Supplementary Information

Ion-Specific Regulation of Epoxy Conversion and Hydroxyl Migration on Graphene Oxide

Jianjun Jiang, [a] Yusong Tu *[b] and Zonglin Gu *[b]

[a] Department of Physics, Sanjiang University, Nanjing 210012, China

[b]College of Physical Science and Technology, Yangzhou University, Yangzhou 225009, China

E-mail: ystu@yzu.edu.cn; guzonglin@yzu.edu.cn

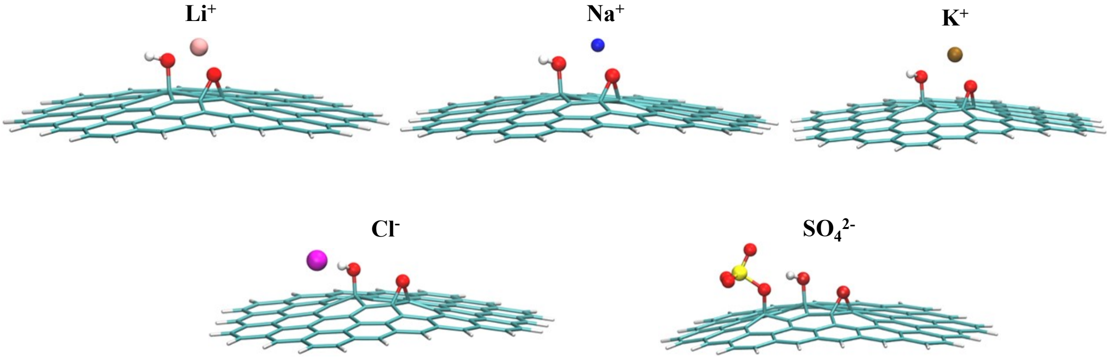

Fig. S1. Reaction configurations of epoxy C-O bond cleavage in ion-adsorbed GO.

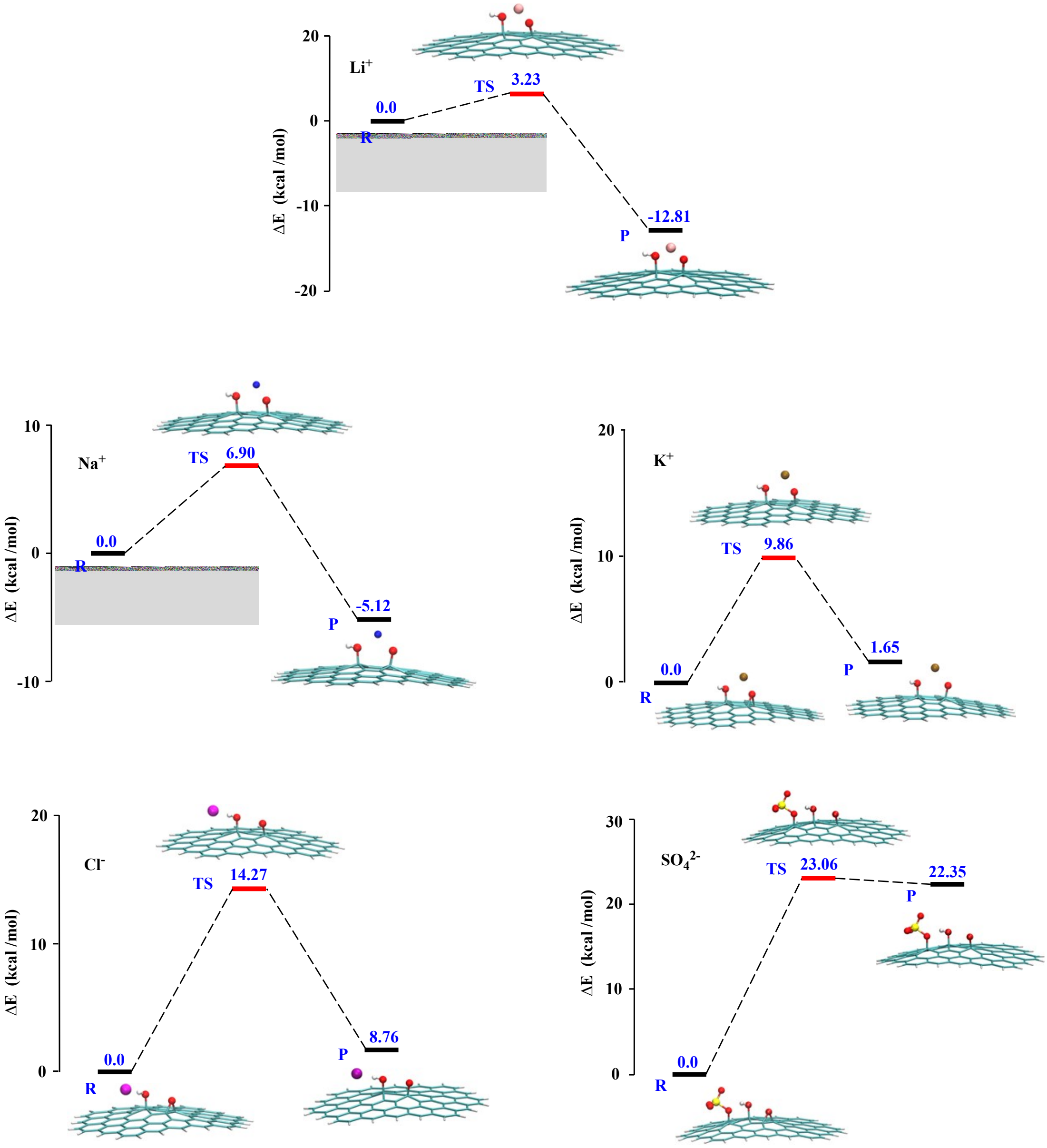

Fig. S2. Reaction pathways of C–O bond cleavage of GO adsorbed with an ion. Notation: reactant (R), transition state (TS), and product (P).

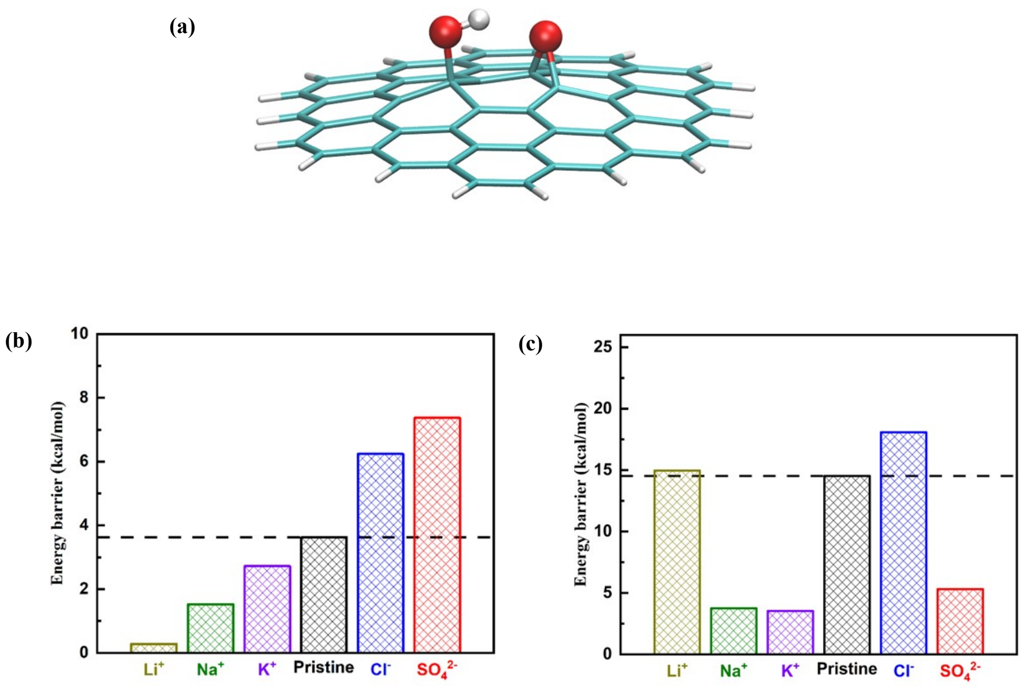

Fig. S3.（a）Atomistic structure of the additional GO model adopted from Ref. [20]. Energy barrier (ΔE) for (b) epoxy C-O bond cleavage and (c) hydroxyl migration in graphene oxide under pristine, cation (Li^+, Na^+, K^+)-adsorbed, and anion (Cl^-, SO_4^{2-})-adsorbed conditions. The horizontal dashed line represents the energy barrier of pristine GO.

As illustrated in Fig. S3(a), the graphene substrate of the GO model adopted from Ref. [20] consists of 54 carbon atoms, passivated by 18 hydrogen atoms at the edges. Its surface is functionalized with one epoxy group and one hydroxyl group.

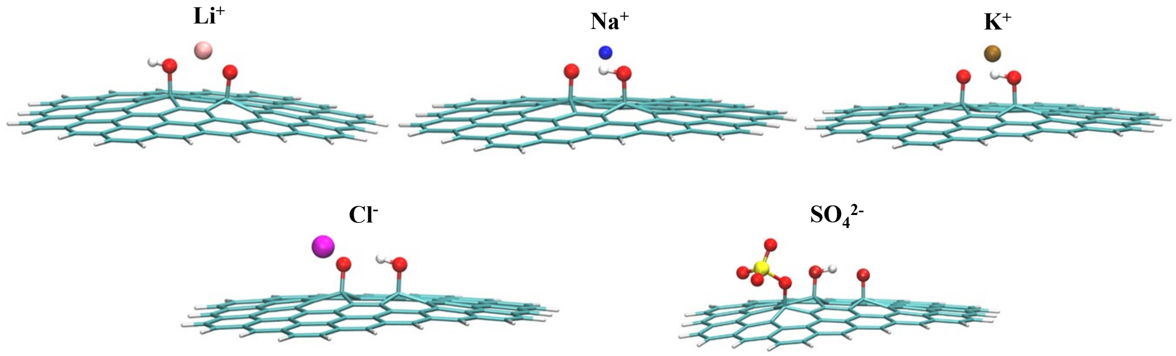

Fig. S4. Reaction configurations of hydroxyl migration in ion-adsorbed GO.

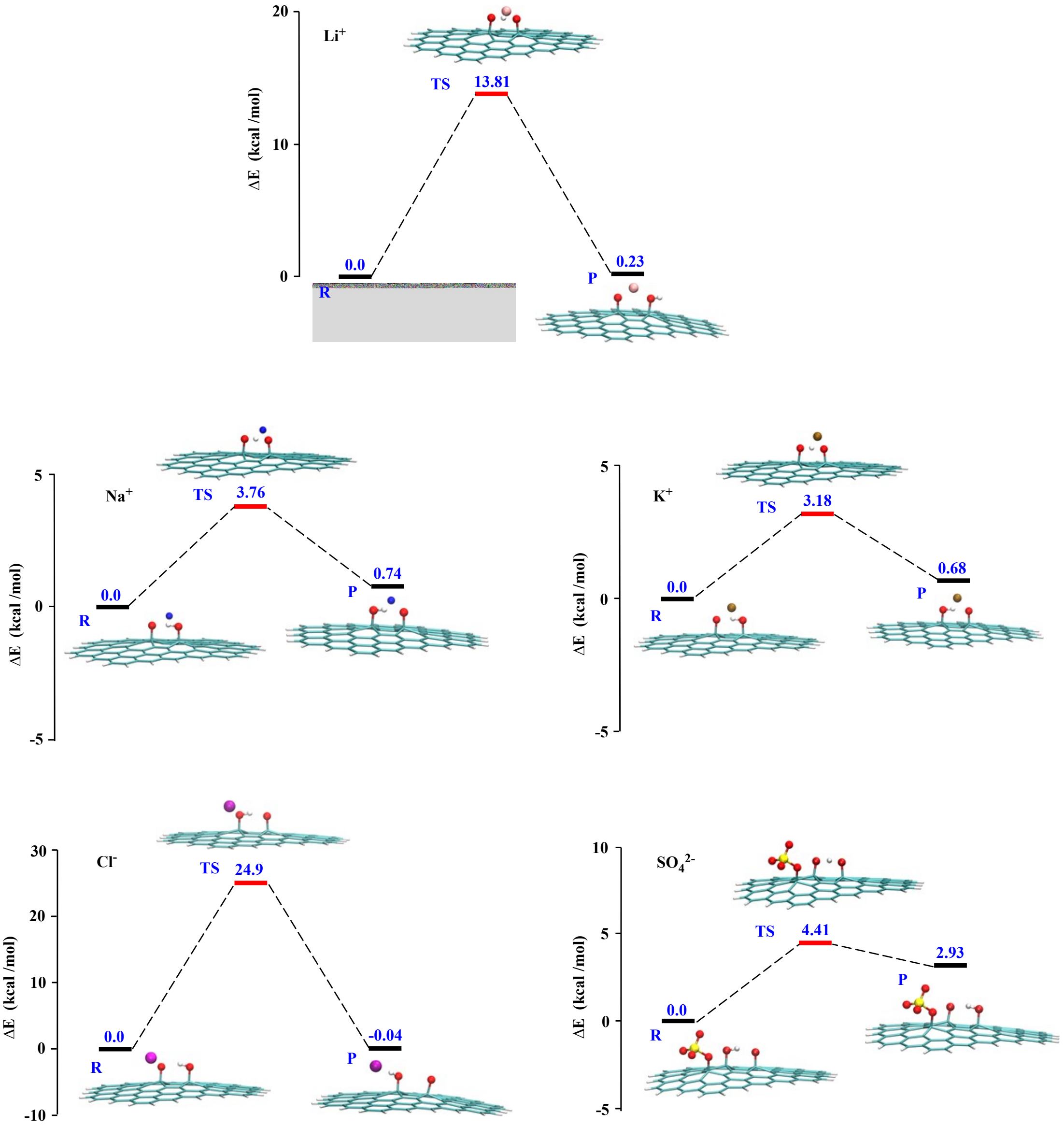

Fig. S5. Reaction pathways of hydroxyl migration of GO adsorbed with an ion.

Implicit solvent computational methods

All implicit solvent calculations were performed using Gaussian 16 with the M06-2X hybrid functional. The solvation model based on density was employed to simulate aqueous environments. Energy barrier calculations for epoxy C-O bond cleavage and hydroxyl migration were conducted using the same basis set assignments as those used in the gas-phase calculations. The 6-31G(d) basis set was used for the GO sheet and cation-incorporated system, while the 6-311+G(d,p) basis set was applied to chloride (Cl^-) and sulfate (SO_4^{2-}) ions. The calculation method for ion adsorption energies followed the procedure described in Ref. [34].

Table S1. Calculated adsorption energies (E_{ads}, kcal/mol) of different ions on the GO model shown in Fig. 1 in the gas phase and aqueous solution (implicit water model). The 6-311G(d,p) basis set was used for the GO sheet and cation-incorporated system, whereas the 6-311+G(d,p) basis set was applied for chloride (Cl^-) and sulfate (SO_4^{2-}) anions.

Ion	E_{ads} (Gas phase)	E_{ads} (Aqueous solution)
Li^+	-84.57	-26.11
Na^+	-62.61	-23.74
K^+	-49.22	-15.72
Cl^-	-17.58	-5.29
SO_4^{2-}	-84.77	-8.96

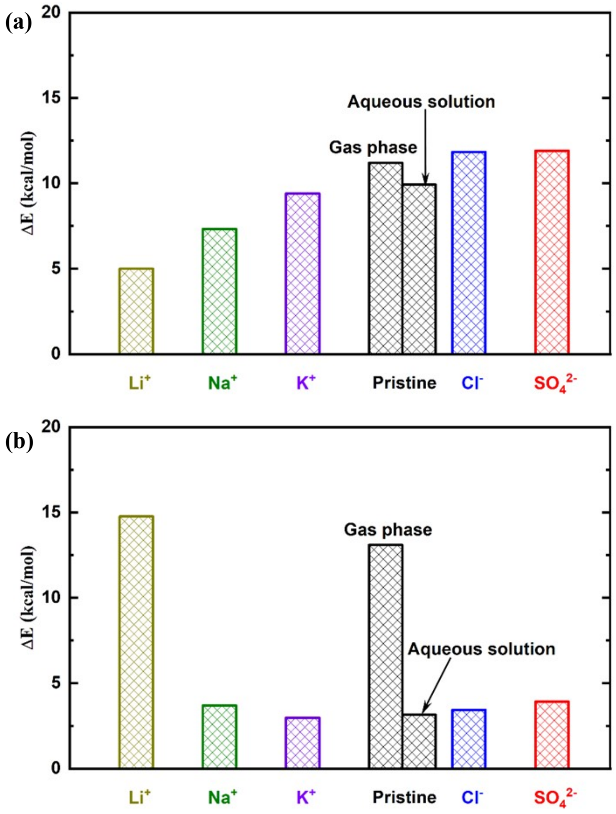

Fig. S6. Energy barriers (ΔE) for (a) epoxy C–O bond cleavage and (b) hydroxyl migration on GO under pristine, cation (Li^+, Na^+, K^+)-adsorbed, and anion (Cl^-, SO_4^{2-})-adsorbed conditions in an implicit water environment. The corresponding gas-phase energy barriers for the pristine system are also included for comparison.