Graphene Supported Single Metal Atom Catalysts for Efficient Hydrogen Oxidation Reaction in Alkaline Media

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Table S1 Calculated binding energy of M with the divacancy graphene (E_b), distance of M−*ortho*-C (d(M−*ortho*-C)), and height (h(M)) of M over the graphene surface for M/G.

Catalysts	E_b (eV)	d(M−*ortho*-C) (Å)	h(M) (Å)
Cr/G	−4.03 (−4.18)	1.974	0.757
Mn/G	−4.27 (−4.41)	1.957	0.693
Fe/G	−5.22 (−5.40)	1.939	0.628
Co/G	−5.64 (−5.77)	1.892	0.491
Ni/G	−6.28 (−6.43)	1.891	0.017
Pt/G	−7.10 (−7.16)	1.981	0.763

Note: (i) Values in the parentheses are the results calculated by the HSE06 functional. (ii) The binding energy (E_b) of M with the divacancy graphene (DG) for M/G was calculated by the equation:

$$E_b = E_{M/G} - (E_M + E_{DG})$$

where $E_{M/G}$, E_M, and E_{DG} are the total energy of M/G, the metal atom M, and the graphene with a divacancy defect, respectively.

Table S2 Calculated adsorption energy (E_{ads}) of H* on M/G with and without OH*.

Catalysts	E_{ads}(H*) (eV)	E_{ads}(H*+OH*) (eV)
Cr/G	−3.08	−2.88
Mn/G	−2.94	−2.87
Fe/G	−2.98	−2.91
Co/G	−3.01	−2.86
Ni/G	−2.97	−2.80
Pt/G	−2.90	−2.68

Table S3 Calculated adsorption energy (E_{ads}) of H_2* on M/G with and without OH*.

Catalysts	$E_{ads}(H_2*)$ (eV)	$E_{ads}(H_2*+OH*)$ (eV)
Cr/G	−0.16	−0.83
Mn/G	−0.16	−0.82
Fe/G	−0.15	−0.30
Co/G	−0.15	−0.31
Ni/G	−0.16	−0.20
Pt/G	−0.19	−0.27

Table S4 Calculated adsorption energy (E_{ads}) of H_2O* on M/G with and without OH*.

Catalysts	E_{ads}(H_2O*) (eV)	E_{ads}(H_2O*+OH*) (eV)
Cr/G	−0.43	−0.62
Mn/G	−0.41	−0.62
Fe/G	−0.39	−0.62
Co/G	−0.38	−0.62
Ni/G	−0.36	−0.58
Pt/G	−0.36	−0.63

Table S5 Calculated bond lengths (d) and bond angle (θ) for the adsorption on M/G.

Species	Parameters	Cr/G	Mn/G	Fe/G	Co/G	Ni/G	Pt/G
OH*	d(M–OH)	1.759	1.747	1.751	1.778	1.842	2.042
H_2*	d(M–H_2)	3.196	3.118	3.041	2.848	2.572	2.569
H_2O*	d(M–H_2O)	3.087	3.041	2.861	2.980	2.764	2.518
H*	d(*ortho*-C–H)	1.131	1.126	1.120	1.129	1.129	1.100
H*	θ(H–C–C)	113.8	114.4	114.8	114.3	116.7	115.5

Table S6 Rate constants (*k*) for the elementary reactions involved in the HOR on M/G at 298 K.

Catalysts	Tafel (s^{-1})	Heyrovsky (s^{-1})	$H_2^*+OH^*$ (s^{-1})	Volmer (s^{-1})	H^*+OH^* (s^{-1})
Cr/G	5.14×10^{5}	5.72×10^{5}	4.88×10^{-7}	3.87×10^{11}	3.87×10^{-4}
Mn/G	4.31×10^{6}	9.81×10^{7}	4.93×10^{-7}	8.32×10^{9}	3.17×10^{2}
Fe/G	2.48×10^{4}	6.98×10^{5}	6.37×10^{-8}	1.89×10^{7}	4.23×10^{2}
Co/G	6.38×10^{3}	5.76×10^{6}	1.37×10^{-11}	6.53×10^{10}	2.17×10^{2}
Ni/G	3.17×10^{2}	8.72×10^{7}	1.36×10^{-9}	3.22×10^{9}	2.13×10^{1}
Pt/G	6.51×10^{6}	2.37×10^{8}	1.41×10^{-2}	5.87×10^{13}	3.47×10^{3}

Table S7 Rate constants *k* for the elementary reactions involved in the HOR on M/G at 340 K.

Catalysts	Tafel (s^{-1})	Heyrovsky (s^{-1})	$H_2^*+OH^*$ (s^{-1})	Volmer (s^{-1})	H^*+OH^* (s^{-1})
Cr/G	1.97×10^{6}	6.48×10^{6}	1.78×10^{-5}	1.18×10^{12}	6.23×10^{-6}
Mn/G	3.41×10^{6}	9.14×10^{8}	5.27×10^{-6}	7.22×10^{8}	5.31×10^{1}
Fe/G	2.89×10^{5}	8.06×10^{6}	6.33×10^{-10}	3.19×10^{8}	7.63×10^{2}
Co/G	4.11×10^{5}	1.33×10^{7}	2.93×10^{-9}	4.13×10^{10}	1.71×10^{3}
Ni/G	3.17×10^{4}	4.73×10^{8}	4.55×10^{-9}	1.10×100^{9}	2.14×10^{3}
Pt/G	9.58×10^{7}	1.01×10^{10}	3.01×10^{0}	8.87×10^{12}	1.58×10^{5}

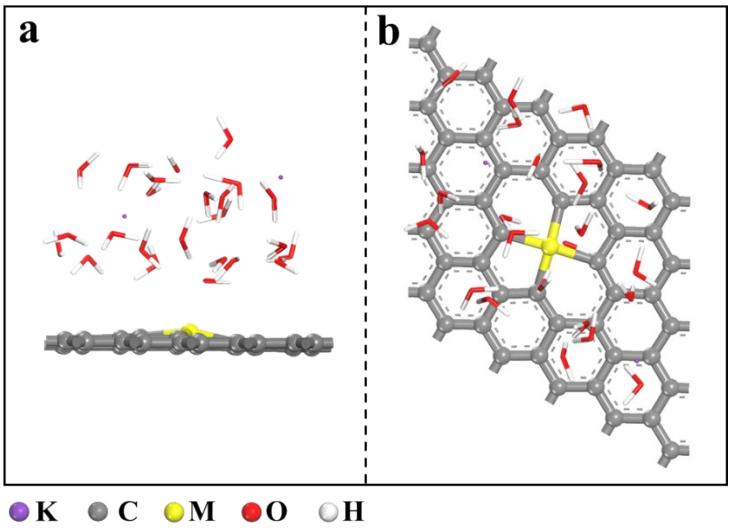

Fig. S1 (a) Side and (b) top views of the configurations for the M/G catalysts with the K^+OH^- solution.

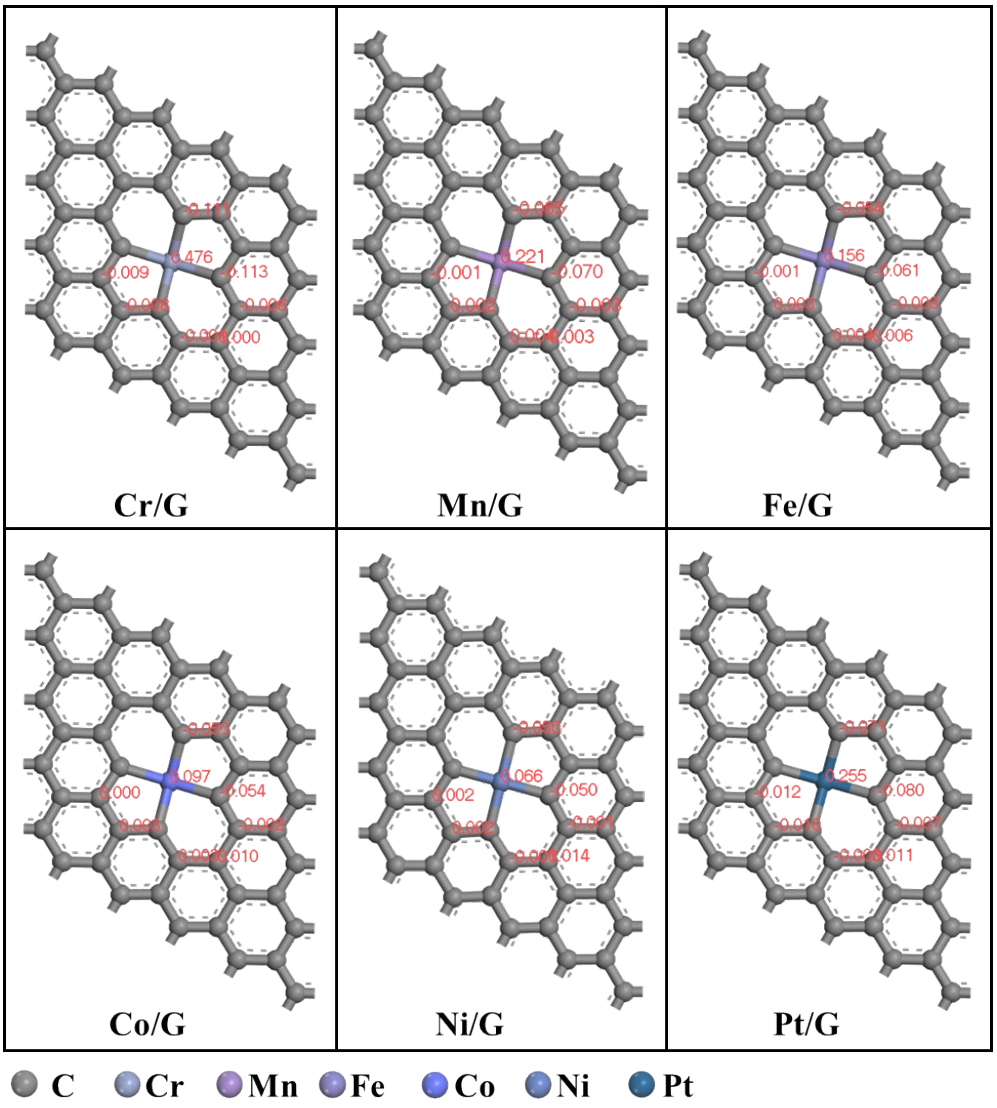

Fig. S2 Population of Hirshfeld charges (in e) in the M/G catalysts.

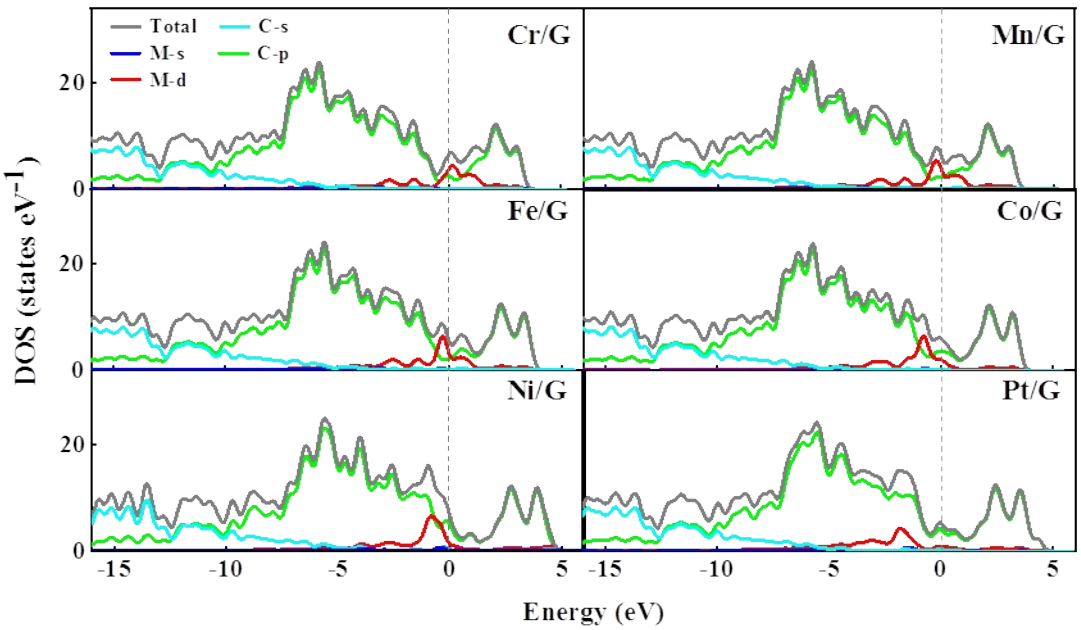

Fig. S3 Partial density of states (PDOS) of the M/G catalysts.

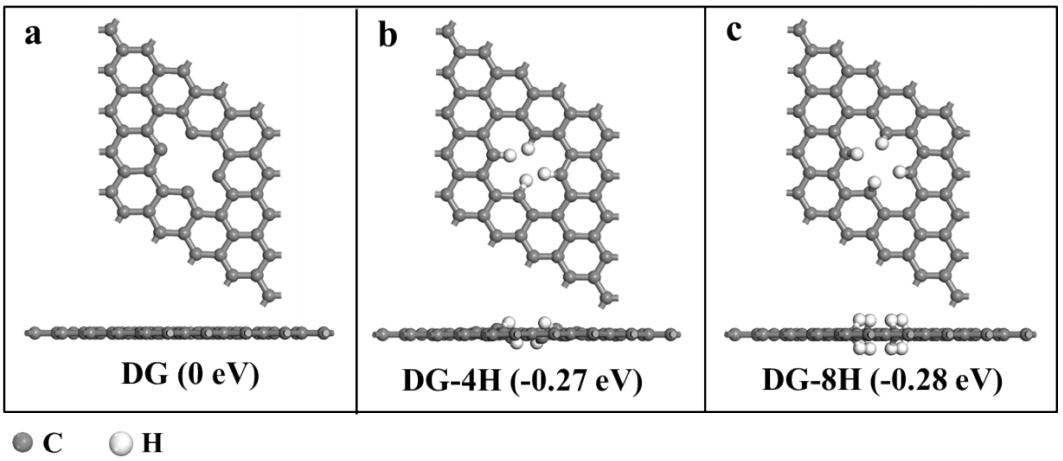

Fig. S4 Optimized structures of DG-nH: (a) DG, (b) DG-4H, and (c) DG-8H. Values in the parentheses are the energies calculated by the following equation: $E_{rel} = E_{DG\text{-}nH} - E_{DG} - \frac{n}{2}\mu_{H_2}$, where $E_{DG\text{-}nH}$ and E_{DG} are the total energy of DG-nH and DG, respectively. μ_{H_2} is the chemical potential of the H_2 molecule.

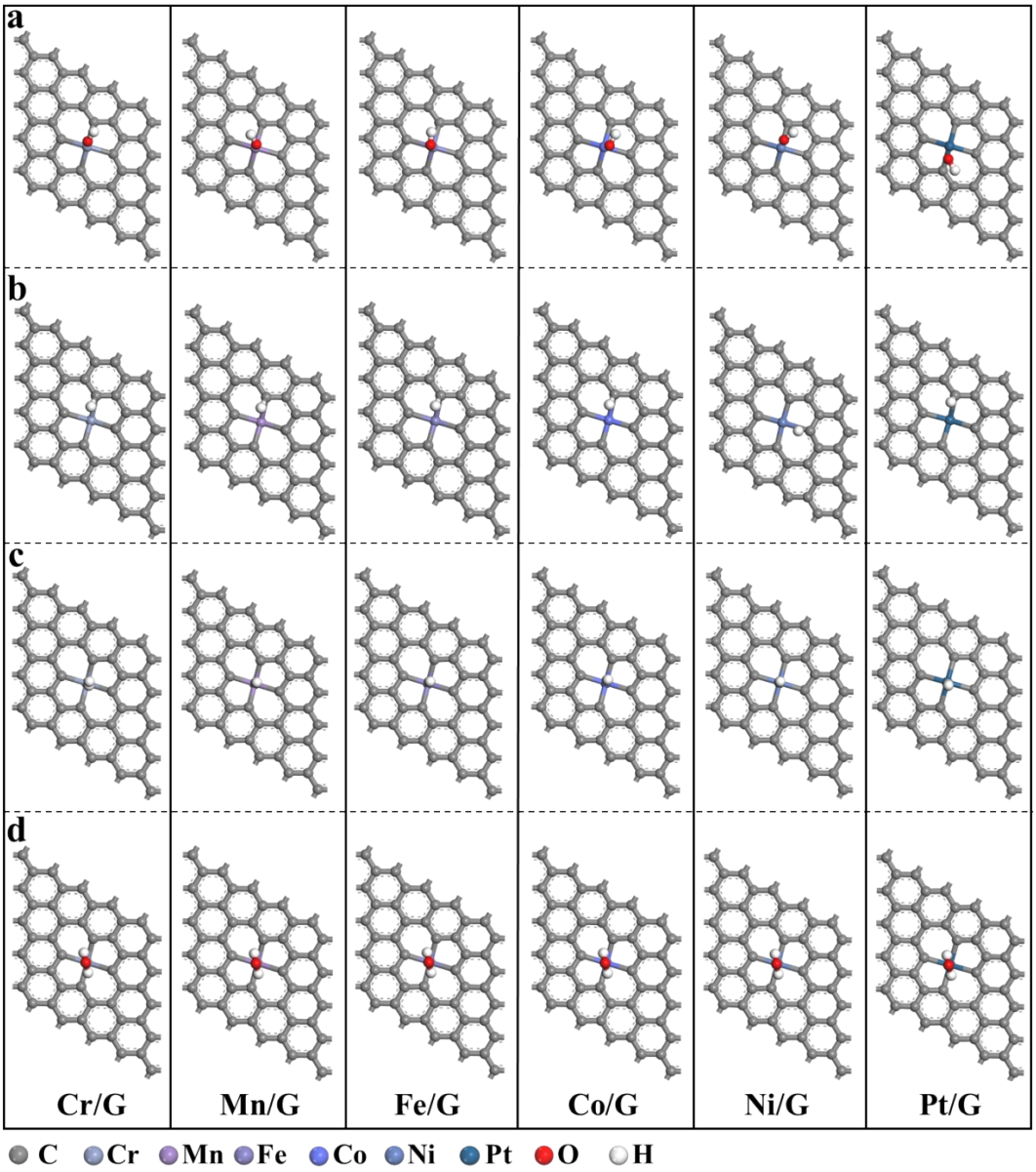

Fig. S5 Adsorption configurations of (a) OH*, (b) H*, (c) H_2*, and (d) H_2O* on the M/G catalysts.

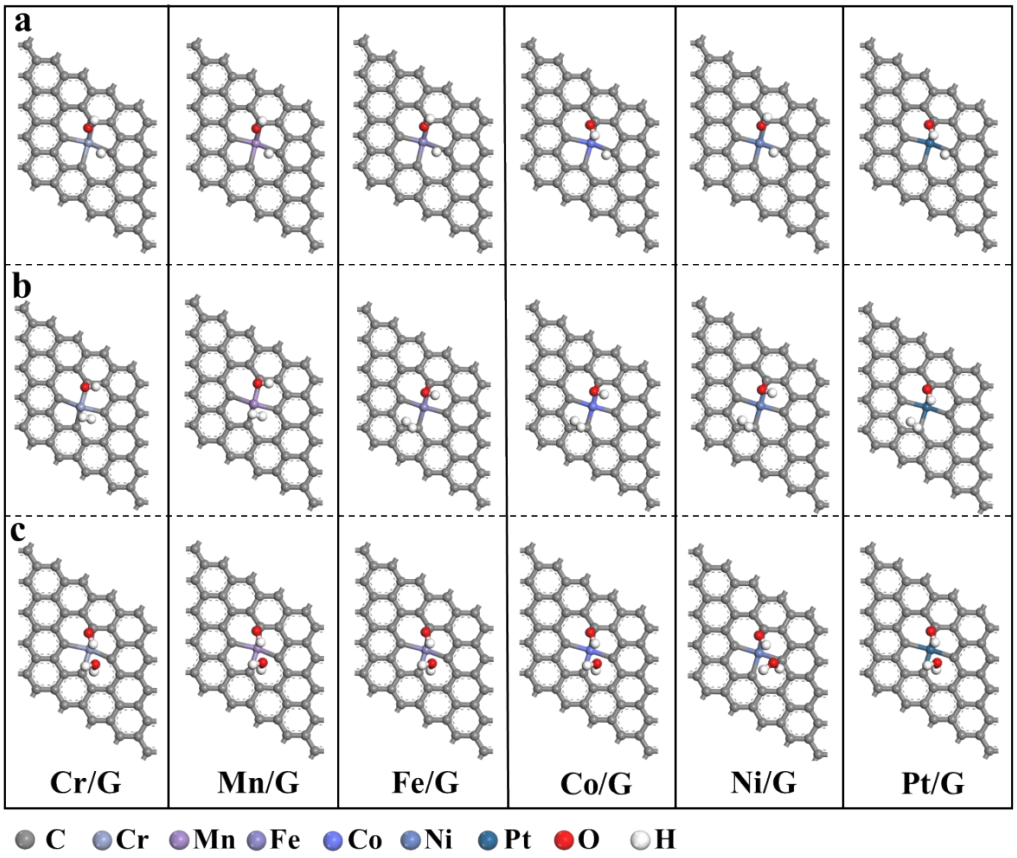

Fig. S6 Co-adsorption configurations of (a) H*+OH*, (b) H_2*+OH*, and (c) H_2O*+OH* on the M/G catalysts.

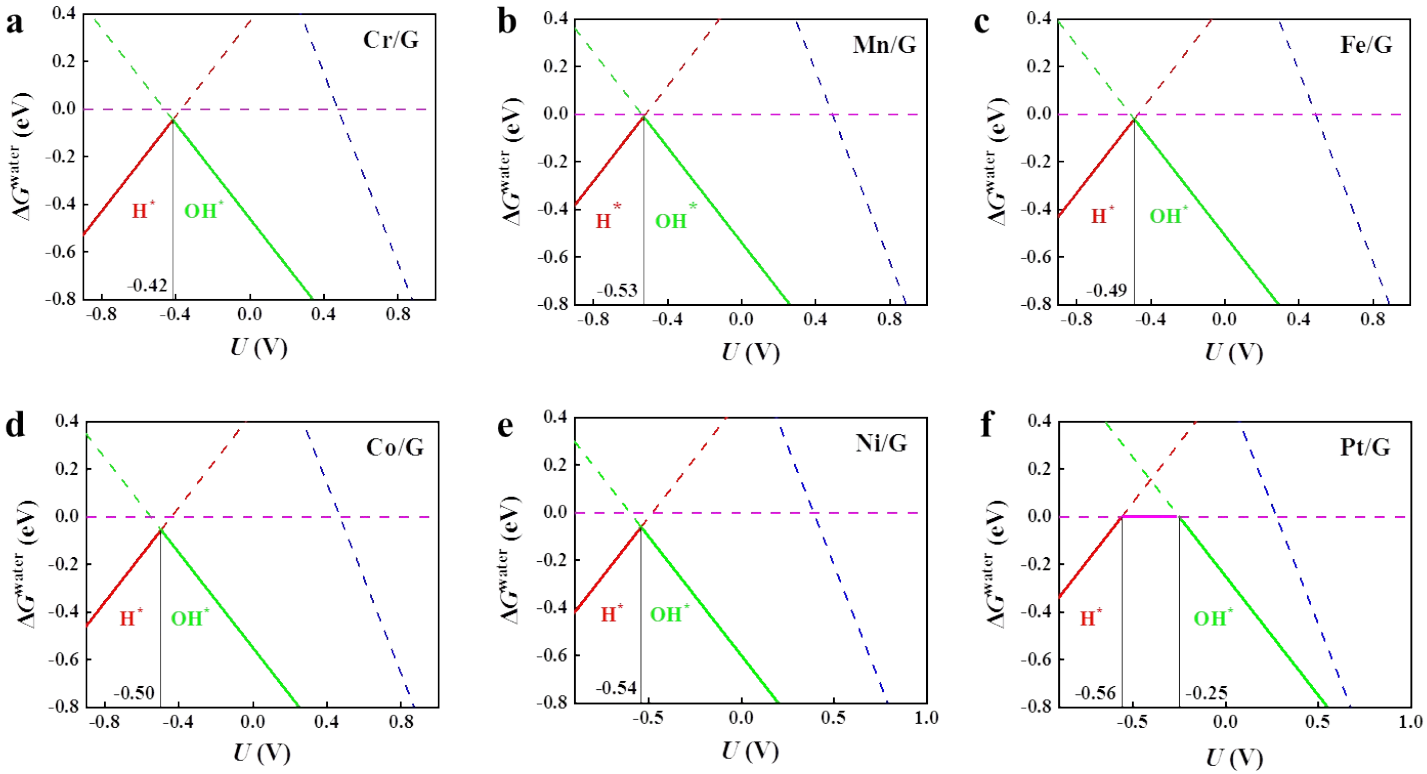

Fig. S7 Phase diagram showing the free energy for different surface structures for water in contact with (a) Cr/G, (b) Mn/G, (c) Fe/G, (d) Co/G, (e) Ni/G, and (f) Pt/G. The free energy for liquid water at 340 K is defined as $\Delta G^{water}(U) = 0$ (pink line). $\Delta G^{water}_{H^*}(U) = \Delta G^{water}_{H^*}(0) + eU$ (red line), $\Delta G^{water}_{OH^*}(U) = \Delta G^{water}_{OH^*}(0) - eU$ (green line), and $\Delta G^{water}_{O^*}(U) = \Delta G^{water}_{O^*}(0) - 2eU$ (blue line).