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Spontaneous Folding Growth of Graphene on h‑BN

Letter

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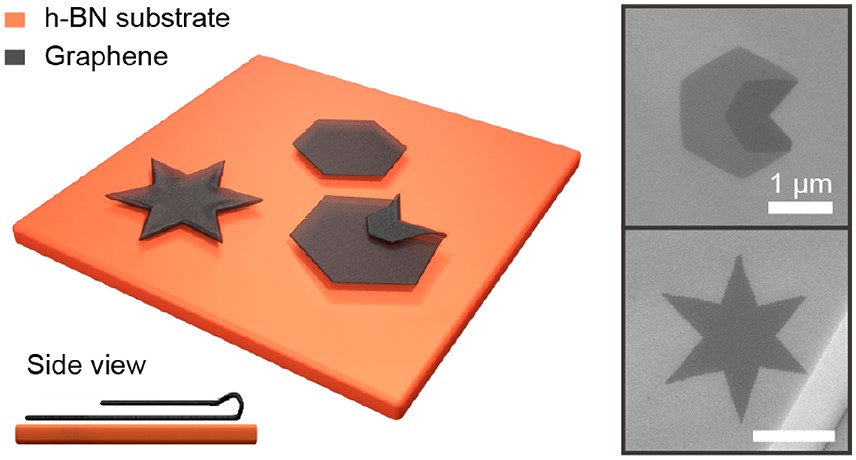
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ABSTRACT: Graphene has been the subject of much research, with structural engineering frequently used to harness its various properties. In particular, the concepts of graphene origami and kirigami have inspired the design of quasi-three-dimensional graphene structures, which possess intriguing mechanical, electronic, and optical properties. However, accurate controlling the folding process remains a big challenge. Here, we report the discovery of spontaneous folding growth of graphene on the h-BN substrate via adopting a simple chemical vapor deposition method. Folded edges are formed when two stacked graphene layers share a joint edge at a growth temperature up to 1300 °C. Using *ﬁ*rst-principles density functional theory calculations, the bilayer graphene with folded edges is demonstrated to be

more stable than that with open edges. Utilizing this novel growth mode, hexagram bilayer graphene containing entirely sealed edges is eventually realized. Our *ﬁ*ndings provide a route for designing graphene devices with a new folding dimension.

KEYWORDS: *graphene, folding growth, folded edge, chemical vapor deposition*

or two-dimensional (2D) materials, structural control is an e*ﬀ*ective way to yield an extensive range of extraordinary properties.[1](#_bookmark4)−[6](#_bookmark4) For instance, 2D materials can be easily stacked into precisely designed constructions,7 with many resulting emergent properties including Hofstadter’s butter*ﬂ*y in graphene/h-BN moirésuperlattice,[8](#_bookmark4)−[10](#_bookmark4) superconductivity in magic-angle bilayer graphene,[11](#_bookmark4),[12](#_bookmark4) and moiréexcitons in transition-metal dichalcogenide heterostructures.[13](#_bookmark4)−[15](#_bookmark4) For atomically thin layers, a new structural degree of freedom

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has been introduced to acquire either bending or folding.[1](#_bookmark4),[6](#_bookmark4),[16](#_bookmark4) Folding is an e*ﬀ*ective route to transfer 2D materials to functional quasi-3D forms. More importantly, this modi*ﬁ*cation allows the ability to tune their physical properties such as hydrophilia, transmittance, and mechanical properties.[3](#_bookmark4),[6](#_bookmark4),[17](#_bookmark4) Indeed, many surprising behaviors at the edges of folded graphene have been theoretically proposed, which include spontaneous electric polarization,18 anomalous magnetism,19 snake states,20 and zero Landau level.2

To date, various approaches have been conducted to achieve edge-folded bilayer graphene (EFBG). The most common method has focused on mechanical techniques, including random folding or self-peeling during exfoliation,[21](#_bookmark4),[22](#_bookmark4) soni*ﬁ*ca- tion or stirring in solution,[23](#_bookmark4),[24](#_bookmark4) and precisely folding by

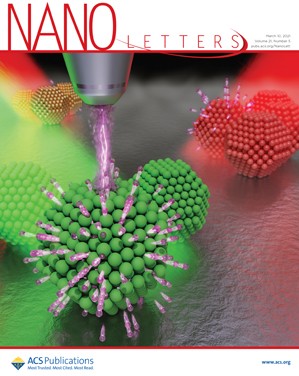
scanning probes.[25](#_bookmark4),[26](#_bookmark4) Besides, Joule heating and chemical modi*ﬁ*cation are also utilized to achieve folded graphene.[27](#_bookmark4)−[32](#_bookmark4) However, some of these methods possess large randomness,

some need complicated operations, and even some will cause the quality decay of graphene sheets. Here, we use a simple chemical vapor deposition (CVD) method to demonstrate that high-quality EFBG can be spontaneously grown on the h-BN

substrate. Speci*ﬁ*cally, this method produces hexagram bilayer graphene containing entirely sealed edges in a controllable manner.

Graphene was grown on h-BN *ﬂ*akes, which were cleaved

onto SiO2/Si substrate in advance. Subsequently, acetylene (C2H2) was introduced to our CVD system as the carbon feedstock with silane (SiH4) acting as a gaseous catalyst.33 The growth temperature was maintained at 1300 °C during the whole growth period. [Figure 1](#_bookmark0)a shows a representative scanning electron microscope (SEM) image of the as-grown samples. Similar to previous reports,[33](#_bookmark4),[34](#_bookmark4) orthohexagonal monolayer graphene sheets (as indicated by the blue circles in [Figure 1](#_bookmark0)a) are obtained with a moirépattern emerging from the lattice mismatch between graphene and h-BN (see [Figure](#_bookmark0) [1](#_bookmark0)a inset). Simultaneously, an unusual bilayer *ﬂ*ake appears with the segmental darker region (as indicated by the red circle in [Figure 1](#_bookmark0)a). This contrast arises from the formation of EFBG, as evidenced by the representative atomic force microscopy (AFM) image shown in [Figure 1](#_bookmark0)b. The corresponding line pro*ﬁ*le ([Figure 1](#_bookmark0)b) further demonstrates that the joint edge (white arrow in [Figure 1](#_bookmark0)b) of the two layers is protruded, which is consistent with the observations of previous studies



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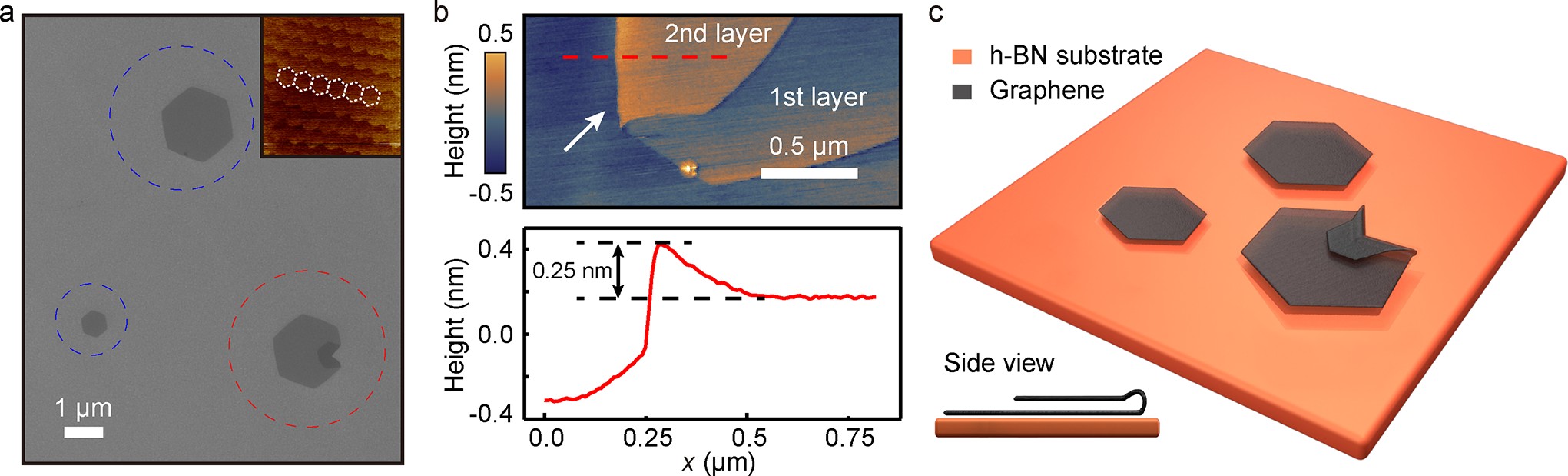
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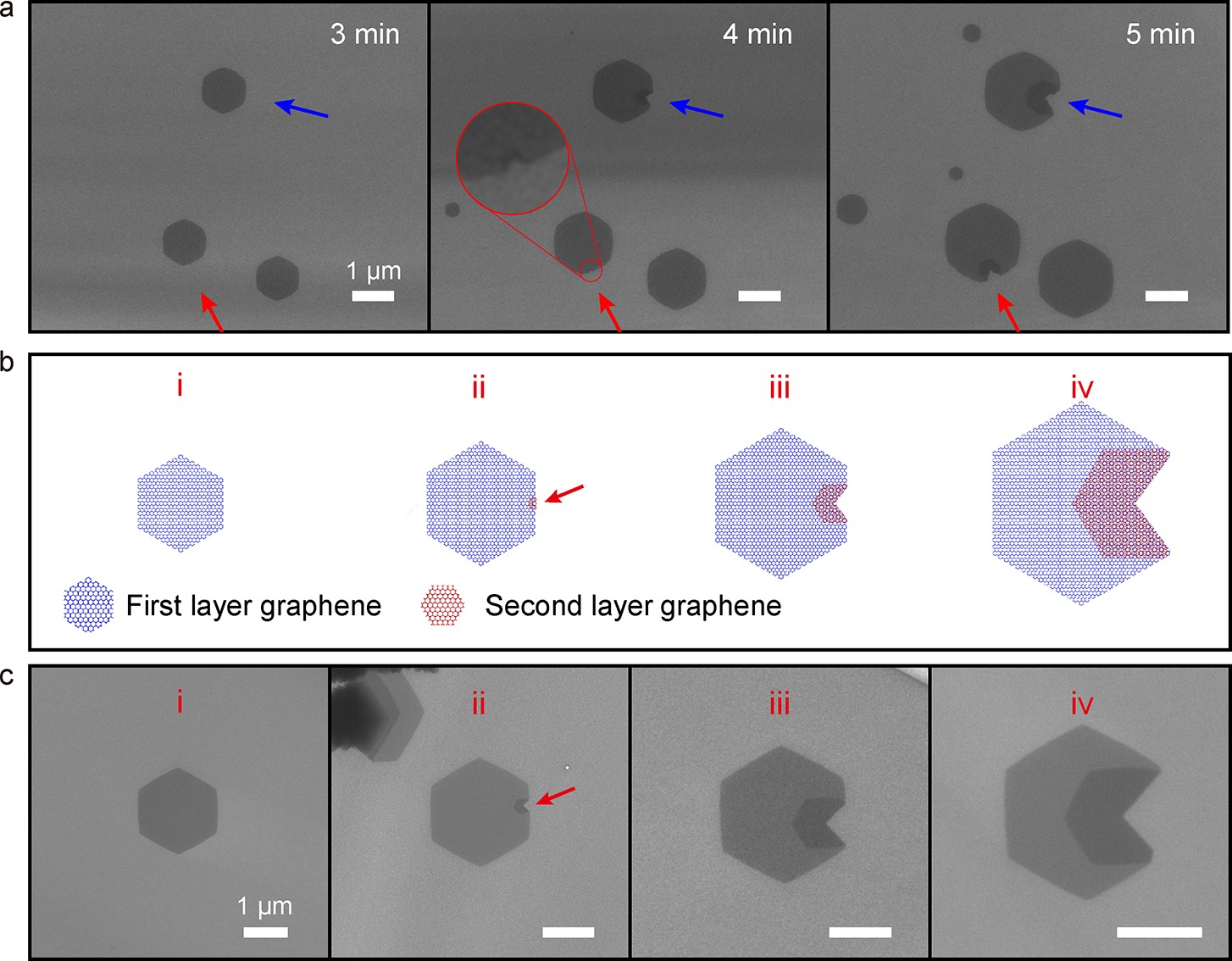
Figure 1. Characterization of edge-folded bilayer graphene (EFBG). (a) Representative SEM image of the epitaxial monolayer graphene (blue circles) and EFBG (red circle) on the h-BN substrate. Inset shows the AFM friction image of the moirépattern for a graphene/h-BN heterostructure with a period of ∼14 nm. (b) Representative AFM image of the folded edge and the corresponding height line pro*ﬁ*le. (c) Schematic of monolayer graphene and EFBG on h-BN.

Figure 2. Formation process of EFBG. (a) SEM images of the continuous growth process of graphene in the same area. Blue and red arrows point to two edge-folding locations, respectively. (b) Schematics of di*ﬀ*erent growth stages of the EFBG. The growth speed ratio of the second layer to the *ﬁ*rst layer is set as 1.5. (c) SEM results corresponding to the four stages in panel b. Red arrows in panels b and c indicate the initial folding points.

about folded graphene.[22](#_bookmark4),[25](#_bookmark4) [Figure 1](#_bookmark0)c shows a schematic diagram of the monolayer graphene and EFBG grown on the h-BN substrate.

Continuous growth (as detailed in [Supplementary Note 1](http://pubs.acs.org/doi/suppl/10.1021/acs.nanolett.0c04596/suppl_file/nl0c04596_si_001.pdf)) was allowed to explore the formation process of the EFBG. [Figure 2](#_bookmark0)a shows the SEM images of graphene *ﬂ*akes corresponding to di*ﬀ*erent intermediate growth stages. It is clearly seen that the folding starts from a single point (see the enlarged view of the 4 min result) and is continuously extended along two directions. After the formation of the folded edges, the joint edges of the two layers stop growing while the size of the graphene bilayer still gets enlarged (see also in [Figure S1](http://pubs.acs.org/doi/suppl/10.1021/acs.nanolett.0c04596/suppl_file/nl0c04596_si_001.pdf)), indicating that the folded edges are closed.

Via measuring the domain sizes at di*ﬀ*erent growth stages shown in [Figure 2](#_bookmark0)a, the growth speeds of the *ﬁ*rst and second layers are estimated to be 379 nm/min and 449 nm/min, respectively. Note that the growth speed superiority of the second layer is a prerequisite for the formation of folded edge, as detailed later. Based on these experimental results, the folding process is summarized as the following stages, which are schematically drawn in [Figure 2](#_bookmark0)b. Initially, the folding begins to occur from a nucleated second layer at/near the edge of the *ﬁ*rst graphene layer (stage ii in [Figure 2](#_bookmark0)b). Then, the joint edge of the two layers is reconstructed to form a folded shape. As the growth speed of the second layer is set to be faster than that of the *ﬁ*rst layer, the edge of the second layer

continually overtakes the corresponding one of the *ﬁ*rst layer. This results in the continuous extension of the folded edges (stages iii and iv in [Figure 2](#_bookmark0)b). Obviously, such intermediate stages are all observed in our experimental SEM data ([Figure](#_bookmark0) [2](#_bookmark0)c), thereby supporting our explanation for the edge-folding process. Here, we would like to address that the nucleation sites for the second graphene layer are randomly distributed on the *ﬁ*rst layer; thus, the folding could start from any position around graphene, e.g., the vertex of the *ﬁ*rst layer graphene (see [Figure S2](http://pubs.acs.org/doi/suppl/10.1021/acs.nanolett.0c04596/suppl_file/nl0c04596_si_001.pdf)).

We next investigate the mechanism of the spontaneous folding growth of graphene on h-BN using *ﬁ*rst-principles density functional theory (DFT) calculations with the inclusion of van der Waals interactions (see [Supplementary](http://pubs.acs.org/doi/suppl/10.1021/acs.nanolett.0c04596/suppl_file/nl0c04596_si_001.pdf) [Note 1](http://pubs.acs.org/doi/suppl/10.1021/acs.nanolett.0c04596/suppl_file/nl0c04596_si_001.pdf)). It has been well-known that the second layer grows underneath the *ﬁ*rst layer on the catalytic copper surface.35 By contrast, it is found that the second layer appears on top of the *ﬁ*rst layer in the present case of the noncatalytic h-BN substrate (detailed in [Supplementary Note 2](http://pubs.acs.org/doi/suppl/10.1021/acs.nanolett.0c04596/suppl_file/nl0c04596_si_001.pdf) and [Figure S3](http://pubs.acs.org/doi/suppl/10.1021/acs.nanolett.0c04596/suppl_file/nl0c04596_si_001.pdf)). The calculated adsorption energies of carbon atoms on h-BN and graphene/h-BN provide an understanding of the di*ﬀ*erent growth speeds of the *ﬁ*rst and second graphene layers. Our results show that the most stable sites of adsorbed carbon atoms on h-BN and graphene/h-BN substrates are (5) and

(15/20) (see [Figure 3](#_bookmark1)a−d) with the adsorption energies of 1.3

and 1.6 eV, respectively. The di*ﬀ*usion barriers of carbon atoms

on h-BN and graphene/h-BN are estimated to be 0.41 and

0.43 eV, respectively. Since the di*ﬀ*usion barriers for the two cases are nearly similar to each other, it is likely that the adsorption energy di*ﬀ*erence (∼0.3 eV) between h-BN and graphene/h-BN leads to a faster growth speed for the second graphene layer compared to the *ﬁ*rst one. Therefore, the second-layer growth overtakes the *ﬁ*rst-layer growth to form

folded edges. It is noteworthy that the resulting spontaneous folding growth of graphene uniquely occurs on the BN substrate, di*ﬀ*ering from the graphene growth on catalytic metallic substrates.[36](#_bookmark4),[37](#_bookmark4)

We further examine the stability of folded edges. The total energy of EFBG is calculated as a function of the length *L*′ of the second graphene layer with *ﬁ*xing the length *L* = 104.6 Å of the *ﬁ*rst graphene layer (see [Figure 3](#_bookmark1)e). As illustrated in [Figure](#_bookmark1) [3](#_bookmark1)f, the energy di*ﬀ*erence between EFBG and the in*ﬁ*nite monolayer graphene decreases as *L*′ increases. Interestingly, there is a critical length *L*′ around 85 Å, above which EFBG becomes thermodynamically more stable than the in*ﬁ*nite monolayer graphene. It is noted that the *ﬁ*nite monolayer graphenes are higher in energy than the in*ﬁ*nite monolayer graphene, owing to their edge energies. Considering such an edge e*ﬀ*ect in *ﬁ*nite monolayer graphenes, the critical length *L*′ would be estimated to be smaller than 85 Å in realistic conditions. We also compare the energies of EFBG and the

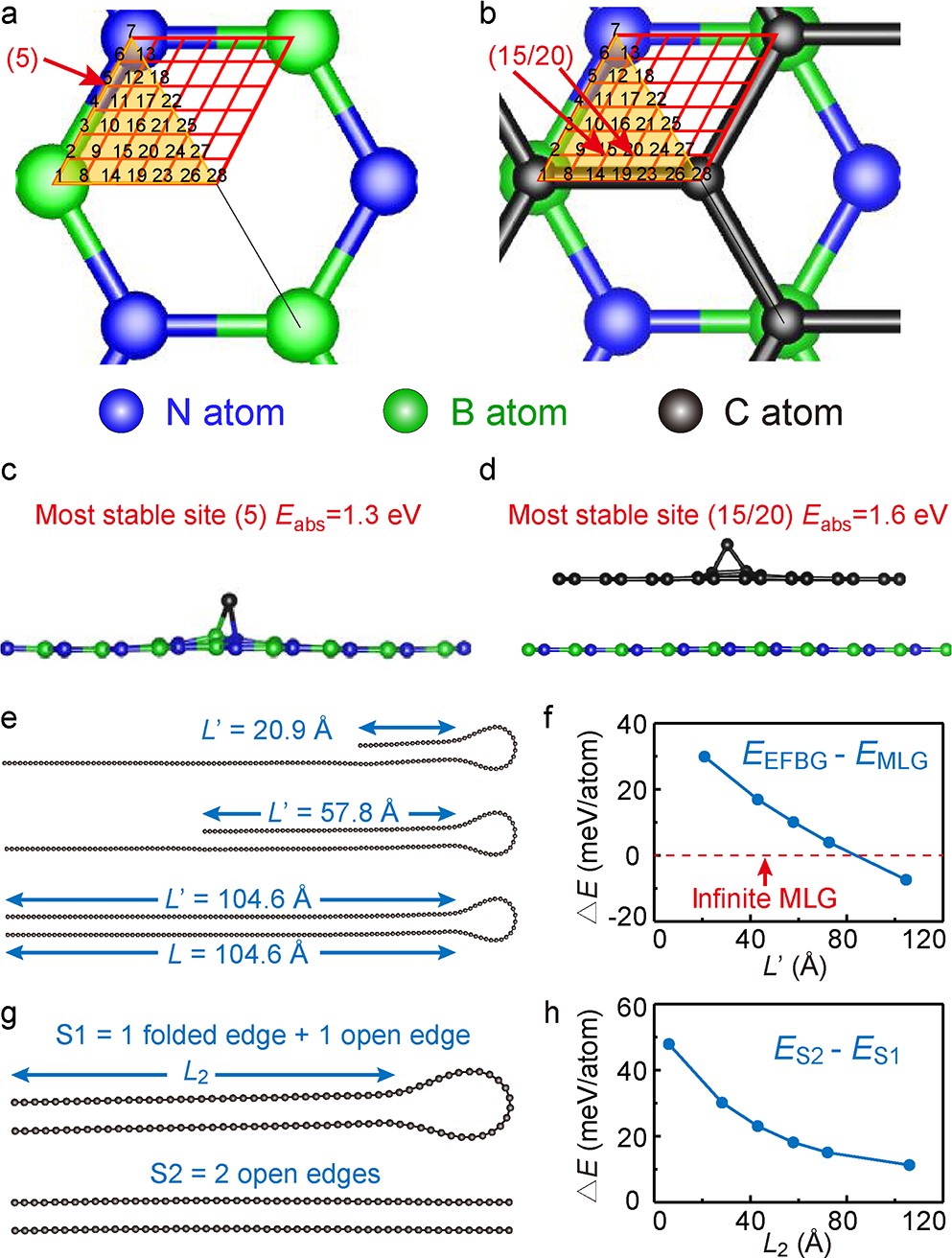


Figure 3. Calculated results. (a, c) Top and side views of the adsorption sites of C atoms on the h-BN surface. The most stable site is (5), as indicated by the red arrow. (b, d) Top and side views of the adsorption sites of C atoms on the graphene/h-BN surface. The most stable site is (15/20), as indicated by the red arrows. (e, f) Calculated formation energy of EFBG relative to the in*ﬁ*nite monolayer graphene (MLG) as a function of the length *L*′ of the second layer. (g, h) Calculated formation energy di*ﬀ*erence between bilayer graphenes with and without folded edges as a function of the length *L*2 of the bilayer graphene.

cost of more than 780 meV/atom, while the EFBG formation from bilayer graphene needs only 120 meV/atom. These values correspond to the temperatures of 8190 and 1260 K, respectively. Since our experimental growth temperature was around 1300 °C, direct bending is unlikely to occur. It is thus concluded that the observed EFBG would be formed by the reconstruction of open joint edges at our growth conditions.

Next, we consider another situation in which the second layer starts to grow around the center of the *ﬁ*rst layer. [Figure](#_bookmark2) [4](#_bookmark2)a shows that a hexagonal domain emerges on top of the *ﬁ*rst graphene layer with a rotation angle of 30° (stage i in [Figure](#_bookmark2)

normal bilayer graphene with the same length *L*2 ([Figure 3](#_bookmark1)g).

[4](#_bookmark2)a). After this, the six apexes of the second layer

Due to the reduced number of dangling bonds, EFBG is always thermodynamically more stable than the bilayer graphene having open edges. As shown in [Figure 3](#_bookmark1)h, the energy di*ﬀ*erence between EFBG and the bilayer graphene keeps positive in the range of calculated length and seems to be converged at a large value of *L*2. On the basis of the theoretically predicted stability of folded edges, we can say that the joint edge of two layers is easily reconstructed to form a folded shape, as demonstrated in our experiments.

According to a previous theoretical work,38 the direct bending from monolayer graphene to EFBG requires an energy

simultaneously catch up on the edges of the *ﬁ*rst layer (stage ii in [Figure 4](#_bookmark2)a). According to our DFT total-energy calculations, the closed edge is more stable than the open edge, leading us to believe that folded edges could be spontaneously formed to lower the involved energy. As the second-layer edges continually overtake the *ﬁ*rst-layer edges, 12 folded edges are extended outward from the six folding start points (stages iii and iv in [Figure 4](#_bookmark2)a). Finally, the folded edges intersect each other, forming a hexagram shape with all edges entirely sealed (stage v in [Figure 4](#_bookmark2)a, see also [Figure S4](http://pubs.acs.org/doi/suppl/10.1021/acs.nanolett.0c04596/suppl_file/nl0c04596_si_001.pdf)). Surprisingly, we observed all intermediate stages presented in

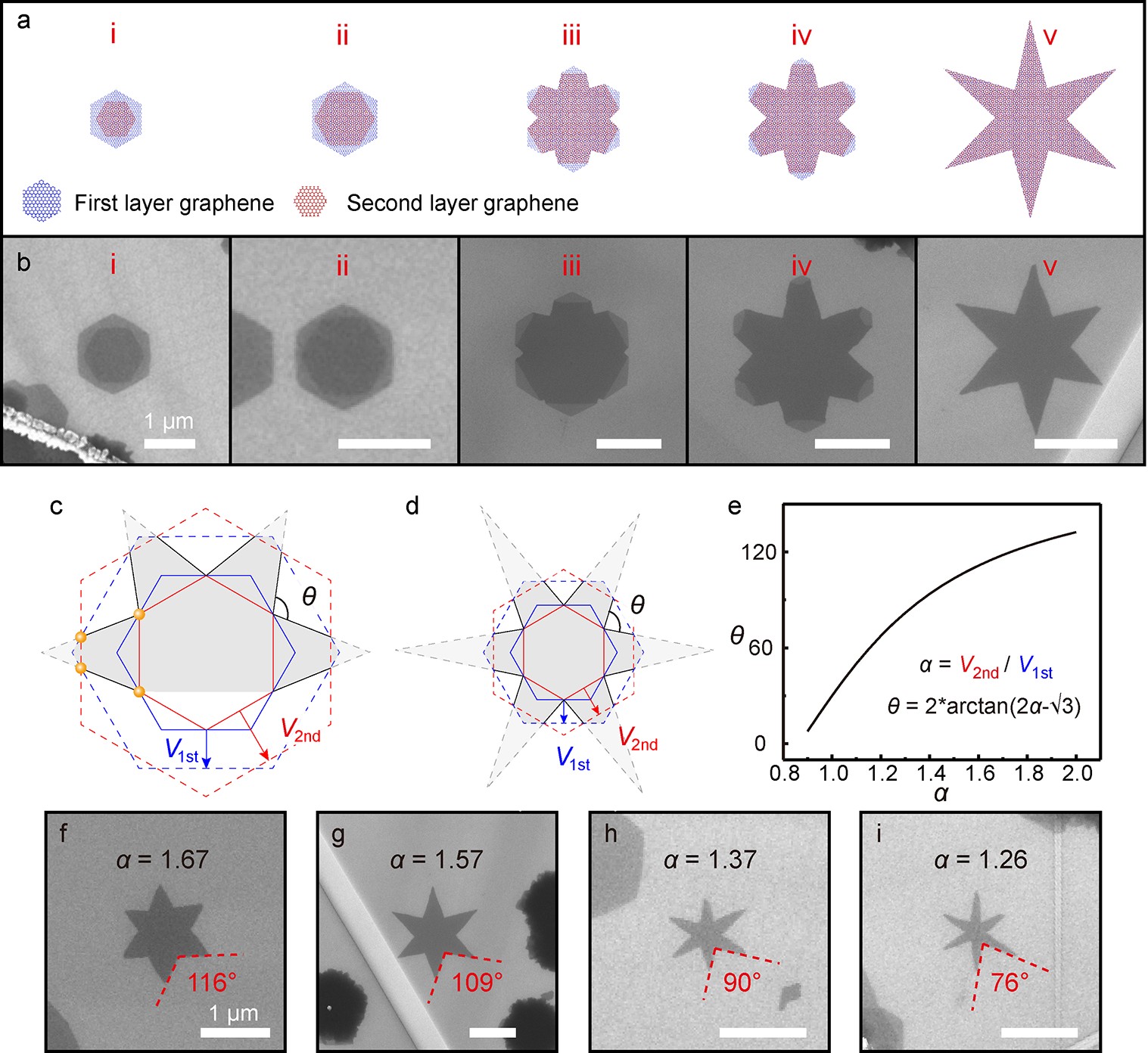


Figure 4. Hexagram bilayer graphene. (a) Schematic of the growth process of hexagram bilayer graphene. (b) SEM results corresponding to the di*ﬀ*erent growth stages shown in panel a. (c, d) Formation processes of hexagram bilayers with di*ﬀ*erent growth speed ratios. Blue and red full-line hexagons represent the *ﬁ*rst and second layers, with their growth speeds designated as *V*first and *V*second, respectively. The growth speed ratios α = *V*second/*V*first are set to be 1.5 and 1.3 for panels c and d, respectively. Blue and red dashed-line hexagons represent the corresponding growth stage,

assuming that the two layers do not form folded edges. Four intersection points of the two layers are marked with orange dots in panel c. Black lines represent the folded edges. The *ﬁ*nal shape of hexagram bilayer graphene is drawn with a gray color. (e) Relation of θ and α. (f−i) SEM results of hexagram bilayers with di*ﬀ*erent shapes. The measured values of θ and the estimated values of α are given in the images.

the schematic diagram (see [Figure 4](#_bookmark2)b), therefore validating our proposal for the growth process of hexagram bilayer graphene. The inclined angle of folded edges (θ in [Figure 4](#_bookmark2)c,d) is determined by the growth speed ratio of the second and *ﬁ*rst layers, which is de*ﬁ*ned as α = *V*second/*V*first. Here, *V*first and *V*second represent the growing speeds of the *ﬁ*rst and second graphene layers, respectively. In [Figures 4](#_bookmark2)c and d, we compare the two examples of hexagram formation, where α values are set to be 1.5 or 1.3, respectively. The full-line hexagons indicate the moment at which the second layer overtakes the *ﬁ*rst layer (equivalently stage ii in [Figure 4](#_bookmark2)a). Assuming that folded edges are not formed, two layers will grow to form the dashed-line hexagons later. In reality, the folding appears when the red and blue hexagons begin to intersect. In [Figure 4](#_bookmark2)c, the four intersection points of the full-line and dashed-line hexagons are marked with orange dots. The black connection lines of the inside and outside orange dots indicate the gradually formed folded edges. We further discuss the di*ﬀ*erent cases of α: if α is larger, the second layer will catch up more quickly on the *ﬁ*rst layer, thereby forming a larger inclined angle θ. As shown in [Figure 4](#_bookmark2)c,d, a relatively obtuse hexagram is obtained, when α is

larger. By geometric operation, the θ−α relation is given as

By tuning the rate of the catalytic silane *ﬂ*ow, we altered the growth speed ratio α. In [Figure 4](#_bookmark2)f−i, four typical hexagram graphene bilayers are displayed with gradually varied θ values.

It is noted that a more obtuse hexagram shape indicates a larger α. Using the measured θ, the speed ratios for the various shapes are estimated as 1.67, 1.57, 1.37, and 1.26, respectively. If θ is less than 60°, the outspread folded edges would no longer cross, leading to an “unclosed hexagram” shape ([Figure](http://pubs.acs.org/doi/suppl/10.1021/acs.nanolett.0c04596/suppl_file/nl0c04596_si_001.pdf) [S6](http://pubs.acs.org/doi/suppl/10.1021/acs.nanolett.0c04596/suppl_file/nl0c04596_si_001.pdf)). Apart from the growth speed adjustment, the growth temperature is also an important factor that in*ﬂ*uences the folding process. Our statistical result ([Figure S7](http://pubs.acs.org/doi/suppl/10.1021/acs.nanolett.0c04596/suppl_file/nl0c04596_si_001.pdf)) shows that the ratio of the folded bilayer signi*ﬁ*cantly increases with increasing growth temperature. This may be attributed to the increase in the nucleated probability of the second graphene layer at a higher growth temperature.

Finally, we note that the closed, folded edges observed in our experiment would have some defects. As shown in [Figure](#_bookmark2)

[4](#_bookmark2)e−i, the angle of folded edges varies, owing to the large-scale variability of α. Therefore, the present folded edges have

di*ﬀ*erent atomic con*ﬁ*gurations. Assuming that such EFBG are unfolded along the folded edge, there will be misaligned orientations between the *ﬁ*rst and second layers in the majority

of cases. A one-dimensional defect line with pentagon−

*θ* = 2 × *arc*tan(2*α* − 3 ): see [Figure 4](#_bookmark2)e.

heptagon (5−7) rings is expected to exist along the edge.[39](#_bookmark5),[40](#_bookmark5)

Such an intrinsic, topological defect line would markedly alter the electronic transport properties in graphene, for instance, unusual electronic transparency, tunable band gap, zero-energy

states, and room-temperature ferromagnetism.[41](#_bookmark5)−[44](#_bookmark5) More

importantly, the defect lines were random with in-plane

polycrystalline graphene but could be designed in our folding growth mode by controlling the growth speed ratio α. As a result, the present folded edges o*ﬀ*er a new platform to explore the novel physics about one-dimensional topological defect lines.

In summary, an entirely new growth mechanism that allows the out-of-plane motion is realized. Such a spontaneous folding growth mode proposes a potential roadmap to achieve designed quasi-3D graphene microstructures by a simple CVD method. The approach presented here allows an easier, more controllable means of folding graphene comparing with other mechanical/chemical methods. Moreover, the tunable, elaborate hexagram constructions o*ﬀ*er ideal platforms for studying the newly emerging physical properties involved in folded edges and topological defect lines. Importantly, this innovative growth mode broadens our prospective horizon for the design of special 3D structures with 2D materials.

# ASSOCIATED CONTENT

\*sı Supporting Information

The Supporting Information is available free of charge at [https://pubs.acs.org/doi/10.1021/acs.nanolett.0c04596](https://pubs.acs.org/doi/10.1021/acs.nanolett.0c04596?goto=supporting-info).

CVD growth of graphene, *ﬁ*rst-principles DFT calcu- lations; stacking order of graphene layers on h-BN; θ−α relations for di*ﬀ*erent types of edge folding processes

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Notes

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# ABBREVIATIONS

2D, two-dimensional; 3D, three-dimensional; EFBG, edge- folded bilayer graphene; CVD, chemical vapor deposition; SEM, scanning electron microscope; AFM, atomic force microscopy; DFT, density functional theory; MLG, monolayer graphene

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