SUPPLEMENTARY MATERIAL:

STUN-BH-DMD search method

To obtain the low-lying binding configuration of STA molecules on graphene, the STUN-BH-DMD method, combining the advantages of stochastic tunneling-basin hopping (STUN -BH) [1], discrete molecular dynamics (DMD)[2] and global minimum search methods, was used. These three methods generally proceed through three basic steps including the change of atom coordinates, energy calculation, and the system evolution evaluated by the Boltzmann factor. For the STUN method, molecular dynamics (MD) simulation at the temperature much higher than 300 K (1100 K used in the original STUN method[3, 4]) was used to change the atomic coordinates, and a larger integration time step of 2 fs was also used to significantly move atoms [ ] for the following Boltzmann factor evaluation. However, the closest local minimum structure after the MD step cannot be obtained in the original STUN method. Consequently, the molecular statics using the conjugate gradient (CG) optimization in the BH method[5] was used to obtain the closest local minimum structure. In the original BH method for finding the most stable LJ nanocluster, the atom coordinates were randomly moved for the next search step. However, if the STA molecules on the graphene were still randomly moved in the same way as the original BH method, the overlap of STA molecules could considerably increase the rejection ratio of the Boltzmann evaluation and make the search process inefficient. Therefore, the MD part of the STUN method is used to replace the random motion of atoms adopted in the original BH method. To extend the local special domain search, the DMD was also used with MD to change the atom coordinates during the search process. The DMD uses a unit step function potential to maintain the repulsive interaction when the distance between two atoms is shorter than a threshold value.

The unit step function potential can significantly reduce the interaction strength between two atoms when the distance between them exceeds a threshold value. Although the advantage of DMD is to expand the spatial search domain, this method could also destroy the stable local configuration built in the previous MD steps without finding a more stable configuration. Consequently, during the STUN-BH-DMD search process, the MD and DMD were iteratively used, by which the MD was conducted in a STUN-BH-MD iteration and the DMD was carried out in a following STUN-BH-DMD iteration. The STUN-BH-D/MD method possesses the ability for a wide spatial domain search, and a stable STA structural retention can also be made at the same time.

The stochastic tunneling (STUN) method was applied to convert the interaction energy into the effective energy[4]. This method allows the configuration to tunnel to the forbidden regions of potential energy surface (PES) by applying a nonlinear transformation to the PES. After the nonlinear transformation, the effective potential, $E_{STUN}(x)$, has the following formula:

$$E_{STUN}(x) = 1 - exp[-\gamma \cdot (f(x) - f_0)] \quad (1)$$

where x stands for the coordinates of atoms, and f_0 is the lowest binding energy formed by STA molecules obtained thus far. The value of f_0 in Eq. (1) will be replaced once a lower binding energy (when the $f_{STUN}(x)$ value is negative) than the current f_0 value is found during the following STUN-BH-DMD search. The value of *f(x)* is the interaction energy between STA molecules at the atom coordinates x. This effective potential preserves all minima locations lower than f_0, and the entire energy space from f_0 to the potential maximum was mapped onto the interval between 0 and 1. The tunneling parameter γ used in Eq. (1) is 1.

The difference between DMD and traditional MD lies in the potential energy function of their interaction. In the original DMD, the unit step function potential was used for the hard sphere interaction, which makes atoms repulsive when they are close to each other, and otherwise no interaction was considered. Consequently, the atoms more easily change their relative coordinates by DMD than when using traditional MD. In the STUN-BH-DMD method, we do not adopt a unit step function potential for the DMD part, and the interaction strengths of non-bonding interaction including the Lennard-Jones and Coulombic interactions were reduced to a 1/100th of their original values. By this way, the interaction between atoms works very similar as using a unit step function potential.

A total of 100,000 STUN-BH-DMD iterations were performed to facilitate the search for the most stable configuration of STA buffer layer on graphene with different STA coverages. To further increase the search spatial domain, the simulated-annealing (SA) method[6, 7] was applied to the MD and DMD parts of the STUN-BH-DMD method. During the 100,000 STUN-BH-DMD iterations, the temperatures of MD or DMD were reduced by 0.008 K every STUN-BH-DMD iterations, decreasing from 1100 to 300 K.

After the MD or DMD part of each STUN-BH-DMD iteration, the energy of the optimized structure by CG method was *f(x)* from Eq. (1). If the value of $E_{STUN}(x)$ is negative, it means that *f(x)* is smaller than f_0 and the energy value of *f(x)* is stored as f_0. The structure is preserved and the STUN-BH-DMD process evolves in the direction of the smaller energy. If the current $E_{STUN}(x)$ is greater than the value of $STUN_{last}$ (the last $E_{STUN}(x)$ stored after the Boltzmann factor evaluation) recorded by the system, it will be determined by generating a random number from 0 to 1 as the acceptance ratio and calculating the Boltzmann's factor. If the value of Boltzmann factor is greater than this random number, the current configuration is accepted;

otherwise, the current structure is skipped, and the configuration corresponding to $STUN_{last}$ was used for the next STUN-BH-DMD iteration. The Boltzmann factor has the following formula:

$$Boltzfactor = \exp\left[\frac{STUN_{last} - E_{STUN}(x)}{kT}\right] \qquad (2)$$

1. If $E_{STUN}(x)$ is lower than or equal to $STUN_{last}$, this STUN-BH-DMD step is accepted. The $STUN_{last}$ is renewed by the current $E_{STUN}(x)$ and xlast (the atom coordinates at $STUN_{last}$) is also replaced by the current atom coordinates.
2. If $E_{STUN}(x)$ is greater than $STUN_{last}$, a random number between 0 to 1 is generated and the Boltzmann factor is determined according to Eq. (2). If the Boltzmann factor is greater than the random number, this STUN-BH-DMD step is accepted. The $STUN_{last}$ is renewed by the current $E_{STUN}(x)$ and xlast is also replaced by the current atom coordinates.
3. If $E_{STUN}(x)$ is greater than $STUN_{last}$ and the corresponding Boltzmann factor is smaller than the random number generated between 0 and 1, this STUN-BH-DMD step is rejected. The system atom coordinates are replaced by xlast for the next STUN-BH step.

The value of kT shown in Eq. (2) was dynamically adjusted every 20 STUN-BH-DMD iterations to keep the acceptance percentage close to 50%. The STUN-BH-DMD method can significantly guide the system to evolve toward the direction of lower energy.

The STUN-BH-DMD method can be summarized in Fig. S1. The STA binding energy obtained by the Drieding force field is first converted to the effective energy according to Eq. (1). Assuming the initial configuration corresponds to the effective energy at Point 1 within Basin A, molecular statistics were determined using the CG method (as adopted in the BH method) to quickly find the nearest local minimum

structure at Point 2 within Basin A, leading to the system evolution from Point 1 to Point 2 ,as can be seen in Fig. S1. By using the CG method, all structures within Basin A correspond to the same local minimum structure at Point 2. This indicates using the CG method can convert the effective energy of each basin into the flat PES, as the dashed horizontal line shows.

Then the DMD or MD for 200 steps are conducted for the STA configuration at Point 2 to generate a different STA configuration for jumping to another Basin. As shown in Fig. S1, the configuration at Point 2 in Basin A changes to that at Point 3 in Basin B after the MD or DMD. Then the local minimum structure at Point 4 in Basin B can be quickly found by the CG method (from Point 3 to Point 4). Many local minimum structures in different Basins can be quickly obtained by repeating the steps above and compared with the previously calculated values of the stable structure by using the Boltzmann factor. The configuration search is guided towards the direction of lower energy and finally, the most stable structure (global minimum structure) can be found.

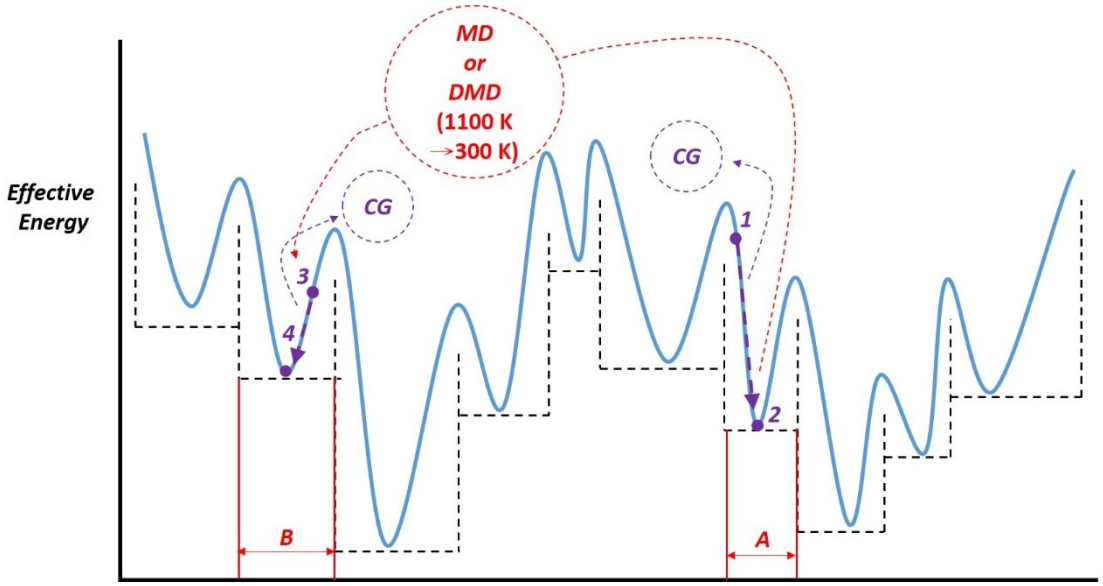

Figure S1. The schematic diagram of the STUN-BH-DMD method. During the STUN-BH-DMD iterations, the temperature of MD or DMD part is quenched from 1100 to 300 K for applying the simulated-annealing method.

List three different coverages buffer-layer animation at Td for long-term MD processes:

Animation 1. STA100 at 380 K

380 K_STA100(2).wmv

Animation 2. STA120 at 400 K

400 K_STA120 (2).wmv

Animation 3. STA140 at 380 K

470 K_STA140 (2).wmv

Reference

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[3] K. Hamacher and W. Wenzel, "Scaling behavior of stochastic minimization algorithms in a perfect funnel landscape," *Physical Review E,* vol. 59, no. 1, p. 938, 1999.

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