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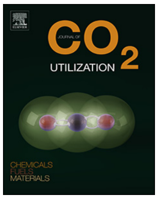

Charge controlled switchable CO_2/N_2 separation for g-$C_{10}N_9$ membrane: Insights from molecular dynamics simulations

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ABSTRACT

Using molecular dynamics simulations, we theoretically demonstrate that the CO_2/N_2 separation performance of g-$C_{10}N_9$ membrane can be controlled by introducing different charges into this membrane. It is found that neutrally charged g-$C_{10}N_9$ membrane is non-selective for CO_2/N_2 separation resulting from its large pore size. However, positively charged g-$C_{10}N_9$ membrane with charge density of 88 × 10^{13} e/cm^2 exhibits 100% N_2/CO_2 selectivity, and the CO_2/N_2 selectivity of negatively charged g-$C_{10}N_9$ membrane with charge density of -60 × 10^{13} e/cm^2 is more than four times higher than that of neutrally charged g-$C_{10}N_9$ membrane. Furthermore, it is shown that the CO_2/N_2 separation performance of charged g-$C_{10}N_9$ membrane is influenced by the number of CO_2 molecules blocking at the pores and the binding energy between CO_2 molecules and charged g-$C_{10}N_9$ membrane, which are determined by positive or negative membrane charge and charge density. Our results manifest that charge control is an excellent method for g-$C_{10}N_9$ membrane to realize switchable CO_2/N_2 separation.

1. Introduction

Carbon dioxide (CO_2) is not only the main greenhouse gas, which excessive emissions from flue gas (mainly composed of CO_2 and N_2) can result in global warming and ocean acidification [1,2], but also an important chemical raw material, which is widely used for enhanced oil recovery and CO_2 conversion [3–7]. Therefore, exploring effective materials and technologies for CO_2 capture and separation is an urgent task [8–11]. Up to now, a variety of CO_2 separation technologies, including cryogenic distillation, pressure swing adsorption and membrane separation [12–14], have been developed. Especially, membrane separation has received significant attention due to facile operation and high-energy efficiency [15–18]. Normally, the gas permeance of a membrane is inversely proportional to its thickness [19]. Hence, two dimensional (2D) membranes with single-atom thickness are ideal candidates for gas separation. Fortunately, graphene was discovered in 2004 and extensive investigations proved that graphene was a good membrane for CO_2/N_2 separation [20,21]. Shan et al. [22] reported that the CO_2/N_2 selectivity of all-N modified pore-16 graphene could reach 11, which was 11 times higher than that of unmodified pore-16 graphene. Wu et al. [23] found that with modifying fluorine around the pore, the CO_2/N_2 selectivity of porous graphene could be greatly enhanced. This was because that the fluorine modification could slightly reduce the diffusion barrier for CO_2 to pass through the porous graphene and greatly increase the diffusion barrier for N_2. Apart from graphene, substantial 2D materials were successfully synthesized, such as graphdiyne, silicene, germanene and graphitic carbon nitrides [24–27]. It should be mentioned that these 2D materials were generally applied for H_2 or He separation, which was attributed to their suitable pore size. Relatively rare studies were conducted to investigate the CO_2/N_2 separation performance of these 2D membranes owing to their limited pore sizes.

Recently, graphitic carbon nitrides received considerable interest for CO_2/N_2 separation. By superacid-catalyzed cross-linking reactions at a much lower temperature, Zhu et al. [28] developed one triazine-framework-based porous membrane (TFM-1) for CO_2 separation. It was demonstrated that TFM-1 exhibited an ideal CO_2/N_2 selectivity of 29 ± 2 with a CO_2 permeance of 518 ± 25 Barrer (1 Barrer = 3.35×10^{-16} mol m m^{-2} s^{-1} Pa^{-1} [29]). Qu et al. [30] proposed a generalized model via distinct quadrupole moments of these two gas molecules to obtain efficient CO_2/N_2 separation membranes. It was reported that the CO_2 permeance of g-$C_{12}N_8$ membrane could reach about 2.8×10^5 GPU (1 GPU = $3.348 \times 10^{-1\circ}$ mol m^{-2} s^{-1} Pa^{-1} [31]) while this membrane was impermeable to N_2. Remarkably, most

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previous studies focused on CO_2-selective membrane, which was suitable for high CO_2 concentration in flue gas [32]. When the CO_2 concentration is not high enough in flue gas, N_2-selective membrane becomes a more appropriate choice due to low energy cost [33,34]. With molecular dynamic (MD) simulations and density functional theory (DFT) calculations, Wang et al. [35] studied the N_2/CO_2 separation performance of poly (triazine imide) (PTI) membrane. They revealed that PTI was an efficient N_2-selective membrane possessing excellent N_2/CO_2 selectivity and high N_2 permeability. Very recently, Zhang et al. [36] proposed one new graphitic carbon nitride framework (g-$C_{10}N_9$) with a band gap of 2.07 eV, which was constructed by s-triazine (C_3N_3) and carbon-rich tri-s-triazine (C_7N_6) through C—C covalent bonds. Since g-$C_{12}N_8$ and PTI can be used for CO_2/N_2 separation [30,35], as well as the structure of g-$C_{10}N_9$ is similar to them, g-$C_{10}N_9$ may be a promising membrane for CO_2/N_2 separation.

Notably, there were some valuable theoretical simulations showing that the charge states of the membrane could affect CO_2 capture and hydrogen purification performance [37–39]. Sun et al. [37] theoretically confirmed that injecting electrons to the BN membrane could drastically enhance CO_2 adsorption energy and the negatively charged BN nanomaterials were excellent absorbents to realize CO_2 capture with high selectivity. Li et al. [38] manifested that injecting negative electrons instead of positive electrons into the C_3N membrane could significantly improve CO_2 adsorption strength. Tan et al. [39] suggested that negatively charged g-C_4N_3 nanosheets with charge density of 73.9×10^{13} cm^{-2} exhibited high CO_2 capture capacities. In addition, they [40] found that injecting positive charges into graphdiyne could significantly enhance its H_2 selectivity and permeance, resulting from lower penetration barrier for H_2 and higher penetration barriers for CO and CH_4.

On the basis of above literature surveys, we find that there are relatively few studies devoted to CO_2/N_2 separation of these porous 2D membrane via controlling membrane charge. Then we obtain a considerable question: could charge controlled g-$C_{10}N_9$ membrane serve as an excellent CO_2/N_2 separation membrane? To answer this question, here, we investigate the CO_2/N_2 separation performance of neutrally, positively and negatively charged g-$C_{10}N_9$ membrane via MD simulations. Furthermore, we study the CO_2/N_2 separation mechanism of charged g-$C_{10}N_9$ membrane from the perspective of energy and structure.

2. Computational methods

2.1. Models

Fig. 1a presents the optimized g-$C_{10}N_9$ structure in a 2 × 2 supercell. The optimized lattice constant for a g-$C_{10}N_9$ cell is 9.42 Å. The maximum distance between atoms (d_{max}) is 8.11 Å and the minimum distance between atoms (d_{min}) is 4.67 Å. The length of C—C bond bridging building blocks is 1.51 Å, the length of C—C bond around the center of the C_7N_6 units is 1.41 Å and the length of C—N bond is 1.35 Å, which are in good agreement with previous studies [36]. Fig. 1b shows the MD simulation model we used to investigate the CO_2/N_2 separation performance of g-$C_{10}N_9$ membrane. The initial model consists of fixed helium wall, fixed g-$C_{10}N_9$ membrane (47.45×48.86 Å^2), feed side (150 relaxed CO_2 molecules and 150 relaxed N_2 molecules) and permeate side.

2.2. Density functional theory calculations

Based on the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) function [41–44], DFT calculations are conducted to optimize the g-$C_{10}N_9$ structure. Double numerical with polarization function (DNP) is adopted to expand electronic wave functions. Self-consistent field (SCF) is used with a convergence criterion of 10^{-6} a.u. on the total energy. Thermal smearing is set as 0.002 eV to speed up the self-consistent field convergence. Grimme's method is adopted to make a dispersion correction. A 6 × 6×1 Monkhorst-Pack k-point mesh is used to express the Brillouin zone integration.

2.3. Molecular dynamics simulations

MD simulations are conducted to investigate the CO_2/N_2 separation performance of charged g-$C_{10}N_9$ membrane. The atomic interactions are expressed by the condensed-phase optimized molecular potential for atomistic simulation studies (COMPASS) force-field. The canonical ensemble (NVT) is adopted in the MD simulations. The thermodynamic temperature of 298 K is controlled by the Andersen thermostat method. The atom-based van der Waals interactions and Ewald electrostatic interaction are performed with a cutoff distance of 12.5 Å. All the simulations are performed 5 ns and the data is collected every 5 ps with a fixed time step of 1 fs.

3. Results and discussion

3.1. The CO_2/N_2 selectivity of g-$C_{10}N_9$ membrane

3.1.1. The CO_2/N_2 selectivity of neutrally charged g-$C_{10}N_9$ membrane

Prior to investigating the gas separation performance of g-$C_{10}N_9$ membrane, we compute the cohesive energy of the g-$C_{10}N_9$ membrane, namely, the energy required to decompose the g-$C_{10}N_9$ structure into isolated C and N atoms, which can be expressed by [45,46]:

$$E_{coh} = (n_C E_C + n_N E_N - E_\varepsilon)/(n_C + n_N)$$

where E_C, E_N, E_ε are the energy of single C atom, single N atom, total g-

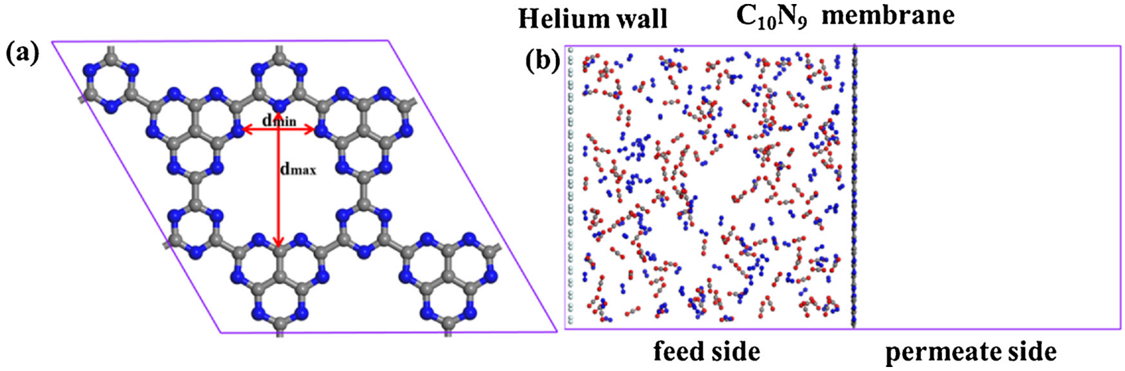

Fig. 1. (a) The optimized structure of g-$C_{10}N_9$ membrane in a 2 × 2 supercell. (b) The MD simulation model of CO_2/N_2 separation for g-$C_{10}N_9$ membrane. (Gray, red, blue, cyan balls represent carbon, oxygen, nitrogen, helium atoms, respectively.) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).