

# Development of Innovative Gas Separation Membranes through Sub-Nanoscale Materials Control

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## Abstract

New membrane types with well-controlled sub-nanostructures were developed from both polymeric and inorganic materials: carbon-based membranes, functionalized mesoporous oxide membranes and molecular sieving zeolite membranes. As for the carbon membranes, a novel carbon membrane with CO<sub>2</sub> affinity enhancement was developed. The prepared membrane showed much a higher separation factor than that of ordinary carbon membranes in the separation of CO<sub>2</sub>/N<sub>2</sub> mixtures. As for the inorganic membrane, a new zeolite membrane and amine-modified mesoporous silica membrane have been prepared.

## Introduction

Carbon dioxide capture and storage (CCS) could allow the utilization of abundant fossil fuel reserves, while significantly decreasing emissions of CO<sub>2</sub> to the atmosphere. However, the cost of CCS, especially of CO<sub>2</sub> capture, is still too expensive to consider as a cost effective technique. This project intends to develop a variety of efficient, low-cost polymeric and inorganic CO<sub>2</sub> separation membranes that will be a game changing technology. Material structure engineering at the scale of gas molecules will be used to increase the permeability and selectivity of the membrane. As for the polymeric based materials, a cardo polymer-based carbon membrane has been prepared by incorporating molecules or atoms which have a strong CO<sub>2</sub> affinity. The effect of the symmetric/asymmetric structure on the resulting sub-nanostructure and separation performance will be investigated. As for the inorganic materials, zeolite / functionalized mesoporous membranes have been prepared. The preparation of ultra-thin, defect-free membranes will be investigated.

## Background

The process of membrane separation of CO<sub>2</sub> from other gases is an active field, but the best membrane today is still considered too energy intensive and expensive to be

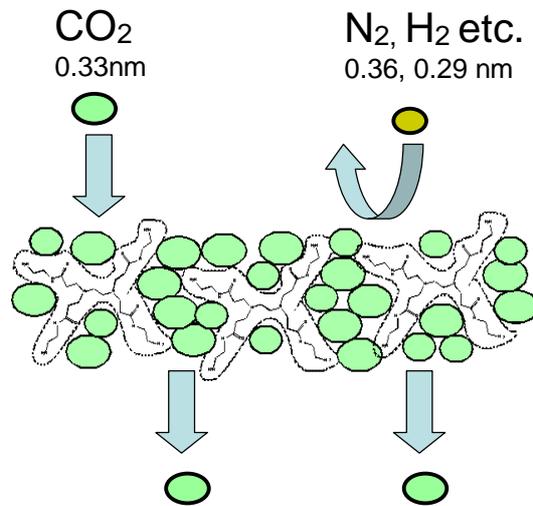
implemented on a large scale. Gas separation in membranes is driven by providing a pressure difference across the membrane. In order to obtain a sufficiently pure stream of CO<sub>2</sub>, the selectivity for CO<sub>2</sub> must be high. In addition, to attain the compact membrane facility, a high permeability is also required. Many current systems require a large membrane area and cascading in order for the gas to permeate through multiple membrane stages to achieve the desired flow rate and purity. As such, new membrane types are required to have high permeability and selectivity, as well as long-term durability. Two areas of gas separation membrane research are currently focused on the development of polymeric and inorganic membranes. Polymeric membranes are relatively easy to manufacture and are well-suited for low temperature applications. The polymer morphology and mobility determine the gas permeability and selectivity. In addition, by carbonizing these polymeric materials it is possible to obtain a molecular sieve capability. Inorganic membranes on the other hand, have much greater thermal and chemical stability. Inorganic materials including zeolites and silicas have appropriately-sized pores that can act as molecular sieves to separate gas molecules by effective size. Surface adsorption and diffusion inside the pores can also play a role in separating gas molecules. Since the effective sizes of CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, and other gases present in fossil fuel conversion systems are very similar, the membrane pore spaces must be controlled on a scale comparable to the size differences among these gas molecules. This will be achieved for a variety of membrane types using several different techniques. In this paper, we describe the development of new membrane types with well-controlled sub-nanostructures prepared from both polymeric and inorganic materials: carbon-based membranes, functionalized mesoporous oxide membranes and molecular sieving zeolite membranes.

## **Results**

### (1) Carbon membrane

#### (1.1) The concept of membrane structure

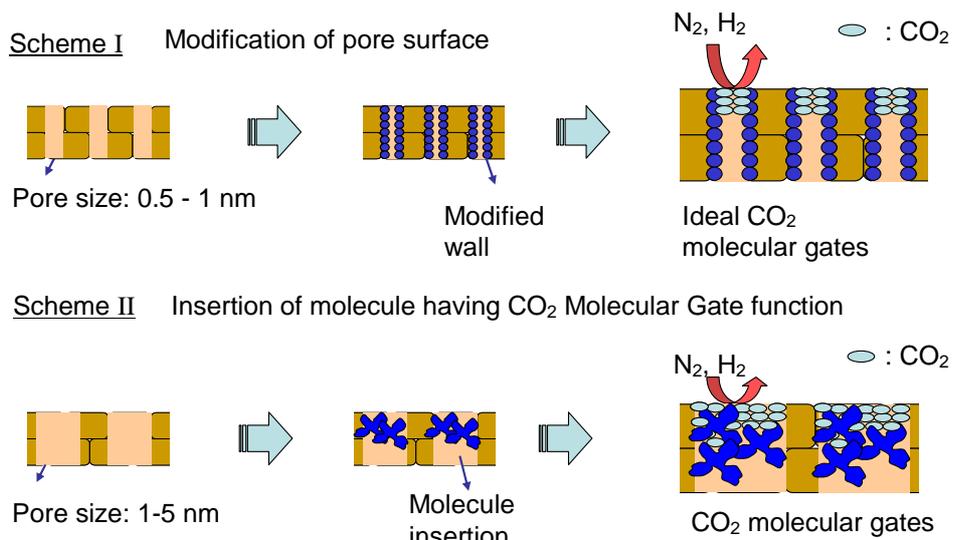
The concept of utilizing molecular gates for high separation performance is shown in Figure 1. In the concept of Molecular Gates, originally claimed by Sirkar et al [1], CO<sub>2</sub> absorbed in organic materials (e.g., the poly(amidoamine) (PAMAM) dendrimer) blocks the permeation of other permanent gases such as N<sub>2</sub> and H<sub>2</sub>, thus high separation performance is obtained. So far, we have developed new dendrimer materials that show a higher separation performance than the conventional PAMAM dendrimer [2]. In addition, we have successfully developed dendrimer composite membrane modules using this PAMAM dendrimer. These PAMAM dendrimer composite membrane modules showed a high CO<sub>2</sub> separation performance under realistic operating conditions (i.e., a pressure difference between the feed and permeate sides) [3, 4].



### CO<sub>2</sub> molecular gates

**Figure 1:** The concept of Molecular Gates for high separation performance.

In this project, the concept of Molecular Gates is combined with nano/ sub-nanostructure materials and the proposed concept is shown in Figure 2. In Scheme I, the pore surface of the sub-nanoporous materials is modified with CO<sub>2</sub> affinity materials to produce ideal CO<sub>2</sub> molecular gates. In Scheme II, the CO<sub>2</sub> affinity molecules such as PAMAM dendrimers are inserted into the pores of the nanoporous materials. In both cases, the CO<sub>2</sub> absorbed in the porous materials blocks the permeation of other permanent gases.

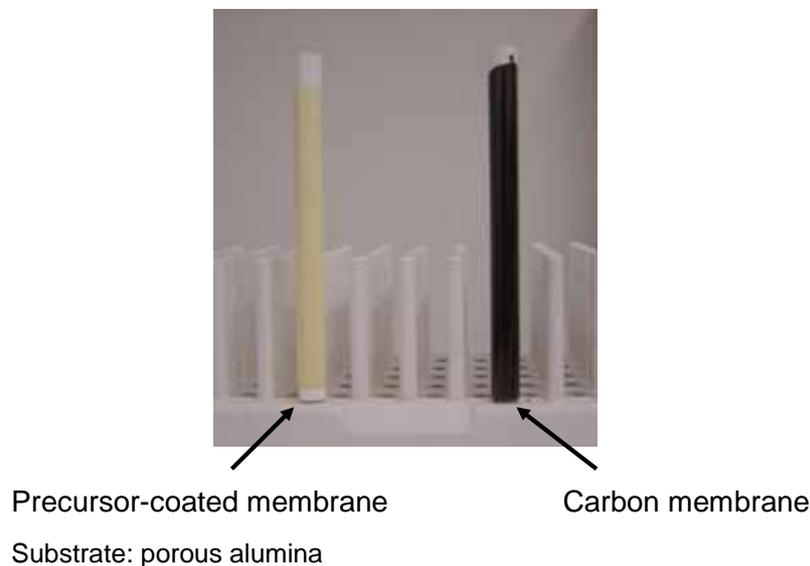


**Figure 2.** Enhancement of CO<sub>2</sub> affinity in sub-nano/nanomaterials.

## (1.2) Membrane preparation

Cardo polyimide was chosen as the precursor for preparing sub-nano/nanoporous carbon membranes. A tubular-type porous alumina membrane (pore diameter 150nm) was used as the porous support. The precursor solution was coated on the outer surface of the alumina support by the dip-coating method. After drying, the precursor-coated membrane was carbonized under vacuum or under a N<sub>2</sub> atmosphere. The separation performance was evaluated using a CO<sub>2</sub>/N<sub>2</sub> gas mixture at 40 °C.

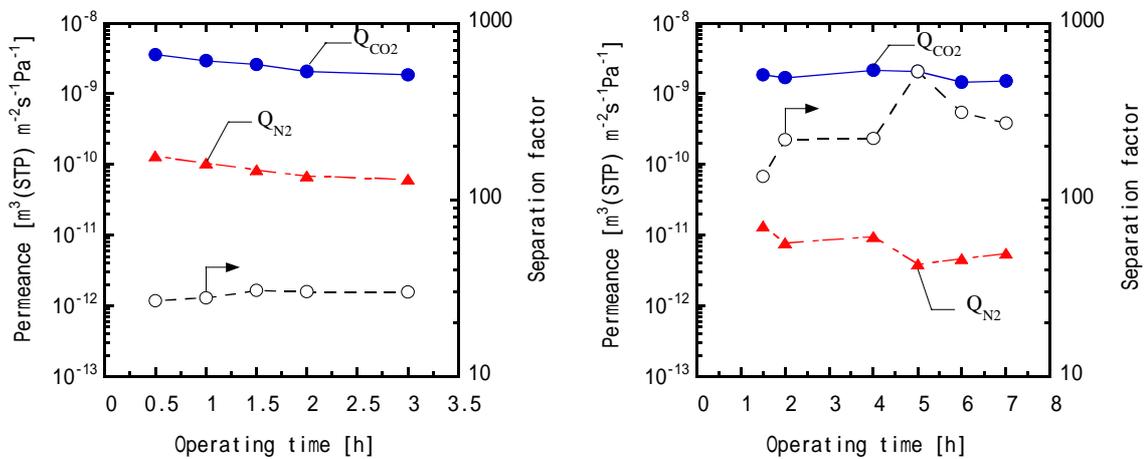
A photograph of a precursor-coated membrane and a carbon membrane is shown in Figure 3. As seen in Figure 3, a yellow precursor layer was formed on the alumina support by dip-coating. Pyrolysis of the precursor layer resulted in the formation of the black carbon layer.



**Figure 3.** Photograph of a precursor-coated membrane and pyrolyzed carbon membrane.

### (1.2.1) Sub-nanoporous carbon membranes with CO<sub>2</sub> affinity enhancement

The CO<sub>2</sub> affinity of a typical carbon membrane was enhanced to improve the separation performance of the membrane based on the concept described in Figure 2 (Scheme I). The separation performance of carbon membranes with/without CO<sub>2</sub> affinity enhancement is shown in Figure 4. In Figure 4 (a), the carbon membrane without CO<sub>2</sub> affinity enhancement showed ordinary separation performance (Permeance: ca.  $10^{-9}$  m<sup>3</sup>(STP) m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>, Separation factor: ca. 30). On the other hand, as shown in Figure 4 (b), the carbon membrane with CO<sub>2</sub> affinity enhancement showed a similar permeance (ca.  $10^{-9}$  m<sup>3</sup>(STP) m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>), but with a much higher separation factor (>200). This research is ongoing to improve the separation performance further.



(a) Carbon membrane without CO<sub>2</sub> affinity enhancement

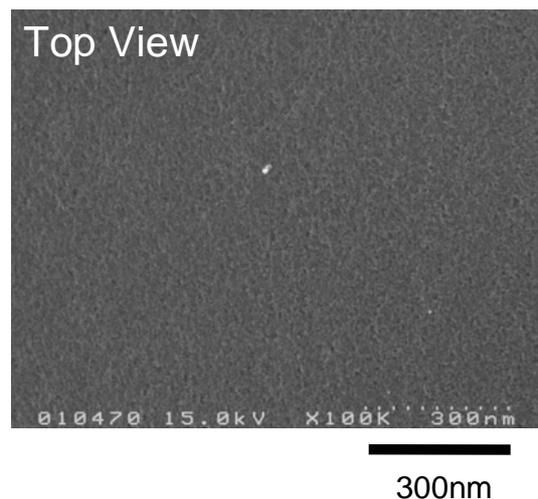
(b) Carbon membrane with CO<sub>2</sub> affinity enhancement

**Figure 4.** Separation performance of carbon membranes with/without CO<sub>2</sub> affinity enhancement (CO<sub>2</sub>/N<sub>2</sub> gas mixture at 40 °C).

#### (1.2.2) Nanoporous carbon membranes with CO<sub>2</sub> affinity molecules

A cardo polyimide/poly(ethylene glycol)-based precursor was selected for the preparation of the nanoporous carbon membranes.

An SEM photograph of the surface of a carbon membrane prepared from the polyimide/poly(ethylene glycol) precursor is shown in Figure 5. As seen in Figure 5, an uneven surface was obtained, which might suggest the formation of a nanoporous structure.

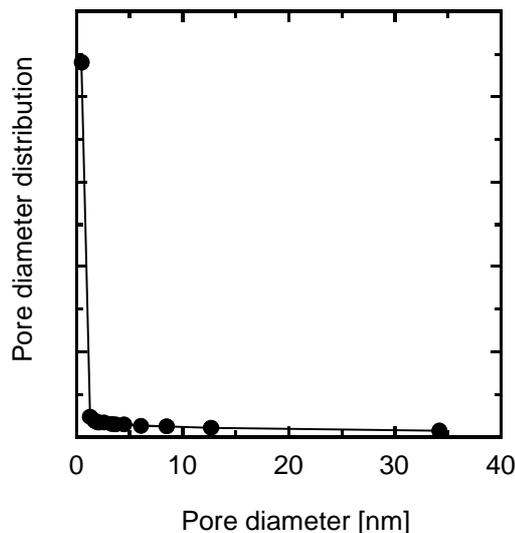


**Figure 5.** SEM photograph of the surface of a carbon membrane prepared from a polyimide/poly(ethylene glycol) precursor.

From the surface structure, it was expected that the nanoporous structure was formed in the carbon layer. However, further examination using nanoporometry showed that neither a nanoporous structure existed or that the nanoporous structure was continuous from the outer surface to the inner surface.

A result of the nanoporometry study is shown in Figure 6. The principle of nanoporometry is as follows: Helium (He) gas permeance was measured under a constant operating pressure, while the vapor pressure of a condensable gas (hexane) was varied in the He carrier gas. The He permeance decreases as the hexane vapor pressure increases, because the hexane becomes condensed and plugs some of the membrane pores by capillary condensation. Since the relationship between the pore diameter of condensation and hexane vapor pressure is described by the Kelvin equation, the pore diameter distribution can be evaluated.

As shown in Figure 6, the pore diameter of the pores contributing to the He permeation is limited to the sub-nano order. Therefore, the pore diameter was deemed too small to insert dendrimers (molecular size > 1 nm). The study to form nanoporous carbon membranes by examining the preparation conditions is ongoing. After a nanoporous membrane structure is realized, it will be necessary to perform experiments to insert dendrimers.



**Figure 6.** Pore diameter distribution of a carbon membrane prepared from a cardo polyimide/poly(ethylene glycol) precursor using nanoporometry.

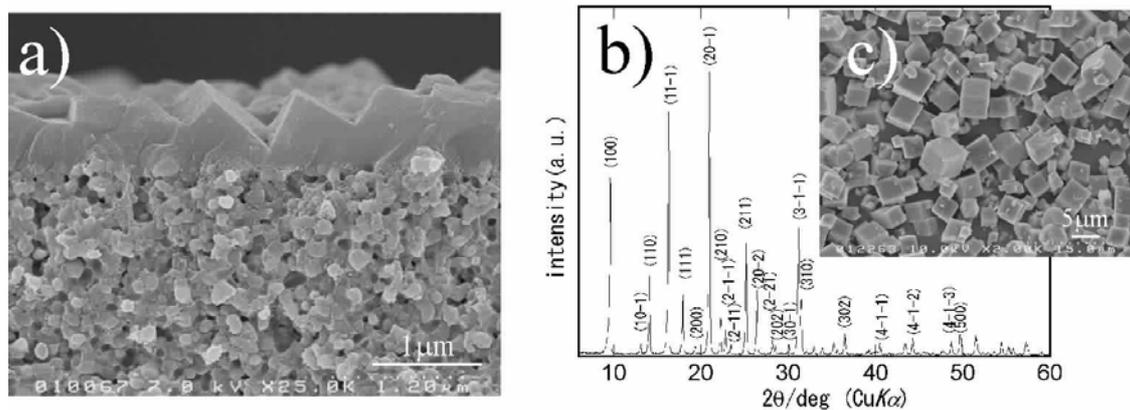
## (2) Inorganic membrane

### (2.1) Synthesis of novel zeolite membranes for CO<sub>2</sub> separation

The preparation method of ultra-thin zeolite membranes was studied using two types of seeding method; i.e., an ultrasonication-based coating method and a rubbing-based seeding method. It was found that the performance and denseness of the membrane prepared by the rubbing-based seeding method was higher than that of the membrane

produced by the ultrasonication-based coating method. The zeolite Y membrane synthesized by the rubbing-based seeding method possessed a complex layer consisted of zeolite and porous substrate particles, and yielded a separation factor of 69.3. Based on these results, we have been investigating the synthesis method of a new type of zeolite membrane effective for CO<sub>2</sub> separation..

In collaboration with the University of Tokyo, we have been undertaking a simulation forecast of the optimum pore structure for CO<sub>2</sub> separation. Based on the simulation results, we have selected a number of candidate zeolite structures for use in CO<sub>2</sub> separation studies and have begun synthesis of new zeolite membranes. In addition, we are continuing to prepare several zeolite seed crystals, from which several new zeolite membranes are anticipated. For example, we have newly prepared a thin KFI zeolite membrane (<1μm), which has not previously been reported, and successfully prepared pure silica CHA zeolite crystals that have previously been difficult to produce (figure 7). Evaluation of the separation performance of these new membrane materials is now in progress.



**Figure 7.** a) SEM cross-sectional image of a thin KFI zeolite membrane, b) XRD pattern and c) SEM image of pure silica CHA zeolite crystals.

## (2.2) Development of a synthetic method of defect-free mesoporous thin films.

The functionalization of the pore walls of mesoporous silicas is effective for selective CO<sub>2</sub> adsorption [5]. In this study, various functionalized mesoporous silica membranes for CO<sub>2</sub> separation were successfully prepared on porous alumina supports by hydrothermal treatment and spin-coating of silica sol. SEM images showed that these techniques deposited dense mesoporous silica layers of 200 and 500 nm, respectively, on the alumina supports. From the TEM and XRD observations, it was shown that these membranes have a highly ordered cubic structure with a pore diameter of ca. 2 nm. The gas permeation properties of these mesoporous silica membranes were governed by the Knudsen diffusion mechanism. Surface modification of the pore walls of these mesoporous silica membranes by grafting amino-silane greatly improved the CO<sub>2</sub> permselectivities. After amine

modification, the thickness of the dense mesoporous silica membrane layer prepared by the hydrothermal method increased to 2000 nm, while no obvious change was observed for the membrane prepared by the spin-coating method. Immersion of the porous alumina substrate into liquid paraffin before spin-coating of the silica sol was effective at preventing the sol from percolating into the pores of the substrate, causing the formation of a dense layer. The amine-modified mesoporous silica membrane prepared by the spin-coating method showed higher CO<sub>2</sub> permeability and selectivity than the membrane prepared by the hydrothermal method, because of the thinner separation layer. Both of the amine-modified membranes showed extremely high CO<sub>2</sub> permselectivity and their  $\alpha(\text{CO}_2)$  values at 373 K were 50 and 800, respectively. It was confirmed that amine-modified mesoporous silica layers work as an effective CO<sub>2</sub> separation layer, and this result showed a possibility of CO<sub>2</sub> separation at high temperature.

However, the CO<sub>2</sub> permeability of the obtained modified mesoporous silica membrane is not sufficient (CO<sub>2</sub> permeance =  $2.2 \times 10^{-11} \text{ m}^3(\text{STP}) \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ ). Therefore, in order to improve the CO<sub>2</sub> permeance, various mesoporous silica membranes with different pore size/structures on porous alumina and glass substrates were prepared by hydrothermal, sol-gel spin-coating and sol-gel dip-coating techniques. It was found that hydrophobizing treatment of the porous substrates was effective for the preparation of thin separation layers. Based on this, we have prepared SBA-16 membrane with high gas permeability (CO<sub>2</sub> permeance =  $5.0 \times 10^{-9} \text{ m}^3(\text{STP}) \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ ). Optimization of the guest material for surface functionalization of the pore walls is now in progress.

## **Progress**

### (1) Carbon membranes

#### (1.1) Sub-nanoporous carbon membranes with CO<sub>2</sub> affinity enhancement

Novel carbon membranes with CO<sub>2</sub> affinity enhancement have been developed. The prepared membranes showed much higher separation factors than ordinary carbon membranes in the separation of CO<sub>2</sub>/N<sub>2</sub> mixtures. Further information will be disclosed when the intellectual property issues are resolved.

#### (1.2) Nanoporous carbon membranes with CO<sub>2</sub> affinity molecules

Efforts were made to prepare nanoporous carbon membranes. So far, the pore diameter of the pores that contribute to gas permeation is of the sub-nano order. Study is ongoing to prepare carbon membranes having nanoporous continuous pores.

### (2) Inorganic membranes

(2.1) It was revealed that the formation of a complex layer of zeolite and the substrate improved the permeation performance when compared with the membrane prepared by arranging crystals on the substrate.

(2.2) In order to improve the CO<sub>2</sub> permeance of the mesoporous silica membrane, it was deemed necessary to pre-treat the porous substrate and optimize the mesopore pore structure for CO<sub>2</sub> separation.

(2.3) Screening tests are ongoing.

### **Future Plans**

#### (1) Carbon membranes

##### (1.1) Sub-nanoporous carbon membranes with CO<sub>2</sub> affinity enhancement

The precursors and CO<sub>2</sub> affinity materials will be optimized to improve the separation performance further. In addition, the preparation conditions will be optimized. Detailed characterization and separation performance measurements will be conducted on the prepared novel carbon membranes.

##### (1.2) Nanoporous carbon membranes with CO<sub>2</sub> affinity molecules

The preparation conditions will be optimized to obtain nanoporous carbon membranes. After nanoporous membrane structures have been realized, CO<sub>2</sub> affinity molecules such as PAMAM dendrimers will be inserted into the nanopores of the carbon membranes, and the separation performance examined.

#### (2) Inorganic membranes

##### (2.1) Development of defect-free zeolite membranes

We will investigate the most suitable condition of the formation of a complex layer of zeolite and the substrate for high CO<sub>2</sub> separation properties. Through these experiments, it is revealed that difference in the coefficient of thermal expansion between the zeolite membrane and substrate needs to be taken into the consideration to prepare defect-free membranes. Therefore, we will develop structures that are effective for thermal stress relaxation above mentioned.

##### (2.2) Functionalized mesoporous membrane with high permeance:

The surface functionalization of the mesoporous oxide membrane by chemical grafting of the guest-material will be studied.

##### (2.3) Screening test:

Various kinds of ultra-thin zeolite membranes with different pore diameters and pore structures, together with various functionalized mesoporous membranes, will be examined in future screening tests.

## **Publications**

1. "Preparation and application of novel carbon membrane", Japanese patent application (in preparation).
2. "A new preparation method of dense zeolite membrane – melt filing of zeolite seed crystals into porous substrate and the formation of dense composite layer –", Japanese patent application (in preparation)

## **References**

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