

Supporting Information

Efficient Hydrogen Isotope Separation by Tunneling Effect Using Graphene-Based Heterogeneous Electrocatalysts in Electrochemical Hydrogen Isotope Pumping

Satoshi Yasuda,^{*,†} Hisayoshi Matsushima,[‡] Kenji Harada,[‡] Risako Tanii,[‡] Tomo-o Terasawa,^{#,†} Masahiro Yano,[†] Hidehito Asaoka,[†] Jessiel Siaron Gueriba,[¶] Wilson Agerico Diño,^{¶,§} and Katsuyuki Fukutani^{#,†}

[†] Research Group for Surface and Interface Science, Advanced Science Research Center, Japan Atomic Energy Agency, 2-4 Shirakata, Tokai, Ibaraki 319-1195, Japan

[‡] Faculty of Engineering, Hokkaido University, North 13, West 8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan

[¶] Department of Applied Physics, Osaka University, Suita, Osaka 565 0871, Japan.

[§] Center for Atomic and Molecular Technologies, Osaka University, Suita, Osaka 565-0871, Japan

[#] Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

Table of contents

1. Chemicals
2. Fabrication of membrane electrode assemblies (MEAs)
3. Optical microscope images of membranes
4. Raman spectra of membranes
5. AFM image of graphene transferred on Nafion
6. Hydrogen isotope separation analysis method and determination of separation factor
7. Representative time evolution of ion current components of Pd-, Pd/C-, and Pt/C-MEAs and calculated molar rates of hydrogen isotope gases generated in cathode outlet at 25 mA cm⁻² for different MEAs
8. Bias dependence of the molar rates for different bias voltages (current densities) of PdGr-MEA observed in Figure 4a
9. Reproducibility of bias dependence of hydrogen isotope ability for PdGr-MEA
10. Potential energy calculation of an H atom passing through the hollow site of a graphene
11. Potential energy calculation of an H ion passing through the hollow site of a graphene
12. Penetration potential calculation of an H ion passing through the hollow site of a graphene under potential
13. Reference

1. Chemicals

Nafion NRE-212 (50.8 μm) and Nafion 5 wt.% dispersed solution were purchased from Sigma-Aldrich (Nos. 676470 and 274704). Single-layer graphene grown on Cu foil was prepared by atmospheric pressure chemical vapor deposition (APCVD) technique or purchased from ACS Material (CVD graphene on Cu foil, 4×2 inch, CVCU1042). Pd wire (Nilaco, diameter: 1.0 mm, 99.9 %, No. PD-341481) was used as a Pd source of electron beam deposition for the fabrication of Pd and PdGr electrodes. Pt/C catalyst supported gas diffusion electrode (Pt/C GDE) which is $0.5 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ Pt/C coated carbon paper (TGP-H-060, TORAY) was purchased from FC Development Co, Ltd. $0.3 \text{ mg}_{\text{Pd}} \text{ cm}^{-2}$ Pd/C GDE was prepared by coating 40 % Pd/C catalyst purchased from Premetek (P30A400) onto carbon paper (TGP-H-060, TORAY). Phosphoric Acid (85.0 +%) (167-02166) and polyethylene glycol (molecular weight 400, 161-09065) for Cu electrochemical polishing, and ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) (012-20503) for Cu etchant were purchased from FUJIFILM Wako Pure Chemical Corporation and used without further purification.

Graphene synthesized by the APCVD was prepared as following procedures. 80 μm -thick copper foils (Nilaco, Cu-113303, 99.9 %) were electropolished in a mixture solution of 80 mL H_3PO_4 and 20 mL polyethylene¹ and then inserted in a quartz furnace with an inner diameter of 15 mm. The foils were pre-annealed at 1050 $^{\circ}\text{C}$ for 60 min under 500 sccm flow of 20 % H_2/Ar , and graphene was grown at 1050 $^{\circ}\text{C}$ for 10 min flowing 780 sccm Ar and 1 sccm 1% diluted CH_4/Ar . After the growth, the furnace was quickly cooled and then grown graphene/Cu foils were removed and stored in a vacuum container (~ 0.01 MPa) at room temperature until usage. H_2 (Tomoe, 99.99999 %) and Ar (Tomoe, 99.9999 %), and 1.0 % CH_4 (Tomoe, Ar base 99.9999 %) were used for the CVD synthesis of graphene.

H_2 (Tomoe, 99.99999 %) and Ar (Tomoe, 99.9999 %) were used for electrochemical measurements. H_2 (Tomoe, 99.99999 %) and D_2 (Cambridge Isotope Laboratories Inc., D_2 :99.6 % + HD:0.4 %, DLM-408-PK) gases were used for hydron isotope analysis. Deuterium hydride (Cambridge Isotope Laboratories Inc., D:97 %, DLM-194-PK) was also used for sensitivity calibration of HD^+ ion current for mass spectroscopy.

2. Fabrication of membrane electrode assemblies (MEAs)

2.1 Fabrication of PdGr - Nafion - Pt/C GDE (PdGr-MEA)

Figure S1 shows a schematic of the procedure of PdGr-MEA, and the MEA was fabricated by a four-step process. At first, graphene on one side of Cu foil was etched away by Ar^+ bombardment at 1.0 keV for 2.5 min under 1.0×10^{-6} Torr (Figure S1a), and then the etched sample was cut into $1.3 \times 1.3 \text{ cm}^2$ squares. 30 μl of 5 wt.% Nafion dispersion solution was deposited on Pt/C GDE ($1.0 \times 1.0 \text{ cm}^2$) square, and then the Nafion deposited GDE was dried at 60 °C for 1 h. Nafion membrane was cut into $2.0 \times 2.0 \text{ cm}^2$ square and used without cleaning. Assembly of a sandwich structure of the Pt/C GDE, Nafion, and the graphene on Cu foil was set and then hot-pressed at 140 °C for 2 min under 1.4 MPa (Figure S1b). The assembly was floated on Cu etchant (0.2 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ aqueous solution) facing Cu foil side at 25 °C for an overnight (typically ca. 12 h) and then rinsed with Milli-Q water for several times to remove residual etchant (Figure S1c). The transferred graphene on the Nafion is difficult to see by naked eye, but the transfer quality of the graphene can be evaluated at a micro-scale by an optical microscope, as shown in Figure S2c. After drying at ambient conditions, the assembly was loaded in a vacuum chamber and 6 nm-thick Pd layer was deposited on the graphene side of the assembly by an electron beam at a rate of 0.1 Å/s (Figure S1d), obtaining a PdGr-MEA (Figure S1f).

2.2 Fabrication of Pd - Nafion - Pt/C GDE (Pd-MEA)

Pt/C GDE, Nafion, and a protective film (0.1 mm thickness Teflon sheet) were positioned and superposed on each other. The assembly was then hot-pressed at 140 °C for 2 min under 1.4 MPa. After the protective film was removed from the assembly, 6 nm-thick Pd was deposited on the Nafion side of the assembly by the electron beam at a rate of 0.1 Å/s.

2.3 Fabrication of Pd/C – Nafion - Pt/C (Pd/C-MEA) and Pt/C - Nafion - Pt/C (Pt/C-MEA)

Pd/C GDE, Nafion, and Pt/C GDE or Pt/C GDE, Nafion, and Pt/C GDE was superposed and then each assembly was hot-pressed at 140 °C for 2 min under 1.4 MPa.

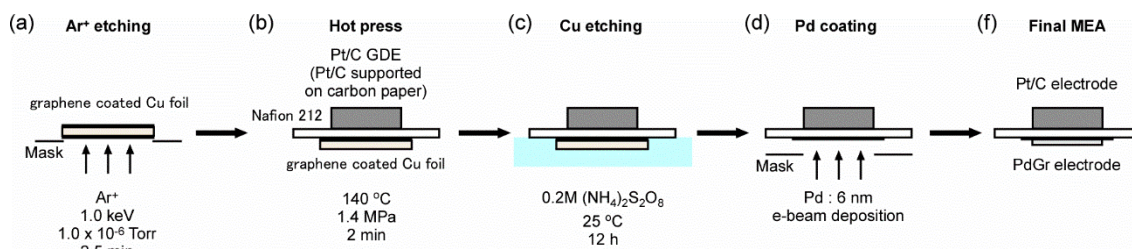


Figure S1. Schematic illustration of PdGr-MEA fabrication.

3. Optical microscope images of membranes

As shown in Figure S2a, the Nafion surface oppositely attached on Pt/C GDE seems to be smooth unevenness. The optical image of Pd deposited on Nafion showed the presence of smooth roughness structure at a microscopic level (Figure S2b), but sub-microscopic AFM measurement confirmed continuous Pd layer formation, as shown in Figure 1c. After graphene transfer onto Nafion, the wrinkles structures which are characteristics of graphene grown on Cu foil by CVD, could be clearly observed (Figure S2c). A few cracks with several micrometer-scale were also occasionally observed due to probably generation during graphene transfer and Cu etching processes. Pd deposited graphene showed metallic luster over the surface, indicating uniformly Pd deposition on graphene (Figure S2d).

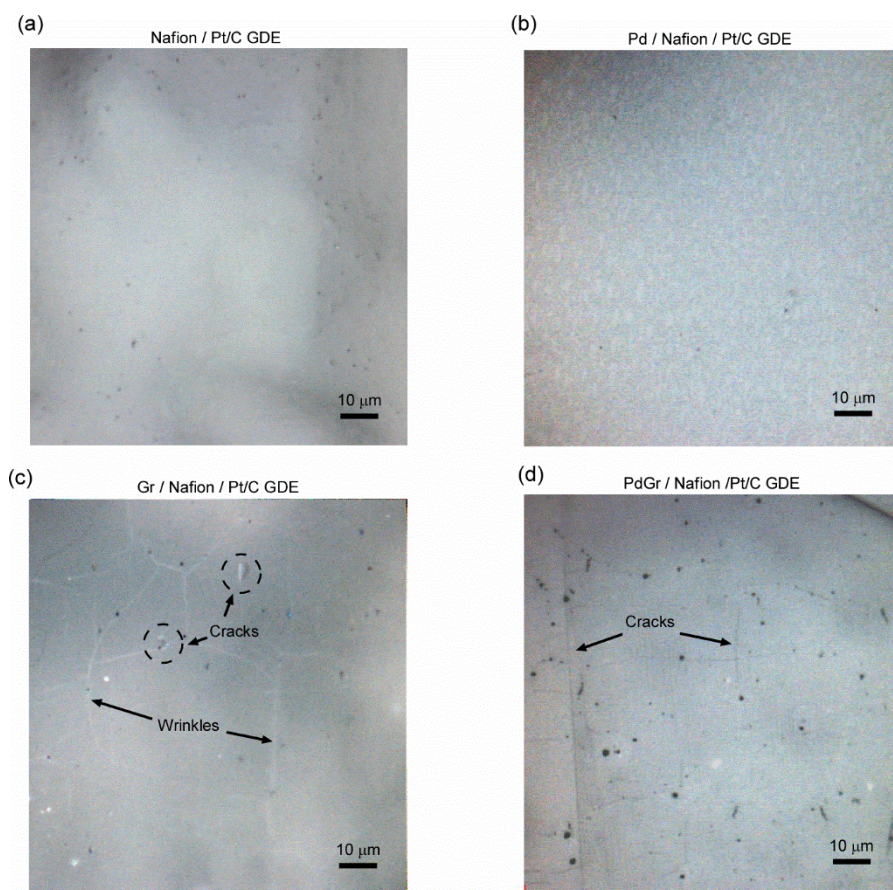


Figure S2. Representative optical microscope images of (a) Nafion, (b) 6 nm-thick Pd deposited on Nafion, (c) graphene transferred on Nafion, and (d) 6 nm-thick Pd deposited on graphene transferred on Nafion. For all samples, Pt/C GDEs are attached on the opposite side of Nafion membranes.

4. Raman spectra of membranes

Figure S3a and b are representative Raman spectra of the CVD synthesized graphene on Cu and Nafion 212 as component materials for MEA fabrication. Raman spectra of the graphene on Cu appears 1600 cm^{-1} (G-band) and 2700 cm^{-1} (2D-band), and the single Lorentzian shape with FWHM of $\sim 25 \text{ cm}^{-1}$ of the 2D-band and the intensity ratios of the 2D- and the G-band peaks (I_{2D}/I_G) of ~ 2 for the graphene on Cu are clear evidence of the formation of a monolayer.² The D-band peak (1340 cm^{-1}) associated with defective structures in graphene was hardly observed, indicating the absence of a significant number of defects for the graphene on Cu. Similar Raman features could be observed for purchased graphene on Cu, indicating that both graphene exhibit similar quality. Typical Raman peak features of the Nafion could be also observed at a frequency range between 200 and 1400 cm^{-1} corresponding to the modes of the perfluoro skeleton (Figure S3b). Raman spectrum of the Pd deposited on Nafion showed a clear reduction of Raman intensity of the Nafion by the Pd deposition (Figure S3c). As for the transferred graphene onto the Nafion (Figure S2d), clear Raman peaks arising from both the graphene and Nafion were observed. Although quantitative defect analysis in domains in the graphene is difficult because of the overlap of several Raman peaks of the Nafion in 1300 - 1400 cm^{-1} , a lack of strong D-band Raman peak around 1340 cm^{-1} arising from defects in graphene indicates no significant presence of defects structures in domain of the transferred graphene. Raman spectrum of the Pd deposited graphene transferred on Nafion also showed a clear reduction of Raman intensity of the graphene by the Pd covering (Figure S3e).

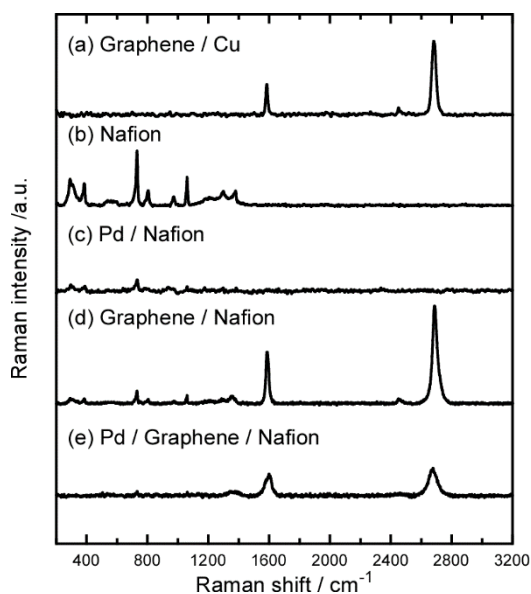


Figure S3. Representative Raman spectra of (a) CVD synthesized graphene on Cu foil, (b) Nafion, (c) 6 nm-thick Pd deposited on Nafion, (d) graphene transferred on Nafion, and (e) 6 nm-thick Pd deposited on graphene transferred on Nafion.

5. AFM image of graphene transferred on Nafion

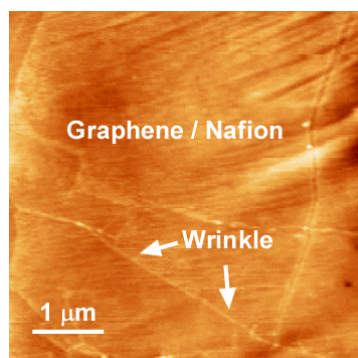


Figure S4. Representative AFM image of graphene transferred on Nafion.

6. Hydrogen isotope separation analysis method and determination of separation factor

Hydrogen isotope gas analysis was conducted by combining the hydrogen isotope pumping cell with a quadrupole mass spectrometer. In this study, separation factor (H/D) is defined as the following equation.

$$H/D = \left(\frac{[H]}{[D]} \right)_{cathode\ outlet} \bigg/ \left(\frac{[H]}{[D]} \right)_{anode\ inlet} = \left(\frac{[H]}{[D]} \right)_{cathode\ outlet} = \frac{2[H_2] + [HD]}{2[D_2] + [HD]}$$

$$\approx \frac{2(i_{H_2^+} - i_{H_2^+_{BG}}) + \alpha(i_{HD^+} - i_{HD^+_{BG}})}{2\beta(i_{D_2^+} - i_{D_2^+_{BG}}) + \alpha(i_{HD^+} - i_{HD^+_{BG}})}$$

[H] and [D] are atomic fractions of protium and deuterium, and the $([H]/[D])_{cathode\ outlet}$ and $([H]/[D])_{anode\ inlet}$ are the ratio of [H] and [D] observed at cathode outlet and anode inlet, respectively. In this study, value of $([H]/[D])_{anode\ inlet}$ is one because a 1:1 H₂/D₂ mixture gas is fed in the anode inlet by the mass flow controller. Actually, we had confirmed that $([H]/[D])_{anode\ inlet}$ value is within 1 ± 0.04 at each experiment by the mass spectrometer. $i_{H_2^+_{BG}}$, $i_{D_2^+_{BG}}$, and $i_{HD^+_{BG}}$ are background ion currents of H₂⁺, D₂⁺, and HD⁺ observed at the cathode outlet under an open circuit condition. $i_{H_2^+}$, $i_{D_2^+}$ and i_{HD^+} are the generated ion currents of H₂⁺, D₂⁺, and HD⁺ under a closed circuit condition. [H] and [D] observed at the cathode outlet were obtained by subtracting each background ion current from each generated ion current. Sensitivity factors of α and β of HD⁺ and D₂⁺ ion currents were estimated by the mass spectrometer flowing known H₂, HD, and D₂ fluxes by the mass flow controller.

7. Representative time evolution of ion current components of Pd-, Pd/C-, and Pt/C-MEAs and calculated molar rates of hydrogen isotope gases generated in cathode outlet at 25 mAcm⁻² for different MEAs

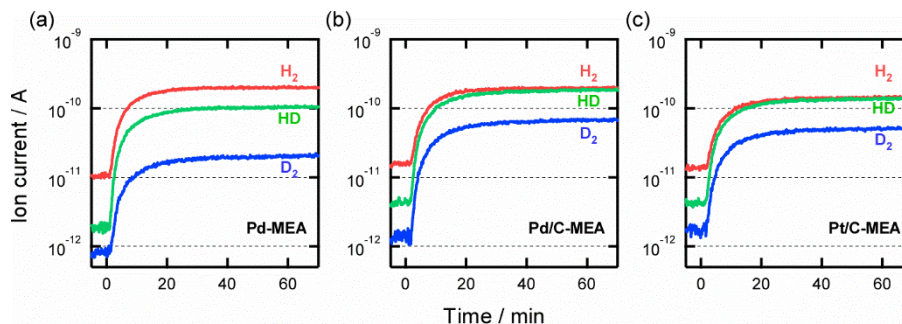


Figure S5. Time evolution of H_2^+ , HD^+ , and D_2^+ ion current observed cathode output for (a) Pd, (b) Pd/C and (c) Pt/C-MEAs. During the measurement, current density of 25 mA cm⁻² was maintained for all electrodes.

MEAs	H/D	Gas fractions in the output gas (%)			Calculated molar rate (10^{-8} mol s ⁻¹ cm ⁻²)		
		H ₂	HD	D ₂	H ₂	HD	D ₂
PdGr	7.4	79.5	17.0	3.5	10.3	2.2	0.5
Pd	2.6	57.1	29.2	13.7	7.4	3.8	1.8
Pd/C	1.2	38.2	33.8	28.0	5.0	4.4	3.6
Pt/C	1.1	34.7	34.9	30.4	4.5	4.5	4.0

Table S1. An example of obtained gas fractions in the cathode output and the corresponding calculated molar rates of H_2 , HD , and D_2 at 25 mA cm⁻² for different MEAs.

8. Bias dependence of the molar rates for different bias voltages (current densities) of PdGr-MEA observed in Figure 4a

Bias voltage Current density	H/D	Gas fractions in the output gas (%)			Calculated molar rate (10^{-8} mol s $^{-1}$ cm $^{-2}$)		
		H ₂	HD	D ₂	H ₂	HD	D ₂
0.143 V (10 mA cm $^{-2}$)	27.4	93.4	6.1	0.5	4.86	0.32	0.03
0.285 V (15 mA cm $^{-2}$)	19.1	90.8	8.4	0.8	7.08	0.65	0.06
0.571 V (20 mA cm $^{-2}$)	10.0	83.7	14.3	2.0	8.71	1.48	0.21
0.687 V (25 mA cm $^{-2}$)	7.4	79.5	17.0	3.5	10.33	2.21	0.45
0.726 V (30 mA cm $^{-2}$)	5.9	75.3	20.5	4.2	11.75	3.20	0.66
0.872 V (40 mA cm $^{-2}$)	4.6	70.0	24.0	6.0	14.56	4.99	1.25
1.006 V (50 mA cm $^{-2}$)	4.0	67.3	25.1	7.6	17.51	6.52	1.97

Table S2. H₂, HD, and D₂ gas fractions in the cathode output and corresponding molar rates for different bias voltages (current densities) of PdGr-MEA observed in Figure 4a.

9. Reproducibility of bias dependence of hydrogen isotope ability for PdGr-MEA

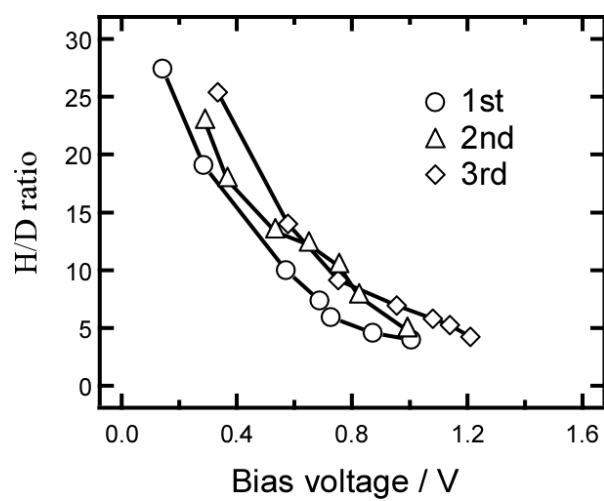


Figure S6. Bias voltage dependence of H/D ratio of PdGr-MEA for each cycle. Data in each cycle was acquired at 10, 15, 20, 25, 30, 40, 50 mA cm⁻².

10. Potential energy calculation of an H atom passing through the hollow site of a graphene

To obtain the potential energy curve (PEC) for a (neutral) hydrogen atom (H^0) passing through the hollow site of graphene³, we performed density functional theory (DFT)-based total energy calculations.⁴⁻⁸ We adopted the projector-augmented wave formalism,^{9,10} with the Perdew-Burke-Ernzerhof generalized gradient approximation exchange correlation functional,¹¹ and a cut-off energy of 550 eV. We adopt the Monkhorst-Pack method¹² to perform the Brillouin zone integrations. We modeled the clean graphene layers as a periodic slab separated by 20 Å of vacuum. As we can see in Figure S7a and S7b (black curve), the potential barrier can be fitted to a $V_0 \cosh^2(\alpha Z)$ -type function,¹³ with a barrier of ca. $V_0 = 4.0$ eV and a width defined by the parameter $\alpha = 1.5 \text{ Å}^{-1}$.

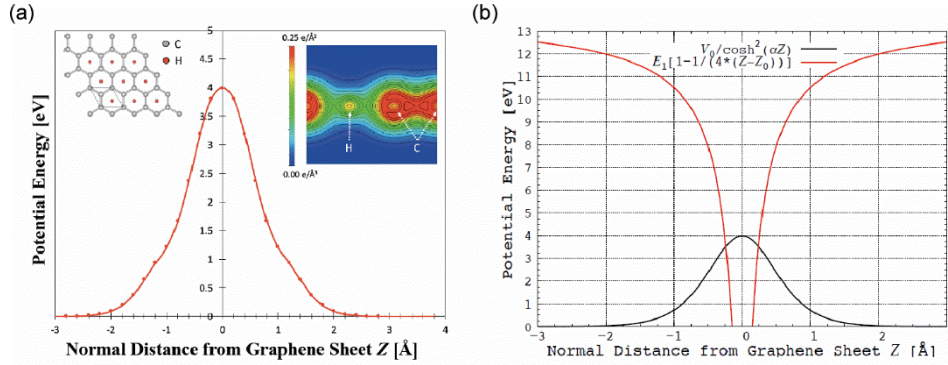


Figure S7. (a) Calculated potential energy curve for the interaction of an H atom passing through the hollow site of graphene, as a function of the H-graphene normal distance Z . Potential energies given in [eV] relative to the case when H is sufficiently far from the graphene. **Left inset:** Top-view of the system, in which the carbon atoms (C, in gray) and hydrogen atoms (H, in red) are shown. **Right inset:** Electron distribution with the H atom at the middle of the graphene, with the positions of C and H showed. (b) **Black curve:** An analytical fit/representation of the calculated potential energy curve shown in (b) for the interaction of an H atom passing through the hollow site of graphene, as a function of the H-graphene normal distance Z Å. Potential energies are given in [eV] relative to the case when H is sufficiently far from the graphene. **Red curve:**

The attractive potential $V = E_1 \left[1 - \frac{1}{4(Z-Z_0)^2} \right]$ experienced by a proton (hydrogen stripped of its electron) interacting with a semi-infinite graphene placed at $Z = 0$, superimposed to that for the case of an H atom passing through the hollow site of a graphene. The ionization energy of hydrogen E_1 is 13.6 eV, and Z_0 is 0.1 Å.

11. Potential energy calculation of an H ion passing through the hollow site of a graphene

A point charge $+e$ placed a distance Z outside the surface of a semi-infinite medium (grounded) with dielectric constant ε would induce an image point charge $q (= \frac{1-\varepsilon}{1+\varepsilon} \varepsilon)$ positioned within the medium at the same distance Z from the surface. For a metal surface ($\varepsilon \rightarrow \infty, q = -e$), the induced charge $q = -e$ attracts the point charge $+e$ towards the surface with a force $F = -\frac{e^2}{(2Z)^2} \hat{\mathbf{z}}$. To move the point charge $+e$ from ∞ towards a distance Z from the surface requires work $W = -\int_{\infty}^Z \mathbf{F} \cdot d\mathbf{l} = \int_{\infty}^Z dz \frac{e^2}{4z^2} = -\frac{e^2}{4} \frac{1}{z} \Big|_{\infty}^Z = -\frac{e^2}{4Z}$. Note that although the induced charge $q_0 = -e$ simultaneously moves over the conductor, this costs us nothing since the whole conductor is at potential zero (grounded). We also note that the electron wavefunctions “leak out” of the surface of a metal (or solid in general). Thus, the image plane that serves as the reference for the Z -coordinate will not be identical to the surface itself, i.e., the plane defined by the coordinates of the nuclei of surface atoms. One therefore has to express the potential as $V = -\frac{e^2}{4(Z-Z_0)}$, where Z_0 usually takes values in the order of half a lattice constant.

To strip an electron from a hydrogen atom requires an energy of ca. $E_1 = 13.6$ eV, producing a proton (a point charge $+e$). When placed outside a conducting graphene, the proton will experience an attractive potential (red curve in Figure S7b) $V = E_1 \left[\frac{1}{4(Z-Z_0)} \right]$, until it reaches distance Z where it overlaps with the potential energy curve corresponding to that for a H atom passing through the hollow site of a graphene. At this instance, the H^0 -graphene and the H^+ -graphene systems would exhibit the same electron distribution. From this moment, the system has no memory of (cannot distinguish) whether the particle passing through the hollow site of the graphene initially came from a proton or a neutral H atom. Energetically, the proton would require a lower activation barrier to pass through the hollow site as compared to a neutral H atom (ca. 0.5 eV for a proton as compared to 4.0 eV for a neutral H atom) as shown in Figure S8. This depends on how close (and how fast) we can bring the proton to graphene before the electron distribution would be indistinguishable from that of a neutral H.

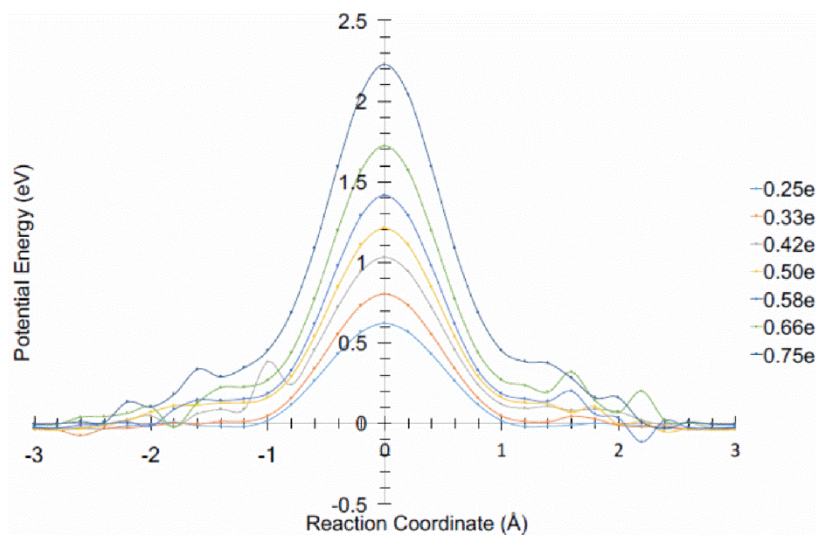


Figure S8. Calculated potential energy curve for the interaction of a hydrogen ion $\text{H}^{+(1-\delta)}$ passing through the hollow site of graphene, as a function of the H-graphene normal distance Z . The energy barrier is found to be reduced with decreasing δ .

12. Penetration potential calculation of a H^+ passing through the hollow site of a graphene under potential

Following the discussions by Nordheim¹⁴ and Fowler¹⁵ on thermionic emissions, we approximate the barrier for a proton passing through a graphene under the influence of some field by the analytic form:

$$V(z) = \frac{[\sqrt{V_0 - Z_0 V_b} + \sqrt{V_0 + (1 - Z_0)V_b}]^2}{4\cosh^2(\alpha Z)} + \frac{V_b}{2}(\tanh(\alpha Z) - 1)$$

V_0 (= 0.5 eV) gives the barrier height for the proton (cf., discussion in the previous section), V_b [eV] is the applied field/potential, a [$\text{\AA}^{-1}$] is the corresponding barrier width parameter, and Z_0 is the position of the transition state. Without an external applied field $V_b = 0$, the potential becomes symmetric with a maximum value of V_0 , and we get back the analytic form $V_0 \cosh^{-2}(a Z)$. Figure S9 shows examples of calculated potential curve at different V_b . Note that exact solutions for the Schrödinger equation (tunneling problem) associated with both these potentials (symmetric and asymmetric forms), can be obtained using hypergeometric functions.

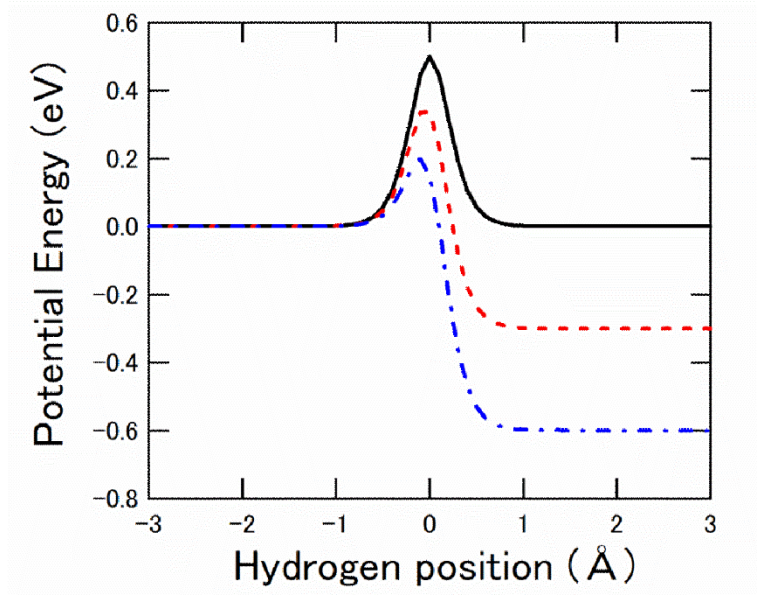


Figure S9. Calculated potential energy curves at different V_b .

References

- (1) Luo, Z.; Lu, Y.; Singer, D. W.; Berck, M. E.; Somers, L. A.; Goldsmith, B. R.; Johnson, A. T. C. Effect of Substrate Roughness and Feedstock Concentration on Growth of Wafer-Scale Graphene at Atmospheric Pressure. *Chem. Mater.* **2011**, 23, 1441–1447.
- (2) Ferrari, A. C.; Meyer, J. C.; Scardaci, V.; Casiraghi, C.; Lazzeri, M.; Mauri, F.; Piscanec, S.; Jiang, D.; Novoselov, K. S.; Roth, S.; Geim, A. K. Raman Spectrum of Graphene and Graphene Layers. *Phys. Rev. Lett.* **2006**, 97 (18), 187401.
- (3) Miura, Y.; Kasai, H.; Diño, W. A.; Nakanishi, H.; Sugimoto, T. Effective Pathway for Hydrogen Atom Adsorption on Graphene. *J. Phys. Soc. Jpn.* **2013**, 72 (5), 995–997.
- (4) Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Computational Mater. Sci.* **1996**, 6 (1), 15–50.
- (5) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for *Ab Initio* Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, 54 (16), 11169.
- (6) Kresse, G.; Hafner, J. *Ab Initio* Molecular Dynamics for Liquid Metals. *Phys. Rev. B* **1993**, 47 (1), 558.
- (7) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, 140 (4A), A1133.
- (8) Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* **1964**, 136 (3B), B864.
- (9) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, 59 (3), 1758.
- (10) Blöchl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, 50 (24), 17953.
- (11) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77 (18), 3865.
- (12) Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone Integrations. *Phys. Rev. B* **1976**, 13 (12), 5188.
- (13) Diño, W. A.; Kasai, H.; Okiji, A. Orientational Effects in Dissociative Adsorption/Associative Desorption Dynamics of H₂(D₂) on Cu and Pd. *Prog. Surf. Sci.* **2000**, 63 (3–5), 63–134.
- (14) Nordheim, L.W. The Effect of the Image Force on the Emission and Reflexion of Electrons by Metals. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* **1928**, 121 (788), 626–639.
- (15) Fowler, R. H. The Thermionic Emission Constant A. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* **1929**, 122 (789), 36–49.