Masoud Arabieh*, S. Mahmood Fatemi and Hamid Sepehrian

Molecular Perspective of Radionuclides Separation by Nanoporous Graphene Oxide Membrane

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Abstract: Graphene-derived membranes has gained much interest recently due to its promising potential in filtration and separation applications. Molecular Sieving phenomena of gas molecules in the interlayer of graphene oxide nanopore have been investigated using molecular dynamic (MD) simulation. We explore I-129 gas radionuclides sequestration from natural air in nanoporous graphene oxide membranes in which different sizes and geometries of pores were modeled on the graphene oxide sheet. In the present work, mean-squared displacement (MSD), diffusion, flow of gas and the number of crossed gas molecules through graphene oxide nanopore membrane have been calculated and the results showed, selective proper nanopores in graphene oxide membrane could dramatically improve separation. The aim of this paper is to show that for the well-defined pore size called P-12, it is possible to separate I-129 from a gas mixture containing I-129, O_2 and N_2. The results would be benefited by the oil industry and others.

Keywords: molecular dynamic (MD) simulation, graphene oxide (GO) nanopore membrane, separation, diffusion coefficient

1 Introduction

Isotopes of iodine play significant environmental roles including, a geochemical tracer (^{129}I), limiting micronutrient (^{127}I), and an acute radiotoxin (^{131}I). ^{129}I is long-lived fission products that produced in significant amounts, this radioactive gas released into the environment by nuclear explosions, nuclear power plants, nuclear weapons and also naturally. Because I-129 is long-lived and relatively mobile in the environment, it is of particular importance in long-term management of spent nuclear fuel. The separation of such an important gas is an interesting subject of scientific investigations. Gas separation membranes allow one component in a gas stream to pass through faster than the others. There are many different types of gas separation membrane, including zeolites, silica and polymers [1,2]. As a novel one-atom-thick planar sheet of sp^2-bonded carbon atoms, packed in a honeycomb lattice, graphene has received much attention in recent years in materials science. Significant progress has been made for the utilization of graphene nanopore in gas separation and purification [3,4]. Furthermore, graphene is easy to produce from natural graphite through chemical oxidation-dispersion-reduction procedure at a low cost. Through chemical oxidation, natural graphite can be effectively oxidized and exfoliated into GO with the introduction of oxygen-containing functional groups. The presence of oxygen-containing functional groups in GO and reduced graphene makes them as excellent supporters for enhancement of wide applications [5,6], to date, there are only a few reports in the separation of gas with GO nanopore

2 Body of article

The molecular permeation of three different diatomic gases, namely I_2, O_2 and N_2 through GO nanopore membranes which different pore sizes were investigated. We considered the Iodine-129 isotopes in the gas mixture system. For simplicity, throughout the text the I-129 is shown by the general I_2 symbol. All MD simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package [7] and structures were visualized using the VMD package [8]. The all-atom optimized potentials for liquid simulations (OPLS-AA) was used for GO, which is able to capture essential many-body terms in the inter-atomic interactions, i.e. bond stretching, bond angle bending, van der Waals, electrostatic interactions and partial charges. The simulation was performed in an NVT ensemble for 5 ns. The Nosé-Hoover barostat and thermostat were applied to maintain the pressure and temperature at 1 atm and 300 K, with damping coefficients 1 ps^{-1} and 0.1 ps^{-1}, respectively and time step of 0.2 fs was

***Corresponding author: Masoud Arabieh,** Nuclear Science and Technology Research Institute, AEOI, P.O. Box 11365/8486, Tehran, Iran, E-mail: arabieh@gmail.com
S. Mahmood Fatemi, Hamid Sepehrian, Nuclear Science and Technology Research Institute, AEOI, P.O. Box 11365/8486, Tehran, Iran, E-mail: mahmoodfatemi@ut.ac.ir; hsepehrian@aeoi.org.ir

used during the simulation. Non-bonded van-der-Waals interactions were modeled in terms of 12–6 Lennard-Jones famous potentials with a cut-off distance of 1.2 nm. SHAKE algorithm was applied for the stretching terms between oxygen and hydrogen atoms of the GO to reduce high-frequency vibrations that require shorter time steps. The particle mesh Ewald (PME) method with a 10.0 Å real-space cutoff, 1.5 Å reciprocal space gridding, and the splines on the order of 4 with a 10^{-5} tolerance was implemented to compute the electrostatic interactions. A simulation box with the dimensions of 30 Å × 30 Å × 80 Å was constructed and a GO nanopore membrane in the middle of the box in Cartesian coordinate origin (0, 0, 0) as the separator and dividing the simulation box with the height of 4 nm into two equal volume chambers, right and left chambers, see Figure 1.

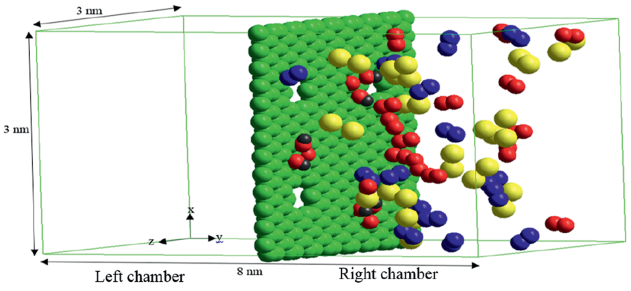

Figure 1: Initially MD snapshot of the gases loaded into the right chamber and the structures of the nanopores employed in the simulation, the colors assigned to each molecule: red, O_2; yellow, I_2 & blue, N_2, green, C; black, H).

Initially, an equal number of 15 molecules of I_2, O_2 and N_2 were loaded into the right chamber (see Figure 1), while the other side (left chamber) was a vacuum. Various sizes of pores were considered, which were called by the number of graphene ring units removed or partially opened, i.e., pore-7 (P-7), P-10, P-11, P-12, P-13, P-14.

3 Result and discussion

In this section, we analyze the plots of mean-squared displacement (MSD) for various pores, in the following diffusion coefficients were investigated.

3.1 MSD

Figure 2 shows MSDs versus time in the pore-12 of the GO nanopore membrane. Figure 2 demonstrates that, only O_2 cross through the membrane because the size of pore is bigger than kinetic diameter of O_2, and is smaller than N_2 and I_2 molecules.

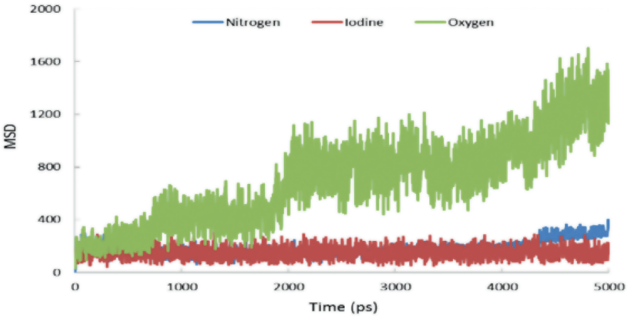

Figure 2: Calculated MSD vs. time for I_2, N_2 and O_2 in the pore-12 GO nanopore membrane.

3.2 Diffusion coefficients

Using MD trajectories, the diffusion coefficients of I_2 and air in the various ring of GO nanopore membrane were calculated. The diffusion coefficients were evaluated from the limiting slope of the MSD curve against time using the Einstein relation [9]. The diffusion coefficients ($Å^2$ ps^{1-}) for titled molecules can be calculated from the MSD vs. time graphs. These quantities are summarized in Table 1.

The results show that: (I) no molecule passes throw the GO nanopore membrane in the pore-7, which is in contrast to the pore-14 case, (II) the pore-12 is more favored for I_2 separation. Accordingly, the results of current simulations candidate the pore-12 of GO nanopore membrane for separation of I_2 from other air.

Table 1: Calculated coefficient diffusions for I_2, N_2 & O_2 at various pore sizes.

Molecule	Pore-7	Pore-12	Pore-14
O_2	0.0000	0.2578	0.4155
N_2	0.0000	0.0910	0.3442
I_2	0.0000	0.0000	0.3327

3.3 The number of crossed gas molecules through graphene membrane

To find the effect of the pore size in passing gas molecules through the GO nanopore membrane, the numbers of gas molecules passed the membrane were calculated. The measure of number of passing gas to be a count of

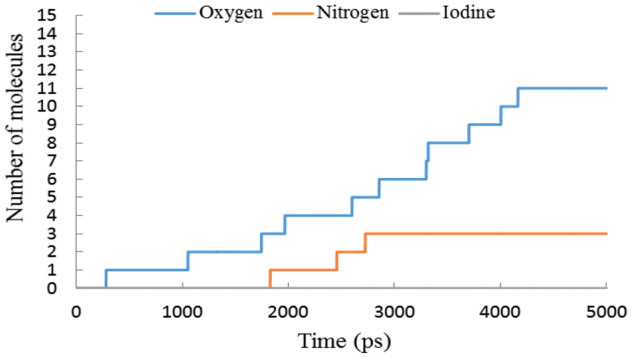

Figure 3: Total number of crossed gases through GO nanopore membrane vs. time for I_2, N_2 and O_2 in the pore-12.

the number of molecules on one side to the other side of the Go nanopore membrane at the current time point. None of gas molecules could cross through p-7 GO nanopore membrane. When the pore size is increased to p-12, still I_2 could not pass the membrane. Figure 3 show total number of crossed gas molecules through GO nanopore membrane vs. time for I_2, N_2 and O_2 in the pore-12 of GO nanopore membrane.

3.4 Calculating flow of gases

The flow is used to characterize the membrane permeability quantitatively. The flow of I_2, O_2, and N_2 was calculated in various pore size models, as shown in Figure 4.

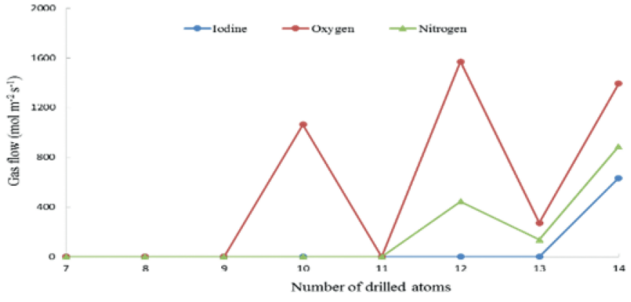

Figure 4: Flow of gases passing through the GO nanopore membranes at different pore areas.

There was a prodigious increase in the flow of I_2 at P-12's area, where the restriction of the size and shape to the N_2 permeation begins to vanish. After that, the flow of O_2 and N_2 molecules became reduced. In the case of the nitrogen and oxygenf molecules, the flow of nitrogen and oxygen molecules reduced at the pore-13, which is due to the different shape of the pore-12 and the pore-13. After that, the nitrogen and oxygen flow increases as the pore area increases.

4 Conclusion

We found that the graphene oxide nanopore membrane could be used to separate iodine-129 gas radionuclides from the air. Selectivity and permeability could be controlled by drilling different shapes and size of pores on a graphene membrane. The separation of I_2 from the air could be achieved by using pore-12 graphene oxide sheet. The restriction of the molecular orientation largely prohibits the permeation of I_2 molecules. When nitrogen and oxygen molecules are not blocked by the pores (e.g., pore-12), there are more oxygen molecules that permeate through the GO nanopore membrane than nitrogen molecules. However, in the pore-12, the best selectivity of I_2 from the air is achieved with the pore size barely bigger than the nitrogen and oxygen molecules and smaller than the I_2 molecules.

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