, if this is achieved, more than four million metric tons of CO_2 would be captured annually from a 1000 MW coal-fired power plant. Our final goal is the creation of a game-changing CO_2 separation membrane, which is applicable to existing power plants and steel works, as well as new plants such as IGCC.

7. Future Plans

The following research will be conducted into an ideal CO_2 molecular gate membrane.

-Improvement of the SC-CO_2 directing method

-Applying the SC-CO_2 directing method to different materials

-Investigating the mechanism of the SC-CO_2 directing method

-Investigating other applications of SC-CO_2, such as interfacial reactions in nanopores

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