COMMENTARY

Nanoripples in graphene: A remarkable structure for proton mass transport

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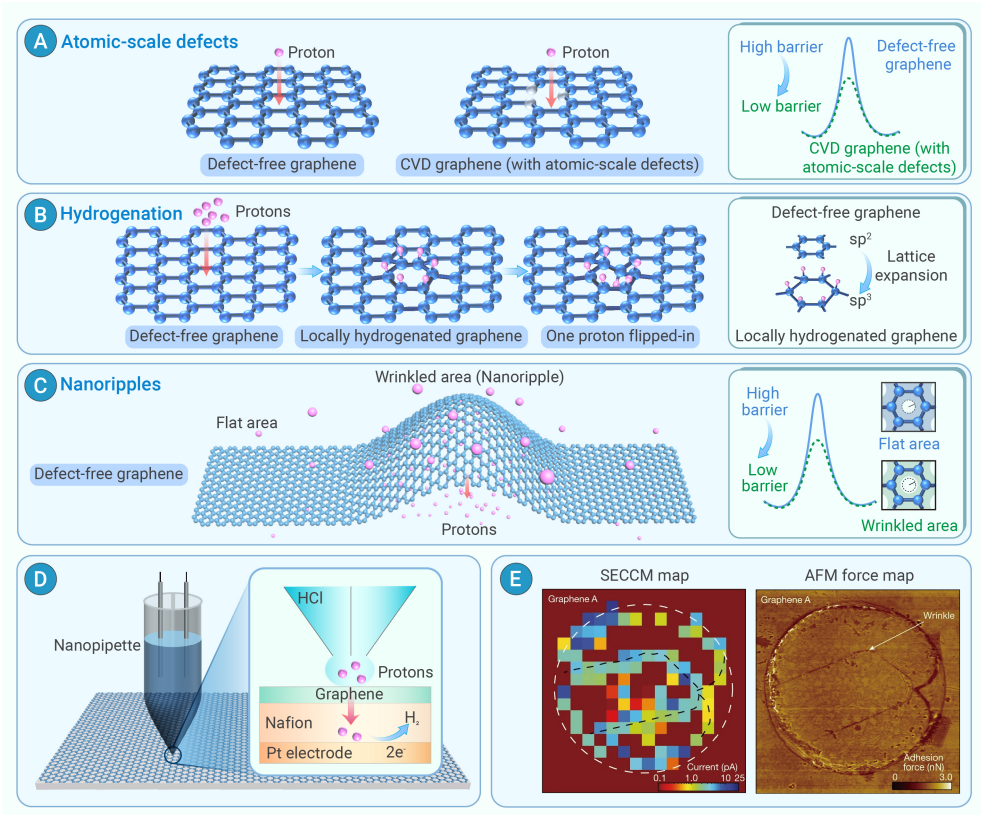

Figure 1. Mechanisms of proton permeation through graphene (A-C) and visualization study of proton permeability using SECCM (D and E) (A) The proton permeation barrier of CVD graphene with atomic-scale defects is smaller than that of defect-free graphene.[2] (B) The hydrogenation mechanism of protons through defect-free graphene. In proton-conductive media, protons form chemical bonds with graphene through chemical adsorption, leading to locally hydrogenated graphene. The hydrogenated six-atom ring exhibits an expansion lattice compared to the original six-atom ring, facilitating the flipping of a proton to the other side of the graphene.[3] (C) Nanoripples facilitate proton permeation through defect-free graphene. The electron cloud density in the graphene wrinkled area (nanoripples) is smaller than that in the flat area, reducing the energy barrier for proton permeation.[4] (D) Schematic of proton transport through the device for studying proton permeability using SECCM.[4] (E) SECCM map and corresponding AFM force map for a graphene device. Reproduced from ref 4 under Creative Commons CC-BY. Copyright 2023 The Authors.

The technology of using graphene as a selective permeation membrane for mass transport has aroused widespread research interest, stemming from the fact that graphene is the thinnest membrane in the world, with a thickness of only one layer of atoms. Perfect graphene that is free of defects does not contain vacancies, grain boundaries, or Stone-Wales defects. The unique characteristics of perfect graphene, being extremely thin and free of defects, have prompted inquiries into whether substances can penetrate it for mass transfer. The research on mass transport in perfect graphene has been ongoing since 2008. It is widely accepted that defect-free graphene is impermeable to all atoms and molecules under ambient conditions.

Nevertheless, defect-free graphene is not impermeable to all substances. Protons, also known as hydrogen nuclei, are subatomic particles with smaller sizes compared to atoms and molecules. In 2014, Hu et al. utilized conductance measurement and mass spectrometry to observe that protons can permeate defect-free graphene.[1] The experimental identification of the high permeability of defect-free graphene to thermal protons is an exciting advancement, indicating the potential for graphene to function as a selectively permeable membrane with broad applications across various fields. In addition, they calculated the energy barrier for proton transport through graphene by measuring proton conductivity at different temperatures. It is essential to highlight that the aforementioned energy barrier was derived from experiments. Actually, the energy barrier for proton transport through graphene deriving from theoretical predictions, such as density functional theory, is higher than the energy barrier deriving from experiments. To account for the difference, an explanation has been proposed that atomic-scale defects in graphene promote proton permeation (Figure 1A).[2] This assumption is based on chemical-vapor-deposited (CVD) graphene, which often has atomic-scale defects. However, atomic-scale defects are absent in the mechanically exfoliated graphene. Another mechanism to explain the difference is hydrogenation (Figure 1B).[3] To be in detail, in aqueous solutions or proton-conducting polymers, graphene can chemically adsorb protons, leading to a change in the hybridization mode of carbon atoms on the hexagonal ring of graphene from sp^2 to sp^3. This results in the expansion of the lattice of hydrogenated graphene, facilitating the flipping of hydrogen atoms from one side of the graphene to the other. While this mechanism is primarily derived from theoretical calculations, the microscopic mechanism that promotes proton transmission has not been directly observed by researchers. Recently, a new mechanism that relates the proton permeability with the extensive nanoscale wrinkles on the surface of graphene, which is attributed to the decrease in electron density compared to the flat area, has been proposed (Figure 1C).[4] Before delving into this mechanism, let us recall some facts of the significant role played by the nanoripples in promoting mass transport.

Graphene is generally considered a flat, two-dimensional crystal. However, in reality, there are numerous nanoscale corrugations on its surface. A study by Sun et al. found that graphene ripples are catalytically active and demonstrate noticeable permeability to hydrogen molecules.[5] Given that the size of hydrogen molecules is larger than that of helium, hydrogen faces higher energy barriers when passing through graphene. Therefore, the only conceivable scenario for hydrogen permeation is through a process in which hydrogen adsorbed on the graphene ripples undergoes catalytic splitting. In this process, hydrogen atoms share electrons with graphene, making it challenging to differentiate between hydrogen atoms and protons. Following this, hydrogen atoms flip to the other side of the graphene and eventually detach

in the form of molecular hydrogen, just like the process shown in Figure 1B. This mechanism highlights the important role of ripples on the surface of graphene in promoting mass transport.

Although previous studies have shown that nanoripples on the surface of graphene can promote proton transport through graphene, proton currents on nanoripples have not yet been observed. As the saying goes, a handy tool makes a handyman. In order to detect the spatial distribution of proton currents on the surface of graphene, a relevant tool is necessary. Scanning electrochemical cell microscopy (SECCM) is a recently developed new pipette-based imaging technique purposely designed to allow simultaneous electrochemical and topographical visualization of surfaces and interfaces. Therefore, it can serve as a tool for studying the electrochemical activity of substances at the micro- and nano-scopic scale and is capable of establishing "structure-property relationships". Recently, Professor Unwin group, in collaboration with Professor Geim and Dr. Marcelo Lozada-Hidalgo group, utilized SECCM as a "microscope" for visualizing proton currents across the surface of defect-free graphene at the nanometer scale.[4]

In this study, to investigate the proton permeability of graphene, the authors constructed a device in which mechanically exfoliated graphene was suspended over micrometre-sized holes in the SiN_x substrates. Within the micrometre-sized holes, graphene was loaded onto a Nafion film (serving as the conductor of protons) which was in contact with a Pt electrode (serving as a proton collector) (Figure 1D).[4] The dual-channel nanopipette filled with HCl served as the proton reservoir. The proton passing through the graphene ultimately reaches the surface of the Pt electrode, where the hydrogen evolution reaction (HER) is catalyzed. The generated current signal is recorded by SECCM and "visualized" by collecting the maps of the current intensity.

It is noteworthy that the mechanically exfoliated graphene utilized in this study is a two-dimensional crystal without defects and micropores, implying that the proton current is not induced by defects. In Figure 1E, the proton permeation current collected by SECCM is displayed, and the morphology of the corresponding area is characterized by atomic force microscopy (AFM).[4] It is evident that the proton conductivity is higher in the wrinkled area (nanoripples) and near the edge of the micrometre-sized holes. The common characteristic of both the nanoripples and the edge region is that the graphene in these areas is under notable strain. The same research also demonstrates that a high proton transmission current is detected in the wrinkles of the single-layer hexagonal boron nitride (hBN).

The authors not only observed higher proton permeability in the wrinkled area by SECCM but also elucidated the mechanism of nanoripples promoting proton transmission through theoretical calculations.[4] On the surface of defect-free graphene, the ability of proton transparency depends on the density of the electron cloud of the graphene lattice. In regions where strain is accumulated (such as the area with nanoripples), there is a lower electron cloud density compared to regions without strain (such as flat graphene areas). This condition is conducive to the transparency of protons.

This work has made a significant contribution to the nanoscopic visualization of the proton permeability of graphene by mapping the proton current with SECCM. By combining with AFM, it reveals, from an experimental standpoint, that nanoripples can facilitate proton transmission through graphene. Indeed, SECCM is a powerful tool for establishing a structure-property relationship at the micro-, or even nano-scale. Particularly concerning two-dimensional crystals, in the future, SECCM can be employed to explore the heterogeneity of intrinsic properties within their microscopic regions. This involves studying variations in basal and edge positions, as well as investigating two-dimensional crystals with different layers, defects, vacancies, and doped structures. However, it is noteworthy that the spatial resolution of SECCM, which depends on various factors including the size of the pipette radius, specific electrochemical processes at interfaces, proper construction of the device loaded with the test sample, and the sensitivity and noise level of the current detection device, still does not perfectly align with the capabilities of AFM and electron microscopy. This imposes a high demand for pushing the limits of the detection resolution of SECCM from the aforementioned aspects.

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DECLARATION OF INTERESTS

The authors declare no competing interests.