# Electronic Supplementary Information for

# Structural transformations of graphene exposed to nitrogen plasma: quantum chemical molecular dynamics simulations

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**Fig. S1**. A schematic picture of a simulation box, drawn in red. The graphene sheet is located at the center of the z axis. The ocher and blue bonds represent the graphene carbon and periodic images, respectively.



**Fig. S2**. Averaged (a) C-C, (b) C-N, and (c) N-N pair distribution functions for the trajectories with the incident energies, 1, 2, and 4 eV. The dashed lines are drawn at 1.6 Å.



**Fig. S3**. B3LYP/6-31g(d)-optimized finite-size models for each configuration of (a, b) SA, (c, d) T, (e) SV, (f) Rec, (g) and (h) ISW, (i, j) Gr-N, (k) and (l) SW-N, and (m) graphene with an isolated nitrogen molecule. Blue spheres, ocher sticks, and white spheres represent nitrogen atoms, graphene carbon, and hydrogen atoms respectively. Both of the optimized (c)  $T_1$  and (d)  $T_2$  configurations converged to the  $T_2$  configurations.



**Fig. S4**. DFTB/mio-1-1-optimized finite-size models for each configuration of (a, b) SA, (c) and (d) T, (e) SV, (f) Rec, (g) and (h) ISW, (i, j) Gr-N, (k) and (l) SW-N, and (m) graphene with an isolated nitrogen molecule. Blue spheres, ocher sticks, and white spheres represent nitrogen atoms, graphene carbon, and hydrogen atoms respectively.

**Table S1.** The relative energies of SA<sub>1</sub> to SA<sub>2</sub> in eV, and C–C distances in the optimized SA<sub>1</sub> and SA<sub>2</sub> configuration models in Å. Two different spin multiplicities, doublet (d) and quarter (q) were employed for each model.

Method	Relative E (SA <sub>1</sub> -SA <sub>2</sub> )	CA–CB distance in SA <sub>1</sub>	CC–CD distance in SA <sub>2</sub>
DFTB	0.4	1.616	2.159
B3LYP (d)	-0.1	1.537	2.053
B3LYP(q)	0.1	1.537	2.055



**Fig. S5.** The schematic structures to count the (a) Gr-N and (b) SW-N configurations. Each configuration is defined by light blue connectivity where one nitrogen atom participates. In the case of SW-N, if three pentagonal rings connected to each other by forming a cyclic SW defects, which is a rare event, we counted it as two SW-N configurations.

#### 1. Configurations containing more than two nitrogen atoms.

We observed diverse configurations and complex structures containing multiple nitrogen atoms, which were difficult to be categorized individually. Thus, we mainly focused on the general topological changes during the simulations. First, we note that a large number of bond cleavages generate graphene large vacancies (Figs. S6a, b).



**Fig. S6.** General topological changes caused by multiple nitrogen atoms. (a) Vacancy on graphene containing linear atomic chain, (b) vacancy on graphene surrounded by CN and NCN groups, (c) Gr-N configuration with Py-N, (d) SW-like configuration with dehydrogenated pyrrolic-N, (e) typical arrangement of two nitrogen atoms on SW defect, (f) interconnection of five-membered ring of SW, ISW defects, and fused-five-membered rings. Blue spheres and ocher sticks represent the nitrogen atoms and C–C bonds, respectively. The orange color was used to emphasize the connection of pentagonal rings.

These vacancies were formed by the concentrated bombardment by nitrogen atoms, which gradually destroyed the carbon bond network of graphene. At the edges of the vacancies, we observed a large number of dangling bonds associated with linear CN and NCN groups, usually oriented in perpendicular direction to the graphene plane. Due to the non-reactive nature of the (negatively

charged) N terminus, these groups prevented rearrangement and recovery of the graphene. The situation is reminiscent of the "wobbling C<sub>2</sub> units" that were observed in earlier simulations of carbon nanotube self-capping processes.<sup>1</sup> Here, one might be tempted to call them "wobbling CN units". Some long linear chains were also observed (Fig. S6b), which is again reminiscent of linear carbon chains created in graphene systems under the influence of an electron beam<sup>2</sup> or during fullerene formation.<sup>3</sup>, <sup>4</sup> The vacancy defects were often combined with substitutional nitrogen configurations to create new configurations, such as Py-N configuration and dehydrogenated-pyrrolic-N configuration (Figs. S6c, d), respectively. Those configurations were usually observed at graphene edges or in pores of graphene, because the nitrogen dopant atom has only two chemical bonds with neighboring carbon atoms.<sup>5, 6</sup>

Another remarkable feature was the prevalent formation of various five-membered ring structures. For example, the combination of Gr-N, SW-N, and ISW built up a multiple-nitrogen-containing fivemembered ring complex (Fig. S6e). These structures are formed by successive appearance of SW-N configurations within the same spatial area, accompanied with nitrogen atoms in Gr-N form. We note that one of the nitrogen atoms is frequently located at the position of a bridge fusing the two SW heptagons (Fig. 3k). The location of nitrogen in SW defects was found to play an important role for the ORR catalytic ability of N-Graphene.<sup>7</sup> As a matter of fact, the increased number of SW and ISW structures results in a structure containing a network of isolated and fused pentagon rings (Fig. S6f) along with some heptagons and even larger rings. The fused pentagon rings increase the local strain in N-Graphene even more,<sup>8</sup> and hence increase the reactivity of the N-doped structures further. The situation is reminiscent of the Haeckelite formation in graphene under the influence of an electron beam<sup>9, 10</sup> with the only difference that here the defects are created by nitrogen bombardment.

#### 2. Changes of chemical composition and chemical bond networks

As nitrogen bombardment went on, we observed considerable changes of the graphene chemical structure including its chemical composition and covalent bond networks. The average number of C–C, C–N, and N–N bonds in 30 trajectories in each incident energy are summarized in Fig. S7a. The total number of covalent bonds increased similarly regardless of the incident energy. The C–C bonds disappeared and C-N bonds appeared more rapidly with 4 eV incident energy, and only small differences between 1 and 2 eV cases. Similar trends were observed in the changes of chemical composition (Figs. S7b, c). The number of carbon atoms decreased and the number of nitrogen atoms increased more rapidly in the case of 4 eV than both of 1 and 2 eV cases. A sudden removal of carbon atoms was observed from 35 ps, resulting from the fragmentation of N-Graphene followed by removal of the fragments like molecule formation during the simulations. As we discussed in the main text, we found a large difference in the number of Gr-N and SW-N configuration between 1 and 2 eV, which cannot be explained by the trends in Fig. S7. This finding suggests that the potential energy barrier for

destruction of graphene and for formation of nitrogen configuration are quite distinct. Fine controlled medium level incident energy, i.e. not too low and not too high, has great potential for controlling graphene nitrogenation.



**Fig. S7.** The trajectory average of the numbers of (a) covalent bonds, (b) carbon atoms, and (c) nitrogen atoms over time. Circle, triangle, inverted triangle and rhombus marks indicate the numbers of C–C, C–N, N–N bonds, and all bonds respectively.

As well as the number of covalent bonds, the bond connectivity changed as a function of time. As already mentioned above, a large number of five-membered ring structures, along with a smaller number of seven- and larger-size ring structures became dominant as the six-membered ring structures were destroyed. It is worthwhile to investigate this transition in greater details, because the electrical properties of graphene greatly depend on these kinds of topological changes. We tried to elucidate effects of the incident energy of nitrogen on the topological changes by plotting the number of five-and six-membered ring structures as a function of time for the different incident energies (Fig. S8).



**Fig. S8.** The trajectory average of the numbers of (a) five- and (b) six-membered ring structures on N-Graphene.

As discussed above, the 4 eV case exhibits a unique behavior that was clearly separated from the others, except for the result obtained before 10 ps. The use of higher projectile incident energy, 4 eV, seems to facilitate the formation of five-membered rings and destruction of six-membered rings. Plotting the number of hexagons as a function of the number of newly created pentagon (Fig. S8a) can clarify that the incident energy of 4 eV "accelerate" the conversion from six-membered ring to five-membered rings relative to the same number of six-membered ring.

Next, we tried to analyze the possibility of selective insertion of nitrogen on either five-membered or six-membered ring by counting the number of nitrogen atom on each ring structure (Figs. S9b, c). However, we could not find a notable difference among incident energies, except for the tendency of high incident energy to insert low amount of nitrogen on five-membered ring. This suggests that selective insertion of nitrogen is not feasible only by regulating the incident energy of the nitrogen source.



**Fig. S9.** (a) The relationships in the numbers of pentagonal and hexagonal rings. (b) The number of nitrogen atom included in each ring structures. (c) The ratio of nitrogen atoms to the all atoms in each ring. Each data point was obtained from the snapshot at the end of each nitrogen shooting, indicating

the average number of ring structures in 30 trajectories.

### **Movie List of MD trajectories**

Movie S1: A representative trajectory in which N-Graphene were destroyed less severely.
Movie S2: A representative trajectory in which N-Graphene were destroyed more severely.
Movie S3: A migration of nitrogen atom to the SA configuration to form the T configuration.
Movie S4: A adsorption of nitrogen atom on the SA configuration to form the T configuration.
Movie S5: Py-N configuration formation from T configuration.
Movie S6: SV configuration formation from T configuration.
Movie S7: SV configuration formation by two nitrogen atoms and pentagonal ring formation.
Movie S8: Rec configuration formation.
Movie S9: ISW1 configuration formation.
Movie S10: ISW2 configuration formation from two SA configurations.
Movie S11: ISW2 configuration formation from Rec configuration.
Movie S12: Gr-N configuration formation through M21 pathway.

Movie S13: Gr-N configuration formation through  $M_{12}$  pathway.

Movie S14: SW-N configuration formation through M<sub>22</sub> pathway.

## References

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