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Adsorption configurations and scanning voltage determined STM images of small hydrogen clusters on bilayer graphene

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By density functional theory calculations, the scanning tunneling microscopy (STM) images of various hydrogen clusters adsorbed on bilayer-graphene are systematically simulated. The hydrogen configurations of the STM images observed in the experiments have been thoroughly figured out. In particular, two kinds of hydrogen dimers (ortho-dimer, para-dimer) and two kinds of tetramers (tetramer-A, -B) are determined to be the hydrogen configurations corresponding to the ellipsoidal-like STM images with different structures and sizes. One particular hexamer (hexamer-B) is the hydrogen configuration generating the star-like STM images. For each hydrogen cluster, the simulated STM images show unique voltage-dependent features, which provides a feasible way to determine hydrogen adsorption states on graphene or graphite surface in the experiments by varying-voltage measurements. Stability analysis proves that the above determined hydrogen configurations are quite stable on graphene, hence they are likely to be detected in the STM experiments. Consequently, through systematic analysis of the STM images and the stability of hydrogen clusters on bilayer graphene, many experimental observations have been consistently explained. © 2013 AIP Publishing LLC.

I. INTRODUCTION

Hydrogenation is one of the most important means to manipulate the properties of graphene and graphite.1–11 In order to understand the mechanism involved, the determination of the hydrogen adsorption state on graphene or graphite surface is essentially important. The related issues have initiated numerous investigations both in theory and in experiment.12–17 In theory, there is a great deal of work trying to understand the stability of hydrogen clusters on graphene or graphite surface.8, 18–23 Small hydrogen clusters containing up to six hydrogen atoms on graphene were systematically studied by Šljivančanin et al., and the stable hydrogen configurations among them have been figured out.24 In experiment, scanning tunneling microscopy (STM), a tool that can provide the real-time image of adsorbate down to atomic scale, is usually used to detect the adsorbed states of hydrogen clusters on graphene or graphite surface. It was reported that the structure of STM images is highly dependent on the size (the number of hydrogen atoms contained) and the configurations (the relative adsorption sites of hydrogen atoms) of hydrogen clusters adsorbed on graphene.12–17, 24, 25 For example, various structures of the STM images of hydrogen clusters were observed in both experiments done by Balog et al.14 on graphene and by Hornekær et al.12 on graphite surface.

Due to the resolution limitation of the STM measurement, the hydrogen clusters corresponding to the STM images cannot be figured out directly in the experiment. Up to now, with the help of density functional theory (DFT) simulations, only two kinds of short ellipsoidal-like STM images, which were observed at low hydrogen coverage, have been thoroughly determined.12, 14 The corresponding hydrogen clusters are ortho-dimer (with two hydrogen atoms adsorbed on the nearest two carbon atoms) and para-dimer (with two hydrogen atoms adsorbed on the opposite carbon atoms of a hexagon of graphene). Their possibility to be observed by STM is supported by their relatively large adsorption energies and desorption barriers, as obtained from DFT simulations.19, 20, 24, 26–28

In addition to the short ellipsoidal-like STM images, many other kinds of STM images with various structures have also been observed in experiments.12–17, 25, 26 For example, both Hornekær et al.12 and Balog et al.14 have observed many more extended ellipsoidal-like images, with some of them looking very slim and some of them being more rectangular. Besides, in the latest work of Hornekær et al., one kind of complex STM images is observed, particularly, these images look star-like at high scanning voltage (874 mV), but they become triangular at low bias voltage (109 mV).15 Detailed observations show that the length, which is the maximum distance between two bright protrusions, of the star-like STM image is the same as the extended ellipsoidal-like ones. Both of them are quite stable and can exist at temperature up to 540 K.15 Extensive work has tried to determine the corresponding hydrogen adsorption states of the above mentioned STM images, and to explain the phenomena observed in the experiments consistently.15–17, 25 As to the extended ellipsoidal-like STM images, many researches

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propose that they are also produced by the ortho-dimers. But, under such assumption, it is hard to explain why these images have the length as large as the star-like ones, which is believed to be produced by complex hydrogen clusters.\textsuperscript{17} On the other hand, other research thinks that they arise from the extended hydrogen dimers, which can have relatively large sizes. However, these extended dimers are not stable enough to coexist with star-like ones at the high temperature of the experiments.\textsuperscript{15} As to the star-like images, due to their scanning voltage dependent shapes and the $C_3$ symmetry, in the work of Hornekær et al.\textsuperscript{15} and Khazaee et al.,\textsuperscript{17} the hydrogen trimers and tetramers with the same symmetry are assumed to be the configurations of these complex images. On the other hand, Ferro et al., by including the interlayer interaction in the graphite, concluded that they can be reproduced by one kind of hydrogen hexamers on graphene.\textsuperscript{16} Consequently, to unambiguously determine the hydrogen configurations of the above mentioned STM images and to fully understand the related phenomena provided by the experiments, further theoretical simulations are necessary.

In this work, the STM images of hydrogen clusters on bilayer-graphene are systematically simulated by first principle calculations. Through full comparison with the experimental observations, ortho-dimer and para-dimer are confirmed to be the hydrogen configurations of those short ellipsoidal-like STM images, and tetramer-A(B) are hydrogen configurations of the extended ellipsoidal-like ones. Hexamer-B, with hydrogen arranging into a big regular hexagon on graphene is hydrogen configuration of the complex star-like STM images. With these determined hydrogen configurations, the phenomena that the ellipsoidal-like images have the same length with the star-like ones and the voltage-dependent shapes in star-like STM images have been consistently explained. Moreover, different from other theoretical work, varied scanning voltage is used in STM image simulation of each hydrogen configuration. A unique scanning voltage dependent character is found in the STM images of each hydrogen configuration. Therefore, varied scanning voltage observation is suggested to further determine the hydrogen adsorption configurations on graphene.

**II. COMPUTATIONAL METHODS**

In our calculations, bilayer graphene in stable stacking (AB style) is chosen as our model since the interlayer interactions felt by the top graphene layer in the STM experiments on graphite surface\textsuperscript{13,25,26} mostly comes from the underneath second layer and thus two layers are necessary and enough to include such interaction. (See the first paragraph of the supplementary material\textsuperscript{29}) A rectangular supercell that contains 144 carbon atoms is used in each STM simulation (see Fig. S1(a) in the supplementary material\textsuperscript{29}). In AB stacking, there are two kinds of non-equivalent carbon atoms as shown in Fig. 1, where the $\alpha$ carbon atom in the upper layer has a neighbor atom directly below, while the $\beta$ carbon atom does not. The hydrogen clusters with two or four hydrogen atoms being arranged in a straight line (Fig. 2) are used to simulate the ellipsoidal-like images observed in the experiments.\textsuperscript{13,15} The hydrogen clusters with three, four, or six atoms being arranged either in a triangle or hexagon (Fig. 3) are used to simulate the star-like images.\textsuperscript{15} More hydrogen clusters considered in the present work could be found in Figs. S4–S12 of the supplementary material.\textsuperscript{29} All the STM images are calculated according to the Tersoff-Hamann theory,\textsuperscript{36} which can be expressed as

$$ I(\vec{r}, V_{bias}) \sim \rho = \int_{E_F}^\infty \sum_i \sum_{\vec{k} \in BZ} |\psi_{ik}(\vec{r})|^2 \delta(E_i - E), $$

where $I(\vec{r}, V_{bias})$ is the transmission current and $\rho$ is the local density of states (LDOS) at the tip position, and $\psi_{ik}(\vec{r})$ is the wave function of the sample surface, which is obtained by the DFT calculation. $V_{bias}$ is the applied scanning voltage, which is used to bias the sample with respect to its Fermi level.

To analyze the stability of the hydrogen clusters on the graphene or graphite surface, the average adsorption energy
of hydrogen clusters is defined as

\[ E_a = (E_{gr} + nE_H - E_{gr+nH})/n, \]

where \( E_{gr} \), \( E_H \), and \( E_{gr+nH} \) are, respectively, the energies of the isolated graphene layer, an isolated hydrogen atom, and the graphene with hydrogen adsorption, and \( n \) is the number of atoms included in the hydrogen clusters. The activation energy for the diffusion and desorption of hydrogen atoms is calculated by the climbing-image nudged elastic band method.\(^{31}\)

In the stability analysis, we use single-layer graphene, and each supercell consists of 72 carbon atoms (see Fig. S1(b) in the supplementary material\(^{29}\)) as well as the bonding hydrogen cluster. This model for analyzing the stability of hydrogen clusters on multilayer graphene or graphite surface is reliable, because the weak interlayer interaction has negligible effect on the chemisorbed hydrogen atoms,\(^{12,13,21,25}\) although it is important for the STM images (shown in this work). In fact, using ortho-dimer in a relative small supercell (4 \( \times \) 4), we have tested its adsorption energy on monolayer (2.69 eV) and bilayer-graphene (2.68 eV), respectively. The result shows that the adsorption energy in these two models is almost the same.

All our calculations are performed within the density-functional theory formalism as implemented in the Quantum Espresso package.\(^{32}\) In the STM simulations the spin-polarized local density approximation (LDA) exchange-correlation function, which is believed to give a good description of the interlayer bonding in graphite, is used.\(^{33,34}\) In the adsorption and activation energy calculation, the Perdew-Burke-Ernzerhof generalized-gradient approximation (GGA)\(^{35}\) function is used to describe the electron-electron interactions, which has a better description of chemical bond. The ultrasoft pseudopotentials\(^{36}\) are adopted to account for the electron-ion interaction. The electron wave function and charge density are expanded in plane waves and the energy cutoffs are 30 and 300 Ry, respectively. The corresponding Brillouin zone is sampled by a 4 \( \times \) 4 \( \times \) 1 mesh using the Monkhorst-Pack scheme.\(^{37}\) All the structures are fully relaxed within the force threshold of 1 \( \times \) 10\(^{-3}\) Ry/bohr. The Methfessel-Paxton smearing\(^{38}\) technique with the width of 0.02 Ry is applied to speed up the convergence.

III. RESULTS AND DISCUSSIONS

STM is one of the powerful means to detect hydrogen adsorption state on graphene or graphite surface. The STM experiments have shown that the images of the adsorbed hydrogen clusters on graphite surface are mainly ellipsoidal-like and star-like at low hydrogen coverage.\(^{13–15}\) More careful observations exhibit that the ellipsoidal-like STM images differ from each other both in shape (either slim or rectangular) and in length (either short or long).\(^{14,25}\) As for the star-like STM images, they only exist at high voltage (874 mV), and become triangular at low voltage (109 mV).\(^{15}\) Our simulations have successfully reproduced all these STM images and the related phenomena with proper hydrogen configurations on bilayer-graphene. As to the short ellipsoidal-like STM images (Figs. 2(a) and 2(b)), the corresponding hydrogen clusters are ortho-dimer and para-dimer. At the high scanning voltage (874 mV) used in the experiments,\(^{15}\) the STM image of the ortho-dimer is short and slim, and that of the para-dimer is short and rectangular. Both of them compare well with those observed in the experiments.\(^{13,14}\) Moreover, our results at high voltage are also consistent with the theoretical investigation given by Hornekær et al.\(^{13}\) Hence we confirm that ortho-dimer and para-dimer are hydrogen clusters generating the short ellipsoidal-like STM images. More interestingly, for both ortho-dimer and para-dimer, we find that their STM images are dependent on the scanning voltage. For example, as shown in Fig. 2(a), the STM image of ortho-dimer is ellipsoidal-like at high scanning voltage, and when the voltage decreases, part of the image disappears and only one bright spot is finally observed at low voltage (109 mV).

In addition to these short ellipsoidal-like STM images, there are also elongated ellipsoidal-like STM images detected in the experiments.\(^{13,14,25}\) It was once assumed that these elongated STM images are also produced by hydrogen dimers on graphene. However, with such assumption, as mentioned in the Introduction, we find that the size of the images and the stability of the hydrogen dimers are in a contradictory situation, since when the explanation for the size is satisfactory, the explanation for the stability will be not and vice versa. Thus, up to now, the hydrogen configurations corresponding to them are still unknown and not accepted. In the following, we will provide three evidences to assign these elongated ellipsoidal-like STM images to be generated by two kinds of tetramers, tetramer-A(-B). First, the STM image of tetramer-A at high scanning voltage (Fig. 2(c)) is ellipsoidal-like and in a long and slim frame, and that of tetramer-B (Fig. 2(d)) is long and more rectangular. Both the STM images of tetramer-A and tetramer-B are almost the same as those extended ellipsoidal-like STM images (slim and rectangular) observed in the experiments.\(^{14,25}\) Second, the adsorption of these two kinds of tetramers on graphene is quite stable, which will be shown in detail later. So they have relatively

FIG. 2. (a) The STM image of para-dimer for the isolated hydrogen atom and the graphene layer (0.02 eV). (b) The STM image of ortho-dimer for the isolated hydrogen atom and the graphene layer (0.02 eV). (c) The STM image of ortho-dimer for the isolated hydrogen atom and the graphene layer (0.02 eV). (d) The STM image of para-dimer for the isolated hydrogen atom and the graphene layer (0.02 eV).
large possibility to exist and be detected on graphene in the experiments. Third, the length of tetramer-A(-B) is about 7 Å (the distance between two hydrogen atoms that are most far away from each other), which is the size of these elongated ellipsoidal-like STM images provided by other works.\textsuperscript{17} It is worthy to note that the simulated STM images of tetramer-A(-B) also depend on the applied scanning voltage (see Figs. 2(c) and 2(d)). Thus, it is highly suggested to adopt variable scanning voltage observation to further clarify the hydrogen configurations of these extended ellipsoidal-like STM images in experiments.

As to the star-like STM images, their scanning voltage dependent characters indicate that the possibly responsible hydrogen clusters could be the triangular trimers, tetramers, or hexagonal hexamers.\textsuperscript{15-17} This is the origin of disputes on the hydrogen configurations corresponding to these star-like STM images.\textsuperscript{16,17} To explicitly figure out the corresponding hydrogen configuration, as shown in Fig. 3, we have simulated the STM images of trimer-A, tetramer-C, and hexamer-A(-B). These hydrogen configurations are chosen because all of them have the C\textsubscript{3v} symmetry, which is the same as the star-like STM images. Other kinds of hydrogen configurations have also been tested (see the supplementary material\textsuperscript{29}), but their STM image structures are not star-like at all, so they are safely excluded from the potential configurations of the star-like STM images. In the following paragraph, we will analyze the STM images of all the mentioned hydrogen configurations, respectively.

Trimer-A (Fig. 3(a)) is the hydrogen configuration of the star-like STM image proposed by Khazaei \textit{et al.}\textsuperscript{17} However, our result clearly shows that it is not the corresponding hydrogen configuration since its STM images are triangular in shape at all scanning voltages (Fig. 3(a)), not star-like at all. Moreover, stability analysis by Šljivančanin \textit{et al.}\textsuperscript{24} as well as our previous work\textsuperscript{22} shows that trimer-A is quite unstable on graphene, so it hardly exists and cannot be detected by the experiments. The STM images of tetramer-C and hexamer-A (Figs. 3(b) and 3(c)) at all scanning voltages are also not star-like, which demonstrates that both of them are not the corresponding hydrogen configurations. For tetramer-C, one interesting thing is that only three bright spots can be observed (Fig. 3(b)) even though four hydrogen atoms are included in its configuration. The reason for this will be given later. Hexamer-B (Fig. 3(d)) is the particular hydrogen configuration of the star-like STM image. The hydrogen atoms involved arrange into the structure of hexagon on graphene with three hydrogens adsorbing on α carbon atoms and the other three on β ones (Fig. 1). The simulated STM image of it at high scanning voltage is star-like (Fig. 3(d)), which is composed of six bright spots with three of them being bigger and brighter than the other three. When the scanning voltage reduces, those three less bright spots disappear and the STM image changes into the structure of triangle including only three bright spots. All the STM images of hexamer-B obtained at different scanning voltages match those observed in the experiments, perfectly.\textsuperscript{15} Moreover, we will identify in the following that hexamer-B is a very stable hydrogen cluster on graphene and it is reasonable that such configuration is detected in the experiments.

We should note that, in the latest STM experiments, the ellipsoidal-like STM images and the star-like ones are detected to have the same length.\textsuperscript{15} Previous explanations are not satisfactory since only dimers (ortho- or para-) are supposed to be the hydrogen clusters of the ellipsoidal-like STM images, but actually these dimers are not large enough to produce images with the same length as those of hexagonal clusters. However, our simulations show that tetramers (-A, -B) are also hydrogen clusters that produce ellipsoidal-like STM images. Since tetramer-A has the same length as that of hexamer-B, their STM images exhibit the same size, as is presented in Fig. 4, and for comparison the observation of the experiment is also given.\textsuperscript{15} This also provides another evidence for the existence of tetramer and hexamer on the graphite surface.

Now we look into why the STM images are voltage dependent. For tetramer-C, as mentioned above only three bright spots can be observed (Fig. 3(b)) even though four hydrogen atoms are included in its configuration, which implies that the applied voltage is not large enough to detect all hydrogen atoms. We do obtain a four-hydrogen image for this configuration when we increase the scanning voltage to 1.073 eV (see Fig. S13(b) in the supplementary material\textsuperscript{29}). The reason is that the hydrogen in the center of the triangle (blue circle, Fig. 3(b)) feels relatively large repulsion from the other three hydrogen atoms (red ones, Fig. 3(b)), which pushes its density of states relatively far away from the Fermi level (see Fig. S13(d) in the supplementary material\textsuperscript{29}), and makes it detectable only at relatively high scanning voltage. In such case the voltage-dependent characters come from the unsymmetrical interactions between hydrogen atoms, due to their special adsorption configurations. For hexamer-B, on the other hand, its hydrogen atoms distribute symmetrically on graphene, so the mechanism involved in its voltage dependent STM images is different from that of tetramer-C. The hydrogen atoms of hexamer-B can be classified into αHs (adsorbed on αC) and βHs (on βC) (see Figs. 1–3). The result in Fig. 5(a) shows that the LDOS (near the Fermi level) on αHs is relatively larger than that on the β ones, which implies that their response to the scanning voltage is different. The projected density of states (PDOS) (Fig. 5(b)) indicates that within the scanning voltage of the experiments, the PDOS on αHs is larger than that on βHs. Especially, near the Fermi level the PDOS on βHs almost vanishes, so its LDOS, as just mentioned, is too
small to be detected in the STM experiments. At low scanning voltage, only αHs can be observed and the STM image of hexamer-B is triangular in shape including three spots. When the scanning voltage increases, the PDOS on βHs slightly increases, and all the βHs become detectable at high scanning voltage. Therefore, the STM images evolve into star-like shapes with six bright spots. Moreover, at each scanning voltage, the PDOS on αHs is always larger than that on β ones, which explains the phenomenon that three spots of the star-like STM images are bigger and brighter than the other three.

The asymmetrical distribution of the PDOS on αHs and βHs is the result of different local interlayer interaction of bilayer-graphene, which is schematically shown in Fig. 5(c). The adsorption of hydrogen atom (αH or βH) on bilayer-graphene will pull the carbon atom beneath out of the graphene plane, and contrarily push its nearest neighbors in the opposite direction. For α carbon atoms, there are carbon atoms directly below them in the underneath layer, while their nearest neighbors do not have. Whereas for β carbons, they have no atoms directly below them, but their nearest neighbors do have. Therefore, the adsorption of αH increases the local interlayer attraction of bilayer-graphene (Fig. 5(c)), which attracts its DOS relatively close to the Fermi level. Nevertheless, for the adsorption of βH, there is enhanced local interlayer repulsion, which pushes its DOS relatively far away from the Fermi level. Therefore, around the Fermi level, the PDOS on αH is always larger than that on β ones. Finally, the explanation of the scanning voltage dependent STM images of hexamer-B as well as tetramer-C could be certainly extended to other hydrogen clusters.

Next we turn to analyze the stability of all the determined hydrogen clusters above. In the STM experiments by Horneckær et al., among all the STM images, the percentage of star-like and ellipsoidal-like images is observed to decrease when the sample is heated even up to 540 K. It means that the corresponding hydrogen clusters adsorbed on graphene are quite stable. In the present work, the stability is analyzed by investigating the adsorption energy and activation energy in the kinetic evolution path of each hydrogen cluster on graphene. In Table I, for stability comparison, the average adsorption energy (Ea) of different hydrogen clusters is presented. As mentioned above, ortho-dimer, para-dimer, tetramer-A, and tetramer-B are hydrogen clusters of ellipsoidal-like STM images, and hexamer-B is the hydrogen cluster of the star-like STM image. The Ea listed in Table I clearly indicates that all these configurations are quite stable on graphene with Ea being even larger than 1.39 eV, which is the adsorption energy of ortho-dimer that has been widely accepted as the very stable hydrogen configuration on graphene.13, 14, 19, 20, 24 and thus can be taken as the reference for judging the stability of hydrogen clusters on graphene. The relatively large Ea of tetramer-A, tetramer-B, and hexamer-B demonstrates that they are even more stable than ortho-dimers.

In addition to the adsorption energy to determine the stability of hydrogen clusters on graphene, the dynamical processes of sticking, diffusion, and recombination also greatly affect the adsorption states of hydrogen clusters on graphene or graphite surface.13, 14, 19, 20, 24 For the well understood stable ortho-dimer (O) and para-dimer (P), our inspected kinetic evolution processes shown in Fig. 6(a) are in good agreement with the literature.13, 14, 19, 20 In particular, para-dimer desorbs directly from graphene with an activation energy of 1.40 eV, while ortho-dimer first diffuses into meta-dimer (M) with an energy barrier of 1.63 eV, and then evolves into para-dimer and finally follows its desorption process (see Fig. 6(a)). As for tetramer-A (tA), it can be considered as being composed by two ortho-dimers, and its desorption paths are shown in Fig. 6(b): tA1 diffuses into tA1 with the energy barrier of 1.66 eV, then tA1 diffuses into tA2 and at last the para-dimer of tA2 desorbs away with the energy barrier of 1.48 eV. On the other hand, tetramer-B (tB) and hexamer-B (Fig. 7) can be regarded as being composed of para-dimers. Their possible kinetic evolution paths are shown in Fig. 7, which clearly demonstrates that desorption path involving two hydrogen atoms in para-positions is the main evolution path, and the corresponding activation energies are 1.26 eV

**TABLE I.** The average hydrogen adsorption energy (Ea) of various hydrogen configurations.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>No. of H atoms</th>
<th>Ea (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho-dimer</td>
<td>2</td>
<td>1.39</td>
</tr>
<tr>
<td>para-dimer</td>
<td>2</td>
<td>1.37</td>
</tr>
<tr>
<td>Trimer-A</td>
<td>3</td>
<td>0.82</td>
</tr>
<tr>
<td>Tetramer-A</td>
<td>4</td>
<td>1.52</td>
</tr>
<tr>
<td>Tetramer-B</td>
<td>4</td>
<td>1.54</td>
</tr>
<tr>
<td>Tetramer-C</td>
<td>4</td>
<td>1.30</td>
</tr>
<tr>
<td>Hexamer-A</td>
<td>6</td>
<td>1.52</td>
</tr>
<tr>
<td>Hexamer-B</td>
<td>6</td>
<td>1.59</td>
</tr>
</tbody>
</table>
FIG. 6. (a) Configurations of ortho-, meta-, and para-dimer as well as the H₂ recombination processes and the corresponding activation energy (eV). The hydrogen (carbon) atoms are noted by dark (gray) spheres. (b) The configurations of tetramer-A(-A1, -A2) and the H₂ recombination processes.

(Fig. 7(a)) and 1.64 eV (Fig. 7(b)), respectively. The data in Figs. 6 and 7 show that the activation energy of tetramer-A(-B) and hexamer-B is comparable with or even larger than that of ortho-dimer and para-dimer, which have been proved to be very stable on graphene.¹³,¹⁴,¹⁹,²⁰,²⁴ So we can confidently conclude that, besides the two most widely accepted ortho-dimer and para-dimer configurations, tetramer-A(-B) and hexamer-B are all stable hydrogen clusters which are important to define the hydrogen adsorption states on graphene or graphite surface. These clusters should be the right hydrogen configurations generating the STM images observed in the experiments.¹²–¹³

IV. SUMMARY

In summary, by taking bilayer graphene as the structural model, the STM images of small hydrogen clusters on graphene or graphite surface are systematically simulated. Our results have fully determined the hydrogen configurations of the STM images observed in the experiments. Specifically, ortho-dimer, para-dimer, tetramer-A, and tetramer-B are hydrogen configurations corresponding to the ellipsoidal-like STM images in different structures and sizes, and hexamer-B is the right hydrogen configuration of the star-like STM image. Due to the interlayer interaction of bilayer-graphene, the STM images of the stable hydrogen clusters have different structures corresponding to various applied scanning voltages. Consequently, the varied scanning voltage detection technique is suggested to definitely determine the hydrogen adsorption states on graphene or graphite surface in the experiments. Additionally, stability analysis with the adsorption energy and kinetic evolution of hydrogen clusters on graphene demonstrates that the predicted hydrogen clusters are quite stable on graphene, and it is reasonable that they could be observed by STM in the experiments.

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35. See supplementary material at http://dx.doi.org/10.1063/1.4832040 for (1) the calculation models used in this work; (2) the LDOS and PDOS distribution of hexamer-B on 1-, 2-, and 3-layer graphene; (3) the STM images of hexamer-B simulated with different probe-graphene distance at varied scanning voltage, and (4) the STM images of other testing hydrogen clusters.