The 70th Japan Society of Applied Physics Spring Meeting 2023
Highlighted Presentations Press Release

April 18, 2023

Hydrogen Isotope Gas Separation by Quantum Tunneling Effect of Graphene

Demonstration of a new purification technology for deuterium using graphene

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Summary

- **One atom thick graphene can efficiently separate hydrogen and deuterium.**
- **The separation ability of graphene originates from the quantum tunneling effect is demonstrated.**
- **It is a high potential as an inexpensive purification method of deuterium, which is an essential material for developing semiconductors, deuterated pharmaceuticals, and nuclear fusion.**

Satoshi Yasuda of the research group for surface and interface science, advanced science research center, Japan Atomic Energy Agency (JAEA), developed a new deuterium separation method utilizing a monoatomic layer of graphene (*1) and the quantum tunneling effect (*2) of hydrogen isotope ions. Unlike conventional purification methods that require a cryogenic environment, the new separation method developed in this study can effectively separate hydrogen and deuterium at room temperature and potentially become an inexpensive deuterium purification method because the technology and equipment already in widespread use can be diverted. It is expected to be an inexpensive purification method for deuterium, which is essential for improving the capacity of semiconductors and optical fibers, and can be used in the future for deuterated pharmaceuticals and as an energy source for nuclear fusion.

Detail

Highly efficient deuterium separation at room temperature by utilizing a single atomic layer of graphene

Deuterium (D_2) is an isotope of hydrogen (H_2) (*3) that is utilized to increase the durability of semiconductor integrated circuits and improve optical fiber propagation capability. It is expected to become essential for developing deuterated pharmaceuticals (*4) and the main fuel for nuclear fusion (*5).

Cryogenic distillation (*6), one of the deuterium production methods, has long been used to separate deuterium from a mixture of hydrogen and deuterium gas, which is the raw material. However, its low-cost performance during production has long been an issue due to the need to cool it to a cryogenic temperature of about -250 degrees Celsius during purification. Low "H/D separation ability" which is the capacity to separate hydrogen and deuterium, also annoys us. Although cheaper deuterium purification methods have been tested for more than half a century, they have yet to be put into practical use, and there is an urgent need to develop an innovative purification method with a new separation mechanism.

Graphene, which has a thickness of only one atom, with carbon atoms arranged in a beehive structure is typical atomic layer material. Recently, Dr. A.K. Geim et al. and his colleagues (*7) have suggested that graphene has the property of an "ion sieve" that allows more hydrogen ions (H^+) to pass through at room temperature than deuterium ions (D^+), and this function has been investigated as a separation membrane for the purification of deuterium. However, monoatomic layer graphene is difficult to handle, and thus few experiments have been conducted to verify its H/D separation ability, and the details of the separation mechanism have not been clarified.

Satoshi Yasuda and his research group members conducted precise verification experiments using a solid polymer electrochemical device that could easily control H^+ and D^+ flow. Simultaneously, they conducted theoretical verification and approached the separation mechanism. Thus, the quantum tunneling effect of H^+ and D^+ through graphene causes a high separation ability at room temperature due to the mass difference of the ions.

Demonstrated effectiveness through experiments and theoretical calculations using existing equipment

Solid-polymer electrochemical devices were used in these experiments. The device is based on a solid electrolyte membrane that can easily produce H^+ and D^+ flow via an electrochemical reaction. Graphene was attached to the membrane, and a palladium metal film was deposited on the graphene to create a double-structured anode. "One atomic layer of graphene is affixed and secured on top of the solid electrolyte membrane, making it easy to handle," says Yasuda.

When voltage is applied between the anode and cathode, the hydrogen and deuterium in the gas mixture supplied to the anode are absorbed by the palladium metal film, ionized, and released to the graphene side. The ionized hydrogen (H^+) and deuterium (D^+) permeate graphene flow to the solid electrolyte membrane, and are released again at the cathode as H_2, D_2, and HD gases. The amount of hydrogen and deuterium ions "sieved" through graphene can be evaluated by analyzing the amount of hydrogen isotope gas released at the cathode by gas analysis (Figures 1 – 3).

Quantitative evaluation of the hydrogen isotope gases observed at the cathode using the device showed that more hydrogen than deuterium was released. For comparative verification, using an anode consisting of only a palladium film without graphene attached to the solid electrolyte membrane showed that less hydrogen was released from the cathode. These results indicate that graphene has ability as an "ion sieve" for hydrogen isotope ions and has great H/D separation capacity.

The experimental results were verified by considering various theoretical models. It was found that the experimental results were best explained by a model in which hydrogen and deuterium ions permeate through graphene owing to the quantum tunneling effect. Lighter H^+ can permeate through graphene than D^+, causing the high H/D separation ability.

Potential for low-cost deuterium mass production

The deuterium separation method using the quantum tunneling effect of hydrogen isotope ions through graphene shows high H/D separation capacity that is ten times higher than that of the conventional method and is expected to significantly reduce production costs because it does not require a cryogenic environment, as conventional methods do. It should be noted that the evaluation system used in this study utilized polymer electrochemical devices, such as fuel cells and water electrolysis, which are already in commercial use. The fact that the verification was conducted using devices already in commercial use suggests that this research has great potential for social implementation.

“The polymer electrochemical devices used in this study were used to verify the H/D separation ability of graphene and its mechanism; however, they can also be used as deuterium purification devices,” said Yasuda. The research group is developing membranes with even higher separation performances while considering atomic layer material other than graphene to further reduce the production costs for practical use.

“If deuterium can be produced domestically at a low cost, it will be a great advantage for the domestic semiconductor industry and the pharmaceutical development sector and is expected to spur the development of future research fields, such as deuterated pharmaceuticals and nuclear fusion,” said Yasuda.

Annotation

*1 **Graphene**: Graphene is a sheet-like nanomaterial that consists solely of carbon atoms. It has a hexagonal structure of carbon atoms and is only one atom thick. Graphene has attracted attention in various fields because of its high electrical and thermal conductivity, high tensile strength, and other characteristics.
*2 **Quantum tunneling effect**: Because of their wavelike characteristics, light particles can pass through the barrier needed for a reaction without requiring energy. For hydrogen and deuterium ions to pass through graphene, they must climb over a "mountain" called the activation barrier, which requires a specific amount of energy. On the other hand, hydrogen and deuterium ions are lighter particles; thus, they can pass through the barrier without requiring energy, owing to the wave nature of the material. In this case, more hydrogen ions, lighter than the deuterium ions, permeate through. This phenomenon is known as the quantum-tunneling effect. The narrower the barrier of the target material, the more pronounced the quantum tunneling effect, which is most effectively manifested in graphene, which is one atom thick.
*3 **Deuterium**: Deuterium is an isotope of hydrogen, and its nucleus consists of one proton and one neutron. Hydrogen has no neutron in the nucleus. Therefore, although they are almost identical in size, deuterium ions (D^+) are approximately twice as heavy as hydrogen ions (H^+).
*4 **Deuterated pharmaceuticals (heavy drug)**: A drug labeled with deuterium. Metabolism slows when the C-H bond at the site where a drug is metabolized is replaced with a more stable C-D bond. This allows the drug to remain stable and effective in the body for long, reducing the number of steps taken and side effects.
*5 **Nuclear fusion**: This is a phenomenon in which light nuclei, such as hydrogen fuse with each other and change into heavier nuclei, such as helium; finally it occurs in the sun. In the DT fusion reaction, deuterium (D) and tritium (T) nuclei fuse to produce helium and neutrons. Because nuclear fusion reactions generate so much energy, it is said that if we can harness this energy, humanity will be free from energy problems.
*6 **Cryogenic distillation**: A method for separating substances by utilizing differences in boiling points. They are commonly used for separating various gases. When a mixture of hydrogen and deuterium gases is liquefied by cooling and then heated to partially evaporate the liquid, the concentration of deuterium in the liquid increases because more hydrogen, which boils easily, evaporates. This process was repeated to separate hydrogen and deuterium.
*7 Dr. A.K.Geim et al.
The following is a report on the properties of H+ ions, which exist more than D+ ions at room temperature.
A. K. Geim et al, Science 351, 68 (2016).
A. K. Geim et al. Nat. Commun. 8, 15215 (2017).
Y. An et al. Adv. Mater. 32, 2002442 (2020)
Incidentally, Dr. A. K. Geim won the 2010 Nobel Prize in Physics for his "innovative experiments on the two-dimensional material graphene.

Figures

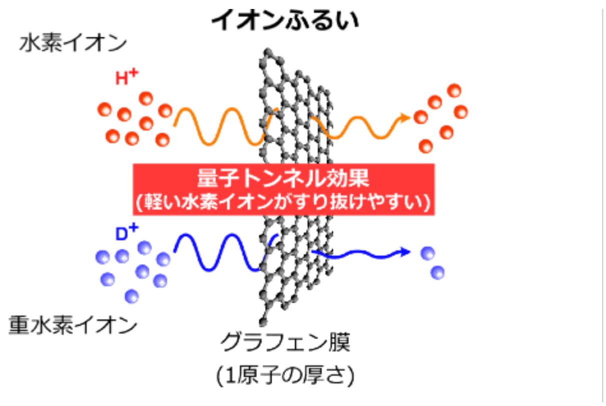

Figure 1 Demonstration that graphene has an H/D separation ability at room temperature.
Separation mechanism of hydrogen ion deuterium ion. Thus, this method is expected to be a low-cost D_2 purification method

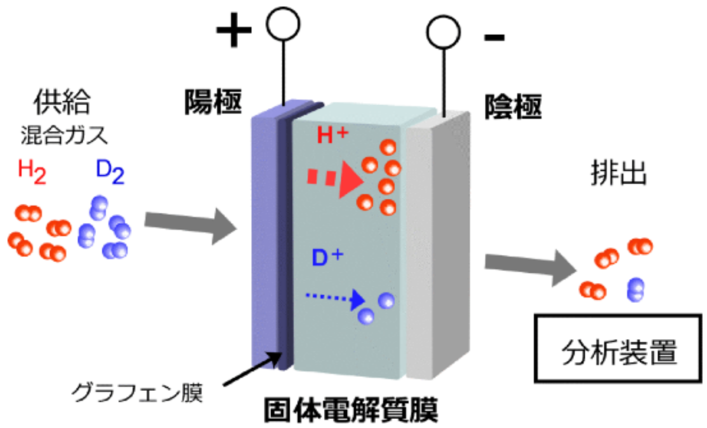

Figure 2 Schematic of the evaluation of H/D separation ability of graphene by hydrogen pumping method.

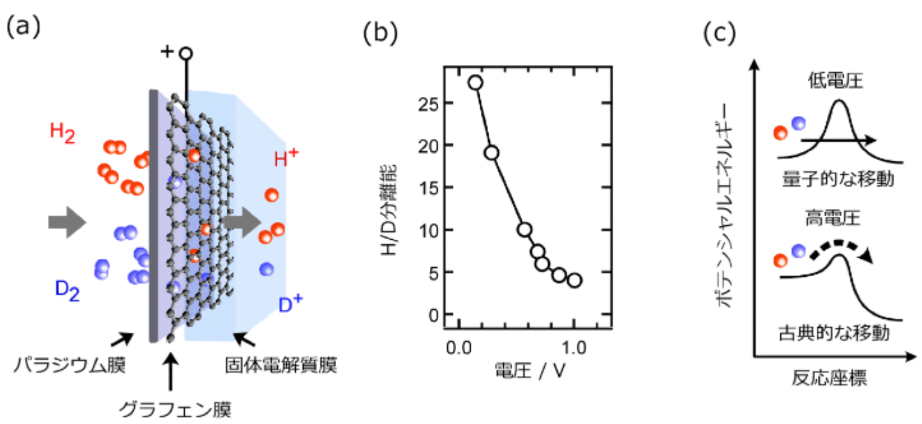

Figure 3 (a) High H/D resolution at room temperature through graphene.
(b) H/D resolution decreases with increasing voltage.
(c) At low voltages, ions slip through the barrier due to the quantum tunneling effect