Gas Separation With Graphene Membranes

By Will Soutter

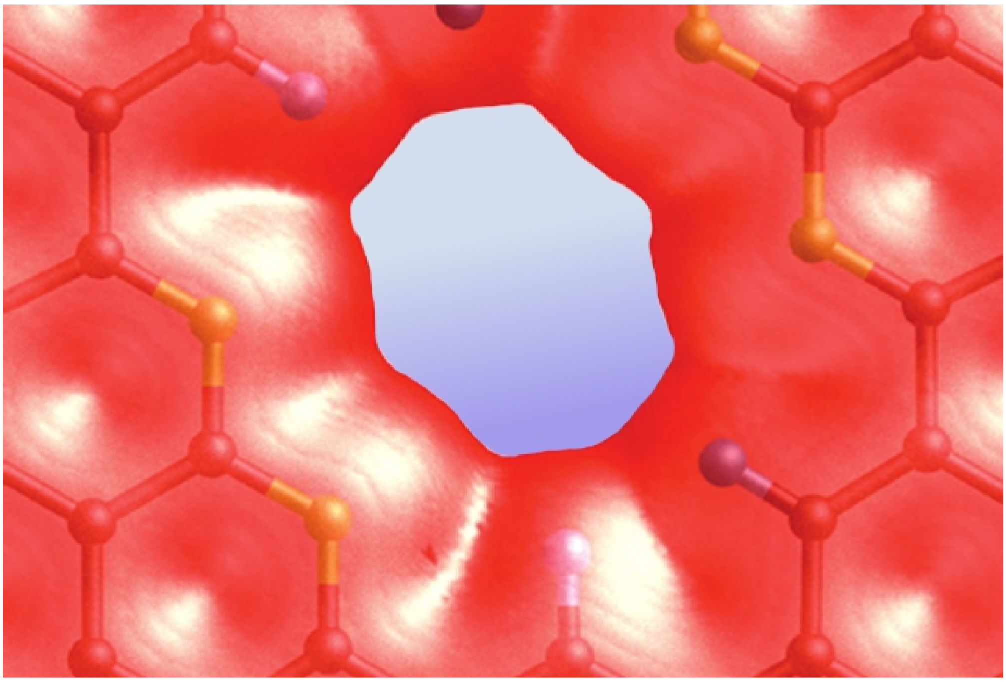
Introduction

The separation of gas mixtures using nanoporous materials is an emerging field of research with many potential applications including fuel cells, batteries, gas sensors and gas purification. The materials that are currently being investigated for these applications include organic polymer-based membranes, porous carbon, and inorganic membranes made of ceramics, metals or glass.

These membranes all have the key properties of chemical resistance and thermal stability. However, one membrane material may be able to beat them all - graphene.

Graphene is extremely strong, very stable and robust, and has properties ideally suited to use as a gas barrier. Tremendous efforts have been undertaken to achieve inexpensive fabrication of graphene sheets with large enough for applications like this since the discovery of graphene in 2004.

Nano-sized pores have to be artificially produced to obtain functional gas membranes using graphene, as the graphene sheet is impermeable even to helium. Post-treatment techniques like electron–hole drilling are suitable for pores in the nanometer range, and smaller pores can be created by catalyzed polymerization at high temperatures.



Sub-nanometer pores in graphene sheets can be used to separate gases based on their molecular size. Image credit: NERSC

What is Graphene?

Graphene is a single atomic layer of carbon atoms, covalently bonded in a regular hexagonal pattern. Graphite is made up of many stacked graphene sheets, and graphene was first isolated by removing a single sheet from a graphite crystal.

This first isolation was achieved in 2004 by Andre Geim and Konstantin Novoselov from the University of Manchester, who were awarded the Nobel Prize in Physics in 2010 for the work. The discovery resulted in a wealth of research work by groups all over the world exploring the physical properties and applications of graphene.

Graphene is the thinnest material in the world, and is impermeable to all gases. These characteristics make graphene an ideal material for gas separation membranes.

Benefits of Graphene in Gas Separation Membranes

The key benefits of using graphene in gas separation membrane include the following:

- Impermeable to all gases
- Thickness of less than a nanometer
- Very high tensile strength
- Can withstand pressure up to 100 mbar
- Pores must be created, allowing control over pore size and therefore gas selectivity.

Recent Developments

In October 2012, researchers from the University of Colorado Boulder showed that atomically thin graphene membranes perforated with small pores can efficiently separate gas molecules using a size-selective sieving technique. The team introduced nanoscale pores into graphene sheets via UV-induced oxidative etching.

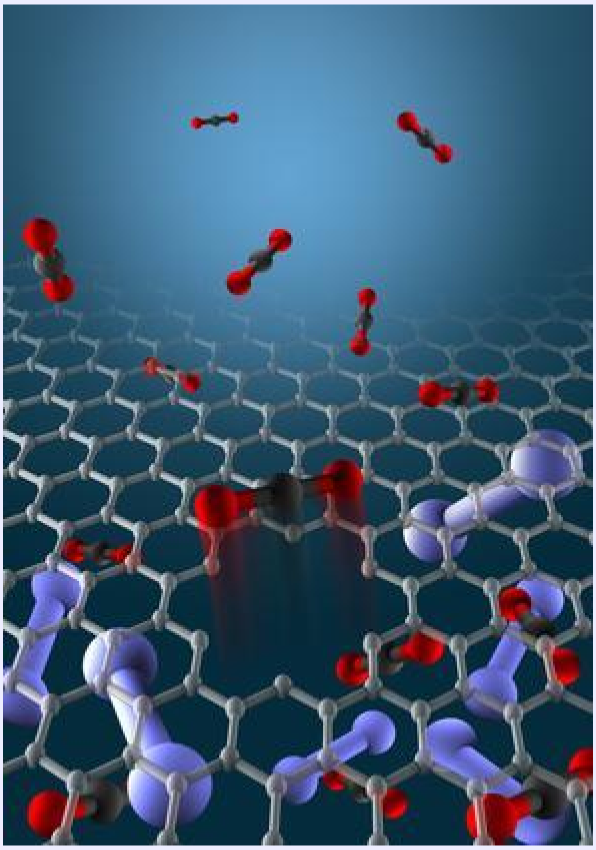


Illustration of a single molecular-sized pore in a graphene membrane separating carbon dioxide from nitrogen. Image credit: Zhangmin Huang, University of Colorado Boulder.

The permeability of the membrane to various gases including sulfur hexaflouride, methane, nitrogen, argon, carbon dioxide and hydrogen was measured. These gases were chosen to cover a wide range of molecular diameters from 0.29 to 0.49 nm.

These experimental results revealed that gas transport through the porous graphene does occur, allowing development of a new range of molecular sieves based on graphene membranes.

In July 2012, researchers from Massey University assessed the capability of functionalized graphene nanopores in separating gases like methane, carbon dioxide and hydrogen from air using a model based on density functional theory.

They modelled the interaction between the pores and selected gas molecules, and concluded that normal and nitrogen-doped graphene pores can separate methane at room temperature.

As part of the study, transmission probabilities and selectivities for the gas molecules were also estimated as a function of temperature.

Despite the supposed inertness of graphene, interactions between the membrane and the gas molecules were shown to have an important role in the performance of the membrane.

This means that chemical functionalization of the pores could be as important as controlling the pore size when developing graphene gas membranes for practical applications.

Conclusion

The fact that the graphene membranes are thin is one of the great advantages of this novel type of membrane. Thin membrane allows large flux of gas to pass through it and does not require much additional energy to push the molecules through, and hence they are highly energy efficient.

In addition, the pore size in graphene membranes can be adjusted to suit the application, giving the membrane a very high selectivity.

The membranes currently being used for various industrial applications have thicknesses in the micron scale. These membranes employed in natural gas processing and power plants are thinner than the diameter of human hair. However, a large volume of gas has to be filtered for industrial uses which need large membranes.

Even these thin films are huge compared to the thickness of a graphene sheet, however. Graphene production technology is now reaching a point where sufficiently large sheets of high-quality graphene are available for gas filtration applications.

Whilst graphene membranes will remain to be an expensive option for some time, certain higher value applications may well begin to find the performance benefits worthwhile in the relatively near future.

References

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