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Electronic Supplementary Information

Theoretical Design on Series of 2D TM-C_3N_4 and TM-C_3N_4@graphene (TM = V, Nb and Ta) Nanostructures with Highly Efficient Catalytic Activity for Hydrogen Evolution Reaction

Ting Wang, Guangtao Yu*, Jingwei Liu, Xuri Huang and Wei Chen*

Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, People's Republic of China

*To whom correspondence should be addressed. Email: yugt@jlu.edu.cn (G.Y.), w_chen@jlu.edu.cn (W.C.)

(I) The possible effect of water as proton resource or serving as a solvent

In hydrogen evolution reaction (HER), water serves as solvent and is possible to participate in the reaction as proton resource. Surface phase changes for the studied systems may occur as a consequence of proton transfer between water and the adsorbents and electron transfer between the absorbents and the electrode. The reactions connecting the different states of the surface can be written such as

$$H_2O + * \leftrightarrow OH* + e^- + H^+ \qquad (1)$$

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

$$* + e^- + H^+ \leftrightarrow H* \qquad (3)$$

where * denotes a free site on the surface, e^- is an electron in the electrode, and H^+ denotes a proton solvated in the electrolyte.

Therefore, dissociation of water may lead to several surface intermediates including OH, O, and H species. In this study, we initially explore the adsorption of OH, O, and H species in solution to get the stable surface phase by using the following correlative formulas. Specifically, adsorption free energy for OH, O and H is calculated by the following equation:

$$\Delta G_w = \Delta E_w + \Delta ZPE - T\Delta S \qquad (4)$$

where the reaction energy in water, ΔE_w, which refers here to the change in the electronic energy between the products and the reactants, is calculated directly from the DFT results. For the eqns (1) and (2), ΔE_w can be calculated via the formula $\Delta E_w = E_{ads} + n/2 E_{H_2} - E_{H_2O}$, where n is 1 and 2 for eqn (1) and eqn (2), respectively. For eqn (3), ΔE_w can be calculated by the formula $\Delta E_w = E_{ads} - 1/2 E_{H_2}$. Note that at standard conditions, the solvated hydrogen (*i.e.* $H^+ + e^-$ in solution) is in equilibrium with H_2 (gas). In addition, H_2O in the gas phase is also employed as reference state, where the entropy for gas phase water is computed at 0.035 bars, since it is the equilibrium pressure in contact with liquid water at 298 K. The free energy of gas phase water at these conditions is equal to the free energy of liquid water. The difference in zero point energies, ΔZPE, and the change in entropy ΔS are determined by using DFT-calculated vibrational frequencies and standard tables for the gas-phase molecule. Note that for all the above details, we follow the schemes proposed by Nørskov *et al.*[1]

Initially, we compute the ΔG_{OH*}, ΔG_{O*} and ΔG_{H*} values on the two dimensional (2D) Nb-C_3N_4 by sampling the possible adsorption sites including the top site (T_{Nb}) over the Nb atom, the top site (T_C) over the C atom and the top site (T_N) over the N atom. The correlative computed results are listed in Table S1. It should be noted that the adsorption of O at T_C and T_N sites and OH at T_N site cannot be obtained, all of which can tend to be at the T_{Nb} during the optimization process. Specifically, we can find that at the T_{Nb} site on one surface of Nb-C_3N_4, the computed ΔG_{O*} value (-2.009 eV) is more negative than ΔG_{OH*} (-1.147 eV) and ΔG_{H*} (-0.602 eV), indicating the strongest interaction of O with Nb-site. Thus, Nb-site is more favorable to be occupied by O rather than OH or H. Based on this structure (denoted by O-Nb-C_3N_4), we further compute the ΔG_{OH*}, ΔG_{O*} and ΔG_{H*} values at the T_{Nb} site on opposite surface of Nb-C_3N_4. It can be found that OH is more likely to occupy the Nb-site from the other side, as reflected by the most negative ΔG_{OH*} value (-1.243 eV). Differentially, the occupation of H can be dominant for non-metallic C/N-sites, as shown in Table S1. Eventually, we can get a stable surface phase, namely O/OH-Nb-C_3N_4, in which the metal Nb-site is occupied by O and OH from two sides (Figure 2a). The similar situation can be also observed in the analogous TM-C_3N_4 (TM = V and Ta) systems, that is, O can occupy T_{TM} site firstly from one side, and then OH occupies T_{TM} site from the other side, as revealed by the correlative computed results (Table S1). Consequently, the stable surface phase for TM-C_3N_4 (TM = V and Ta) can be also obtained, namely O/OH-V-C_3N_4 and O/OH-Ta-C_3N_4, respectively (Figure 4a and 4b). Moreover, we calculate the ΔG_{OH*}, ΔG_{O*} and ΔG_{H*} values on TM-C_3N_4@G (TM = V, Nb and Ta), and the correlative computed results are collected in Table S1. We can find T_{TM} site is more energetically favorable to be occupied by O, in view of the more negative ΔG_{O*} value at T_{TM} site (Table S1). As a result, we can obtain the stable surface phase for TM-C_3N_4@G (TM = V, Nb and Ta), namely O-V-C_3N_4@G, O-Nb-C_3N_4@G and O-Ta-C_3N_4@G, respectively (Figure 6).

Subsequently, based on the correlative structural models, we explore the HER catalytic activity of these systems in solvation and in vacuum to examine the solvation effect, by computing ΔG_{H*} values of three representative sites including T_O, T_C and T_N. The computed results are presented in Table S2. It can be found that all the computed ΔG_{H*} values are almost no change ($\leq$ 0.079 eV) between the two situations, indicating the negligible solvation effect. Therefore, to make the computational cost less demanding, in this study we compute ΔG_{H*} value in the vacuum condition for estimating the HER activity for the studied systems. The correlative computed results have been presented and discussed in the main text.

Reference

1. J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov and U. Stimming, *J. Electrochem. Soc.*, 2005, **152**, J23-J26.

Table S1 The computed ΔG_{OH*}, ΔG_{O*} and ΔG_{H*} values in solvation for the sampled T_{TM}, T_C and T_N sites on TM-C_3N_4 and TM-C_3N_4@G (TM = V, Nb and Ta) systems. Note that I represents one side of TM-C_3N_4, while Π means another side for TM-C_3N_4 after O occupying Nb-site.

System	Adsorption site	ΔG_{OH*}（eV)	ΔG_{O*}（eV)	ΔG_{H*}（eV)
Nb-C_3N_4	I-T_{Nb}	-1.147	-2.009	-0.602
	I-T_C	-0.327	--	-0.700
	I-T_N	--	--	1.099
	Π-T_{Nb}	-1.243	-0.183	0.203
	Π-T_C	-0.563	--	-0.857
	Π-T_N	--	--	0.930
V-C_3N_4	I-T_V	-1.010	-1.386	-0.346
	I-T_C	-0.183	--	-0.705
	I-T_N	--	--	1.063
	Π-T_V	-0.432	0.190	0.965
	Π-T_C	-0.103	--	-0.250
	Π-T_N	--	--	0.731
Ta-C_3N_4	I-T_{Ta}	-1.554	-2.706	-0.754
	I-T_C	-0.466	--	-0.830
	I-T_N	--	--	1.003
	Π-T_{Ta}	-1.428	-0.256	0.010
	Π-T_C	-0.546	--	-0.866
	Π-T_N	--	--	1.049
V-C_3N_4@G	T_V	-0.880	-1.159	-0.078
	T_C	0.037	-0.026	-0.302
	T_N	--	--	0.910
Nb-C_3N_4@G	T_{Nb}	-1.051	-1.810	-0.422
	T_C	-0.131	-0.027	-0.469
	T_N	--	--	1.261
Ta-C_3N_4@G	T_{ta}	-1.438	-2.507	-0.766
	T_C	-0.287	-0.155	-0.623
	T_N	--	--	1.230

Table S2 The computed ΔG_{H*} values in solvation and in vacuum for the sampled T_O, T_C and T_N sites on O/OH-TM-C_3N_4 and O/OH-TM-C_3N_4@G (TM = V, Nb and Ta)

Adsorption site	ΔG_{H*} (eV)	O/OH-Nb-C_3N_4	O/OH-V-C_3N_4	O/OH-Ta-C_3N_4	O-V-C_3N_4@G	O-Nb-C_3N_4@G	O-Ta-C_3N_4@G
T_O	vacuum	0.857	0.129	0.714	0.386	0.873	1.124
	water	0.922	0.160	0.789	0.327	0.794	1.072
T_C	vacuum	-0.245	-0.234	-0.329	-0.372	-0.537	-0.607
	water	-0.288	-0.278	-0.398	-0.347	-0.564	-0.643
T_N	vacuum	1.217	0.453	1.246	0.725	1.109	1.156
	water	1.283	0.526	1.312	0.664	1.049	1.085

(II) The computational test on employing PBE functional to predict HER activity on the single atom catalyst Cu@graphdiyne with known experimental performance

In this work, a computational test is performed through computing the adsorption free energy of hydrogen by PBE functional to predict HER activity on the single atom catalyst (SAC) Cu@graphdiyne with known experimental performance. Figure S1a presents the optimized structure of Cu@graphdiyne, where the Cu atom is inclined to interact with the acetylenic bonds. By comparing the calculated ΔG_{OH*} (2.455 eV), ΔG_{O*} (0.195 eV) and ΔG_{H*} (0.163 eV), we can find that H is more energetically favorable to occupy metal Cu-site (Figure S1b). Such a small ΔG_{H*} value (0.163 eV) at Cu site, which is even close to zero, can reflect the high HER catalytic activity. This is well consistent with the known experimental result, confirming the reliability of PBE calculation in predicting the HER activity for SAC system.

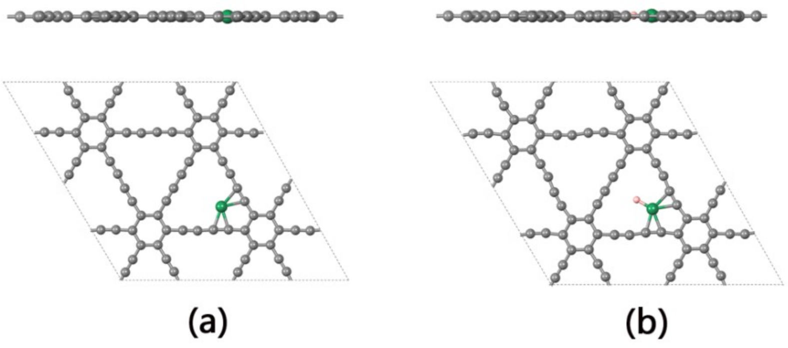
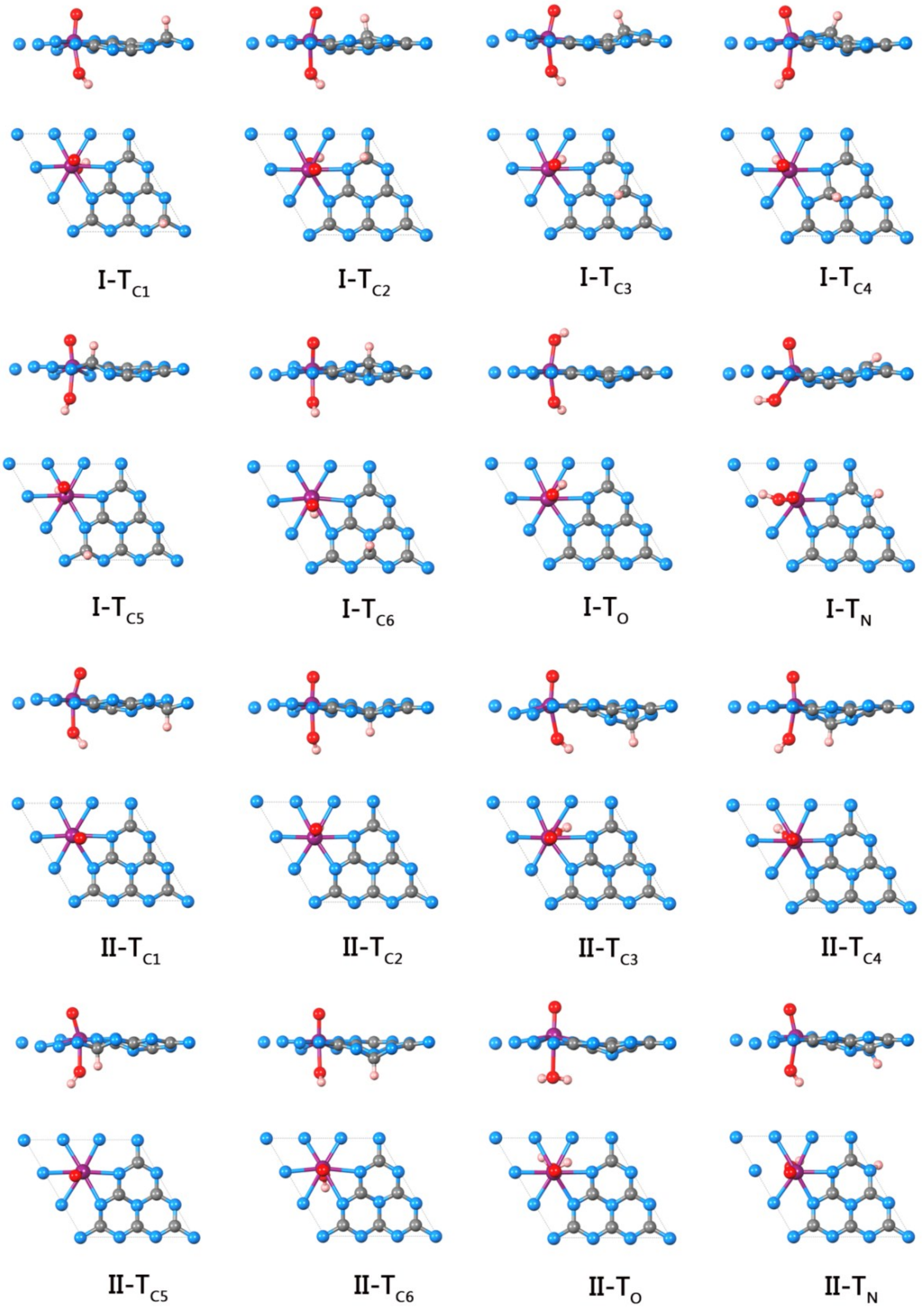


Figure S1 The top and side views of optimized structures for Cu@graphdiyne without (a) and with (b) the adsorption of H* at Cu-site. Note that pink, grey and green spheres represent H, C and Cu atoms, respectively.

(III) The optimized structures with the adsorption of H* at the different sits on O/OH-TM-C_3N_4 and O/OH-TM-C_3N_4@G (TM = V, Nb and Ta)



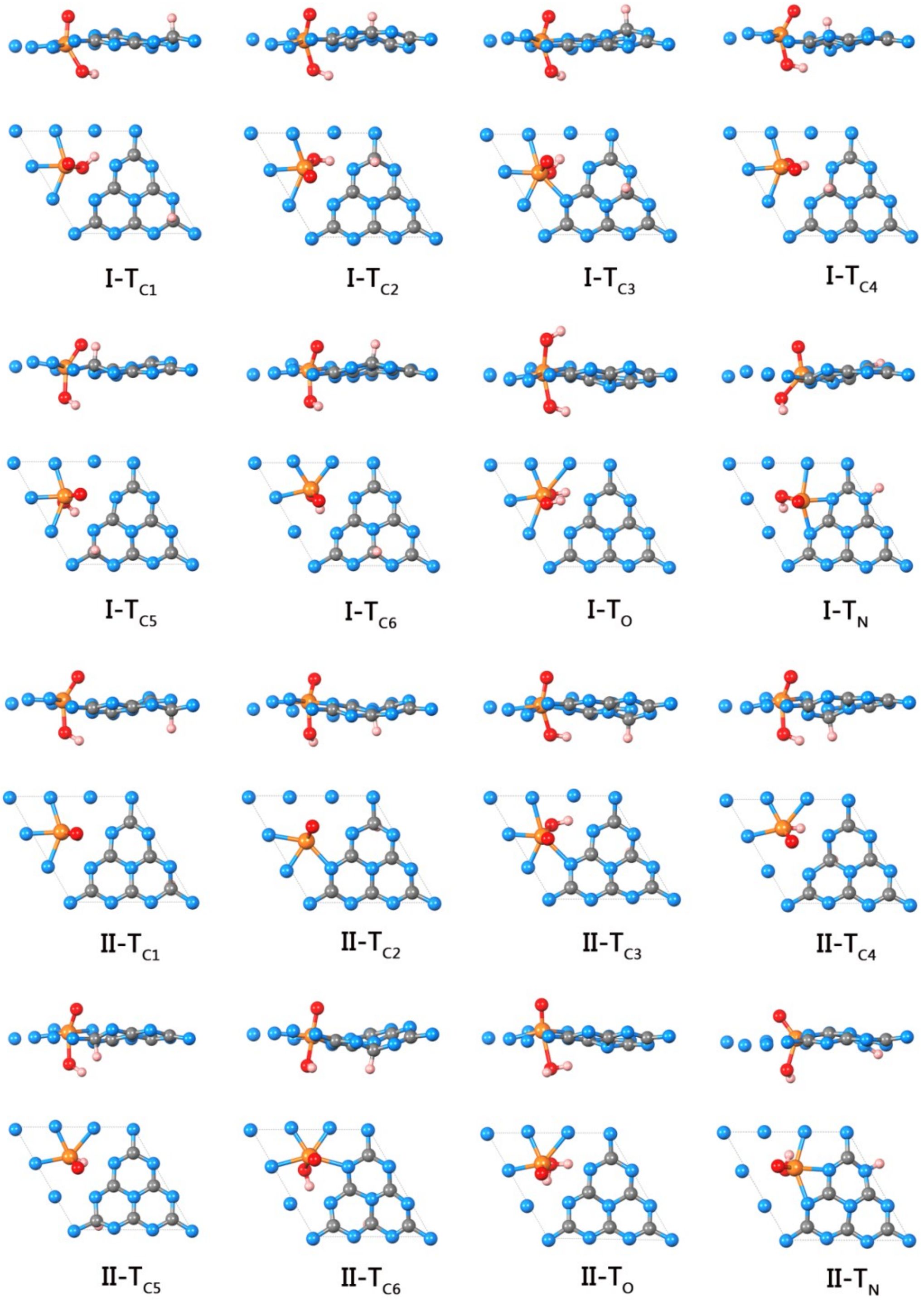
I-T_{C1} I-T_{C2} I-T_{C3} I-T_{C4}

I-T_{C5} I-T_{C6} I-T_{O} I-T_{N}

II-T_{C1} II-T_{C2} II-T_{C3} II-T_{C4}

II-T_{C5} II-T_{C6} II-T_{O} II-T_{N}

(a)



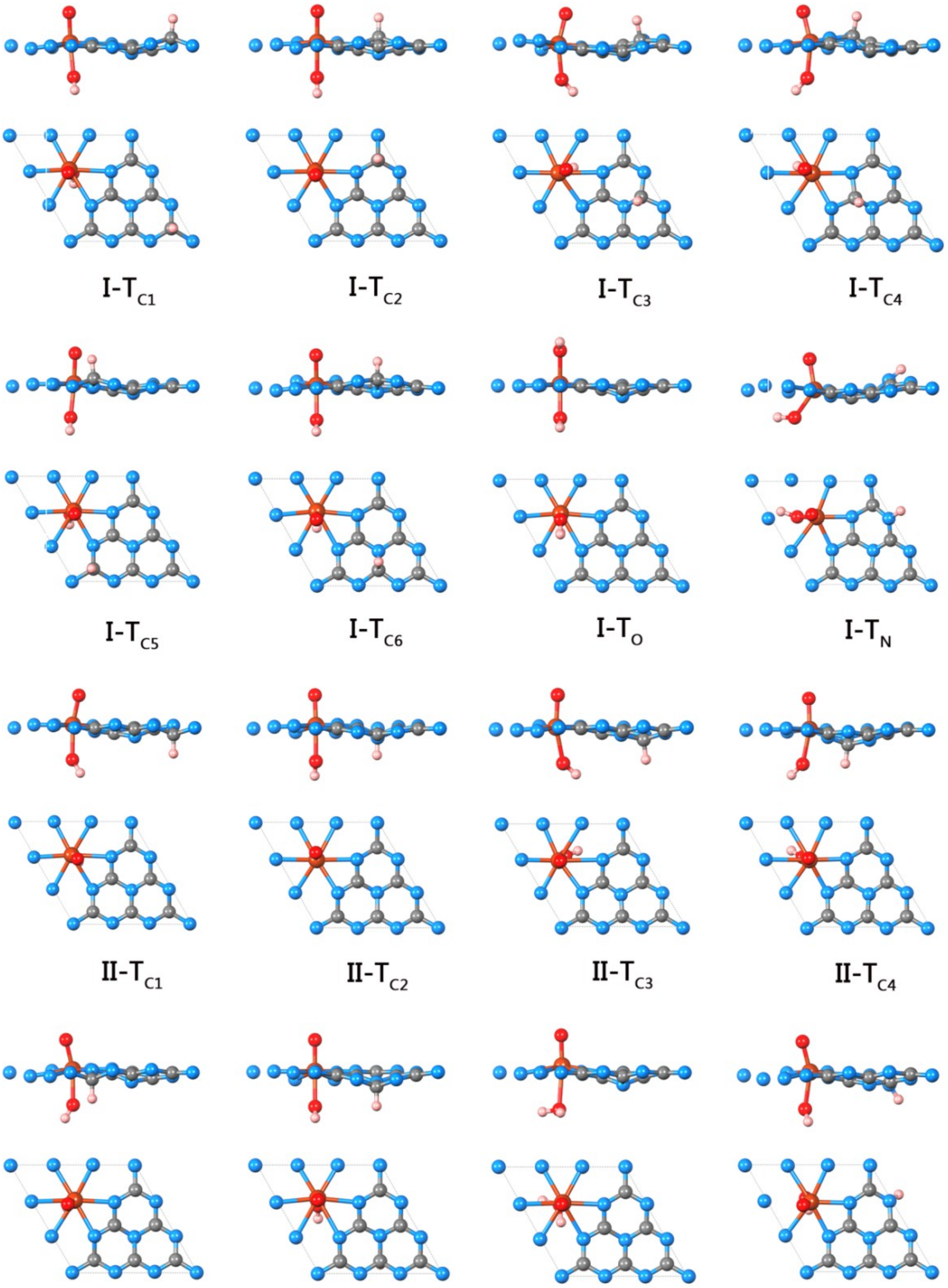
I-T$_{C1}$ I-T$_{C2}$ I-T$_{C3}$ I-T$_{C4}$

I-T$_{C5}$ I-T$_{C6}$ I-T$_{O}$ I-T$_{N}$

II-T$_{C1}$ II-T$_{C2}$ II-T$_{C3}$ II-T$_{C4}$

II-T$_{C5}$ II-T$_{C6}$ II-T$_{O}$ II-T$_{N}$

(b)



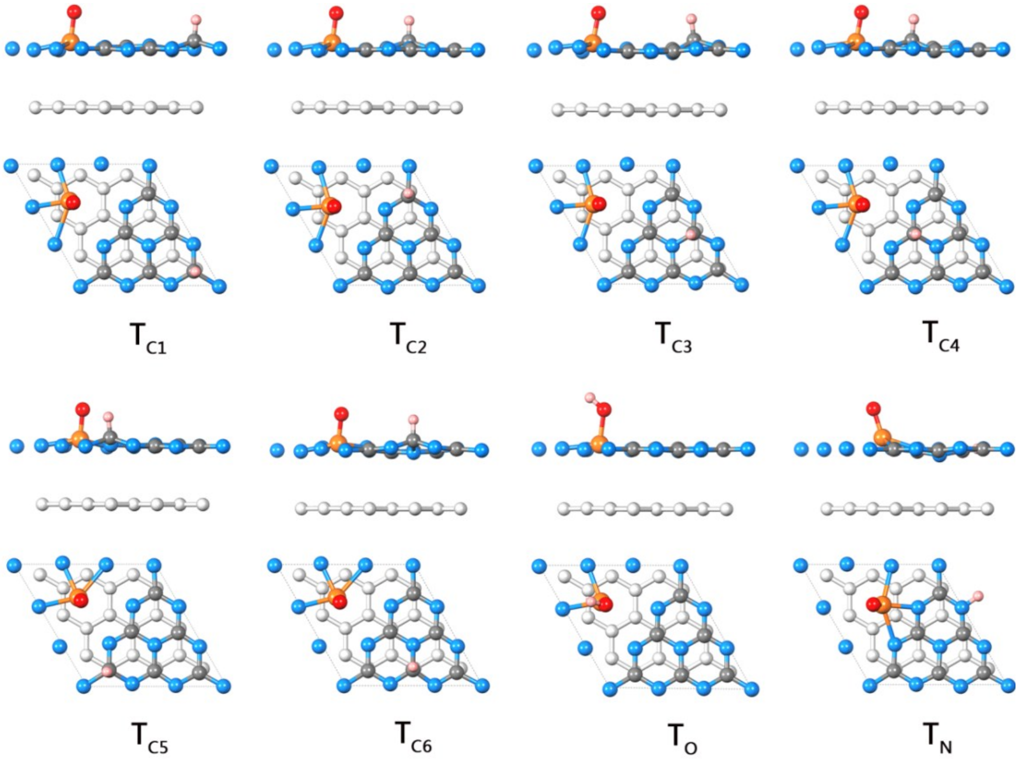
I-T$_{C1}$ I-T$_{C2}$ I-T$_{C3}$ I-T$_{C4}$

I-T$_{C5}$ I-T$_{C6}$ I-T$_{O}$ I-T$_{N}$

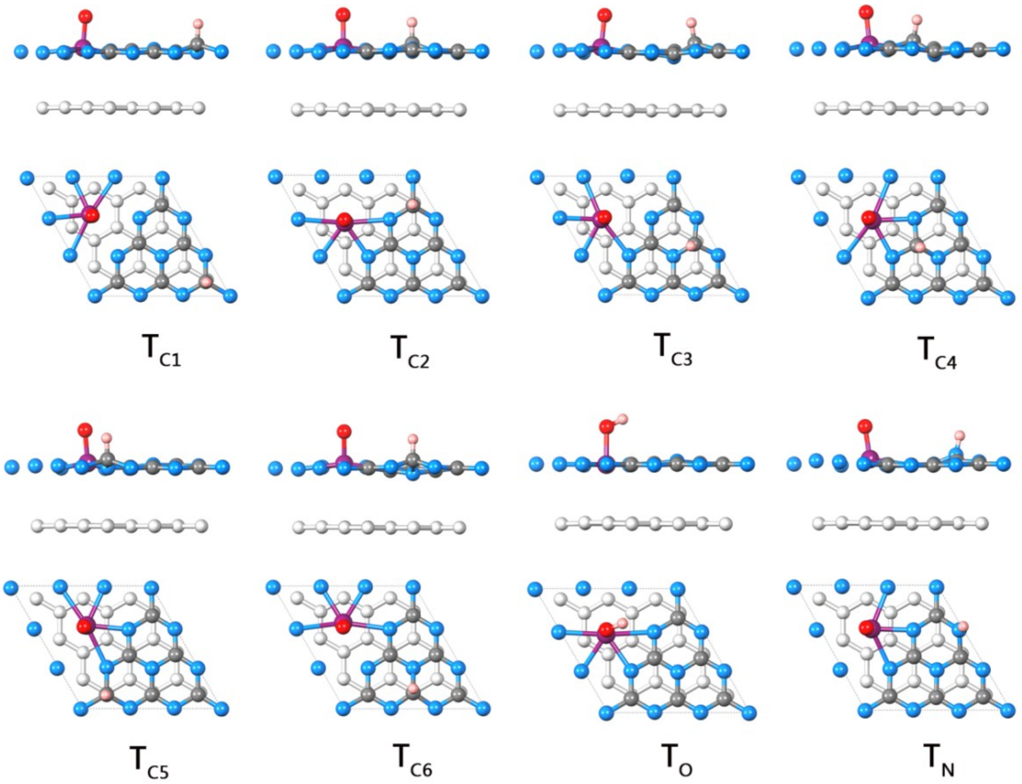
II-T$_{C1}$ II-T$_{C2}$ II-T$_{C3}$ II-T$_{C4}$

II-T$_{C5}$ II-T$_{C6}$ II-T$_{O}$ II-T$_{N}$

(c)



(d)



(e)

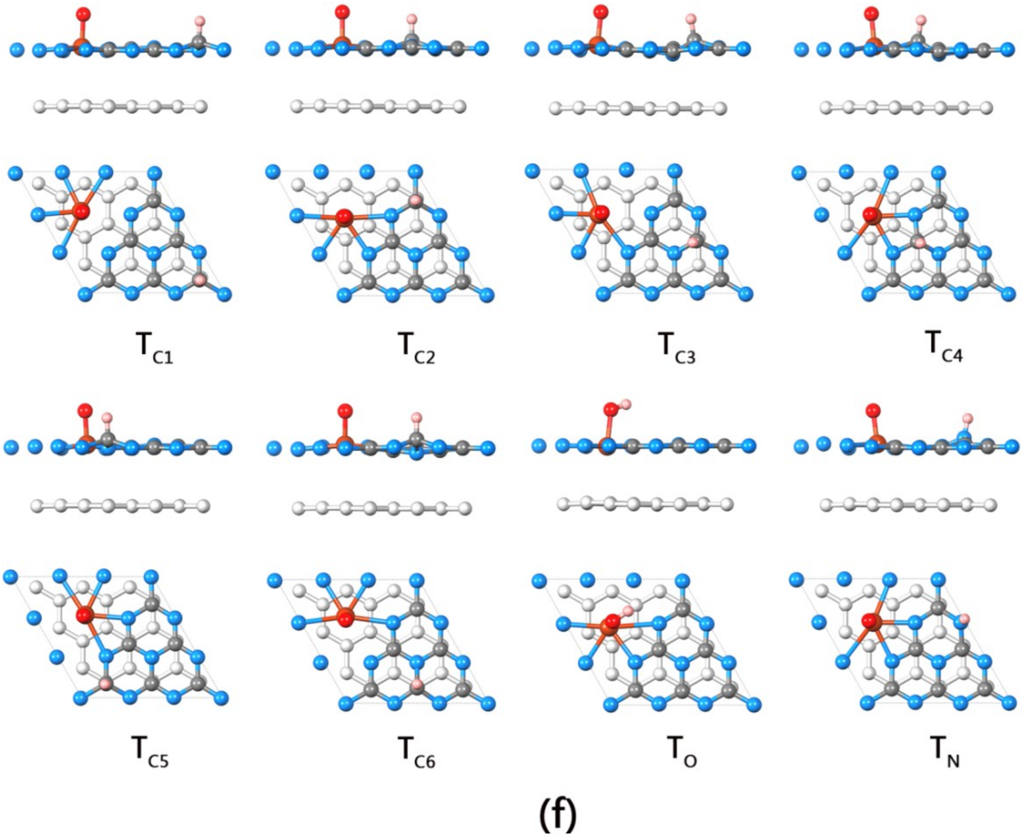


Figure S2 The top and side views of optimized structures with the adsorption of H* at different sites on O/OH-Nb-C_3N_4 (a), O/OH-V-C_3N_4 (b), O/OH-Ta-C_3N_4 (c), O-V-C_3N_4@G (d), O-Nb-C_3N_4@G (e) and O-Ta-C_3N_4@G (f). Note that pink, red, grey, blue, yellow, purple and brown spheres represent H, O, C, N, V, Nb and Ta atoms, respectively, while white sphere represents C atom in the graphene substrate.