Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Formation and Topological Structure of Three-Dimensional Disordered Graphene Networks

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1. Annealing method to construct DGNs from an FCC carbon lattice.

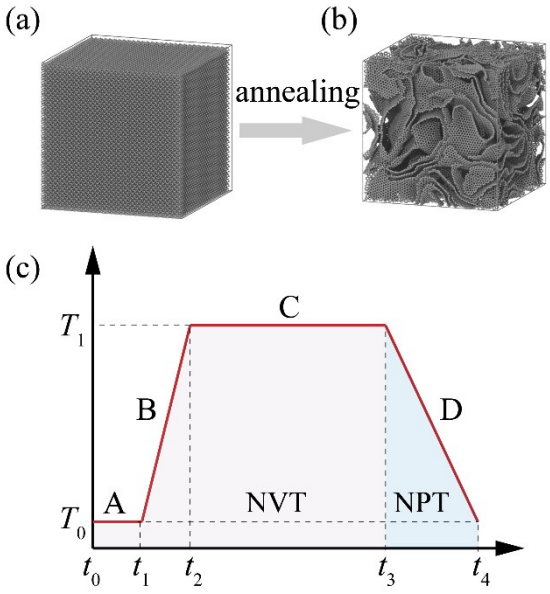

Figure S1. During the annealing process, the system changed from (a) an FCC lattice of carbon atoms to (b) a disordered graphene network. (c) Settings of temperature and ensemble used during the annealing process.

The annealing process starts from an FCC carbon lattice containing 108000 atoms, and the density is 1.0 g/cm^3. During stage A, the system was simulated at 300 K for 10 ps, and models of different densities can be obtained by deforming the simulation box. During stage B, the temperature was raised to the target annealing temperature T_1 in 10 ps, and the temperature was held during stage C until t_3, 2 ns. We used the canonical (NVT) ensemble from stage A to C. During stage D, the temperature was gradually lowered to 300 K in another 10 ps, using the isothermal-isobaric (NPT) ensemble.

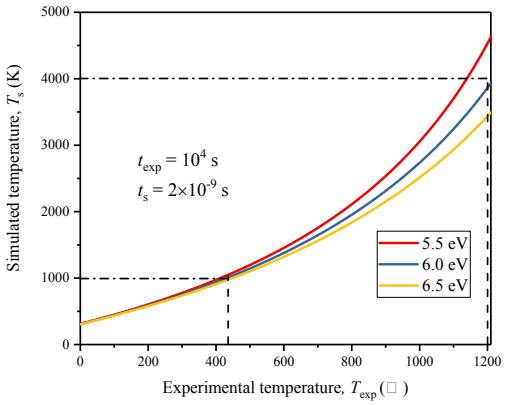

Figure. S2 Relationship between simulating temperature and experimental temperature based on Arrhenius' equation.

Due to the limits of computing resources, full-atom MD simulations are usually on a time scale of several nanoseconds, several orders smaller than experimental annealing time. To investigate the annealing process that takes several hours in practical experiments, we used raised simulating annealing temperature to achieve the same reaction probability. The simulated annealing temperature and simulated time can be associated with experimental annealing temperature and time based on Arrhenius theory. The frequency of a reaction event is

$$f = Ae^{-\frac{E}{k_B T}}, \tag{1}$$

where E is the energy barrier of the reaction, k_B is the Boltzmann constant, T is temperature and A is the attempt frequency. To make the reaction in such a limited simulated time comparable to a long-time experimental condition, one should raise the temperature to improve the frequency of reaction in annealing simulation, to satisfy:

$$f_s t_s = f_{exp} t_{exp}, \tag{2}$$

where f_s and t_s are the simulated frequency and time, and f_{exp} and t_{exp} are the experimental frequency and time. From Eqs. (1) and (2), the relations between simulated temperature, T_s and the equivalent real temperature T_{exp} is

$$T_s = (-\frac{k_B T_{exp}}{E} \ln \frac{t_{exp}}{t_s} + 1)^{-1} T_{exp} \quad . \tag{3}$$

We draw the curves of t_s as a function of t_{exp} in Figure S2, using three energy barriers, which are in the same order of magnitude as atomistic rearrangements of graphite defects.

2. Densities of DGNs

During the pre-annealing stage, we gradually changed the simulation box's side length to get a series of models with different initial densities, ranging from 0.1 to 2.3 g/cm3. After the same annealing time, the smaller-density models have more free atoms. The following simulation includes deleting free atoms and releasing the pressure, during which the box size changed. So the final density are different from the initial density

Initial density (g/cm^3)	Final density (g/cm^3)
0.10	0.10
0.20	0.22
0.30	0.33
0.40	0.45
0.50	0.56
0.80	0.90
0.90	1.01
1.00	1.12
1.25	1.24
1.50	1.35
1.75	1.46
2.00	1.54
2.30	1.64

Table S1. Initial densities during annealing and their corresponding final densities after annealing and subsequent energy minimization.

3. The discrete grid method to compute local angular defects

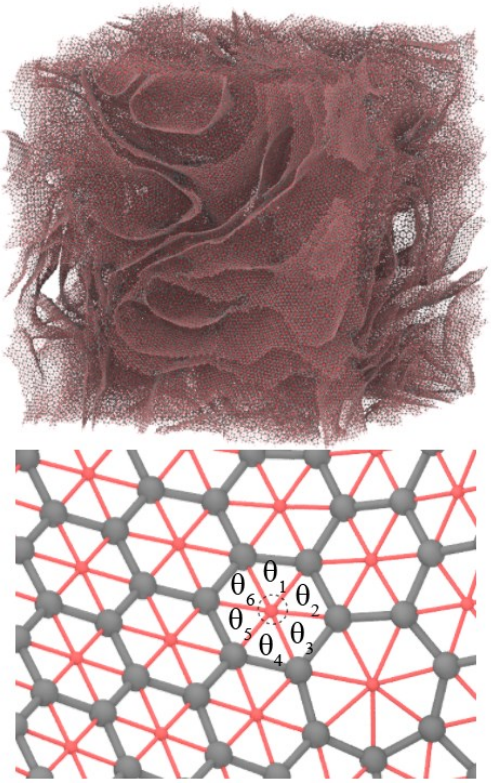

Figure S3. The disordered graphene networks were divided into triangles. Angular defect was calculated at each vertex.

Fragments of carbon rings were identified. A discrete grid method was used to calculate the local angular defects on the surfaces. The mesh of triangles was constructed by connecting the vertexes of atom sites and vertexes at the rings' centers, as shown in Figure S3. Then, the local angular defect was calculated by the summation of the angles at each vertex. Vertexes on the edges were ignored in statistics.

4. Different graphitization level in DGNs annealed at different temperatures.

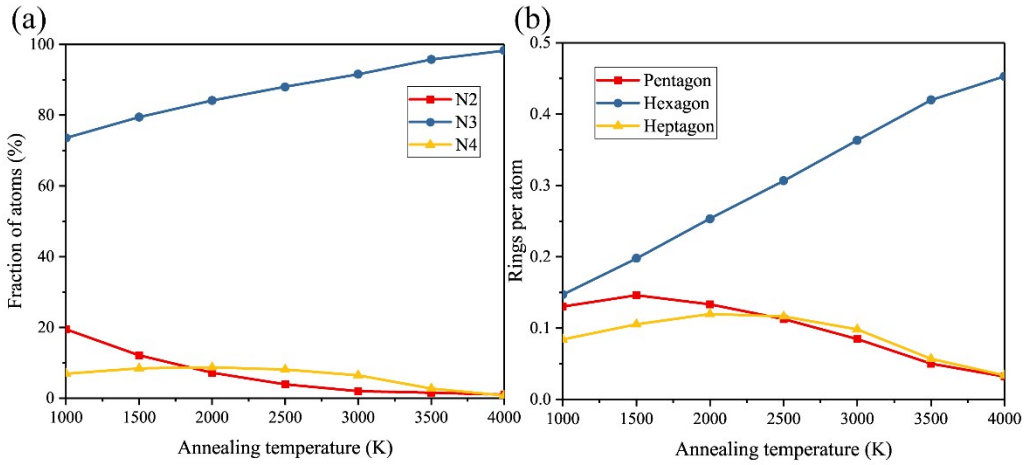

Figure S4. (a) The fraction of N2, N3, and N4 atoms in the final DGNs as a function of annealing temperatures. (b) Statistical numbers of different carbon rings in DGNs annealed at different temperature. The fraction of N2 atoms and the number of heptagons increase with the increase of annealing temperature, indicating higher annealing temperature results in higher graphitization.

5. Influence of relaxation by AIREBO potential after annealing simulation.

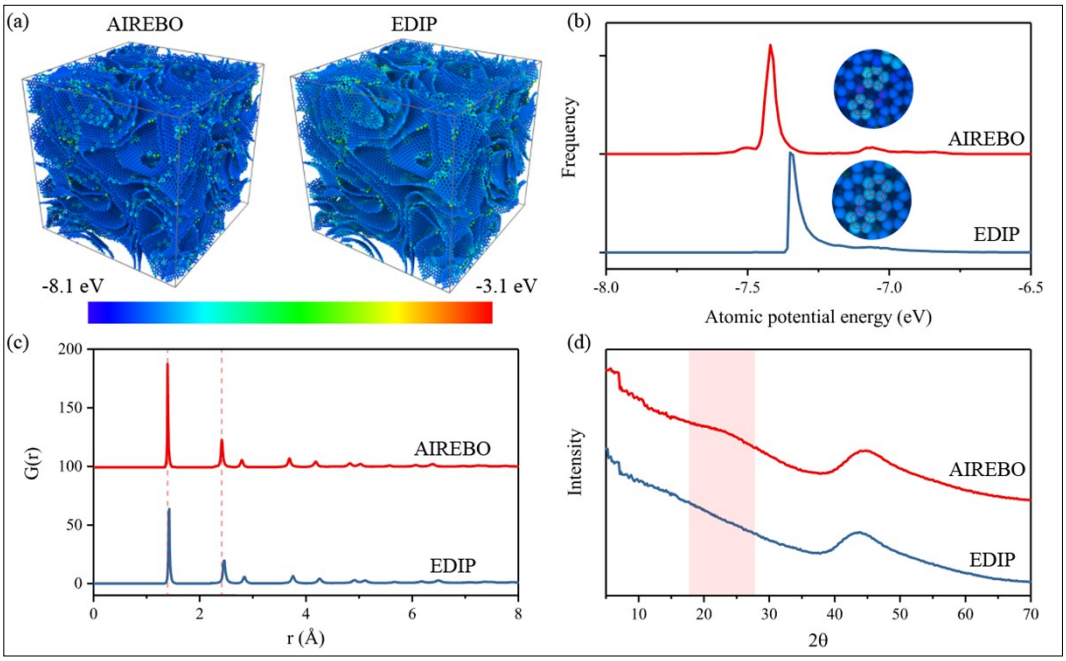

Figure S5. (a) The box of AIREBO showed a shrink. The atoms were colored by atomic potential energy. (b) The histogram of atomic potential energy shows the energy was reduced because of the LJ term. (c) The radial pair distribution function shows little difference between the two structures. (d) The peak in the computed XRD spectrum shifted to the right and became stronger, indicating the reducing stacked spacing.