The Mechanism of Alkali Promoting Water Splitting on g-C$_3$N$_4$

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(a)
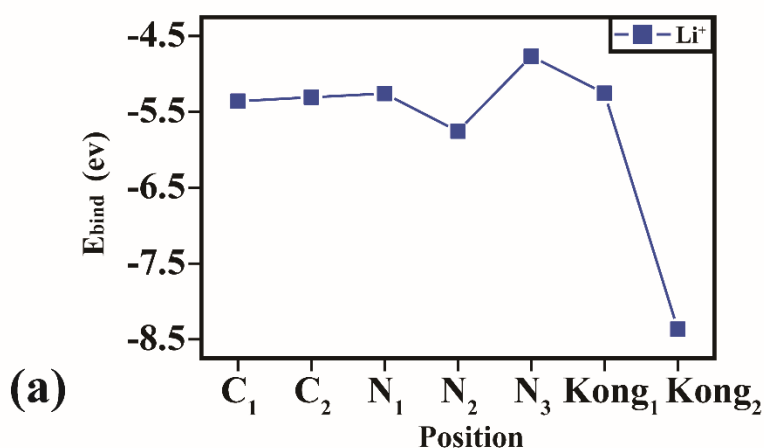
Pure g-C$_3$N$_4$	C$_1$	C$_2$	N$_1$	N$_2$	N$_3$
electron	-1.54	-1.58	+0.98	+1.20	+1.16

(b)

Figure S1 (a) is the binding energy (E$_{bind}$) for Li$^+$ absorbed on g-C$_3$N$_4$, where the positions are marked in Figure 1. (b) is the electron gain and loss of various atoms compared with isolated atoms, where the positive one represents the gain of electrons and the negative one represents the loss of electrons.
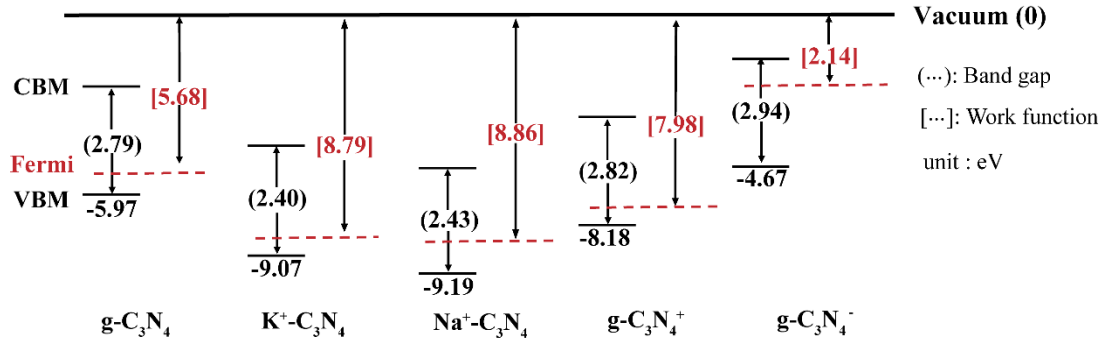
Figure S2 The energies of VBM, band gap and work function for the g-C_3N_4, K^+ absorbed g-C_3N_4, Na^+ absorbed g-C_3N_4, positively charged g-C_3N_4 and negatively charged g-C_3N_4, where the vacuum is set 0. In the K^+ (Na^+) absorbed g-C_3N_4, it can be seen as that negative ion is far away from the base, so only the influence of cations needs to be considered.

E (eV)	·H·OH	H₂O	(·H—*·OH)			(·H—*·O)			(·H—*·OOH)			(·H—*·OO)		
	·H·OH	H₂O	H₂O	NaCl	KCl	Pure	NaCl	KCl	Pure	NaCl	KCl	Pure	NaCl	KCl
Ed(n=0)	5.33		4.36	4.01	4.13	6.02	6.06	6.01	1.62	1.36	0.98	3.43	3.48	3.53
S(n=0)	10^{-37}		10^{-20}	10^{-14}	10^{-16}	10^{-48}	10^{-49}	10^{-48}	10^{26}	10^{31}	10^{37}	10^{-4}	10^{-5}	10^{-6}
Ed(n=1⁺)			5.68	5.10	5.07	4.48	4.87	4.89	2.37	2.22	1.97	2.07	2.36	2.52
S(n=1⁺)			10^{-43}	10^{-33}	10^{-32}	10^{-22}	10^{-29}	10^{-29}	10^{14}	10^{16}	10^{20}	10^{19}	10^{14}	10^{11}
Ed(n=1⁻)			3.89	3.17	3.36	5.23	5.18	5.19	1.12	0.77	0.71	2.27	3.06	2.73
S(n=1⁻)			10^{-12}	10	10^{-3}	10^{-35}	10^{-34}	10^{-34}	10^{35}	10^{41}	10^{42}	10^{15}	10^{2}	10^{7}

Table S1 The dissociation energies (eV) for ·H (Ed) from H_2O and the relative rates of H–O bond dissociation (S). The values of n, 0, 1+ and 1 represent the neutral, losing electron and obtaining electron states of porphyrin and g-C_3N_4.

Electrostatic interaction		$q_{H1}(h^+)$	$q_{H2}(h^+)$	$q_O(e^-)$	d_1(Å)	d_2(Å)	$\dfrac{q_{H1}q_O}{d_1{}^2}$	$\dfrac{q_{H2}q_O}{d_2{}^2}$
	pure	0.62	0.66	1.28	0.97	0.97	0.84	0.90
*OH₂	NaCl	0.66	0.69	1.33	0.96	0.96	0.95	1.01
	KCl	0.69	0.68	1.35	0.97	0.97	1.00	0.98
	pure	0.59		0.83	0.99		0.50	
*OH	NaCl	0.59		1.18	0.96		0.75	
	KCl	0.63		1.25	0.97		0.84	
	pure	0.75	0.78	0.47	0.95	0.95	0.39	0.40
*O-OH₂	NaCl	0.62	0.77	0.48	1.00	0.96	0.30	0.41
	KCl	0.66	0.78	0.53	1.00	0.93	0.35	0.47
	pure	0.64		0.44	0.95		0.31	
*O-OH	NaCl	0.66		0.60	1.01		0.39	
	KCl	0.63		0.51	1.01		0.32	

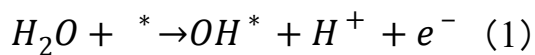**Table S2** The q_H(h+), q_O(e-) and d (Å) represent the positive charge on H, the negative charge on O, and the distance between O and H. Therefore, the electrostatic interaction between O and H is expressed as $\frac{q_H q_O}{d}$.
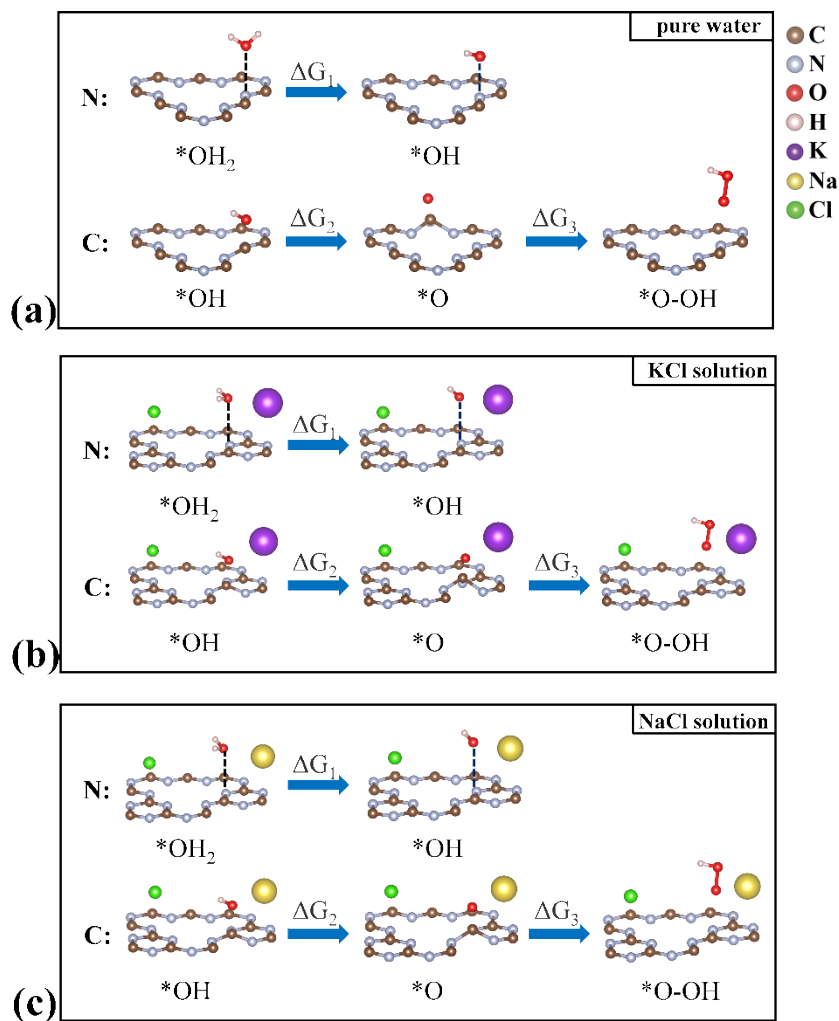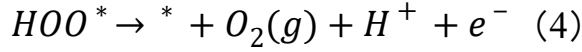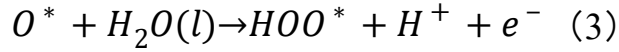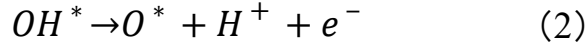
Figure S3 The corresponding configurations of the reaction intermediates in OER, while the absorbed site for *OH$_2$→*OH is N, other steps are all C.

Free energy calculation

The process of oxygen evolution reaction (OER) is as following:

$H_2O + \; ^* \rightarrow OH^* + H^+ + e^-$ (1)

$$OH^* \rightarrow O^* + H^+ + e^- \qquad (2)$$

$$O^* + H_2O(l) \rightarrow HOO^* + H^+ + e^- \qquad (3)$$

$$HOO^* \rightarrow {}^* + O_2(g) + H^+ + e^- \qquad (4)$$

In computational hydrogen electrode (CHE) model[1], the free energy of a proton-electron pair at 0V *vs* RHE is defined to be to ½ of the H_2 free energy at 101,325 Pa, meaning that the Gibbs free energy change ($\triangle$G)is 0 for the reaction $H_{(aq)}^+ + e^- \rightleftharpoons \frac{1}{2}H_{2(g)}$. Therefore, the $\triangle$G for each elemental step is

$$\Delta G_1 = G_{HO^*} + \frac{1}{2}G_{H_2} - G_* - G_{H_2O}$$

$$\Delta G_2 = G_{O^*} + \frac{1}{2}G_{H_2} - G_{OH^*}$$

$$\Delta G_3 = G_{HOO^*} + \frac{1}{2}G_{H_2} - G_{O^*} - G_{H_2O}$$

$$\Delta G_4 = 4.92 - \left[\Delta G_1 + \Delta G_2 + \Delta G_3\right]$$

The Gibbs free energy is calculated using

$$G = E + ZPE - TS + eU$$

where E is the energy of optimized structure; *e* and *U* are the number of electrons transferred and the electrode potential applied; the zero point energies (ZPE) and enthalpic entropy correction (TS) were obtained as G(T) using Vaspkit.[2]

1.   Jiao, Y.; Zheng, Y.; Chen, P.; Jaroniec, M.; Qiao, S. Z., Molecular Scaffolding Strategy with Synergistic Active Centers To Facilitate Electrocatalytic CO_2 Reduction to Hydrocarbon/Alcohol. *J. Am. Chem. Soc.* **2017,** *139* (49), 18093-18100.

2.   Wang, V.; Xu, N.; Liu, J. C.; Tang, G.; Geng, W. T., VASPKIT: A Pre- and Post-Processing Program for VASP code. . *arXiv: Mater. Sci.* **2019**.