

Diagram of Multiple Vacancies and Defect Self-Healing in Graphene

Supplementary Information

Computational Details:

All geometric structures are fully optimized with the conjugate gradient method and the force field using density functional based tight binding (DFTB) method with the DFTB+ package. A force threshold of 1×10^{-6} a.u. is applied as convergence criterion, and the conjugate gradient method is employed. To test the accuracy of the DFTB method, we have compared with the results from density functional theory (DFT) with the Perdew-Burke-Ernzerhof approximation.¹ Frozen-core all-electron projector-augmented wave method,² as implemented in the VASP code is used.³ The cut-off energy for the plane-wave basis expansion is 400 eV. Periodic supercells and a 10-Å-thick vacuum region to separate the graphene sheet from adjacent images are used. Atomic positions are relaxed until the forces on all atoms are less than 0.02 eV/Å. The compared results from DFTB and DFT are shown in **FIG. S1**.

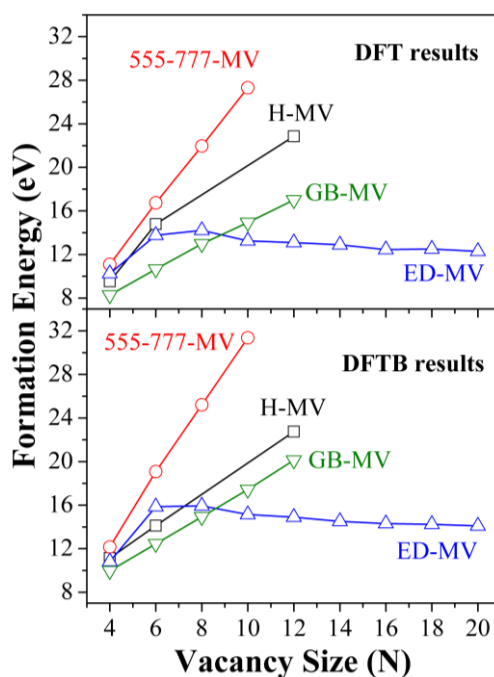


FIG. S1. Comparison between the DFT and DFTB results on the formation energies for different types of multiple vacancies.

References:

- 1 J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* 1996, **77**, 3865.
- 2 Kresse and D. Joubert, *Phys. Rev. B* 1999, **59**, 1758.
- 3 Kresse and J. Furthmuller, *Phys. Rev. B* 1996, **54**, 11169.

Modeling Details:

We use graphene nanoribbons with different widths w to investigate the width effect on structural stability for multiple vacancies. The nanoribbon lengths depend on the vacancy size, which are long enough to separate the adjacent defect from the periodic supercells.

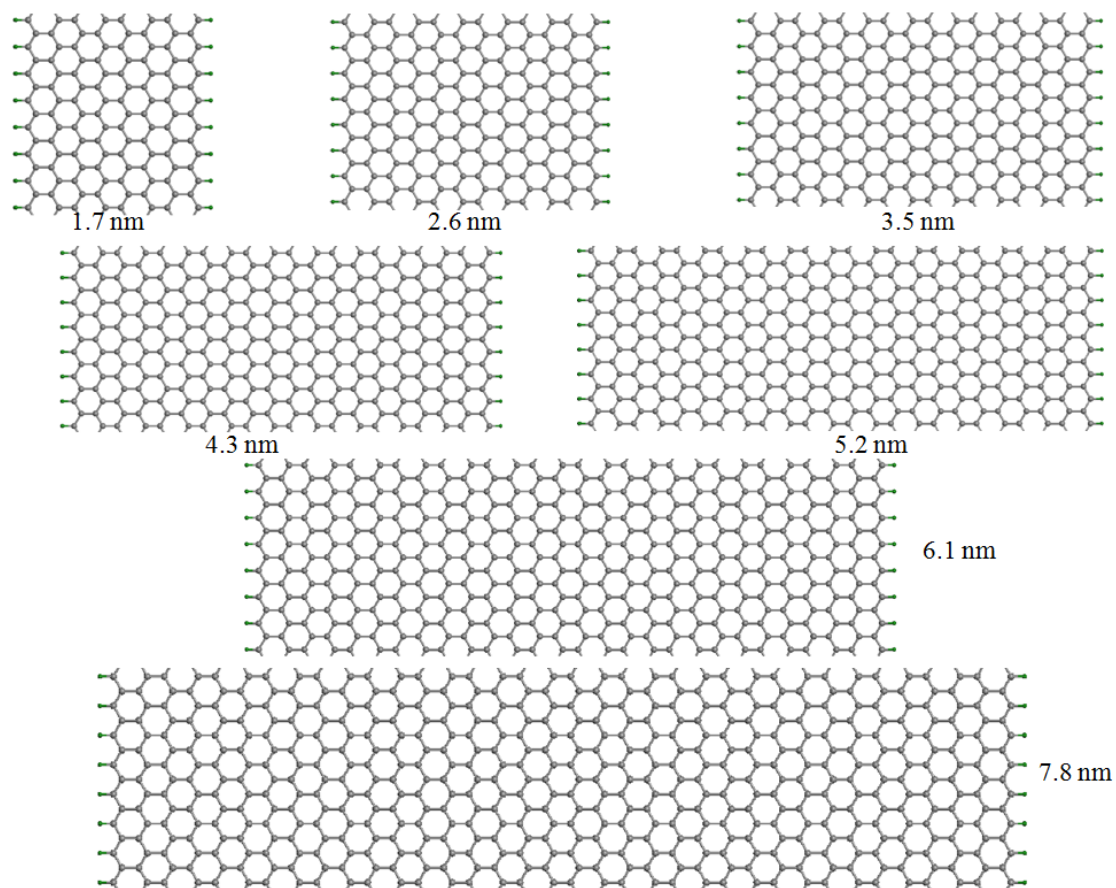


FIG. S2. Periodic structural models for GNRs with different widths w used in this study.

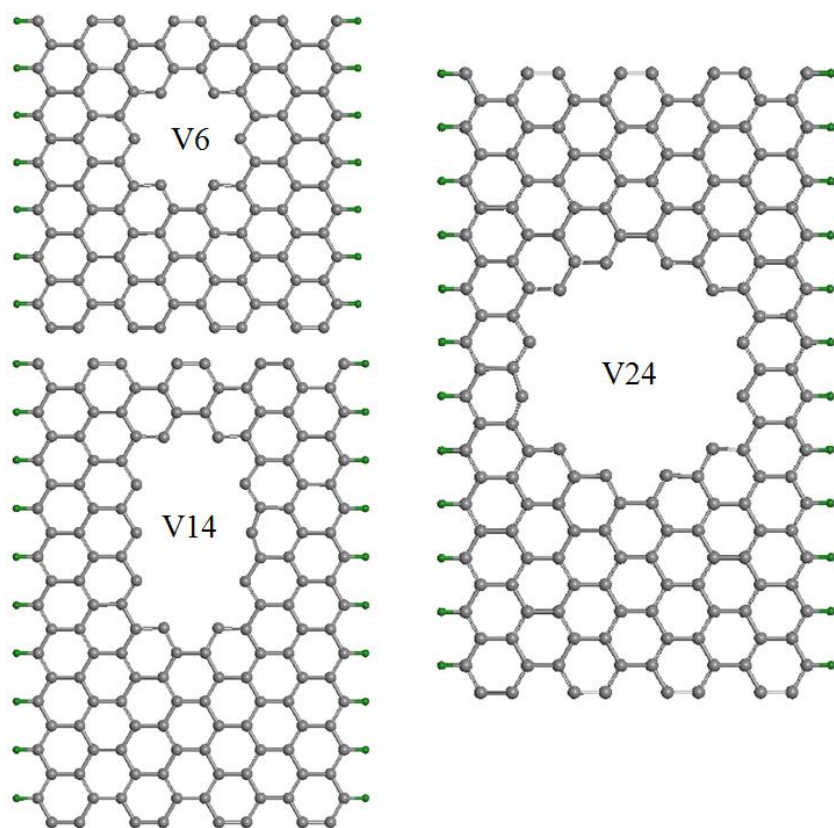


FIG. S3. Representative structures for **H-MV** after fully relaxation.

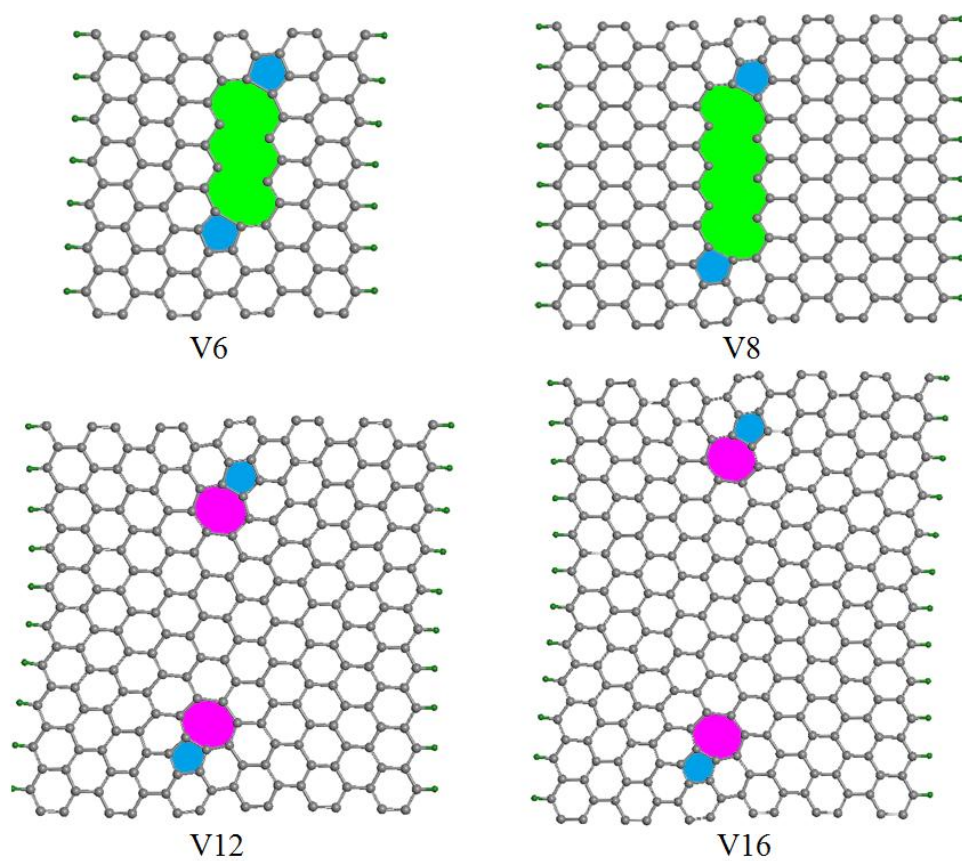


FIG. S4. Representative structures for **ED-MV** after fully relaxation.

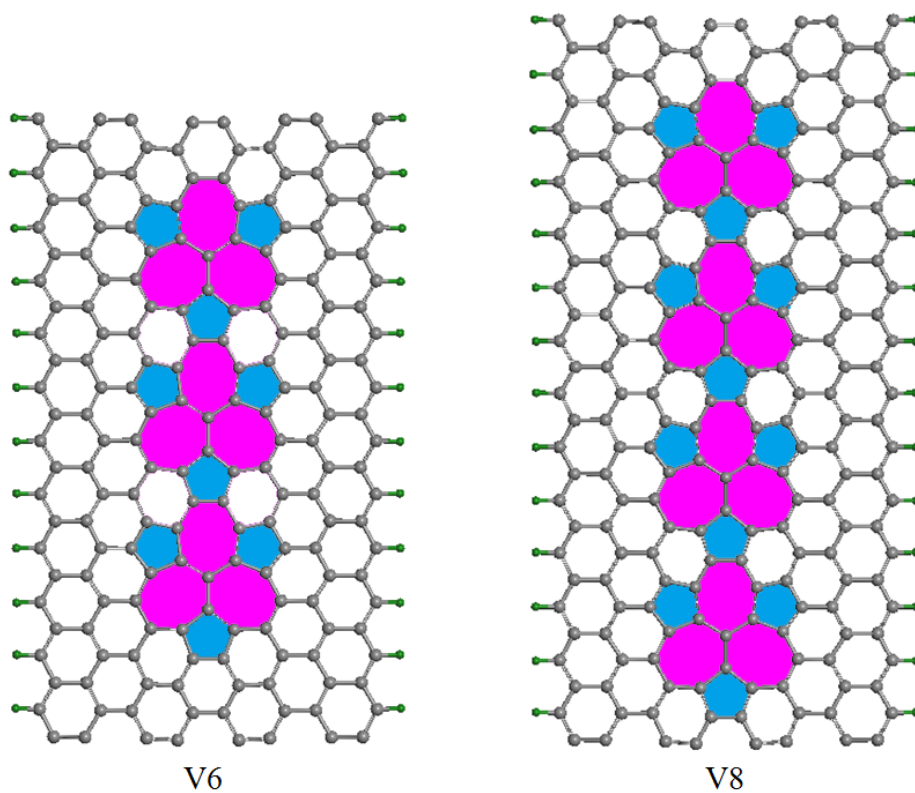


FIG. S5. Representative structures for **555-777-MV** after fully relaxation.

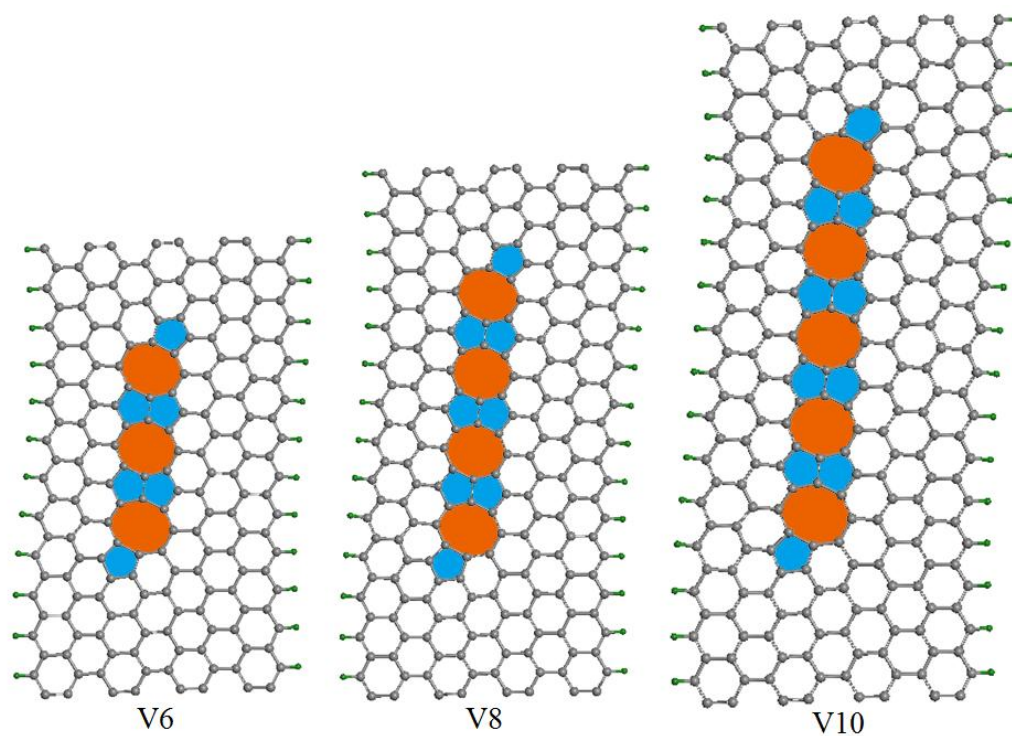


FIG. S6. Representative structures for **GB-MV** after fully relaxation.

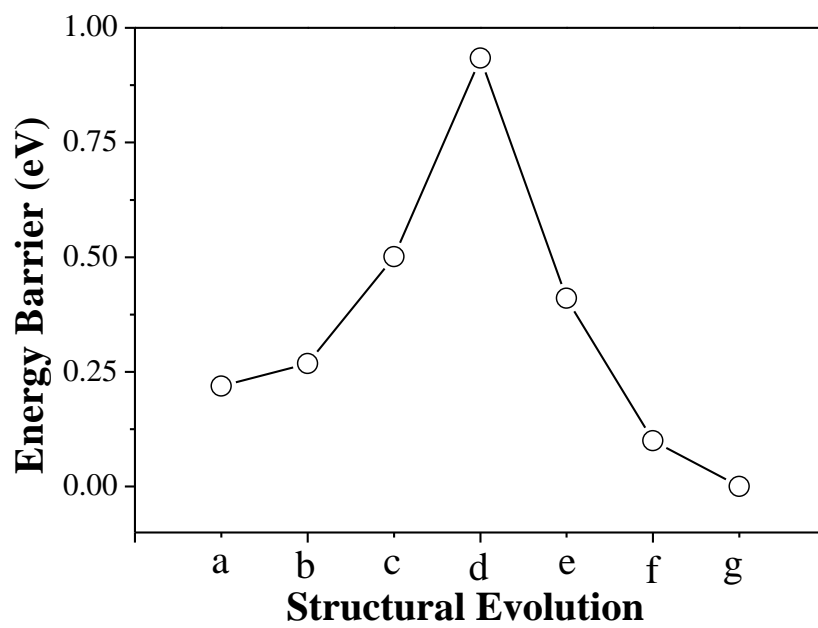
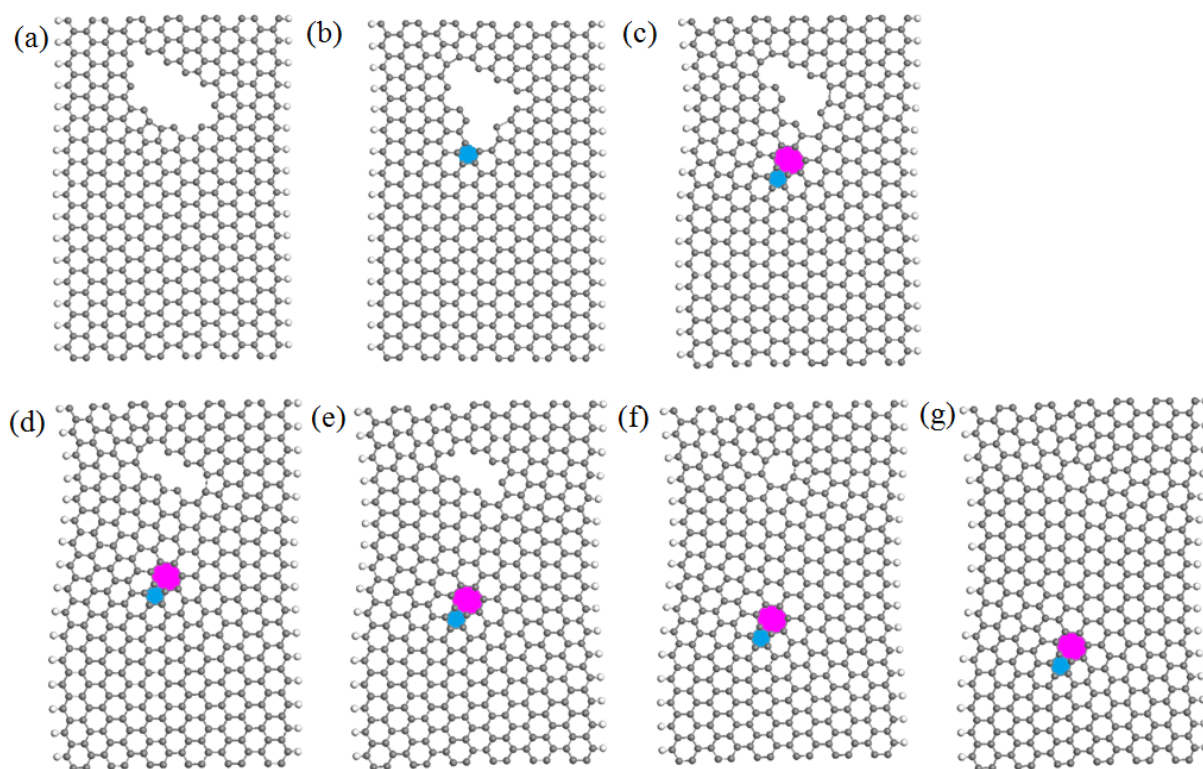


FIG. S7. Structural evolution and energy barrier from **H-MV** to **ED-MV** in GNR with the width of 2.6 nm.