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

Enhanced Catalytic Activity of SO_x-Incorporated Graphene for Hydrogen Evolution Reaction

Chi Ho Lee[†], Eun Bi Nam[†], and Sang Uck Lee[†,‡,]*

†Department of Bionano Technology, Hanyang University, Ansan, 15588, Korea

‡Department of Chemical and Molecular Engineering, Hanyang University, Ansan, 15588, Korea

Table S1. Zero point energies (ZPE) and entropic (TS) corrections for SO_x-incorporated graphenes (SO_2@G, SO_3@G and SO_4@G) at 298 K.

SO_x@G	ZPE	TS	△ZPE	T△S	△ZPE- T△S
SO_2@G-H*	0.29	-	0.15	-0.21	0.36
SO_3@G-H*	0.29	-	0.15	-0.21	0.36
SO_4@G-H*	0.29	-	0.15	-0.21	0.36
H_2	0.27	0.41	-	-	-

The gas phase values were from Ref. 1, while the values for the adsorbed species were taken from DFT calculations. We used the same values for the adsorbed species in the same SO_X@G structures (X= 2, 3 and 4), because it has been known that the vibration frequency is much less dependent on similar surfaces than the bond strength.

$$\frac{1}{2}\mathrm{H_2} + * \rightarrow \frac{1}{2}\mathrm{H_2^*}$$

$$\triangle \mathrm{ZPE} = \mathrm{ZPE}_{\frac{1}{2}\mathrm{H_2^*}} - \frac{1}{2}\mathrm{ZPE}_{\mathrm{H_2}}$$

$$\triangle \mathrm{S} = \mathrm{S}_{\frac{1}{2}\mathrm{H_2^*}}(\simeq 0) - \frac{1}{2}\mathrm{S}_{\mathrm{H_2}}$$

Table S2. Frequencies of adsorbed species of SO_x-incorporated graphenes (SO_2@G, SO_3@G and SO_4@G).

Adsorbed Species	Frequency (cm^{-1})
SO_2@G-H*	2603.518, 1009.251, 1008.691
SO_3@G-H*	2623.925, 1056.074, 1009.948
SO_4@G-H*	2613.050, 1024.342, 995.391

Table S3. Formation energy (E_f) of SO_x@G (x=2, 3 and 4).

Material	E_f (eV)[a]	
	Basal plane	Zigzag edge
SO_2@G	0.98	2.75
SO_3@G	-0.75	2.07
SO_4@G	0.03	-0.47

[a] The formation energies (E_f) of SO_x@G are calculated as $E_f = (E_{SO_x@G} + \mu_c) - (E_G + \mu_S + \mu_O + \mu_H)$, where $E_{SO_x@G}$ and E_G are total energy of the SO_x@G and G, respectively, and μ_c, μ_S, μ_O and μ_H are the chemical potentials of C, S, O and H elements.

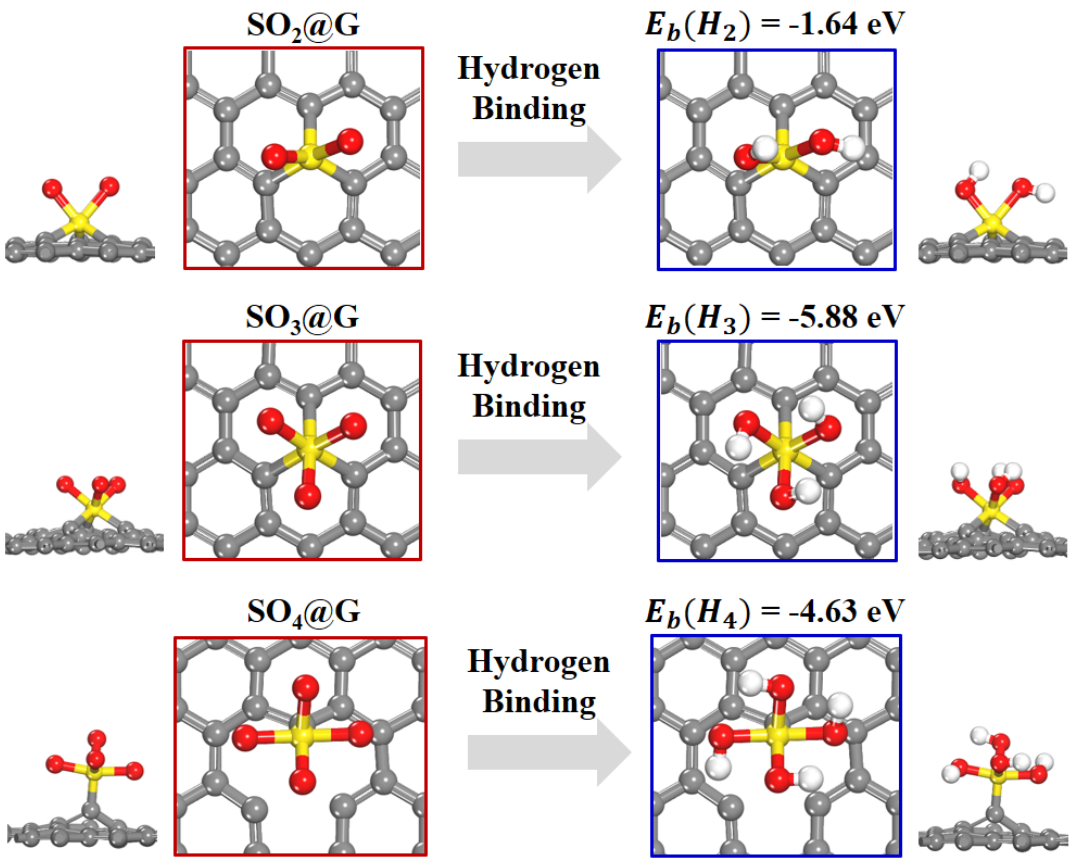

Fig. S1. Hydrogen binding energies on the oxygen sites of SO_x@G (x=2, 3 and 4) on basal plane.

$E_b(H_x)$[a] (x=2, 3 and 4) indicates hydrogen binding energy.

[a] $E_b(H_x) = \left[E_{SO_x@G+Hx} - E_{SO_x@G}\right] - \frac{x}{2}E_{H_2(g)}, (x = 2, 3\ and\ 4)$

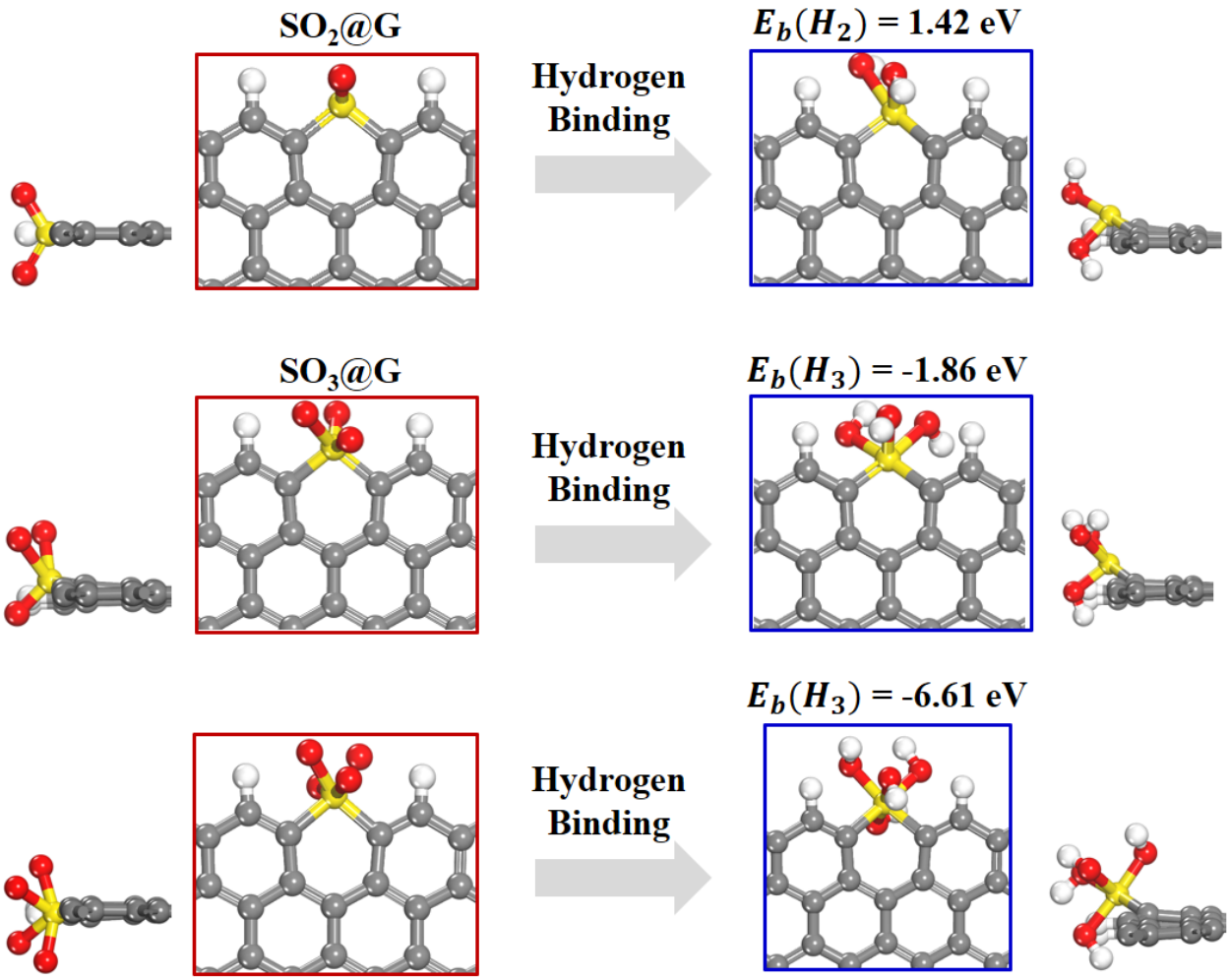

Fig. S2. Hydrogen binding energies on the oxygen sites of SO_x@G (x=2, 3 and 4) on zigzag edge.

$E_b(H_x)$[a] (x=2, 3 and 4) indicates hydrogen binding energy.

[a] $E_b(H_x) = \left[E_{SO_x@G+Hx} - E_{SO_x@G}\right] - \frac{x}{2}E_{H_2(g)}, (x = 2, 3\ and\ 4)$

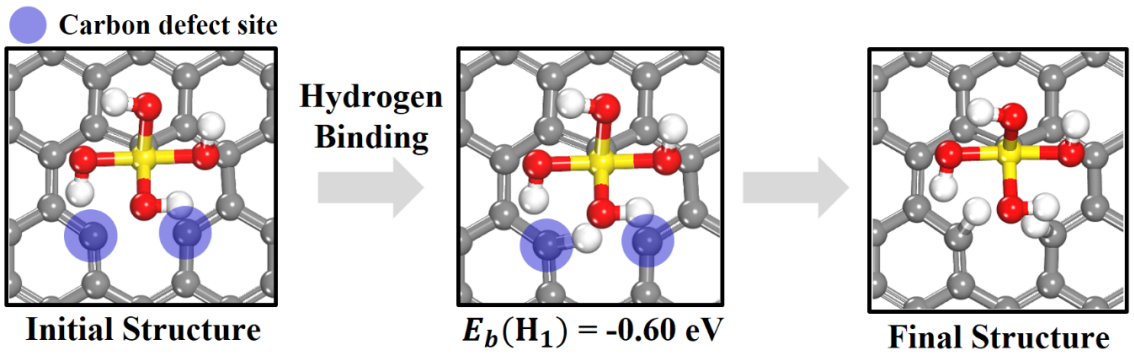

Fig. S3. Hydrogen binding energy ($E_b(H_x)$) on the carbon defect sites of SO_4@G.

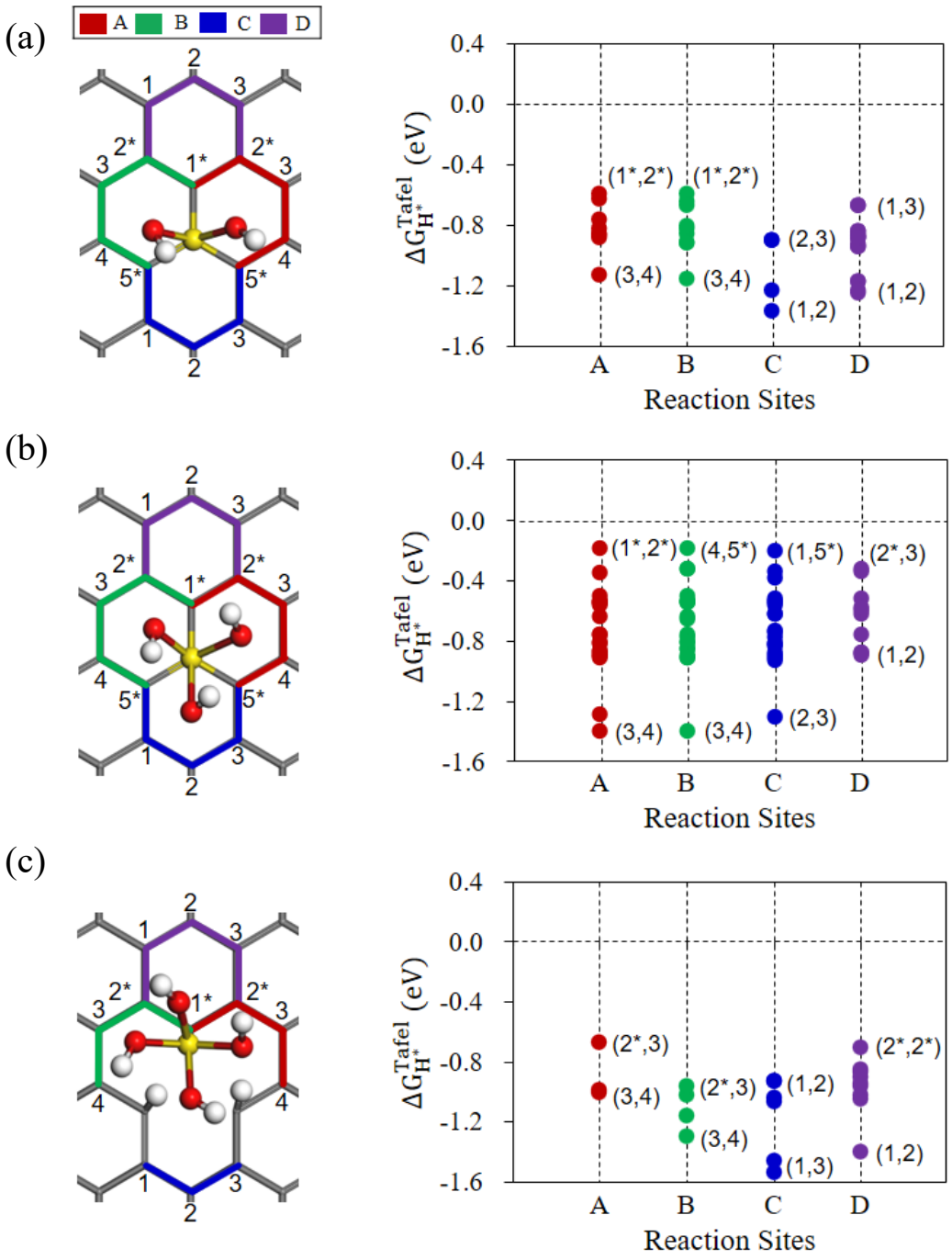

Fig. S4. HER activities, $\Delta G_{H^*}^{Tafel}$ of (a) SO_2, (b) SO_3, (c) SO_4-incorporated graphene structures (SO_x@G, x=2, 3 and 4) as a function of various active sites. Arabic numbers and insets indicate the active sites and structures, respectively. If the active site regions overlap, * is marked on the active site.

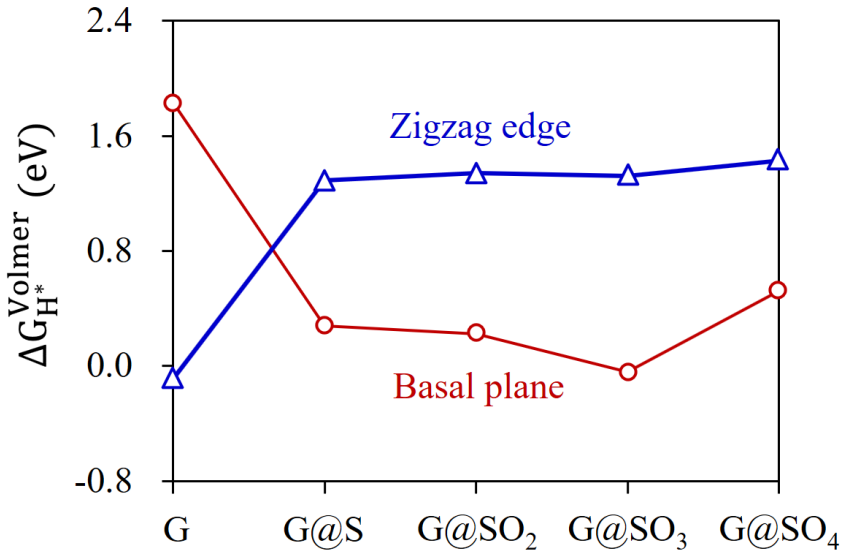

Fig. S5. HER activities, $\Delta G_{H^*}^{Volmer}$ of G, G@S, G@SO_2, G@SO_3 and G@SO_4.

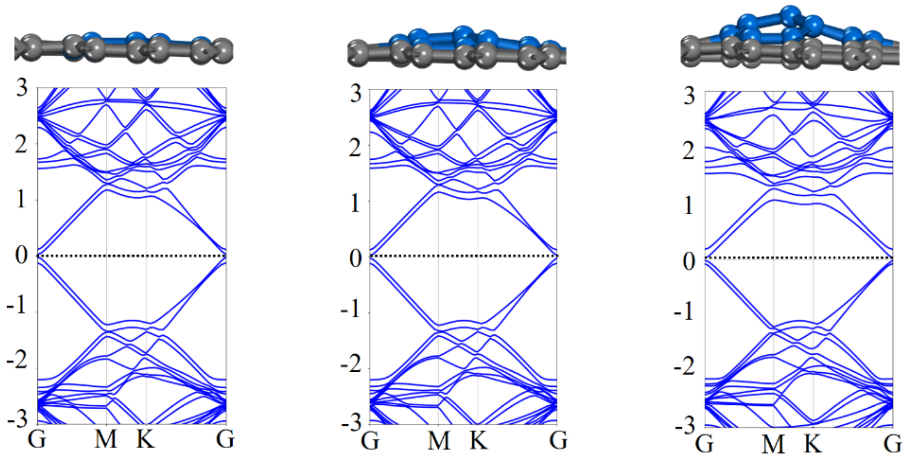

Fig. S6. Band structures of G with structural deformation. Blue marked carbon sites indicate the deformed area.

We investigated the correlation between band structure variation and structural deformation, which can be induced by SO_3. We systematically changed graphene sheet from in-plane to out-of-plane structures. However, we cannot observe any change in the electronic band structure, even though the in-plane graphene sheet is largely deformed to out-of-plane. It confirms that the geometric effect has no associated with a *p*-type doping effect of SO_3@G.

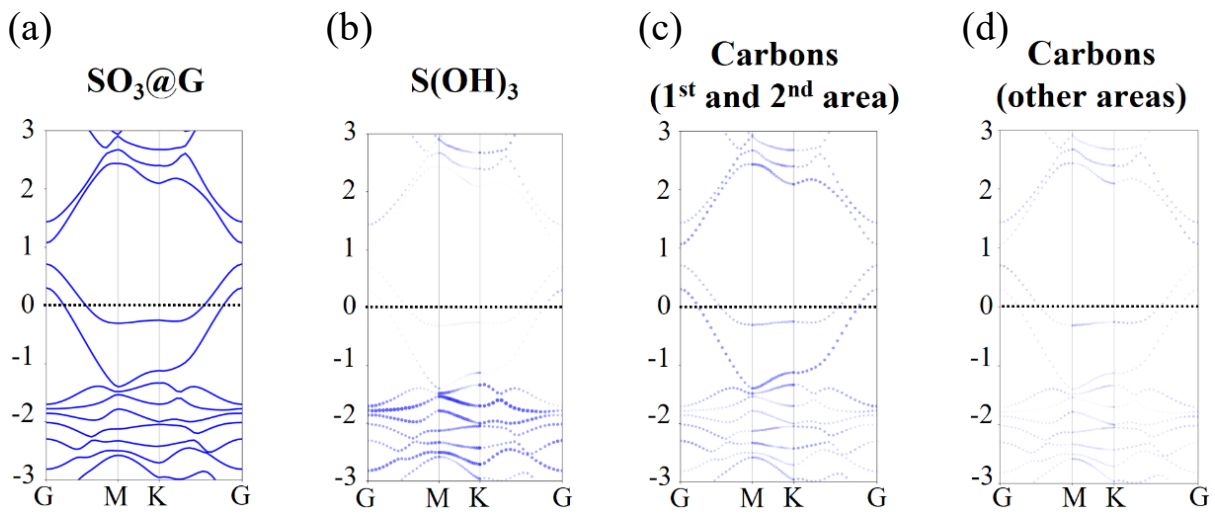

Fig. S7. Decomposed band structures of (a) SO_3@G, (b) $S(OH)_3$, (c) carbons of 1st and 2nd area, and (d) carbons of other areas. Black dotted line indicates the Fermi level.

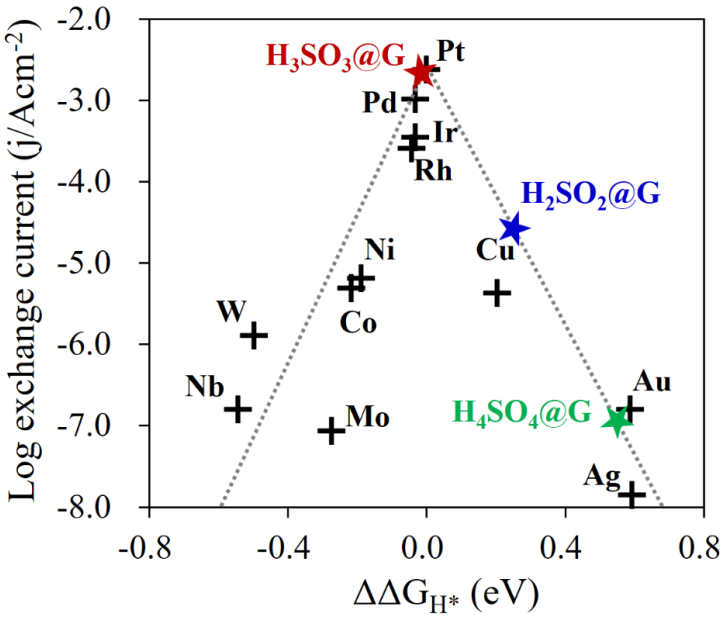

Fig. S8. Relative hydrogen adsorption free energies ($\Delta\Delta G_{H*}$) of the SO_x@G (x=2, 3 and 4). The volcano plot (gray dashed lines) for pure metal catalysts can be illustrated by the relation between the experimental exchange current and theoretical $\Delta\Delta G_{H*}$

With understanding in HER activity of SO_x@G, we turned to infer the experimental log exchange currents of SO_x@G by using the volcano plot for pure elemental metals, which was obtained from the relation between experimental exchange currents and theoretical ΔG_{H^*} values for Pt, Pd, Ir, Rh, Ni, Co, Cu, W, Nb, Mo, Ag, and Au, as shown in Fig. S8.[2-5] For easy comparison of the HER activity with Pt, we used relative hydrogen adsorption free energies ($\Delta\Delta G_{H*}$) of SO_x@G compared to ΔG_{H^*} of Pt, defined by $\Delta\Delta G_{H^*} = \Delta G_{H^*} - \Delta G_{Pt-H^*}$.

Looking at the exchanged current values of SO_x@G based on $\Delta\Delta G_{H^*}$, we can deduce that the SO_3@G has exchanged current value of -2.68 Acm^{-2} locating close to the peak of volcano plot, which is close to Pt as -2.63 Acm^{-2}. On the contrary, in the case of SO_2@G with -4.61 Acm^{-2} and SO_4@G with -6.94 Acm^{-2}, these are HER-inactive due to the unfavorable H adsorption locating on the right side of volcano plot. After theoretically confirming log values obtained from the

correlation between i_0 and $\Delta\Delta G_{H^*}$, we can once again verify the crucial role of SO_3 in acidic environment for HER.

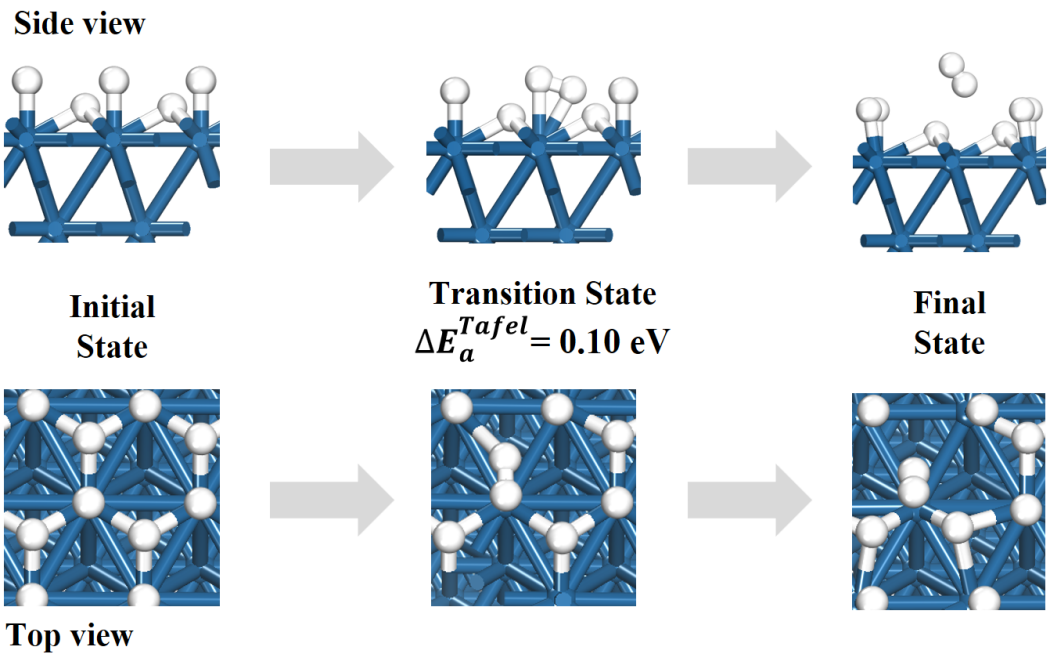

Fig. S9. Tafel reaction on the Pt(111) surface. E_a indicates the activation energy barrier for the Tafel process.

In the case of Pt(111) surface, the Gibbs free energy close to zero ($\Delta G_{H^*} \cong 0$) occurs around 100% H coverage. Therefore, it is most likely that the hydrogen evolution reaction is mainly driven by the hydrogen adsorption/desorption at 100% coverage. This is in quite good agreement with the experimental work of Markovic *et al*.[6] After confirming the optimal H coverage on the Pt(111) surface, we examined activation energies for the Volmer and Tafel reaction using this optimal structure. From Fig. S9, one can see that the activation energy for Tafel is 0.10 eV.

References

1. P. Atkins, Physical Chemistry. 10th ed.; Oxford University Press: Oxford, U.K., 2014, 1–1008.
2. S. Trasatti, *J. Electroanal. Chem.* 1972, **39** (1), 163-184.
3. J. Perez, E. R. Gonzalez, H. M. Villullas, *J. Phys. Chem. B.* 1998, **102** (52), 10931-10935.
4. D. Eberhardt, E. Santos, W. Schmickler, *J. Electroanal. Chem.* 1999, **461** (1-2), 76-79.
5. O. Savadogo, K. Amuzgar, D. L. Piron, *Int. J. Hydrogen. Energ.* 1990, **15** (11), 783-788.
6. N. M. Markovic, B. N. Grgur, P. N. Ross, *J. Phys. Chem. B.* 1997, **101**, 5405.