Electronic Supplementary Information

Charge Carrier Exchange at Chemically Modified Graphene Edges: a Density Functional Theory Study

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The molecular geometry of hydronium (H_3O^+) is trigonal pyramidal with three bonding pairs and one lone pair, as illustrated in Fig. S1a. The calculated O-H bond length d and ΔHOH angle θ are 0.991 Å and 112.5°, respectively, agreeing well with the experimental data with a deviation no larger than 2.0% [1]. The energy level diagram of hydronium based on band energy calculation is shown in Fig. S1b. In this energy window there appear four occupied MOs of hydronium: the lowest lying a_1 bonding orbital, the double degenerate e, and the lone-pair a_1 orbital. The isosurface of the lowest five eigenstates of H_3O^+ have been identified in the right panel of Figure 1b as mainly of C_{3v} symmetric bonding character.

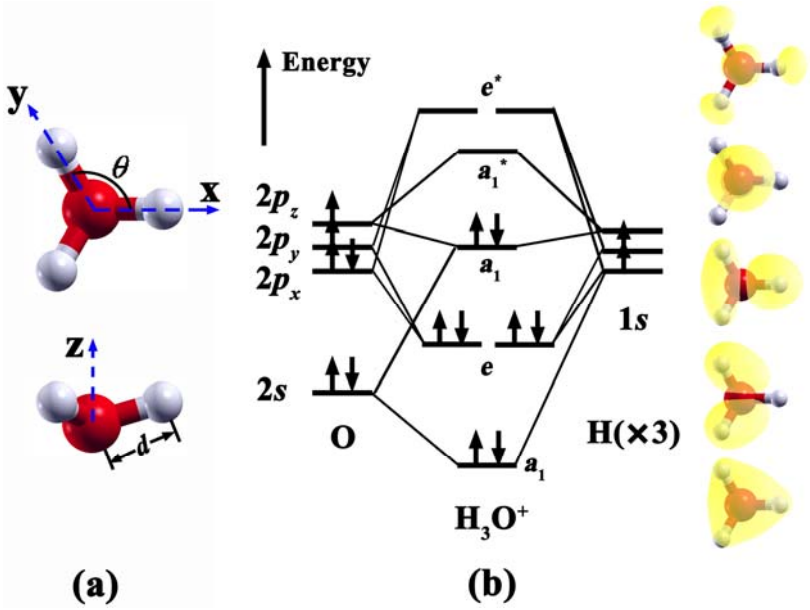

Fig. S1 (a) Top and side views of molecular structure of hydronium, (b) Energy level diagram and the views of the isosurface of the lowest five eigenstates of hydronium.

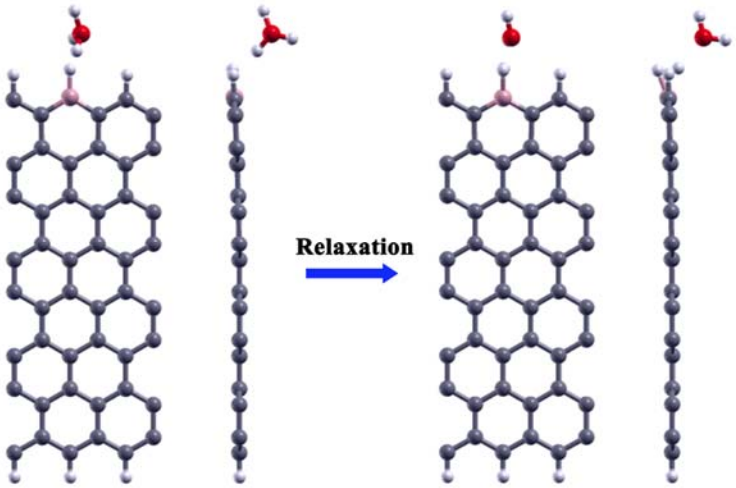

Fig. S2 Top and side views of proton transferred to hydrogen passivated B-doped ribbon edge from hydronium H_3O^+.

	Mulliken Charge (e) Before H* transfer			Mulliken Charge (e) After H* transfer		
	Edge atom	H*	C*	Edge atom	H*	C*
B-doped ribbon	2.49	0.59	4.31	2.66	0.91	4.24
Undoped ribbon	4.17	0.52	4.03	4.22	0.66	4.00
N-doped ribbon	5.42	0.50	3.84	5.49	0.54	3.84
O-doped ribbon	6.43	0.49	3.75	6.44	0.49	3.80

Table. S1 Mulliken population charge of proton H*, edge atom and the carbons atoms C* in proximity to the edge atom when proton was transferred from hydronium H_3O^+ to the doped ribbon edge.

References

1 J. Tang and T. Oka, *J. Mol. Spec.* 1999, **196**, 120.