Electric-Field Control of Giant On/Off Current Ratio in Graphene Through Reversible Hydrogenation

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Abstract

Graphene-based electronic devices have attracted tremendous attention owing to its single-atomic-layer thickness and high electron mobility for potential applications in the next-generation electronics. The main obstacle for widespread implementation of graphene transistors is the poor on/off current ratio arising from the absence of essential bandgap in the Dirac-like dispersion. A promising approach for opening an energy gap in graphene is by the hydrogenation process that transforms graphene into highly insulating graphane with sp³ bonding. Here we demonstrate an electric-field control of conductor–insulator transition in microscale graphene through highly reversible hydrogenation reaction in a liquid electrolyte. Most remarkably, the sheet resistance of fully hydrogenated graphene shows a lower limit of 200 GΩ/sq, leading to a giant on/off current ratio larger than 10⁸ at room temperature. Similar behaviors are also demonstrated in bilayer graphene, while the trilayer one remains highly conductive after the hydrogenation. In-situ Raman spectroscopy reveals lattice deformation due to the change of C-C bond from sp² to sp³ hybridization, which is supported by first-principles calculations. Our finding lays out a new roadmap for the graphene-based electronics, and the electric-field-controlled hydrogenation method may also be generalized to other two-dimensional materials.

Main Text

Graphene, a two-dimensional (2D) crystal with carbon atoms tightly packed into a honeycomb lattice, can be considered as the composition of benzene rings with their hydrogen atoms stripped off from the basal plane. Likewise, hydrogen atoms can be bonded back to the carbon sites of graphene lattice through hydrogenation reaction, which produces a stable alkane compound named graphane. The decoration of hydrogen atoms changes the hybridization of carbon atoms from sp² into sp³, resulting in a drastically different electronic structure with a huge energy gap. A reversible and in situ hydrogenation method is crucial to control the conductor–insulator transition in graphene, which can produce sufficient on/off current ratio for the realization of
The hydrogenation of graphene requires rather powerful reagents to initiate the chemical reactions owing to its weak hydrogen affinity and chemical inertness\textsuperscript{4}. Therefore, all hydrogenation approaches require the activation of either hydrogen or the graphene lattice to make the reaction feasible\textsuperscript{5}. A number of precursive routes to hydrogenated graphene have been demonstrated since its initial synthesis in 2009 (Ref. 6). The main approaches fall into three categories: (1) atomic/plasma hydrogen reaction\textsuperscript{6–14}, (2) chemical reduction\textsuperscript{15–18}, and (3) electrochemical hydrogenation\textsuperscript{19–21}. Although all these methods can produce hydrogenated graphene that mostly exhibits insulating behavior and gap-opening characteristics, additional processings, such as thermal annealing\textsuperscript{6–20}, electron-beam\textsuperscript{22} or laser-pulse irradiation\textsuperscript{21,23}, are generally employed to restore the pristine graphene, which is too intractable to integrate into a field-effect transistor (FET). However, electric-field-controlled electrochemical gating represents a highly versatile approach to produce systematic functionalization, as the ion implantation and extraction can be precisely controlled by the gate voltage ($V_G$)\textsuperscript{24–28}.

In our experimental setup (Fig. 1a), the graphene devices are immersed in a hydrogen-ion electrolyte (HIE). A thin Pt foil close to graphene is used as the gate electrode (see detailed structure in Fig. S1). When a positive $V_G$ is applied between the gate and source electrode of graphene, the electric field drives hydrogen ions (H$^+$) to accumulate on top of the graphene surface. Thus, the resistance of graphene is strongly modulated due to the formation of an electric double layer (EDL) at the interface between graphene and HIE. With increasing $V_G$ to above the hydrogenation potential, graphene lattice becomes highly activated and the chemical bonding between H$^+$ ions and C atoms starts to form, as illustrated in Fig. 1b.

Figure 1c displays the source-drain current ($I_{DS}$) of a monolayer graphene (MLG), which reveals a characteristic V-shaped profile\textsuperscript{29–31} for -1 V < $V_G$ < 1.5 V arising from the linear dispersion of relativistic Dirac fermions intrinsic to graphene\textsuperscript{1,4}. Surprisingly, when $V_G$ is increased to 1.7 V, $I_{DS}$ drops dramatically to nearly zero and remains pinch-
off up to $V_G = 4 \text{ V}$ (Fig. S2). Therefore, the hydrogenated MLG transforms into a wide-bandgap insulator analogous to graphane$^{2,3}$. When $V_G$ is swept back from 2.2 V, $I_{DS}$ stays in the “off” state till 0.2 V and then starts to increase gradually. It nearly recovers the original “on” state at -1 V, where the MLG is dehydrogenated and the sp$^2$ bond hybridization is restored. The subsequent two cycles of gate sweeping between -1 V to 2.2 V generate nearly identical $I_{DS}$ traces. Such unprecedented consistency further demonstrates the highly reversible hydrogenation and dehydrogenation processes without the degradation of graphene lattice.

To accurately determine the high resistance value of hydrogenated MLG, we carefully restrain the leakage current ($I_G$) between the gate and graphene electrodes. By linearly fitting the $I_{DS} + I_G$ as a function of $V_{DS}$ as shown in Figs. S3 and S4, we can derive that the sheet resistance of hydrogenated MLG has a lower limit of 200 GΩ/sq at room temperature (see more discussion in the Supplementary Information). When the cell is cooled down to 0 °C to further suppress $I_G$, the sheet resistance can reach up to 300 GΩ/sq (Fig. S5), approaching the measurement limit of our instrument. Such high resistance offers an ideal “off” state for graphene-based logic devices. In the “on” state at 1.5 V and -1 V, the MLG is highly conductive with sheet resistance merely $\sim 410 \Omega$/sq. Therefore, the on/off ratio can reach a record high value of $4.9 \times 10^8$ at room temperature, which is seven orders of magnitude higher than that ever reported on microscale MLG FETs (less than 20)$^{32}$.

The changes of graphene lattice induced by hydrogenation are corroborated by Raman spectroscopy, as shown in Fig. 1d. The main features in the Raman spectra of MLG are the G and 2D peaks at around 1580 and 2670 cm$^{-1}$, resulting from the in-plane vibrational (E$_{2g}$) mode and two-phonon inter-valley triple resonance scattering, respectively$^{33,34}$. The single and sharp 2D peak at charge neutral point ($V_G \sim 0.3 \text{ V}$) are unambiguous fingerprints of MLG$^{33,34}$. As more electrons are injected at $V_G \sim 1.5 \text{ V}$, the G peak becomes sharper and shifts to 1590 cm$^{-1}$, consistent with previous reports$^{29,35}$. With the further increase of $V_G$ to 2.0 V, the hydrogenation reaction results in three distinctive features in Raman spectra: (1) the appearance of sharp D and D' peaks at
1340 and 1600 cm⁻¹, (2) the significant broadening of the 2D peak, and (3) the emergence of combined (D + D′) and overtone (2D′) modes around 2930 and 3190 cm⁻¹. The D peak is undetectable in disorder-free MLG because its activation requires a defect via an inter valley double-resonance Raman process. Therefore, the intensity of D peak relative to G peak can serve as a measure for the defect density in graphene. Here, the sharp D peak in hydrogenated graphene reflects the breaking of translational symmetry of C-C sp² bonds and the formation of massive C-H sp³ bonds, behaving like a large amount of defects in graphene lattice. Besides, the observation of D′, D + D′, and 2D′ peaks further proves the presence of defect-assisted activation during the resonance Raman processes. It is worth noticing that the intensity of all Raman peaks are greatly increased compared to that without hydrogenation, which is probably caused by the surface-enhanced Raman scattering induced by the enhanced electromagnetic field between neighboring isolated and randomly-sized nanoscale pristine graphene domains embedded in the hydrogenated area, as further supported by the broad fluorescence background in the Raman spectra (Fig. 1d). The restoration of graphene lattice during the dehydrogenation reaction for \( V_G \) from 2 V to -1 V is also confirmed by the Raman spectroscopy (Fig. 1d). When \( V_G \) is lowered from 2 V, all the hydrogenation-induced Raman peaks (D, D′, D+D′, and 2D′) gradually decrease in intensity and completely disappear at around -0.5 V, leaving only the G and 2D peaks characteristic of graphene. These observations clearly demonstrate that the hydrogenated graphene can be fully recovered to its original lattice by electric-field control, which is further proved by the highly reversible and reproducible Raman spectra with multicycle sweeps (Fig. S6). Moreover, the agreement between Raman spectra and transport measurements indicates that the insulating graphene is indeed caused by the hydrogenation-induced transformation from sp² to sp³ hybridization.

To confirm that the current pinch-off is due to hydrogenation rather than bad connection between drain/source electrodes and graphene flake, we performed the control experiments in a three-segment device on a single graphene ribbon with shared drain/source electrodes as shown in Fig. 2a-c. Only the middle segment is exposed to
HIE, while the left and right ones are covered by a layer of 300-nm poly(methyl methacrylate) (PMMA) to obstruct the hydrogenation reaction. We first ground the shared electrode 2 and record the $I_{DS}$ of both the left and middle segments simultaneously. The middle segment reproduces the pinch-off state at $V_G \sim 2$ V (Fig. 2b), while the $I_{DS}$ of the left segment remains “on” at the same $V_G$ (Fig. 2a). This proves that the shared electrode 2 has a good electrical connection with the graphene ribbon even when the middle segment is fully hydrogenated. We then performed similar measurements in the middle and right segments. Likewise, the results in Fig. 2b and 2c completely rule out the possibility that electrode 3 is detached from the graphene ribbon during hydrogenation. It is worth mentioning that $I_{DS}$ of the left and right segments still presents V-shaped behavior (Fig. 2a and c) despite the PMMA cover layer. This is probably caused by the diffusion of H$^+$ ions from the middle segment via the interface between graphene and PMMA or SiO$_2$ substrate, other than through the PMMA layer (Fig. S7). The obstruction of hydrogenation in the left and right segments at $V_G \sim 2$ V is attributable to the blockage of the electric field by the PMMA layer, further demonstrating the decisive role of the electric field in controlling the graphene hydrogenation.

The gate-controlled switching capability is another key factor for the application of graphene FETs. As shown in Fig. 2d, when $V_G$ is quickly switched between -0.5 V and 2.4 V, the $I_{DS}$ should exhibit sharp transitions between on and off states, which is explicitly demonstrated by the alternating $V_{DS}$ across graphene channel in the voltage divider circuit (Fig. S8). After one million switching cycles (Fig. 2e), the graphene FET remains readily functional without any decay of the divided voltage, indicating the outstanding reversibility and stability of the hydrogenation and dehydrogenation in MLG. All these findings provide a long-sought solution to obtain a giant on/off current ratio and reliable switching capability in graphene FETs, which would significantly advance the applications of graphene logic devices.

Figure 2f and g present the switching speeds of the MLG device under the control of switching $V_G$ between -1 V and 2.6 V. We find that the rise time (10 % – 90 %) of
\( V_{DS} \) is 0.4 ms and the turn-off delay time is around 2.2 ms, which strongly depends on the turn-off gate voltage and the distance between gate electrode and graphene channel. Thus, this delay time can be attributed to the migration time of H\(^+\) ions onto graphene surface driven by the electric field. In Fig. 2g, the fall time to the “on” state is hard to evaluated due to the presence of undesired signal when switching \( V_G \) from 2.6 V to -1 V, which probably arises from the large parasitic capacitance in our electrochemical FET. Here we hypothesize the trace of switch curve (blue dashed line) by following the tendency of \( V_{DS} \). Thus, the fall time can be estimated to be around 0.13 ms, much lower than the rise time (0.4 ms). And the delay time is around 1.1 ms. This can be interpreted that the strip off of H atoms from graphene should be faster than the migration and accumulation to the graphene surface. Compared with the previous studies on electrochemical graphene FETs\(^{24,25}\), the performance of our MLG device is much more superior in terms of degradation, response time, and on/off ratio. The key improvement in our devices is utilizing the HIE with dissociative H\(^+\) ions other than that from the hydrolysis of residual water in the moister air\(^{24}\) or organic dielectrics\(^{25}\). Moreover, we only applied low gate voltages (between -1 and 2.6 V) to avoid the electrolysis of electrolyte and the irreversible reaction with anions (e.g. TFSI\(^-\) or OH\(^-\)), which may induce strong physical stress and break the C-C bonds in the graphene channel.

Besides monolayer graphene, the electric-field-driven reversible hydrogenation in multilayer graphene has also been studied. As shown in Fig. 3a, the \( I_{DS} \) of bilayer graphene (BLG) presents a characteristic V-shaped feature\(^{31}\) similar to MLG before the occurrence of hydrogenation (\( V_G < 1.5 \) V). A new feature here is that BLG presents a layer-by-layer hydrogenation behavior, as reflected by the two-step falloff of \( I_{DS} \) for \( V_G > 1.6 \) V. Fully hydrogenated BLG is also highly insulating with the sheet resistance larger than 50 G\(\Omega\)/sq (Fig. S9). As \( V_G \) is swept back to -1 V, \( I_{DS} \) of hydrogenated BLG progressively recovers its original conducting state. Two subsequent cycles of reversible hydrogenation display reproducible \( I_{DS} \) traces (Fig. 3a), with a slight difference in the onset voltages of the second jump at \( V_G > 1.7 \) V, which presumably corresponds to the hydrogenation of the bottom layer. The Raman spectra in Fig. 3b
further corroborate the electric-field control of reversible hydrogenation in BLG. Near the charge neutral point ($V_G \sim 0$ V), both the significant broadening and blue-shift of the 2D peak (to 2700 cm$^{-1}$) reveal the fingerprint of BLG. When the top graphene layer is hydrogenated at $V_G = 1.7$ V, the Raman spectrum exhibits similar changes as that in MLG and remains nearly unchanged during the hydrogenation of bottom layer at $V_G = 2.1$ V, which indicates consistent hydrogenation mechanism and structure both for the MLG and BLG. As the dehydrogenation is induced by sweeping $V_G$ to -1 V, the Raman spectrum progressively restores its original characteristics of pristine BLG.

For the trilayer graphene (TLG), the $I_{DS}$ traces in Fig. 3c are nearly identical to that of MLG and BLG before the hydrogenation (-1 V < $V_G$ < 1.5 V). However, the hydrogenation of TLG (1.7 – 1.9 V) only decreases the $I_{DS}$ but cannot completely pinch it off. With further increase of $V_G$ to 2.5 V, no more hydrogenation process is detected except for the increase of $I_{DS}$. As $V_G$ is swept back to -1 V, the $I_{DS}$ first decreases monotonically, then fluctuates during the dehydrogenation process and finally merges into the original V-shaped profile. More cyclic electric-field controls of $I_{DS}$ demonstrate the high stability and reversibility of hydrogenation in TLG, as further proved by the representative Raman spectra in Fig. 3d. The consistent Raman results of MLG, BLG, and TLG demonstrate the similar C-H configurations and defect types in the hydrogenated graphene.

To understand the microscopic mechanism of the electrochemical reaction between hydrogen and graphene, we performed density functional theory (DFT) calculations. Figure 4a displays the potential energy curves for single atomic H on top of the C sites with a fully relaxed MLG lattice as a function of the distance between H and adjacent C atoms. It can be clearly seen that the potential energy curves have a local minimum with the binding energy around 0.8 eV and H-C distance about 1.2 Å. A detailed analysis of the charge density distribution shows that charge transfer occurs between the H atom and graphene lattice, indicating the formation of chemical bond. In this case, the C atom under the H atom moves 0.38 Å upward relative to the graphene plane. Before the formation of H-C bond, there is an energy barrier of $\sim 0.2$ eV corresponding
to the H atom at ~1.8 Å above the C atom, consistent with previous reports\textsuperscript{3,37}. When the electric field is applied on top of graphene, a linear background is superposed to the potential energy of the graphene and H atom system. Accordingly, the energy barrier gradually flattens with increasing electric field to ~ 2 V/nm, which is readily achieved in our experiments at $V_G = 2$ V by the strongly localized electric field of the ~1 nm EDL on graphene surface\textsuperscript{30,31}. Moreover, as illustrated in Fig. 4b, the energy barrier is lowered by electron doping to an experimentally accessible level of ~ $1 \times 10^{14} \text{ cm}^{-1}$ (Ref. 29,31). This finding indicates that the hydrogenation can be greatly facilitated by the strong electric field and high electron doping, in good agreement with our observation that MLG is highly conductive at $V_G \sim 1.5$ V, which is right before the reaction. For the dehydrogenation process, it is unexpected that MLG gradually becomes conductive with $V_G < 0.2$ V because the energy barrier of H desorption is as high as 1.0 eV. We attribute such discrepancy to the metastable hydrogenated lattice susceptible to Eley-Rideal reactions between H$^+$ ions in HIE and chemically bonded H atoms\textsuperscript{37,38}, or the desorption of recombined H atom pairs on graphene surface\textsuperscript{39,40}.

Among all the structures of fully hydrogenated graphene, the most stable one is supposed to have the chair conformation with the hydrogen atoms alternating on both sides of the plane\textsuperscript{2}. Although only the top surface of MLG is exposed to HIE in our devices, we believe that hydrogen atoms are chemically bonded to carbon atoms on both sides based on the following reasons. Firstly, the most stable composition for single-side hydrogenation is C$_4$H as demonstrated both experimentally and theoretically\textsuperscript{10,41–43}. However, the binding energy of C$_4$H (1.98 eV/H atom)$^{41}$ is much smaller than that of double-side hydrogenated chair conformer (6.56 eV/H atom)$^2$. Additionally, in the general case with two H atoms bonded to the nearest C atoms, H positions on opposite sides of the graphene sheet are much more favorable than those on the same side\textsuperscript{3}. Secondly, the single-side hydrogenated graphene can only be obtained when the hydrogen is completely restricted to one side$^{41}$. Given the high diffusivity of H$^+$ ions under electric field\textsuperscript{26–28}, they can easily penetrate through the top surface\textsuperscript{44,45} or intercalate into the interface between graphene and SiO$_2$ substrate.
through the exposed edges\textsuperscript{46}. Therefore, H atoms prefer to bond both sides of graphene, which is further facilitated by the progressive reduction of formation energies with the increase of H concentrations\textsuperscript{3,47}. Thirdly, due to the frustrated hydrogenation domains arising from the random bonding of H atoms to A or B sites of graphene lattice\textsuperscript{48}, the single-side hydrogenated C\textsubscript{4}H with strong disorders is still conductive\textsuperscript{10} with sheet resistance much lower than our results. Finally, compared with the plasma-induced single-side hydrogenation\textsuperscript{6–10}, our Raman spectra are more analogous to that from the chemical reduction method, which has been used to produce high H coverage over 50\% (Ref. 15–17).

Based on the above analyses, we employ the chair conformer as the structure of fully hydrogenated MLG and calculate the density of states (DOS). As shown in Fig. 4c, the hydrogenation process converts gapless MLG into an insulator with bandgap up to 3.5 eV. BLG with only the top layer hydrogenated is equivalent to a graphane/graphene (B-A) heterostructure, which is still conductive. Upon complete hydrogenation, the highly insulating BLG possesses a large bandgap corresponding to bilayer graphene (Fig. 4d). For the case of TLG, the applied electric field is strongly localized on the top one/two layers, thus at least one bottom graphene layer cannot be fully hydrogenated and serves as a gapless conducting channel as displayed in Fig. 4e with the graphane/BLG (B-A-A) and bilayer-graphane/MLG (B-B-A) configurations. The electronic structure calculations thus are highly consistent with the transport behavior of all the devices with different numbers of graphene layers.

The electric-field-induced reversible hydrogenation provides a powerful way to create and annihilate a sizable bandgap in the microscale graphene. The giant room-temperature on/off current ratio and stable switching behavior pave the road for practical applications of graphene-based electronics. These findings shed new lights on the construction of an all-graphene-based integrated circuit with MLG working as the essential FET and TLG as the interconnection line\textsuperscript{49}. Compared with the chemical method\textsuperscript{3,50}, the electric-field control of reversible adsorption of H atoms also represents a feasible approach for hydrogen storage in atomic-thin graphene membranes.
According to the previous studies of H\(^+\) ion control in metal oxides\(^{26–28}\), we believe that our electric-field-induced hydrogenation can be used as a universal method for reversibly tuning the atomic bonding and band structures of various 2D crystals, which opens up new opportunities in searching for emergent materials with novel functionalities.

**Methods**

**Sample preparation**

Graphene crystals were mechanically exfoliated on silicon wafers with 285 nm SiO\(_2\). The thickness was identified by the atomic force microscope and Raman spectroscopy. After that, standard electron-beam lithography and thermal evaporation were used to deposit Cr/Au (3/50 nm) on the ends of the graphene samples to serve as the drain and source electrodes. A long strip of Pt foil (5 mm × 2 mm × 25.4 μm) was used as the gate electrode. Then a layer of sealant and cover glass were employed to seal all these electrodes in liquid electrolyte cell as detailed in Ref. 51. The injection of hydrogen ion electrolyte was carried out in argon-filled glovebox and the filling openings were fully sealed by the epoxy before taking it out of the glovebox for the electric transport measurements.

**Electric transport measurements**

A direct voltage \(V_{DS} = 5 \text{ mV}\) was applied between the drain and source electrodes by Keithley 2400 SourceMeter, and \(I_{DS}\) was recorded simultaneously. Another 2400 SourceMeter was used to apply \(V_G\) between the Pt electrode and graphene source electrode and measure \(I_G\) in the meanwhile. The change of \(V_G\) was performed only at room temperature (~ 25 °C) with the changing rate at 2 mV/s. When measuring the resistance of hydrogenated graphene, \(V_G\) was kept unchanged while \(V_{DS}\) was swept back and forth with the rate at 5 mV/s. All the sheet resistance values were obtained from the two-terminal resistance by considering the size effect.
Raman spectroscopy measurements
Raman spectroscopy was measured by HORIBA LabRAM HR Evolution Spectrometer with 532 nm laser excitation and 1800 l/mm grating. All the Raman spectra have subtracted the background signals contributed by HIE. During Raman measurements, two Keithley 2400 SourceMeters worked together to control $V_G$ and monitor $I_{DS}$ respectively. When $V_G$ reached the target voltage, the Raman signals were acquired until $I_{DS}$ became nearly stable.

Theoretical calculations
First-principles calculations were performed in the framework of density functional theory using the Vienna ab initio Simulation Package\(^5\). The energy cutoff of the plane-wave basis was fixed at 500eV. The projector augmented wave (PAW) method and the Perdew-Burke-Ernzerhof type generalized gradient approximation (GGA)\(^5\) were adopted to model the electron-ion interactions and the exchange correlations between electrons, respectively. The crystal structure relaxations were performed with the force criteria of 0.01 eV/Å. The van der Waals interaction between neighboring layers was considered by the DFT-D3 methods\(^5\). A vacuum layer of 20 Å was added in the direction perpendicular to 2D planes to avoid interactions between adjacent periodic images. The Monkhorst-Pack k-point meshes of 40×40×1, 9×9×1 were adopted for pristine lattices and supercells of 3×3, respectively.

Data availability:
All raw and derived data used to support the findings of this work are available from the authors on request.

Acknowledgments:
We thank Yong Xu for helpful discussions and technical supports. This work is supported by the Basic Science Center Project of NSFC (grant No. 51788104) and the National Key R&D Program of China (grants No. 2018YFA0307100 and
2016YFA0301001). This work is supported in part by the Beijing Advanced Innovation Center for Future Chip (ICFC). J.S.Z acknowledges support from the National Thousand Young Talents Program.

**Author contributions**

J.S.Z. and Y.Y.W. proposed and supervised the research. J.S.Z designed the device structure and proposed the electrolyte. S.R.L., Y.C.W., C.L.Y., and Y.X.L. fabricated the devices and carried out the electric measurements. S.R.L and Y.C.W. measured the Raman spectra. W.H.D. and J.H.L. performed theoretical calculations. J.S.Z., Y.Y.W., and S.R.L. prepared the manuscript with comments from all authors.

**Competing interests:**

The authors declare no competing interests.

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Fig. 1 | Electric-field control of reversible hydrogenation in MLG. a, Schematic structure of HIE gated graphene device and electric measurement configuration. b, Illustration of the hydrogenation process between graphene lattice (blue) and H⁺ ions (red). c, Three consecutive cycles of $I_{DS}$ measurements in device M1 as a function of applied gate voltage $V_G$ at room temperature (25 °C). It represents a highly reproducible conductor-insulator transition in MLG. The black arrows indicate the sweep directions of $V_G$. The applied $V_{DS}$ is fixed at 5 mV. d, Raman spectra of MLG at different $V_G$'s in device M2. The corresponding $I_{DS}$ of labeled $V_G$ is represented by the solid dot and circled number with the same color in c. The correspondence of $I_{DS}$ and Raman spectra at different $V_G$'s is highly reproducible in different devices. To clearly present all the Raman spectra, the intensity of $V_G = 2.0$ V is divided by four.
Fig.2 | Characterization of the insulating and switching behaviors of hydrogenated MLG.

**a**, The current between electrode 1 and 2, $I_{12}$, versus $V_G$ in the three-segment device M3 as shown in the inset. The middle segment is exposed to HIE, whereas the left and right ones are covered by a layer of 300-nm PMMA. **b**, The current between electrodes 2 and 3, $I_{23}$, as a function of $V_G$. The black curve is obtained simultaneously with that in **a**. The inset shows the optical image of our device and the scale bar is 10 μm. **c**, The current between electrodes 3 and 4 measured simultaneously with the red curve in **b**. The measurement configuration is displayed in the inset. **d**, The $V_{DS}$ across the drain and source electrodes of MLG device M4 (black line, left scale) and the square waveform of $V_G$ (red line, right scale) measured by the oscilloscope simultaneously. When $V_G$ is periodically changed between -0.5 V and 2.4 V, the $V_{DS}$ can be quickly switched accordingly in the voltage divider circuit with the input voltage of 0.5 V. The period of $V_G$ is 0.1 s. **e**, Same measurements as **d** after one million switching cycles with $t \sim 28$ hours. The $V_{DS}$ remain unchanged as the beginning, which indicates the high stability of reversible hydrogenation in MLG under the electric-field control. **f-g**, The characterization of respond time in MLG device M4. The rise time of $V_{DS}$ (10 % - 90 %) from on to off state is 0.4 ms and the fall time is estimated around 0.13 ms. The $V_G$ is switched between -1 V and 2.6 V with the changing time of 1 ms. The blue dashed line in **g** is the extrapolated trace of $V_{DS}$ from the tendency.
Fig. 3 | Electric-field control of reversible hydrogenation in BLG and TLG. 

**a**, Three consecutive cycles of $I_{DS}$ in BLG as a function of applied gate voltage $V_G$ of device B1. The black arrows indicate the sweep directions of $V_G$. The applied $V_{DS}$ is fixed at 5 mV. **b**, Raman spectra of BLG at different $V_G$’s in device B2. The corresponding $I_{DS}$ of labeled $V_G$ is represented by the solid dot and circled number with the same color in **a**. The intensity of Raman spectra for $V_G = 1.8$ and 2.2 V is divided by four. **c-d**, The same measurements of $I_{DS}$ (**c**) and Raman spectra (**d**) in TLG devices (T1 and T2).
**Fig.4 | DFT calculations of hydrogenated MLG, BLG, and TLG.**

**a,** Potential energy as a function of the distance between H atom and the subjacent C atom under different electric fields. The insets present the configurations of H atom (red) and graphene lattice (blue) with different distances. The effect of electric fields is assumed to add linear backgrounds to the potential energy curves. The barrier becomes nearly flattened with the increase of the electric field up to 2 V/nm.

**b,** The energy barrier as a function of doped electron density with different electric fields.

**c,** Density of states of MLG (blue) and graphane with chair conformation (red). The crystal structures of single-layer graphene (A) and graphane (B) are presented in the insets.

**d-e,** DOS of different stacking configurations in the bilayer (d) and trilayer cases (e). The stacking sequences are indicated in the top right legends.