Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.


# Supporting Information

## Lithiation Mechanism and Lithium Storage Capacity of Reduced Graphene Oxide Nanoribbons: A First-Principles Study

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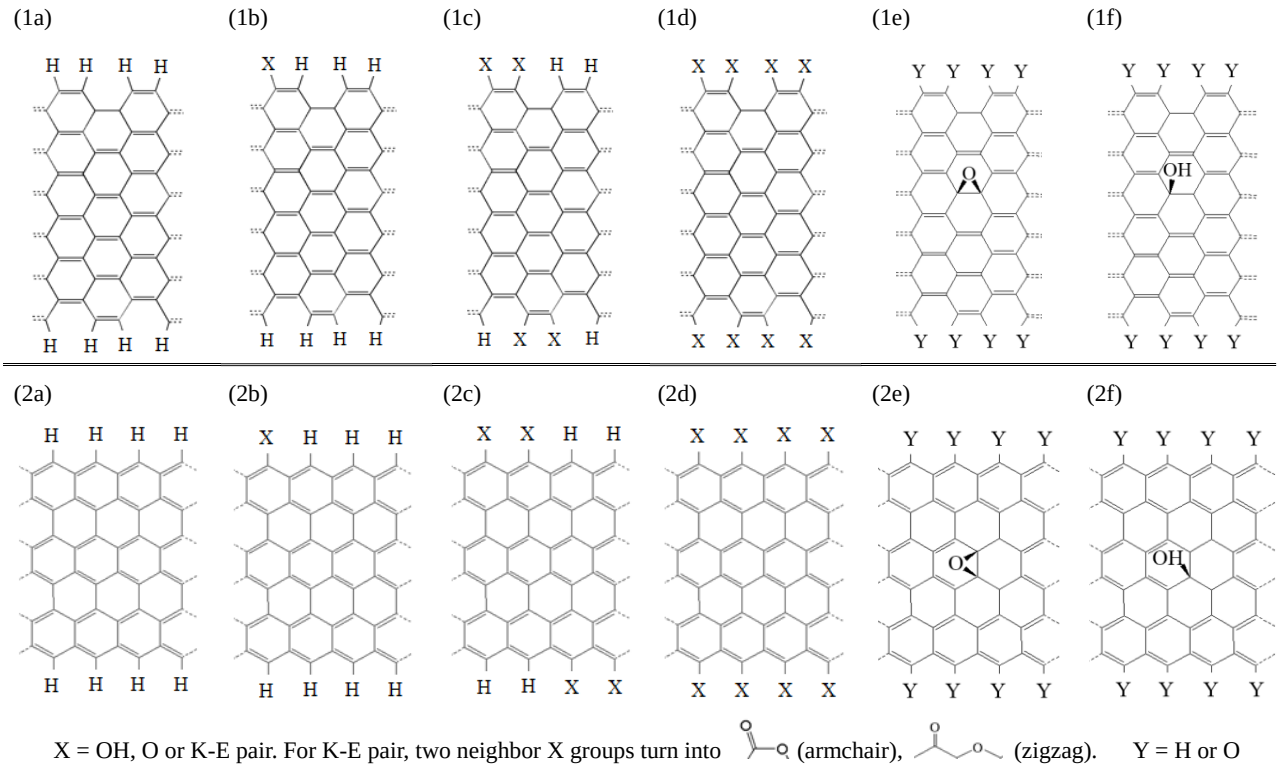



Figure S1. Different concentrations of functional groups on the armchair (1) and zigzag (2) GNRs, respectively: (a) 0X, (b) 1X, (c) 4X and (d) 8X at the edge sites, and an (e) epoxy and (f) hydroxyl group on the basal plane.

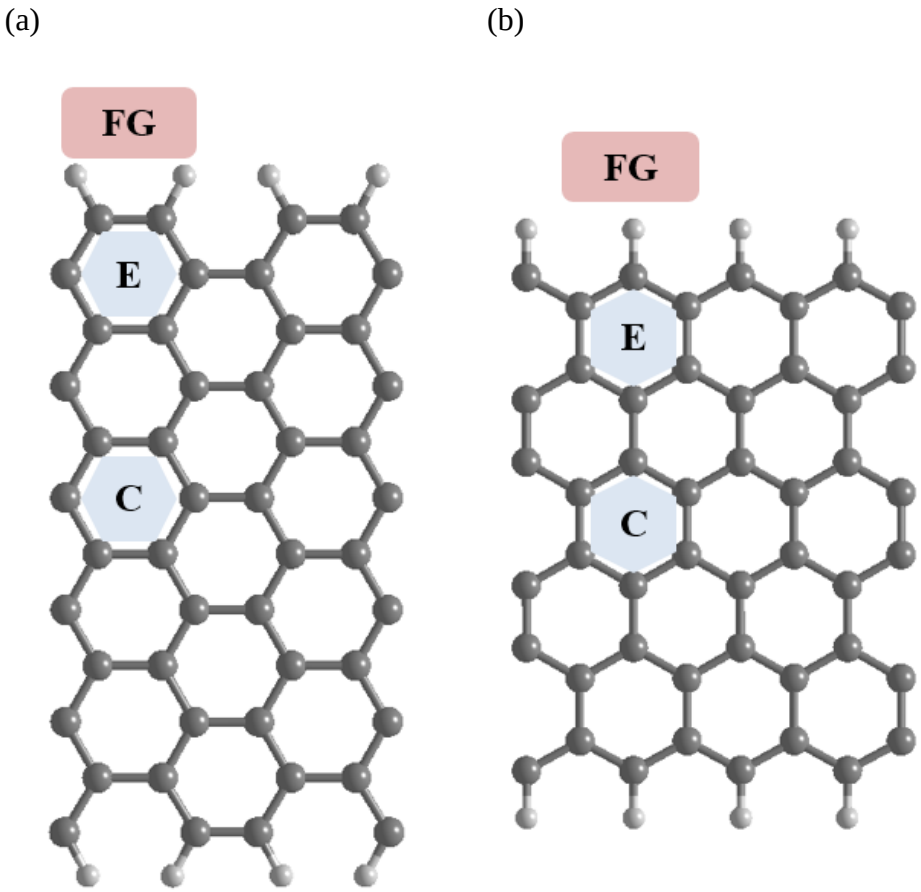



Figure S2. Possible adsorption sites on the (a) armchair and (b) zigzag GNRs considered in this work. Here **FG, E,** and **C** denote the cases for Li adsorption on the functional groups, an edge hollow site, and the central hollow site of the basal plane, respectively.

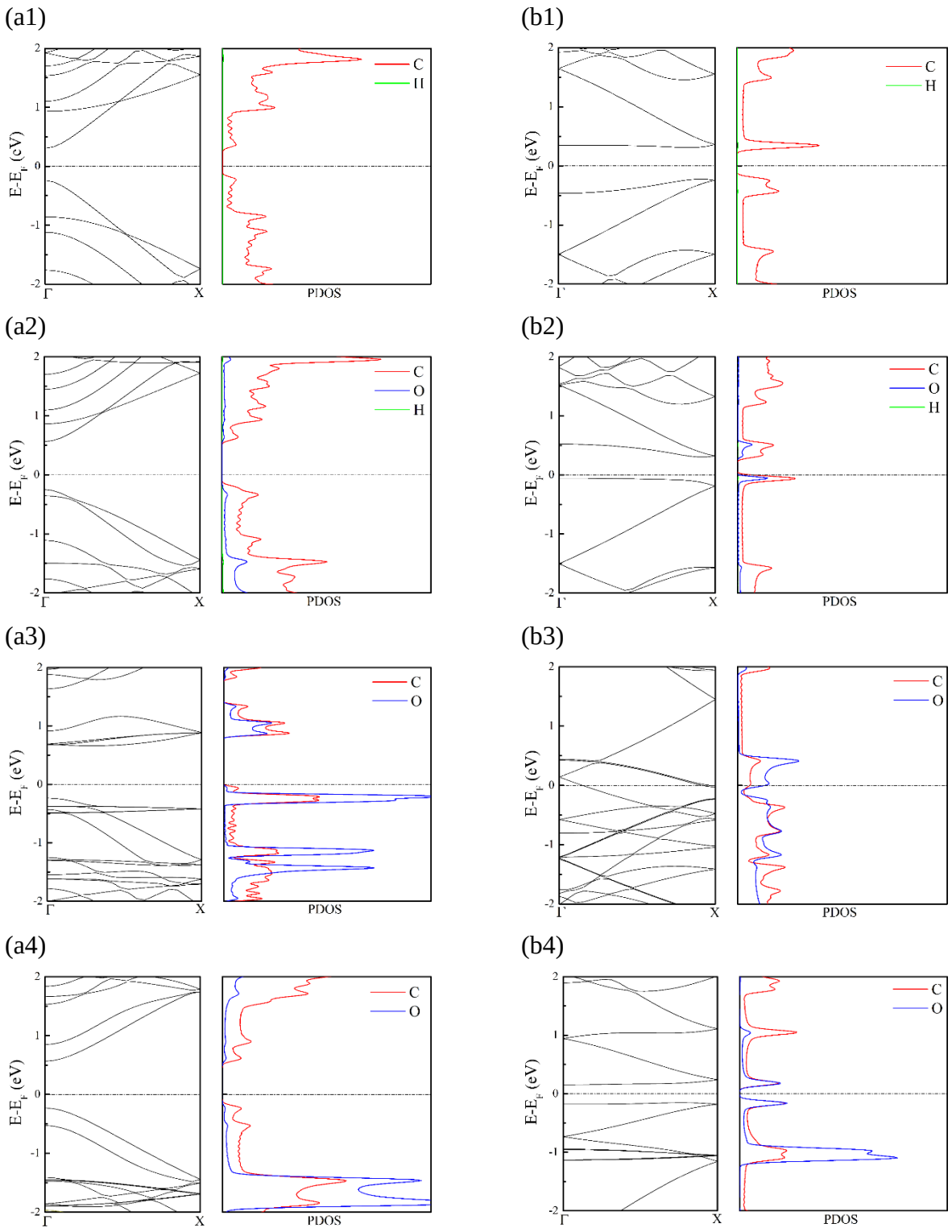



Figure S3. Band structures and PDOS of the (a) armchair and (b) zigzag graphene nanoribbons terminated with (1) -H, (2) -OH, (3) -C=O, and (4) K-E pairs, respectively.

Table S1. Calculated adsorption energies on various sites of the armchair and zigzag GNRs terminated with different functional groups using VASP and Gaussian09. “X” means that Li cannot adsorb on functional groups and “FG” means Li adsorbed on functional groups after relaxation.

| Armchair | # of groups | Adsorption energy (eV) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Edge | | Center | | Functional Groups | |
| | | VASP | G09 | VASP | G09 | VASP | G09 |
| H | - | -1.165 | -0.965 | -1.112 | -0.913 | X | X |
| OH | 1 OH | -1.093 | -0.848 | -1.105 | -0.902 | X | X |
| | 4 OH | -1.070 | -0.830 | -1.110 | -0.848 | X | X |
| | 8 OH | -0.858 | -0.902 | -0.981 | -0.909 | X | X |
| O | 1 O | -2.485 | -2.467 | -1.761 | -1.765 | -2.713 | -2.832 |
| | 4 O | -1.828 | -1.868 | -1.568 | -1.597 | -3.834 | -3.888 |
| | 8 O | FG | FG | -1.484 | -1.502 | -4.244 | -4.270 |
| K-E pair | 2 K-E | -1.202 | -0.983 | -1.334 | -1.043 | -1.836 | -1.721 |
| | 4 K-E | -1.225 | -1.085 | -1.277 | -1.077 | -3.189 | -3.139 |
| Zigzag | | | | | | | |
| H | - | -1.739 | -1.974 | -1.406 | -1.599 | X | X |
| OH | 1 OH | -1.637 | -1.807 | -1.432 | -1.572 | X | X |
| | 4 OH | -1.538 | -1.647 | -1.361 | -1.423 | X | X |
| | 8 OH | -1.296 | -1.220 | -1.252 | -1.138 | X | X |
| O | 1 O | -1.545 | -1.316 | -1.464 | -1.319 | -1.928 | -1.897 |
| | 4 O | -2.328 | -2.299 | -2.047 | -1.764 | -4.520 | -1.608 |
| | 8 O | FG | FG | -2.272 | -2.179 | -4.777 | -4.751 |
| K-E pair | 2 K-E | -1.959 | -1.842 | -1.718 | -1.555 | -3.170 | -3.210 |
| | 4 K-E | -1.923 | -1.800 | -1.629 | -1.490 | -4.102 | -4.229 |

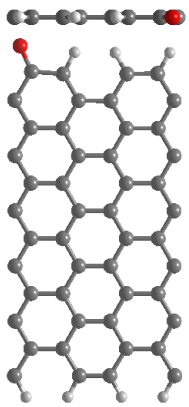
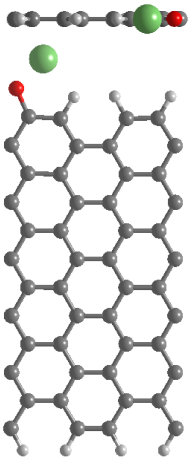
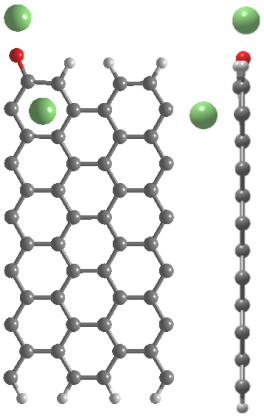
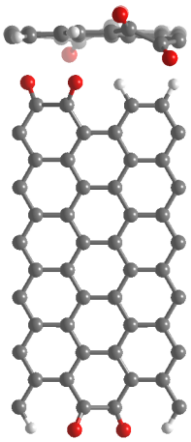
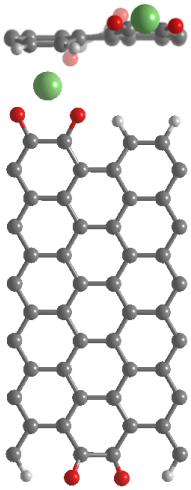
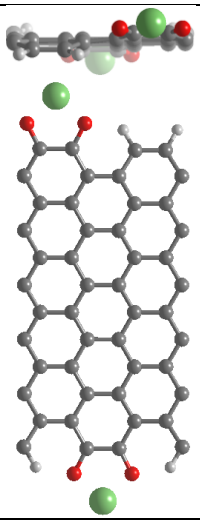
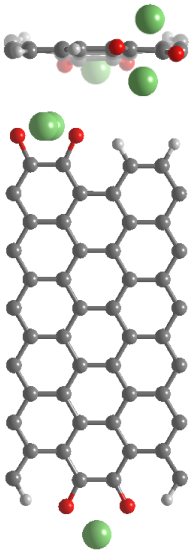
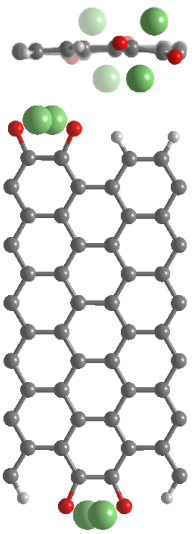
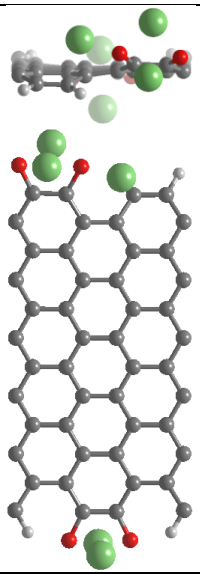
| 0 Li | 1Li | 2Li |
|---|---|---|
|  |  |  |

Figure S4. The most stable configurations at various stages of lithiation on the armchair GNR model terminated with one ketone group.

| 0 Li | 1Li | 2Li |
|---|---|---|
|  |  |  |
| **3 Li** | **4 Li** | **5 Li** |
|  |  |  |

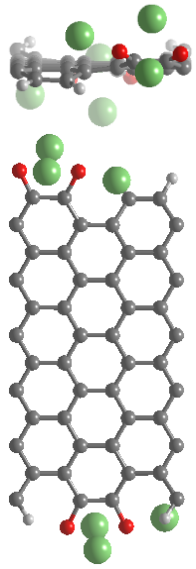
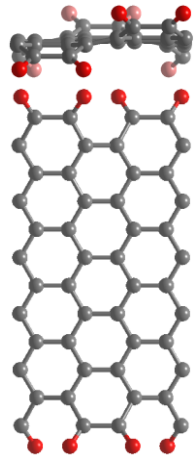
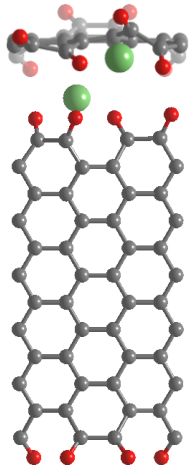
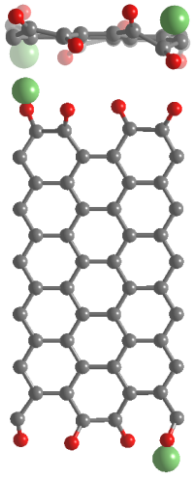
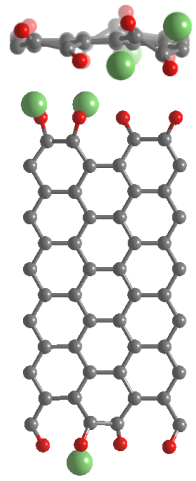
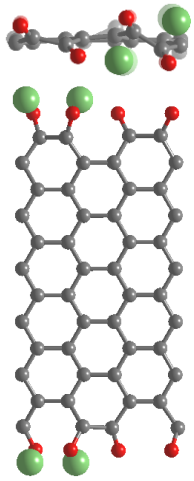
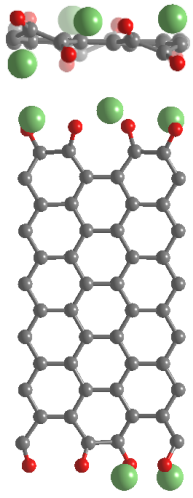
| 6 Li | | |
|---|---|---|
|  | | |

Figure S5. The most stable configurations at various stages of lithiation on the armchair GNR model terminated with four ketone groups

| 0 Li | 1Li | 2Li |
|---|---|---|
|  |  |  |
| **3 Li** | **4 Li** | **5 Li** |
|  |  |  |

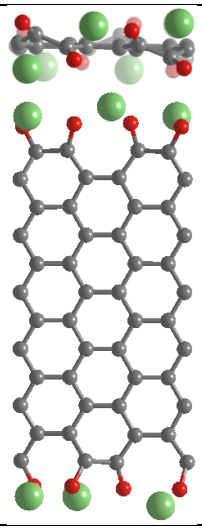
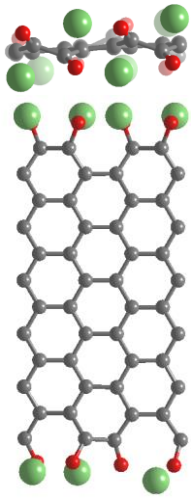
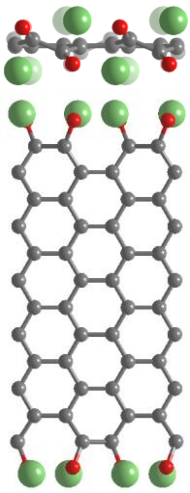
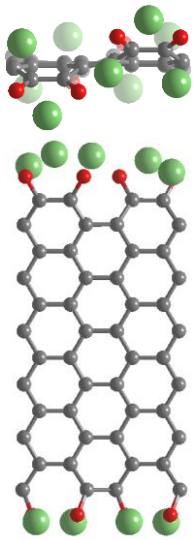
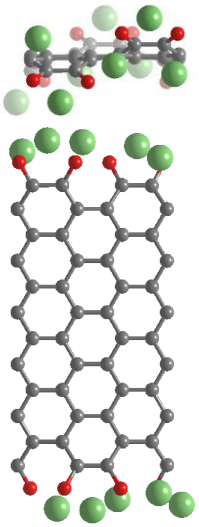
| 6 Li | 7Li | 8Li |
|---|---|---|
|  |  |  |
| **9 Li** | **10 Li** | |
|  |  | |

Figure S6. The most stable configurations at various stages of lithiation on the armchair GNR model terminated with eight ketone groups

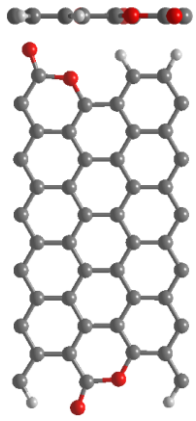
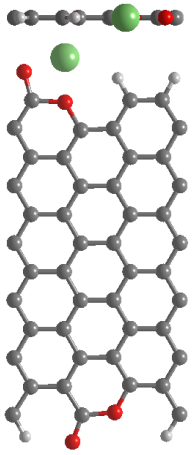
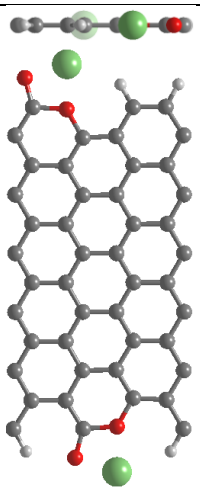
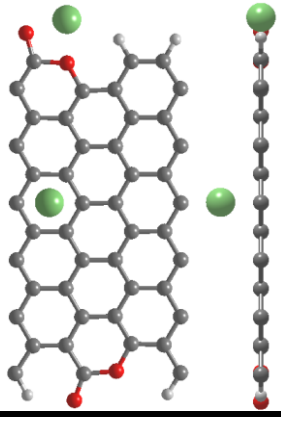
| 0 Li | 1Li | 2Li |
|---|---|---|
|  |  |  |
| **3 Li** | | |
|  | | |

Figure S7. The most stable configurations at various stages of lithiation on the armchair GNR model terminated with two K-E pairs.

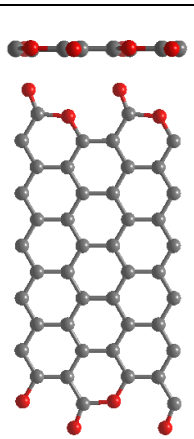
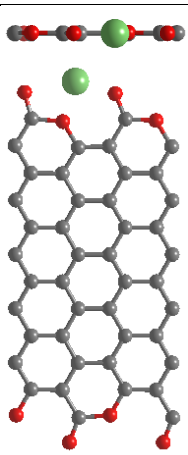
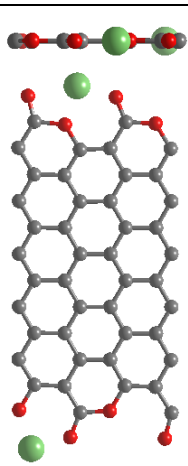
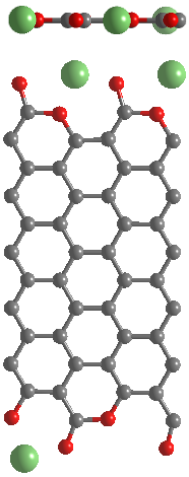
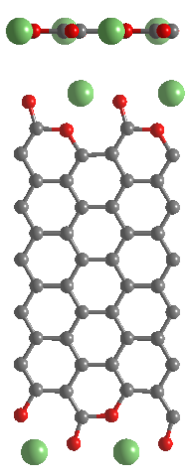
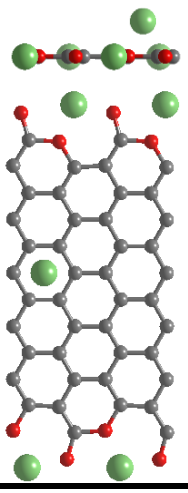
| 0 Li | 1Li | 2Li |
|---|---|---|
|  |  |  |
| **3 Li** | **4 Li** | **5 Li** |
|  |  |  |

Figure S8. The most stable configurations at various stages of lithiation on the armchair GNR model terminated with four K-E pairs.

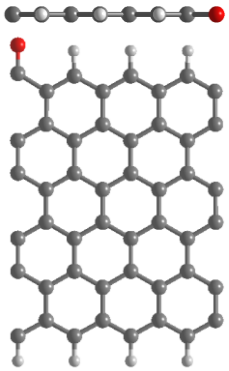
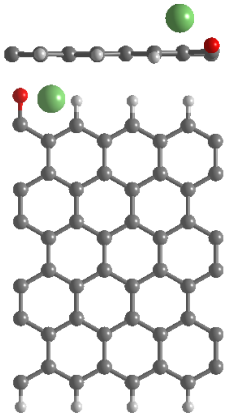
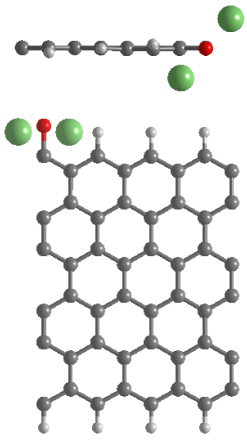
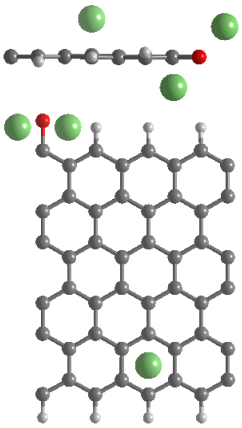
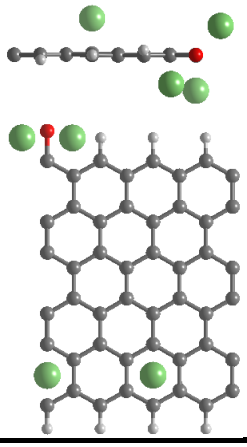
| 0 Li | 1Li | 2Li |
|---|---|---|
|  |  |  |
| **3 Li** | **4 Li** | |
|  |  | |

Figure S9. The most stable configurations at various stages of lithiation on the zigzag GNR model terminated with one ketone group.

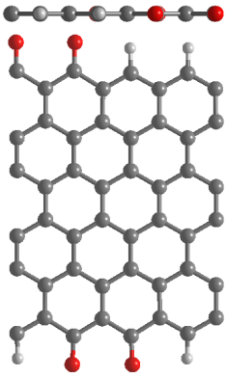
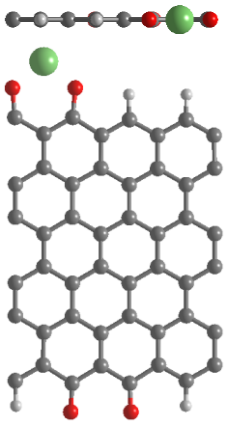
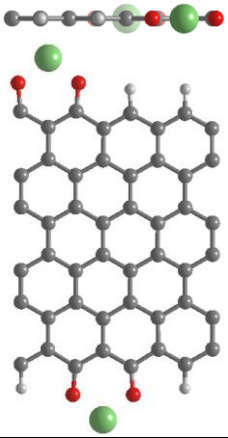
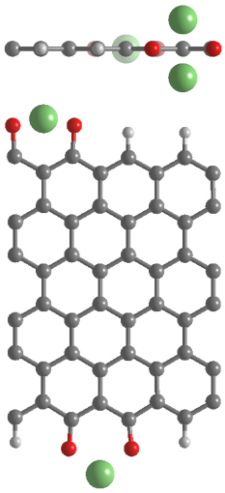
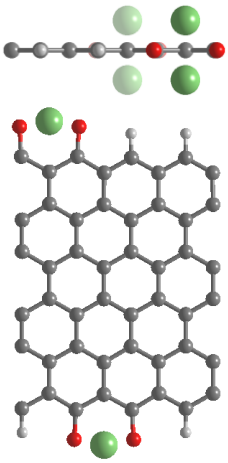
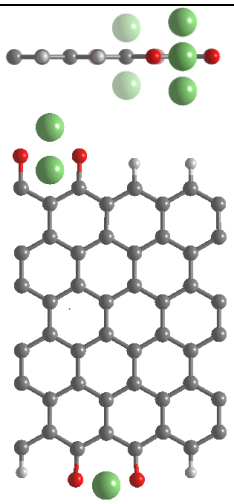
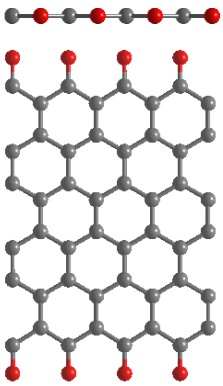
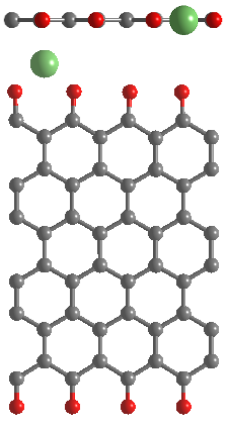
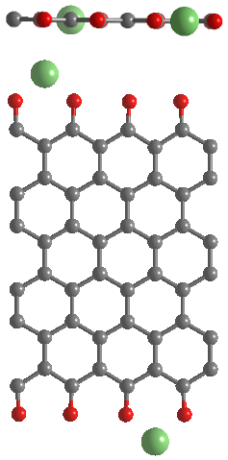
| 0 Li | 1Li | 2Li |
|---|---|---|
|  |  |  |
| **3 Li** | **4 Li** | **5 Li** |
|  |  |  |

Figure S10. The most stable configurations at various stages of lithiation on the zigzag GNR model terminated with four ketone groups.

| 0 Li | 1Li | 2Li |
|---|---|---|
|  |  |  |

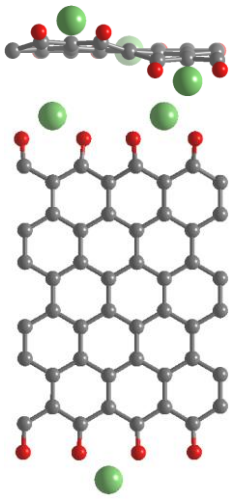
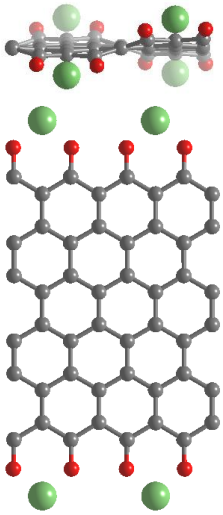
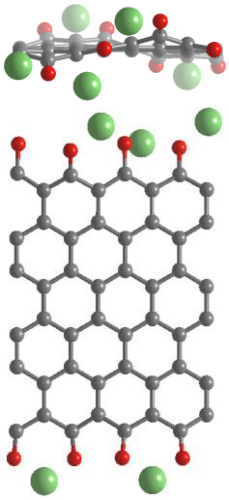
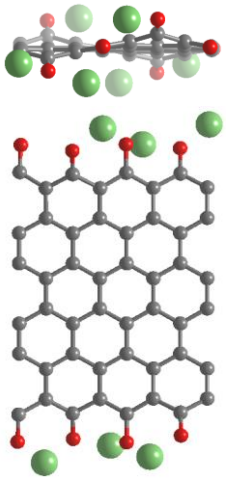
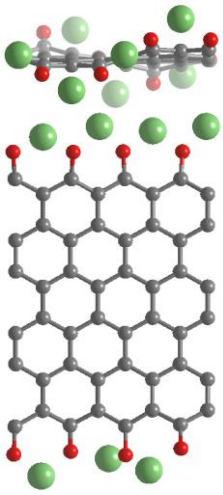
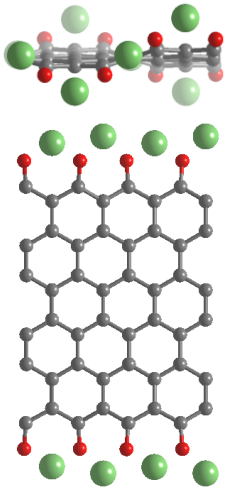
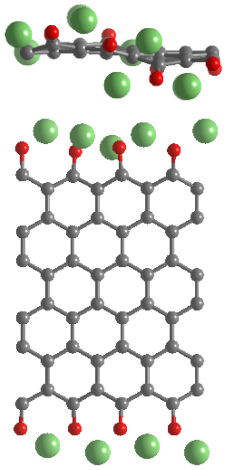
| 3 Li | 4 Li | 5 Li |
|---|---|---|
|  |  |  |
| **6 Li** | **7Li** | **8Li** |
|  |  |  |
| **9Li** | | |
|  | | |

Figure S11. The most stable configurations at various stages of lithiation on the zigzag GNR model terminated with eight ketone groups.

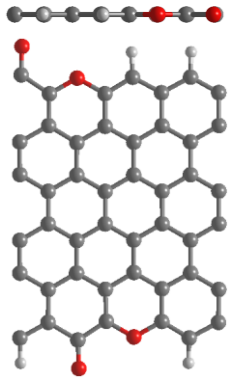
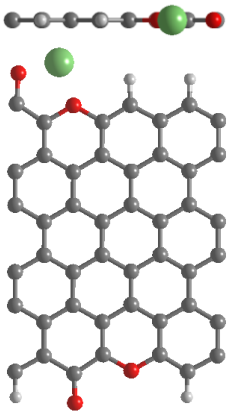
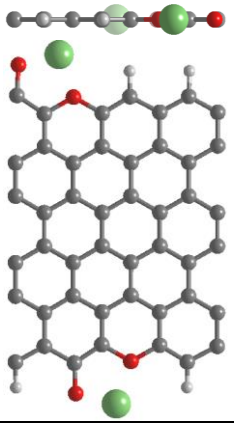
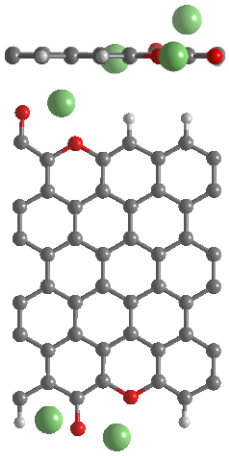
| 0 Li | 1Li | 2Li |
|---|---|---|
|  |  |  |
| **3 Li** | | |
|  | | |

Figure S12. The most stable configurations at various stages of lithiation on the zigzag GNR model terminated with two K-E pairs.

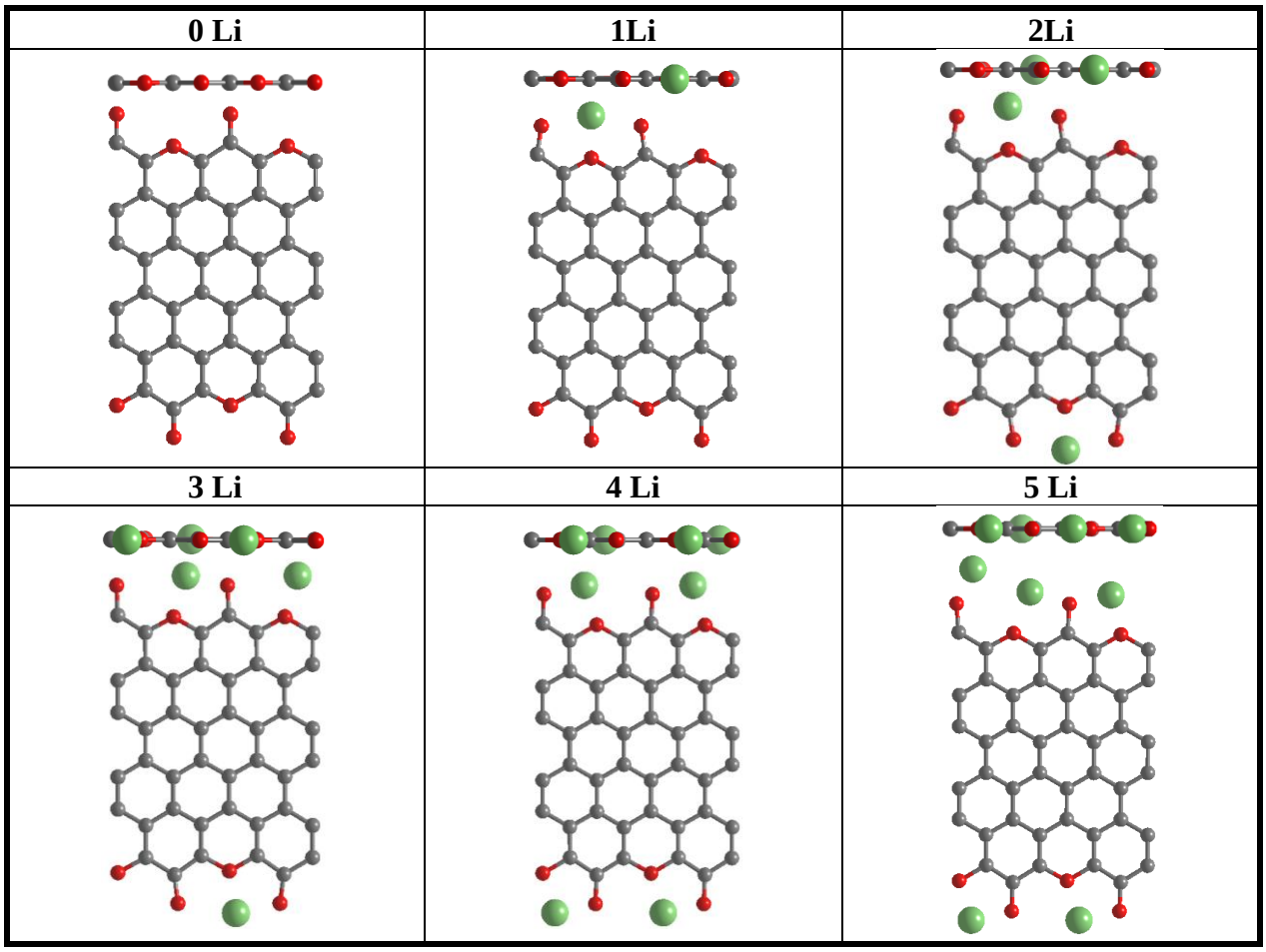



Figure S13. The most stable configurations at various stages of lithiation on the zigzag GNR model terminated with four K-E pairs.

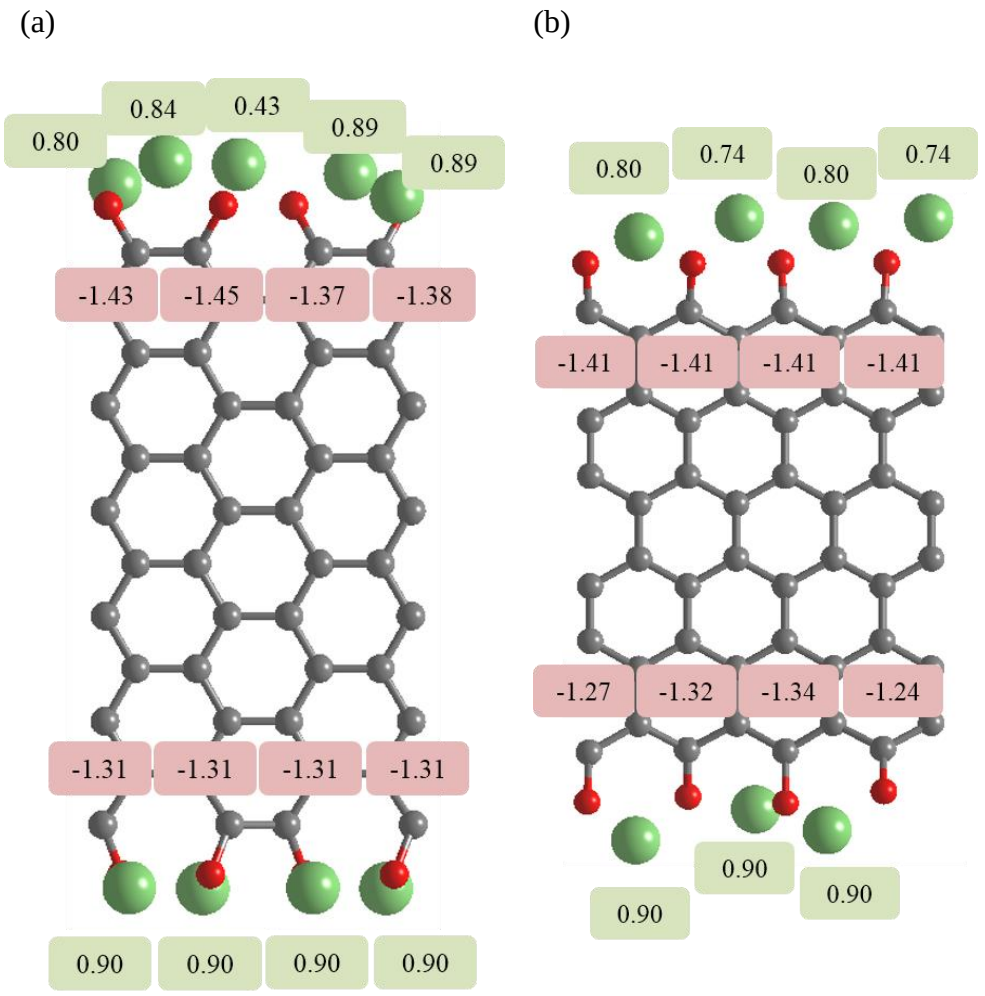



Figure S14. Configuration of the fully ketone-terminated (a) armchair GNR with 9 adsorbed Li atoms and that for the (b) zigzag GNR with 7 adsorbed Li atoms. The numbers in the green blocks indicate the Bader charges of the adsorbed Li atoms, while those in the red blocks indicate the Bader charges of the O groups.

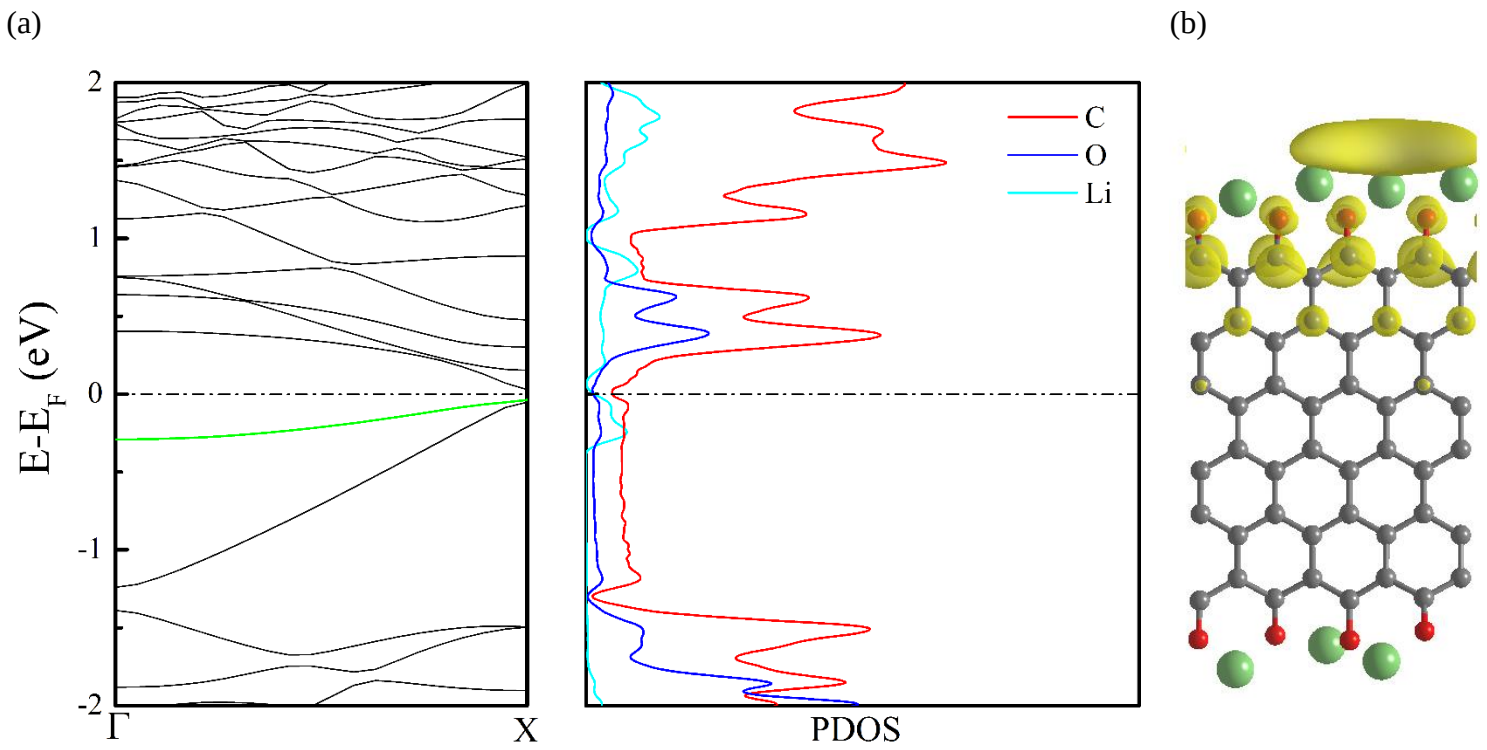



Figure S15. (a) Partial density of state and band structure of the fully ketone-terminated zigzag GNR with 7 adsorbed Li atoms; (b) The charge distribution of the highest occupied energy band in (a) (green line in band structure).

Table S2. Adsorption energies of Li on GNRs grafted with an in-plane epoxy or hydroxyl group. Adsorption type A and B are defined in Figure 6.

| Edge | Functional groups | Adsorption Type | Adsorption energy range (eV) |
|---|---|---|---|
| Armchair fully H-terminated | None | A | -1.100 ~ -1.165 |
| | Epoxy | A | -1.226 ~ -1.530 |
| | | B | -2.590 ~ -2.615 |
| | Hydroxyl | A | -1.609 ~ -1.877 |
| | | B | -4.005 ~ -4.043 |
| Zigzag fully H-terminated | None | A | -1.406 ~ -1.739 |
| | Epoxy | A | -1.621 ~ -1.844 |
| | | B | -2.839 ~ -2.876 |
| | Hydroxyl | A | -1.805 ~ -1.890 |
| | | B | -3.656 ~ -3.925 |

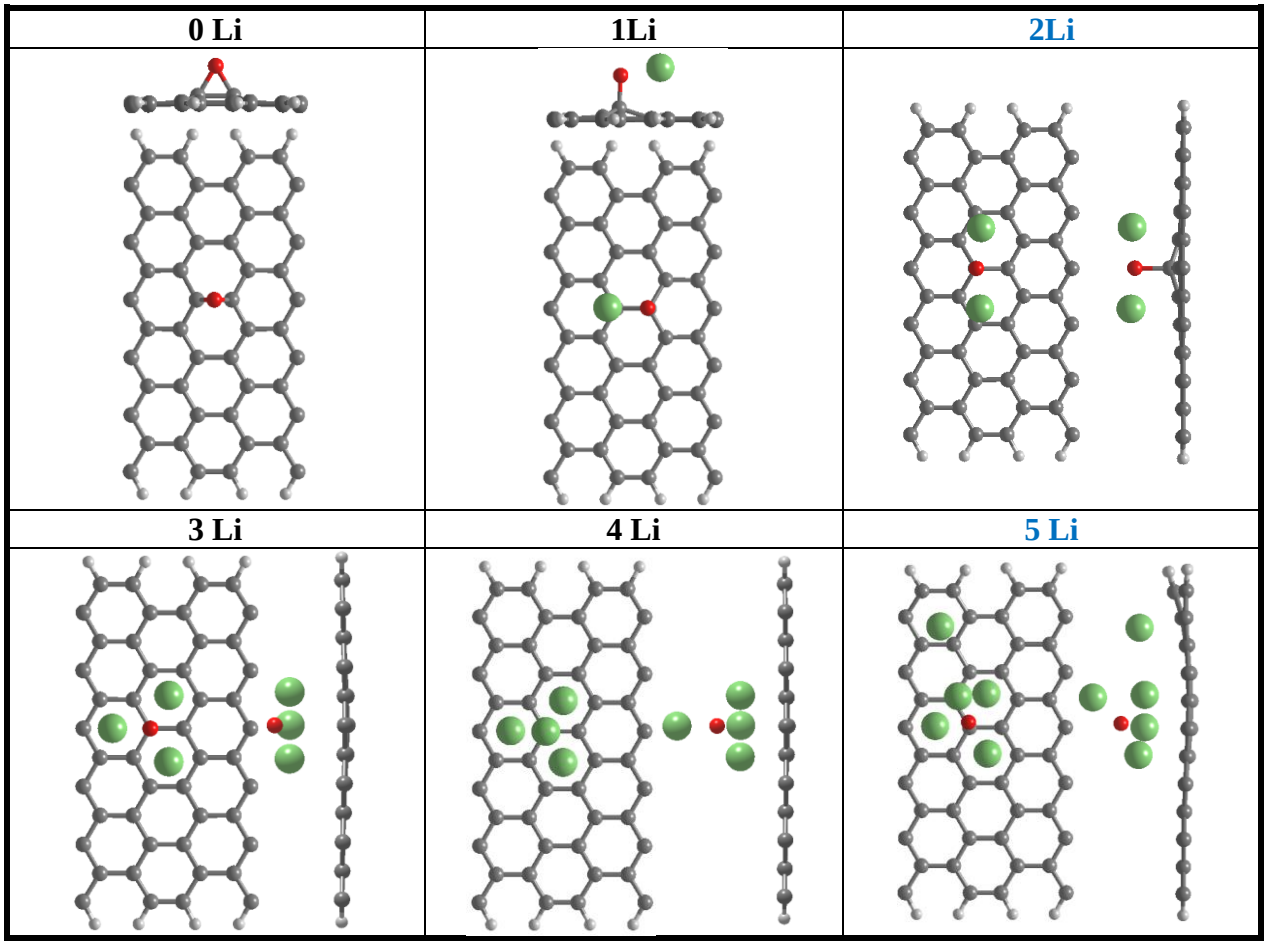



Figure S16. The most stable configurations at various stages of lithiation on the armchair GNR model grafted with one epoxy group.

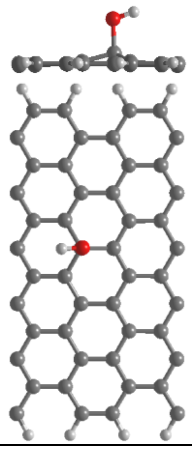
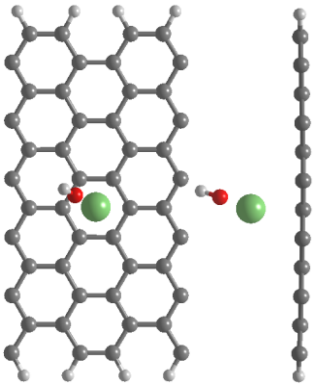
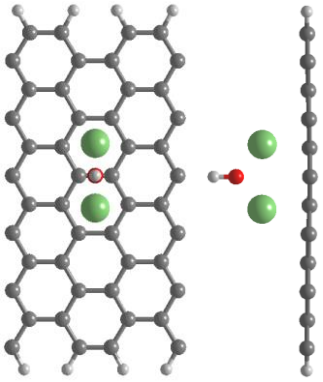
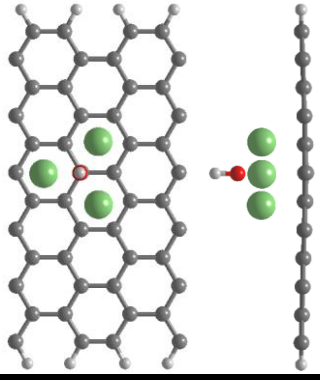
| 0 Li | 1Li | 2Li |
|---|---|---|
|  |  |  |
| **3 Li** | | |
|  | | |

Figure S17. The most stable configurations at various stages of lithiation on the armchair GNR model grafted with one hydroxyl group.

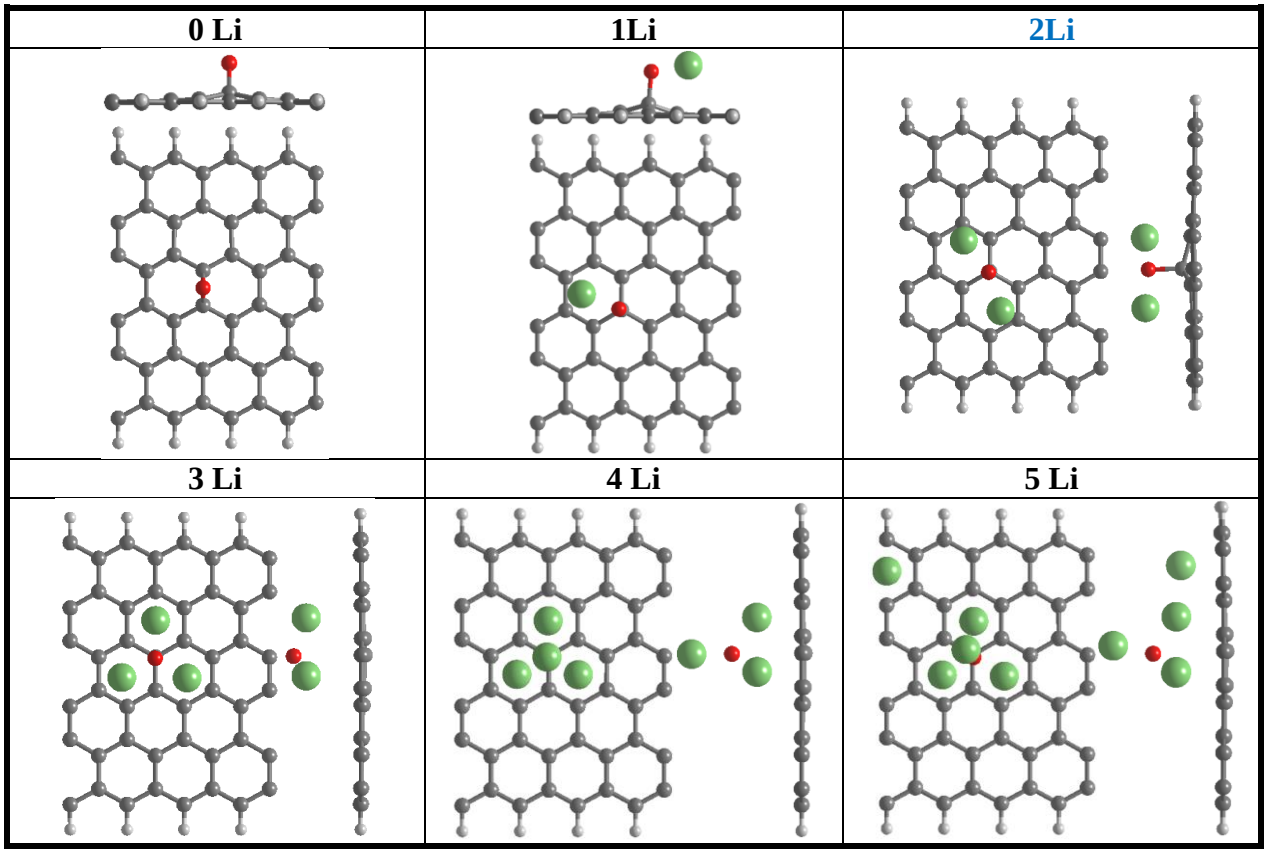



Figure S18. The most stable configurations at various stages of lithiation on the zigzag GNR model grafted with one epoxy group.

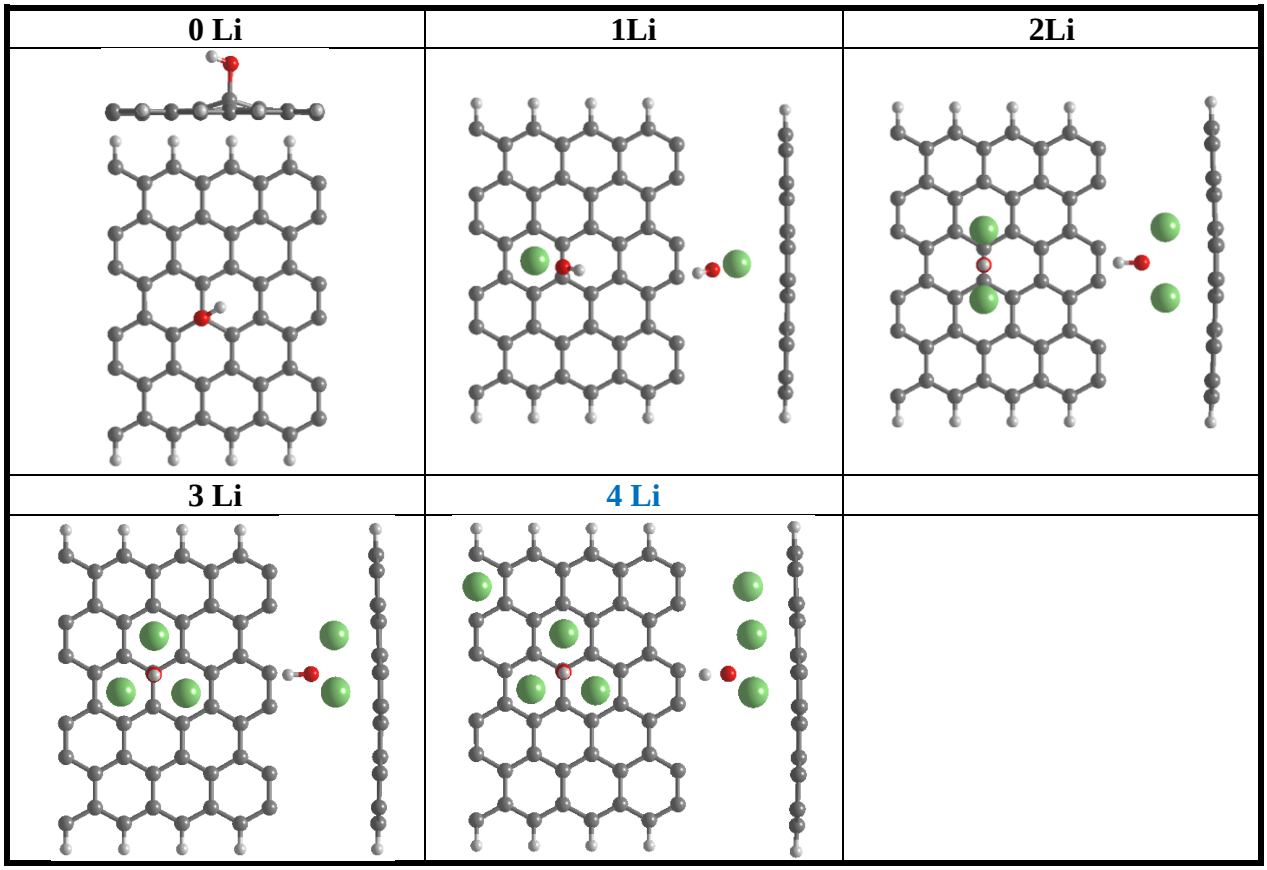



Figure S19. The most stable configurations at various stages of lithiation on the zigzag GNR model grafted with one hydroxyl group.

Table S3. Calculated Bader charges for the Li and O atoms of a $Li_4O$ cluster on the armchair and zigzag GNRs, respectively.

| | Li1 | Li2 | Li3 | Li-pyramid top | O |
|---|---|---|---|---|---|
| Armchair | 0.89 | 0.89 | 0.89 | 0.68 | -1.80 |
| Zigzag | 0.89 | 0.89 | 0.89 | 0.91 | -1.73 |

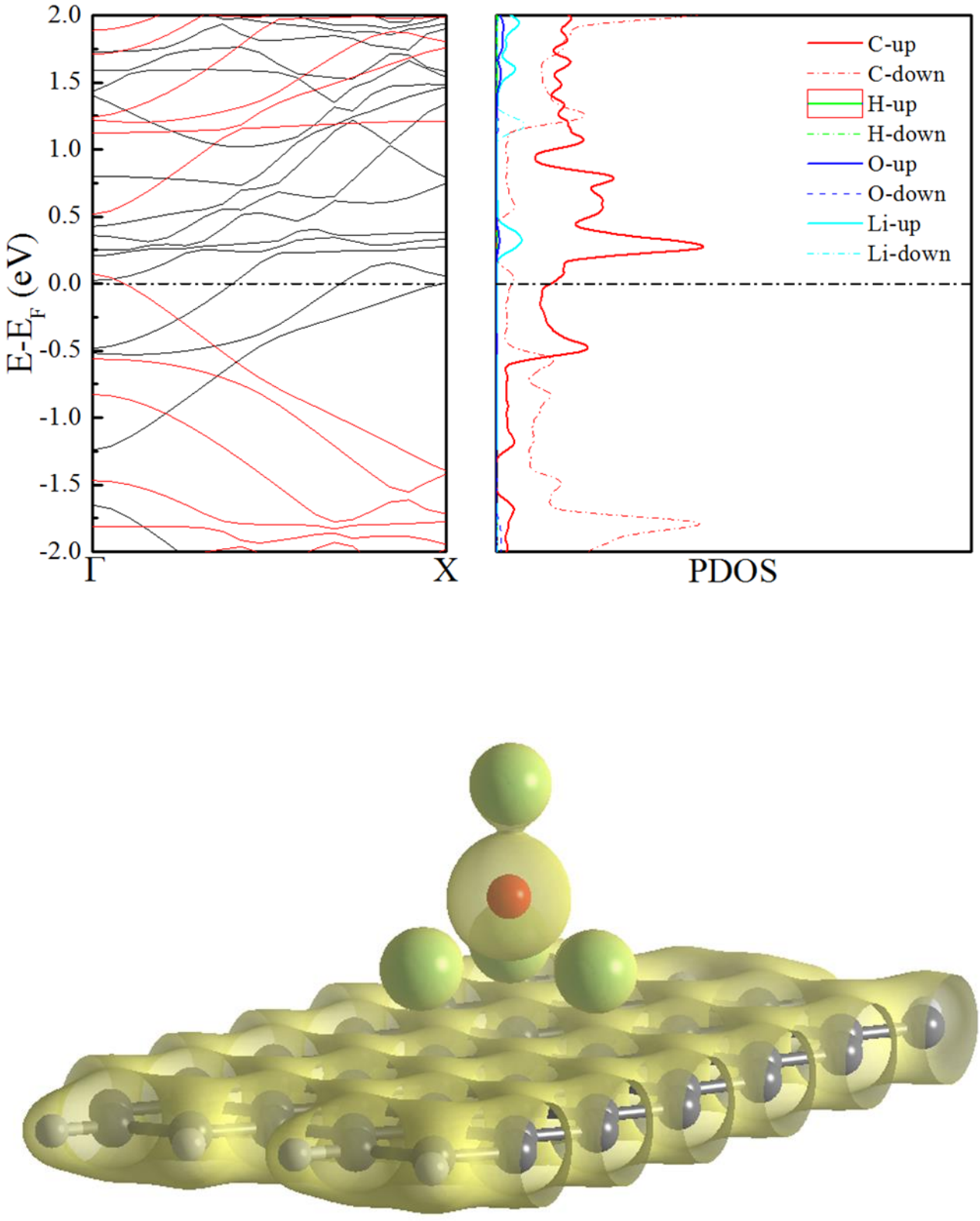



Figure S20. The electronic band structure and charge density analysis of a $Li_4O$ cluster on the graphene nanoribbon.

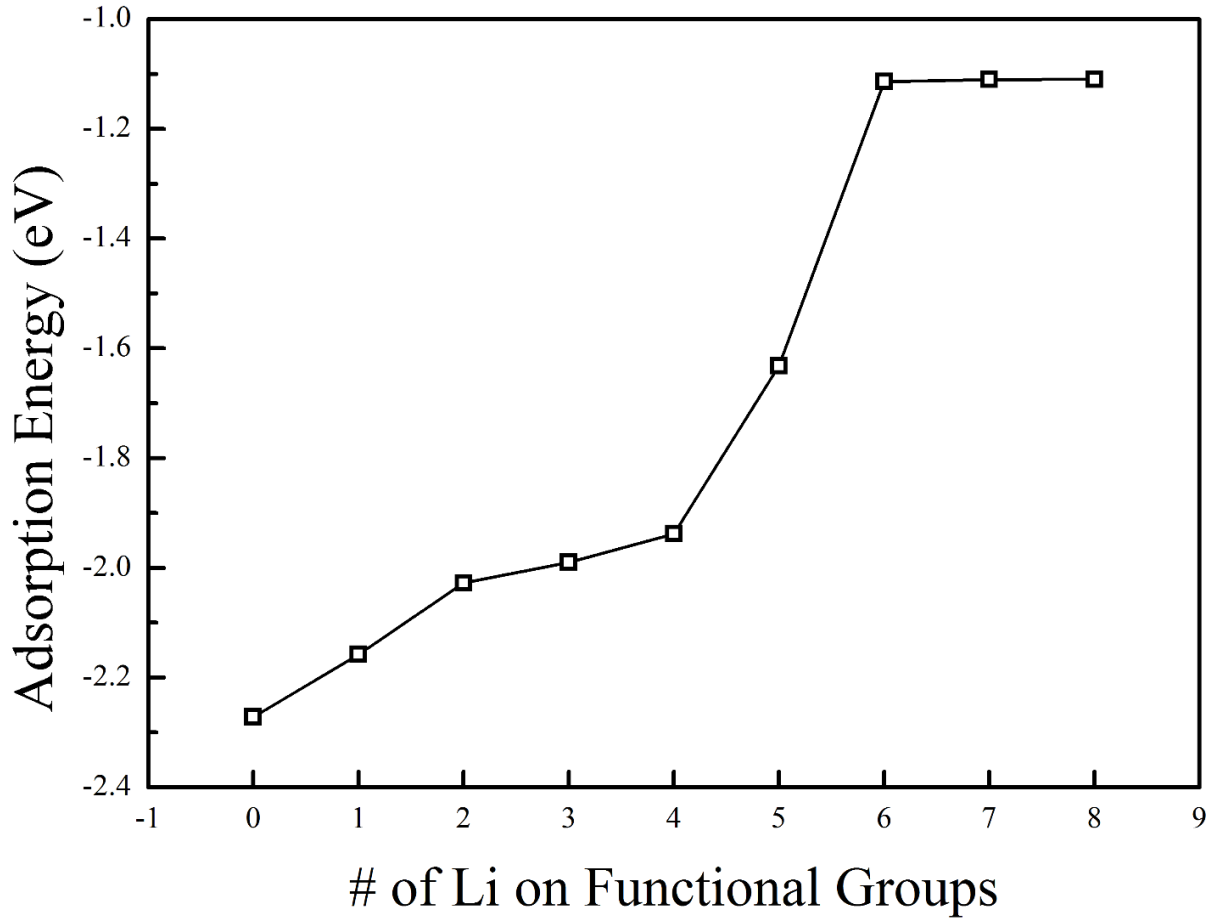



Figure S21. The adsorption energy of a Li atom on the central hollow site of a zigzag GNR terminated with 8 ketone groups when *n* Li atoms were adsorbed on the edge functional groups.