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Microporous CO2 Capture Membranes Promoted by Carbonic Anhydrase-Mimetic Catalyst

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GHALEI, Behnam

3,200,000

CO2

ZnCl2   0.001, 0.01, 0.1 mM

Zn2+

~0.59M1s-1   PEG   CO2   SEM

CO2/N2   100%

CO2

CO2 emission from fossil fuel combustion is the main cause for the climate change. Biological CO2 capture provides ecofriendly solution to address this issue. Here, a novel biomimetic enzyme synthesized and incorporated in polymers to fabricate high performance membranes for practical CO2 capture.

Here, we develop novel mimic enzyme promoted CO2 facilitated transport membranes for CO2 capture. The hystidyl bolaamphiphile compound with amino acid heads and alkyl chain body was synthesized. The bolaamphiphile solution were incubated with ZnCl2 in different concentrations (0.001, 0.01 and 0.1 mM) to generate CA-mimetic particles through coordination of Zn2+ ions with the histidine imidazole groups. The self-assembled particles with the highest catalytic efficiency (~0.59 M1.s-1) was selected as the nanofiller to enhance the CO2 separation performance of PEG-based polymers. The SEM image showed the uniform dispersion of the particles inside the polymer matrix due to the strong interactions. The significant enhancement (up to 100%) in the CO2/N2 selectivity of the composite membranes compared with the pure polymer matrices was observed. The high CO2 adsorption of the CA-mimic particles and their catalytic functionality are the main reasons for this observation.

Membrane gas separation processes for CO2 capture

Gas separation Membranes Enzyme mimetic CO2 capture

１．研究開始当初の背景

Greenhouse gas emission and its impact on global warming has brought great attention to the need of separating CO_2 from flue gases (Carbon capture and storage). Currently chemical absorption of CO_2 in a liquid stream is the most investigated strategy for CO_2 capture. However, it is also known as an energy intensive process, which requires high capital investment and suffers from several operational challenges [1].

Membrane technology has emerged as a practical method because of its relatively low energy consumption, high packing density, small foot print, and scale-up capabilities. This process enables CO_2 to be concentrated at the downstream side of the membrane. Membrane should possess several characteristics including high CO_2 permeability, high CO_2/N_2 selectivity, thermal and chemical stability, and resistance to aging to be considered as effective materials for carbon capture from flue gas. However, conventional polymer membranes suffer from a trade-off between membrane properties such as permeability and selectivity. Different approaches have been utilized to enhance the gas separation performance and to suppress the industrial limitations of membranes including: synthesizing functionalized polymer structures, surface modification, chemical and thermal cross-linking, UV photo-oxidation and adding nano-fillers [1].

The biomimetic approach represents a promising eco-compatible scenario for carbon dioxide capture due to its specificity for CO_2 and the ability to hydrate CO_2 rapidly to form water soluble ions (HCO_3^-). For example, the enzyme carbonic anhydrase has been proposed as a rate promoter for CO_2 absorption due to its high catalysis efficiency and high selectivity for carbon dioxide hydration. Carbonic anhydrase (CA) is an enzyme that in found in mammals, marine species and bacteria. It is responsible for rapid catalyzing of CO_2 hydration reaction with water to form bicarbonate, 10^4-10^6 CO_2 molecules per second. The active site of CA is containing one distorted zinc (Zn) center coordinated to three imidazolic nitrogen atoms of histidine (His) residues and an aqua ligand in the fourth coordination site. The attached water molecule is supplying an O-H unit to fabricate bicarbonate ion (HCO_3^-) from CO_2. The imidazole coordinated Zn^{2+} ion facilitates the swift removal of hydrogen by polarizing the O-H bond [2].

２．研究の目的

Enzymatic membranes containing bio-organic enzymes (e.g. CA) is a type of facilitated transport membranes that could achieve efficient CO_2 separation by mimicking the function of mammalian respiratory system. However, several technical issues, including the thermal instability, short lifetime, pH-sensitivity, and high purification cost of CA, limited their practical applications. To overcome these hurdles, artificial CA-mimetic catalysts with high CO_2-philic properties have been considered in this proposal for designing highly efficient CO_2 capture membranes [3].

This work presents the development of novel mimic enzyme promoted CO_2 facilitated transport membrane for CO_2 separation from post-combustion flue gas. First, molecular self-assembly of a bolaamphiphilic molecule containing His motifs have been utilized as a facile way to replicate the triple-His imidazole of CA active center. Bolaamphiphile compounds

could create rigid and stable solid particles. Second, the synthesized particles were coordinating with metal ions such as Zn_{2+} to imitate the nature of CA active site and finally the functionalized self-assembled particles were applied to fabricate a thin film composite membrane in combination with a water-soluble polymer matrix.

３．研究の方法

(1) Enzyme mimic particles synthesis

The hystidyl bolaamphiphile compound with two amino acid heads and alkyl chain body with seven carbons was synthesized [3]. The L-histidine bolaamphiphiles were synthesized by the reaction of L-histidine methyl esters with azelaic acid (Sigma-Aldrich) (TCI, Japan) in the presence of N-ethyl-N-(gama-dimethylaminopropyl)carbodiimide (Sigma-Aldrich) and l-hydroxybenzotriazole (Sigma-Aldrich). The conjugation reaction was performed at 0-5 ℃ for 6 h to produce the intermediate ester product. Then sodium hydroxide hydrolysis and acid neutralization of the ester functions produces bolaamphiphiles. To prepare the self-assembled particles, the synthesized bolaamphiphile was dissolved in pH-controlled water (pH of 6 to 9) at a concentration of 5 mM. The bolaamphiphiles solution were incubated for 12 h to be self-assembled, then $ZnCl_2$ in different concentrations (0.001, 0.01 and 0.1 mM) was added to complete the production of the CA-mimetic particles through coordination of Zn_{2+} ions with the histidine imidazole groups.

(2) Polymer Synthesis

The polyethylene glycol based polyurethane polymer (PU) was synthesized by a two-step bulk polymerization method. 19.0 g Pluronic L-35 (Sigma-Aldrich) was reacted with 6.7 g isophorone diisocyanate (IPDI, Wako Pure Chemical) in the presence of dibutyltin dilaurate (DBTDL, Sigma-Aldrich) at 70 ℃. After 2 h mixing with a mechanical stirrer, 2.9 g 1,8-octanediamine (ODA, Sigma-Aldrich) in 50 mL anhydrous dimethylacetamide (DMAc, Wako Pure Chemical) was added to the mixture to obtain a high molecular weight PU. The synthesized PU was dried under vacuum at 80 ℃ overnight.

(3) Composite membrane preparation

The self-assembled particles (CA-mimic) were used as a filler to enhance the CO_2 separation performance of water-soluble PEG-based polymers, i.e. Pebax 1657 and PU. The PU and Pebax 1657 nanocomposites at various enzyme mimic particle loadings (5 and 10 wt%) were prepared in Ethanol/Water solution (70/30 v./v.). The membranes were fabricated by the solution casting method in Teflon Petri-dishes at 50 ℃ overnight. The membranes were removed and dried under vacuum at 70 ℃ for 24 h. The average thickness of the membrane was bout 70-micron as measured by a micrometer (Mitutoyo, Model S406, Japan). CO_2 and N_2 gas permeability of the membranes was measured using the constant volume–variable pressure method at room temperature and 2 bar. For each sample, three membranes were tested, and the average permeability coefficients were reported.

4．研究成果

The nuclear magnetic resonance spectroscopy ($_1$HNMR) confirmed that dicarboxylic acids were properly conjugated with the histidine methyl ester and the hydrolysis reaction is completed (Fig. 1-a). The SEM image showed aggregated structure of the self-assembly prepared at pH 7 (Fig. 1 c). However, the self-assembled structures changed to bloblike aggregates, with more discrete morphology when the pH increased to 9 (Fig. 1 b).
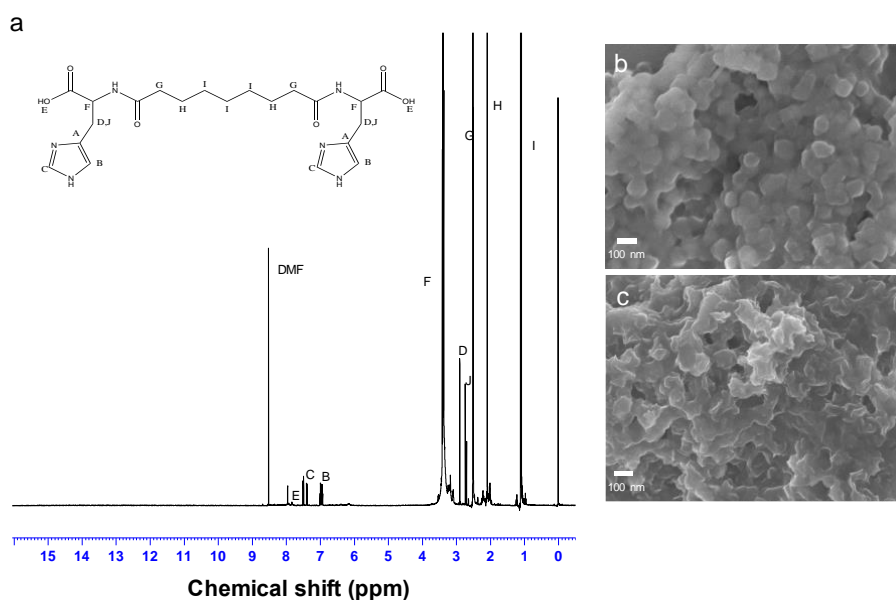

Fig. 1. (a) $_1$HNMR spectroscopy analysis of L-histidine bolaamphiphile. SEM images of the self-assembled synthesized L-histidine bolaamphiphile at (b) pH 9 and (c) pH 7.

The self-assembled L-histidine bolaamphiphile with Zn^{2+} ions functioned as a CA-mimic, and were used as catalyst to hydrate CO_2. The catalytic activities were tested at various Zn^{2+} concentrations. The activity of the CA-mimetic catalyst was determined from the deacetylation of para-nitrophenylacetate (p-NPA), following Michaelis–Menten kinetic model. This reaction has similar mechanism as CO_2 hydration. The effect of the Zn^{2+} ions content on the catalytic activity of the CA-mimic particles was investigated to determine the optimal concentration of the Zn^{2+} ions and presented in Table 1. The catalytic efficiency of mimic enzymes decreased as the concentration of the Zn^{2+} ions increased. This might due to the formation of hydroxide bridge between two Zn^{2+} ions. An increase in the concentration of the Zn^{2+} ions could deteriorate the active Zn–imidazole complex by creating bridged Zn^{2+} ions.

Table 1. The catalytic efficiency of mimic-CAs with different Zn^{2+} concentrations.

Zn^{2+} (mM)	V_{max} (mM/s)	K_m (mM)	K_{cat} (s^{-1})	Catalytic efficiency (k_{cat}/K_m) (1/M.s)
0.001	0.002309	2.01	0.0012	0.59
0.01	0.001879	2.56	0.0009	0.35
0.1	0.0004544	1.59	0.00045	0.28

The average molecular weight (M_w) and polydispersity index (PDI) of the synthesized polyurethane were determined using gel permeation chromatography (GPC, Shimadzu, 800 series) and found to be 65 000 g/mol and 1.4, respectively. The chemical structure of the polymer is shown in Fig. 2 (a).

The CA-mimic enzyme with the highest catalytic efficiency (0.001mM Zn^{+2}) was selected as the filler for the development of composite membranes. The dispersion and miscibility of the CA-mimic particles in the PU matrix were further explored by microscopy images (Fig. 1c). The SEM image in Fig.2 (b) shows the uniform dispersion of the particles inside the polymer matrix which confirmed the strong interaction of the CA-mimic fillers with the Pebax chains.

Table 2. The gas separation of membranes at 2 bar and 25 ℃.

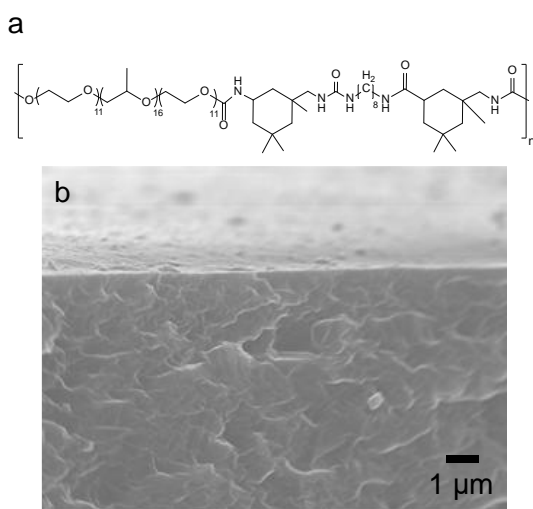| Membrane	Permeability (Barrer)		Selectivity
	N_2	CO_2	CO_2/N_2
Pure Pebax	1.8	92.7	51.5
Pebax+5 wt% filler	0.9	74	82.2
Pebax+10 wt% filler	0.7	73.1	104.4
Pure PU	3	129	43
PU+5 wt% filler	2.2	115	52.4
PU+10 wt% filler	1.8	102	56.7

Fig. 2. (a) Chemical structure of synthesized PU, (b) Cross-section SEM image of Pebax/10 wt% CA-mimic filler.

The gas permeability and selectivity of the PU and Pebax based membranes were tested at 2 bar and 25°C. The impact of CA-mimic fillers on the transport properties of membranes is presented in Table 2. The considerable enhancement (up to 100%) in the CO_2/N_2 selectivity of the membranes comprising CA-mimic fillers compared with the pure polymer matrices was observed. The high CO_2 adsorption of the CA-mimic particles and their catalytic functionality are the main reasons for this observation. The effect was more significant for the membranes based on Pebax which could be due to the morphological changes in the Pebax structure in the presence of the fillers.

In summary, we synthesized CA-enzyme mimic particles and utilized them as efficient nanofillers to enhance the selectivity of the polymer matrices for CO_2 capture. The resulting composite membranes showed exceptional CO_2 separation property due to the catalytic effect of the enzyme mimic particles on the hydration of CO_2 molecules.

References:
[1] Ghalei, Behnam, et al. *Nat. Energy* 2.7 (2017): 17086.
[2] Yao, Kai, et al. *ChemComm* 48.12 (2012): 1766-1768.
[3] Kim, Min-Chul, and Sang-Yup Lee, *CHEM-EUR J* 20.51 (2014): 17019-17024.

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Ali Pournaghshband Isfahani , Morteza Sadeghi , Somaye Nilouyal , Ansori Muchtar , Guoji Huang , Masateru Ito , Daisuke Yamaguchi , Easan Sivaniah and Behnam Ghalei							-	
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