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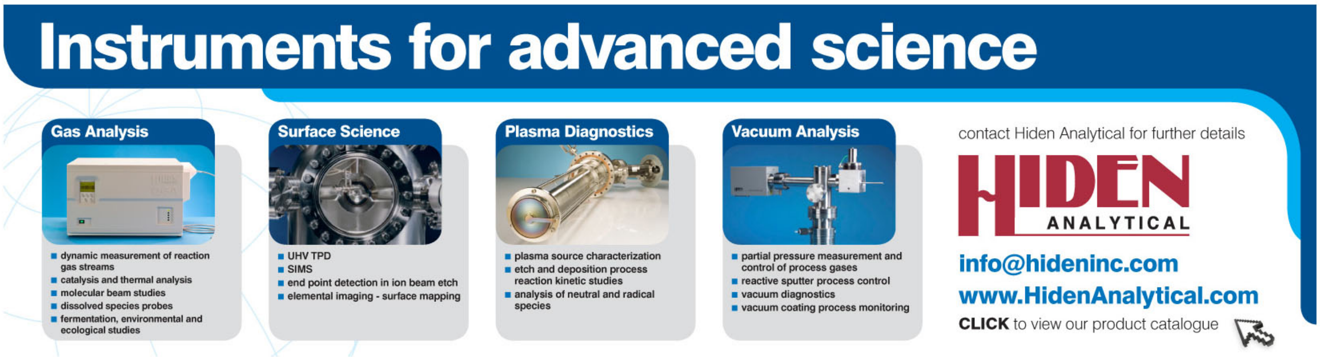

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Line defects guided molecular patterning on graphene

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Graphene emerges as a candidate scaffold for patterning molecules. Despite existing progresses, it still remains unclear how to achieve molecular self-assembly in domains of desirable geometry. We reveal a barrier effect of line defects (e.g., open slits) in graphene, which can potentially enable molecular confining and patterning in a domain of desirable geometry. Using molecular dynamics simulations, we demonstrate that fullerene molecules can be readily patterned into a stable cluster of various shapes and sizes. Such a strategy is expected to be applicable to pattern various types of molecules that interact with graphene via van der Waals force. *© 2014 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4867534]

Molecular self-assembly has received great attention in nanotechnology, driven by its promising potential to pattern random molecules into structures with desired property and function,[1–4] which, in turn, can find possible applications such as molecular storage,[5] chemical reaction,[6] and biomedical systems.[4] Various self-assembly techniques have been studied recently. In particular, the advent of graphene motivates its use as a template for molecular self-assembly. Simulations have shown that hydrogenated graphene can adopt well-defined three-dimensional geometries, which serve as energy walls to trap molecules.[5] Other experiments have demonstrated that guest particles can be packed between two stacks of graphene, forming a sandwich like structure.[6] However, the molecular packing geometry in these existing techniques is relatively limited, and it still remains unclear how to achieve molecular self-assembly into an arbitrary geometry. To address such a challenge, in this Letter, we use molecular dynamics simulation to demonstrate a feasible and robust approach to patterning molecules into domains of desired shapes and sizes on graphene simply by introducing line defects (e.g., open slits) in graphene.

Recent progresses in graphene engineering have made it feasible to tailor graphene into desirable shapes and to introduce defects into graphene with atomic resolution. It is reported that cutting graphene with sub-nanometer-precision can be achieved using scanning tunneling microscopy lithography[7] and focused electron-beam etching.[8] Research has also shown that using a scanning transmission electron microscope, graphene can be sculpted into patterns of predefined position and sizes.[9] Point defects and line defects (e.g., open slits) can be introduced into graphene by knocking off carbon atoms using focused electron-beam[10] or high-energy ion-beam irradiation.[11,12] These progresses on programmable introduction of defects in graphene make the proposed molecular patterning on graphene in this Letter feasible to achieve in experiments.

At the center of line defects guided molecular patterning on graphene is the barrier effect of open slits in graphene, as demonstrated in Fig. 1. An open slit is introduced in a graphene monolayer by knocking off a row of carbon atoms. The resulting slit has a width of about 3 Å and is composed of two zigzag edges. A fullerene (C_{60}) molecule is placed near the slit. Energy minimization is performed using large-scale atomic/molecular massively parallel simulator (LAMMPS),[13] in which the carbon material structure is described by the adaptive intermolecular reactive empirical bond order (AIREBO) potential.[14] The interaction between the graphene and the C_{60} molecule is van de Waal (vdW) type. The total vdW force acting on the C_{60} molecule can be computed by summing all carbon-carbon atomic pair potentials between the C_{60} molecule and the graphene. When the C_{60} molecule is placed on a perfect graphene sheet (or far away from the slit), the total in-plane vdW force acting on the C_{60} molecule is nearly zero, given the symmetry of the graphene lattice. By contrast, when the C_{60} molecule is placed near the open slit, the missing carbon atoms at the slit result in a net vdW force acting on the C_{60} molecule in the direction perpendicular to the slit and pointing to the direction away from the slit. In other words, the open slit serves as a barrier by exerting a net force on the C_{60} molecule to push it away. To demonstrate such a barrier effect, Fig. 1 plots the net in-plane vdW force acting on the C_{60} molecule as a function of its distance to the open slit. Initially, the C_{60} molecule is placed on the right with a distance d to the center of the slit of 10 Å. The C_{60} molecule is displaced along the horizontal direction towards the open slit with a displacement step of 0.5 Å. The distance from the center of the C_{60} molecule to graphene in out-of-plane direction is fixed at its equilibrium value (~8 Å). At each location, the energy minimization is performed, and then the resultant force along the horizontal direction is documented. In this fashion, we can obtain the net vdW force in horizontal direction as a function of the distance from the C_{60} to the center of the open slit. As shown in Fig. 1, when the C_{60} molecule is far from the slit edge, the net vdW force approaches to zero as the molecule cannot feel the open slit and the vdW force is zero-balanced. As the C_{60} molecule moves toward the slit, the net vdW force increases, which peaks at a distance about 3 Å to the center of the slit in the direction that prevents the C_{60} molecule to move further toward the slit. The net force decreases to zero only when the C_{60} molecule is placed right above the center of the open slit due to symmetry. Essentially, such a net force results from the difference between the carbon

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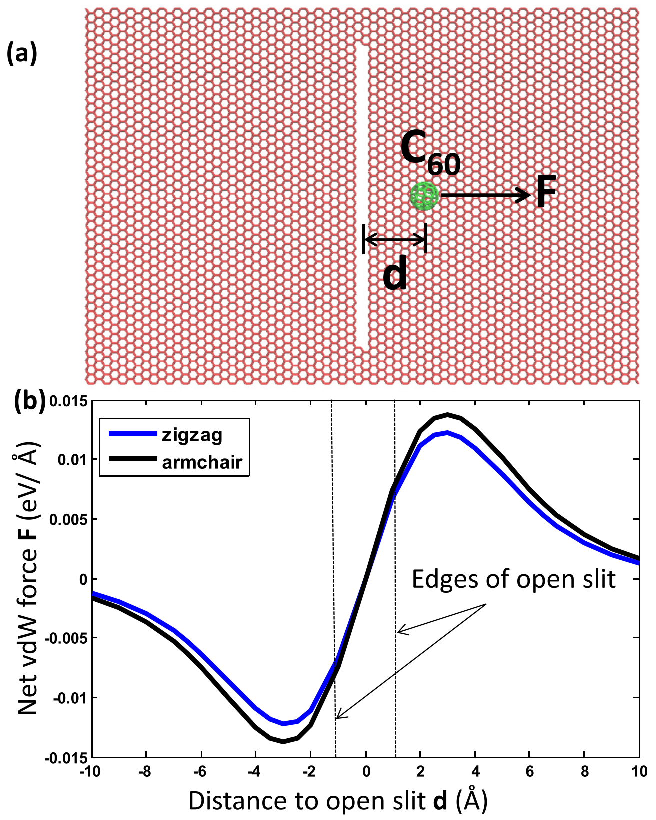

FIG. 1. (a) A 3 Å-wide open slit is introduced in a graphene monolayer by knocking off a row of carbon atoms and is composed of two zigzag edges. A C_{60} molecule is placed near the slit with an out-of-plane distance of 8 Å to the graphene sheet. (b) Net in-plane vdW force acting on the C_{60} molecule as a function of the distance of C_{60} to the open slit. Dashed lines mark the location of the edges of the open slit.

atom density of graphene on the right side and that on the left side of the C_{60} molecule as it approaches the open slit. The higher atom density side (i.e., away from the open slit) provides a vdW force greater than the less dense side. As a result, the net force effectively pulls the C_{60} molecule away from the edge of the open slit. Figure 1 also plots the net force vs. the distance of C_{60} from the edge of an open slit along the armchair direction, which shows a rather similar trend. Due to the symmetry of the graphene lattice, the two curves in Fig. 1 set the upper and lower limits of the net force due to an open slit along arbitrary direction in graphene. The barrier effect of an open slit in graphene demonstrated in Fig. 1 is the physical origin of the proposed approach to packing molecules in a domain of desirable shape, as shown in the following.

As an example of the above mentioned barrier effect of open slits, we demonstrate molecules packing in a square-shaped domain. As shown in Fig. 2, four slits with length of 50 Å and width of 3 Å are introduced in a graphene sheet (100 Å × 100 Å), demarcating a square-shaped domain. Nine C_{60} molecules are randomly introduced to the central square-shaped domain (Fig. 2(a), e.g., by dispersing C_{60} molecules over the graphene), and then the system evolves freely at 300 K. Driven by thermal fluctuation, the C_{60} molecules start to move around. When a C_{60} moves toward the open slits, it will be bounced back into the square-shaped domain due to the barrier effect. Figures 2(a)–2(c) show the snapshots of the confined motion of the C_{60} molecules and the corresponding patterning process. In Fig. 2(b), five out of the nine C_{60} molecules cluster together in a triangular pattern, as highlighted by the solid line. Figure 2(c) shows that further self-assembly eventually patterns all C_{60} molecules into a cluster in a triangular lattice. Such a cluster moves around as a whole within the domain. The triangular pattern shown in Fig. 2 is dictated by the vdW interaction among C_{60} molecules and is in agreement with simulation and experimental results of previous research.[15]

Next, we investigate the maximum packing capacity by adding more C_{60} molecules into the square-shaped domain. It is shown that further added C_{60} molecules into the square-shaped domain can readily self-assemble into the existing cluster, leading to an even larger cluster (Figs. 2(d)–2(f)). The first two snapshots in Fig. 3 show the evolution of the newly added three C_{60} molecules to the final configuration in Fig. 2. The similar self-assembly process is observed. As the C_{60} cluster grows in size, its random migration under thermal fluctuation within the square-shaped domain becomes more confined. It is shown that in total of 23 C_{60} molecules can be densely packed in a 50 Å × 50 Å square-shaped domain (Fig. 3(h)).

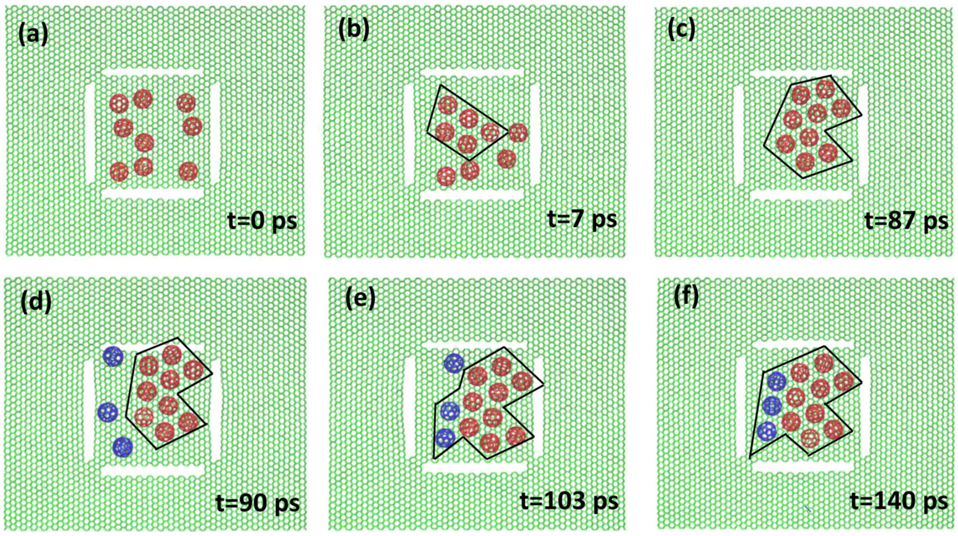

FIG. 2. (a) Initial configuration of the simulation, nine C_{60}s are randomly distributed in the square-shaped domain enclosed by four slits. (b) At 7 ps, five of nine C_{60}s start to cluster into a triangular pattern. (c) At 87 ps, all nine C_{60}s self-assemble into a larger cluster with a triangular lattice. (d) Three more C_{60}s are added to the existing system. (e) Two of the three newly added C_{60}s are self-assemble into the cluster. (f) All the 12 C_{60}s form a larger cluster with triangular lattice (Multimedia view). [URL: http://dx.doi.org/10.1063/1.4867534.1] [URL: http://dx.doi.org/10.1063/1.4867534.2]

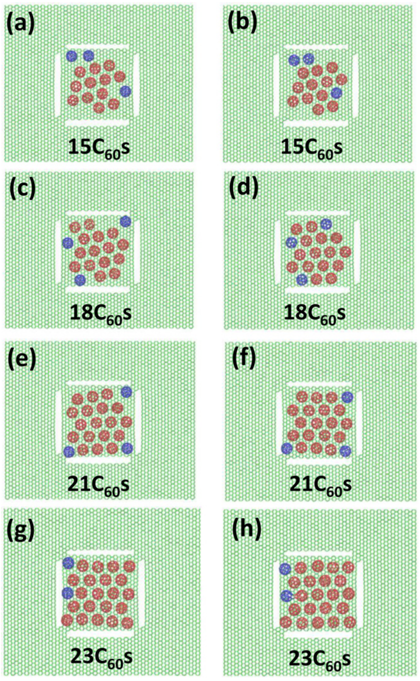

FIG. 3. More C$_{60}$s (in blue color) are continuously added into the square-shaped domain (left column), which can readily self-assemble into the existing cluster (right column) in a well-defined triangular lattice. Eventually, the squared domain can accommodate 23 C$_{60}$s.

As suggested by the results in Fig. 1, the barrier effect holds for open slits of any arbitrary direction in a graphene sheet. This renders versatile design of the confining domain, which in turn can enable molecules patterning into desirable geometry. As a demonstration, Fig. 4 shows patterning C$_{60}$s into other different shapes, such as triangular, circular, and hexagonal. Since the C$_{60}$ cluster self-assembled inside a prescribed confining domain is dictated by the inter-C$_{60}$ vdW interaction and, thus, energetically favorable (as evident by the thermal motion of the cluster as a whole), it is expected that such a C$_{60}$ cluster will remain self-assembled even if the confining domain is removed. Above said, programmable molecular packing in an arbitrary geometry can be achieved by a self-assembly process of the molecules in a confining domain of desirable geometry and followed by transferring the patterned molecular cluster to the final designated location (e.g., another substrate).

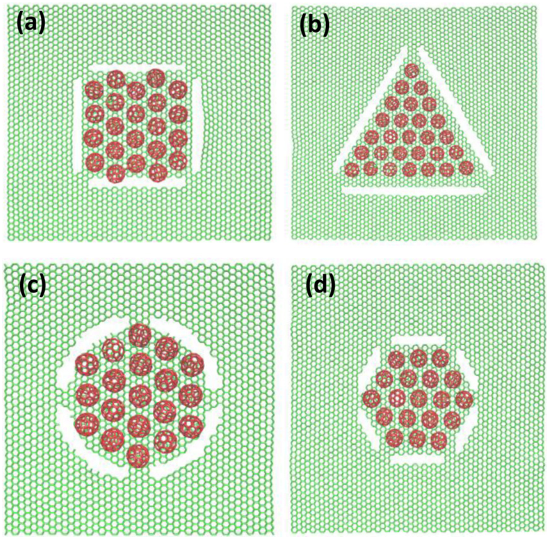

FIG. 4. Domains of different shapes, e.g., (a) square, (b) triangular, (c) circular, and (d) hexagonal, can be generated in graphene to pattern C$_{60}$s into a cluster of designated geometry.

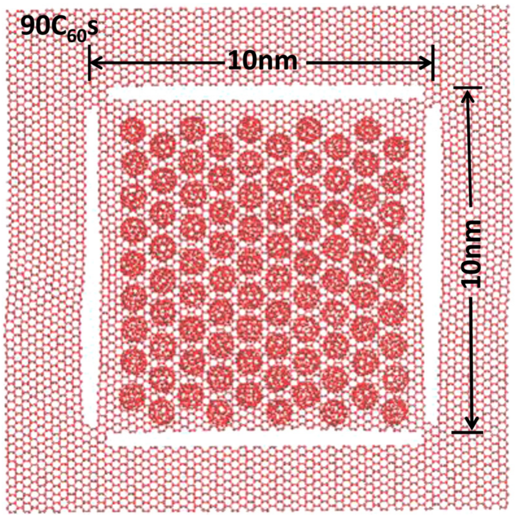

FIG. 5. A large square-shaped confining domain with side length of 10 nm is generated in a graphene sheet, which can accommodate 90 C$_{60}$s densely packed into a triangular lattice as a giant molecular cluster.

Finally, we demonstrate the feasibility of forming a giant molecular cluster by self-assembling a large number of C$_{60}$ molecules in a confining domain defined by open slits in a graphene sheet. Figure 5 shows a large square-shaped domain with a side length of 10 nm and slit width of 4 Å. A total of 90 C$_{60}$ molecules can be patterned with a triangular lattice into a square-shaped cluster, which remains stable and moves as a whole under thermal fluctuation.

In summary, we reveal the barrier effect of an open slit in a graphene sheet, resulting from a net force pushing a molecule away as the molecule approaches the open slit. Such a barrier effect is nearly independent of the orientation of the open slit in the graphene sheet, therefore a molecule-confining domain of desirable shape can be readily created by simply introducing open slits that demarcate the confining domain. These appealing features can enable molecular self-assembly into an arbitrary geometry, a desirable but hard-to-achieve nanofabrication strategy. As a benchmark, we demonstrate that C$_{60}$ molecules can self-assembly into stable clusters of various shapes and sizes inside confining domains of various geometry enclosed by open slits in a graphene sheet. Given that the barrier effect of an open slit is essentially due to a net vdW force acting on a molecule near the slit, it is expected the line-defect enabled molecular patterning on graphene demonstrated in the present work should be applicable to other material systems, such as nanoparticles and DNA. In this sense, the present findings shed light on a potential approach for molecular storage and patterning at nanoscale.

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