Supplementary Information for

Work function-regulated two-dimensional porous C_7N_6-based single-atom catalysts for hydrogen evolution reaction

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To better evaluate the interaction strength between transition metal (TM) and support, the adsorption energies of different TM atoms anchor on C_7N_6 monolayer (TM@C_7N_6) were calculated, as the following formula:

$$E_{ad}=E_{total}-(E_{sub}+E_{TM}$$

where E_{total} represents the total energy of the system, Esub denotes the energy of the substrate, and E_{TM} corresponds to the energy of the adsorbed TM atom. This definition implies that a more negative value of E_{ad} indicates a more stable adsorption structure.

To examine the electrochemical stability of TM@C_7N_6, the dissociation potential (U_{diss}) was calculated:

$$U_{diss}=U^0_{diss}-\frac{E_f}{Ne}$$

where U^0_{diss} and N represent the standard dissolution potential of elements in their bulk structure and the number of electrons involved in the dissolution process, respectively.

Additionally, to evaluate the catalytic activity of HER process, Gibbs free energy of H adsorption (ΔG_{H*}) was calculated based on computational hydrogen electrode (CHE) model, as shown in the following formula:

$$\Delta G=\Delta E_{DFT}+\Delta E_{ZPE}-T\Delta S$$

where ΔE_{DFT}, ΔE_{ZPE}, and ΔS represent the adsorption energy of intermediates, change in zero-point energy, and entropy, respectively.

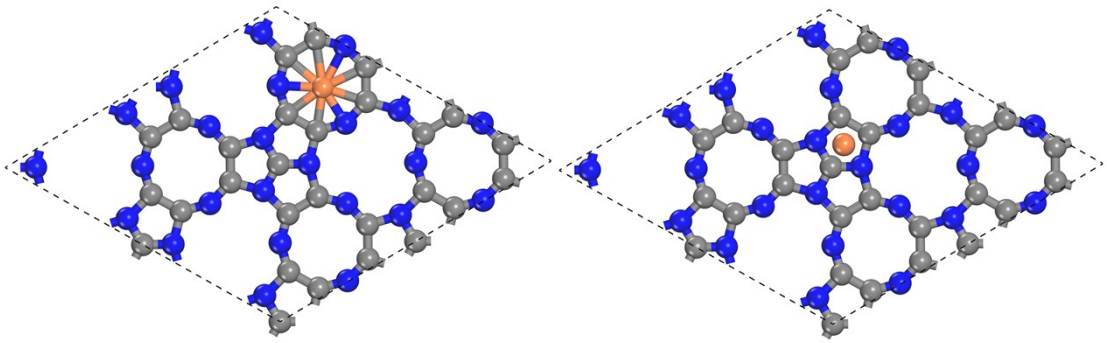


Fig. S1 Geometry structures of TM supported on C_7N_6 in (a) C_6N_3 centers and (b) pentagonal core. The grey, blue, and orange spheres represent C, N and TM elements, respectively.

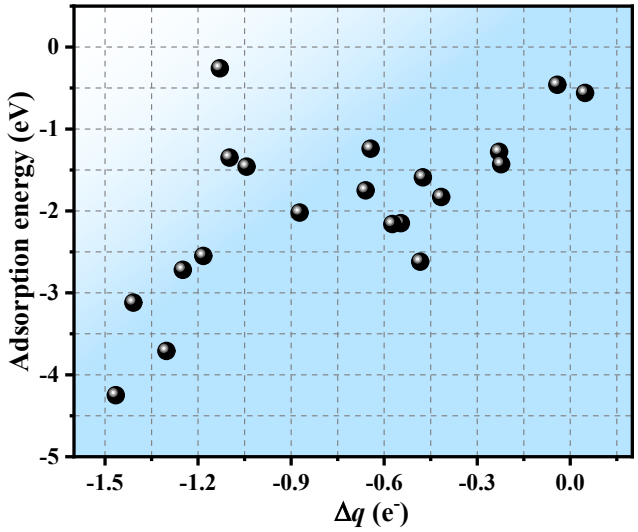
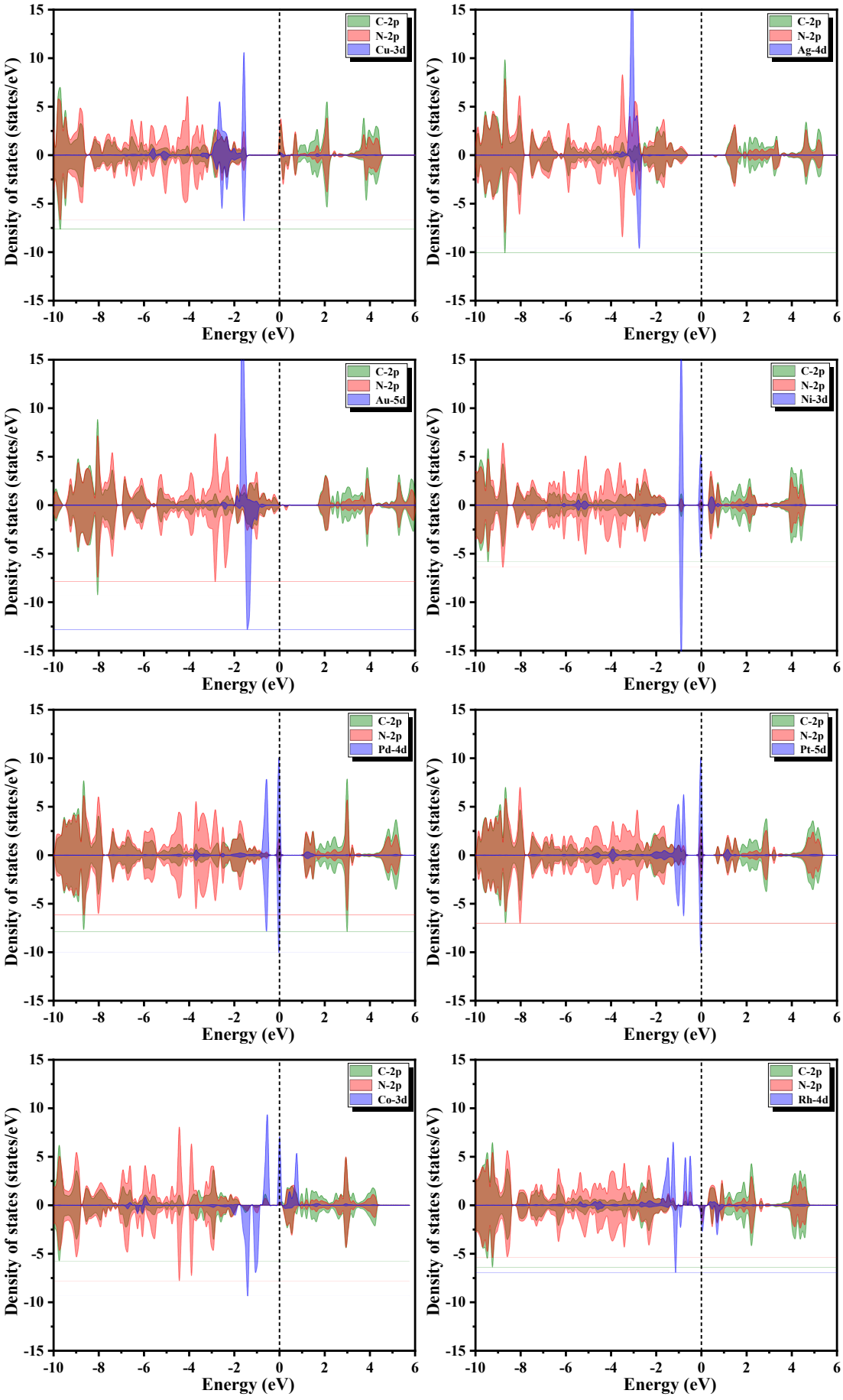
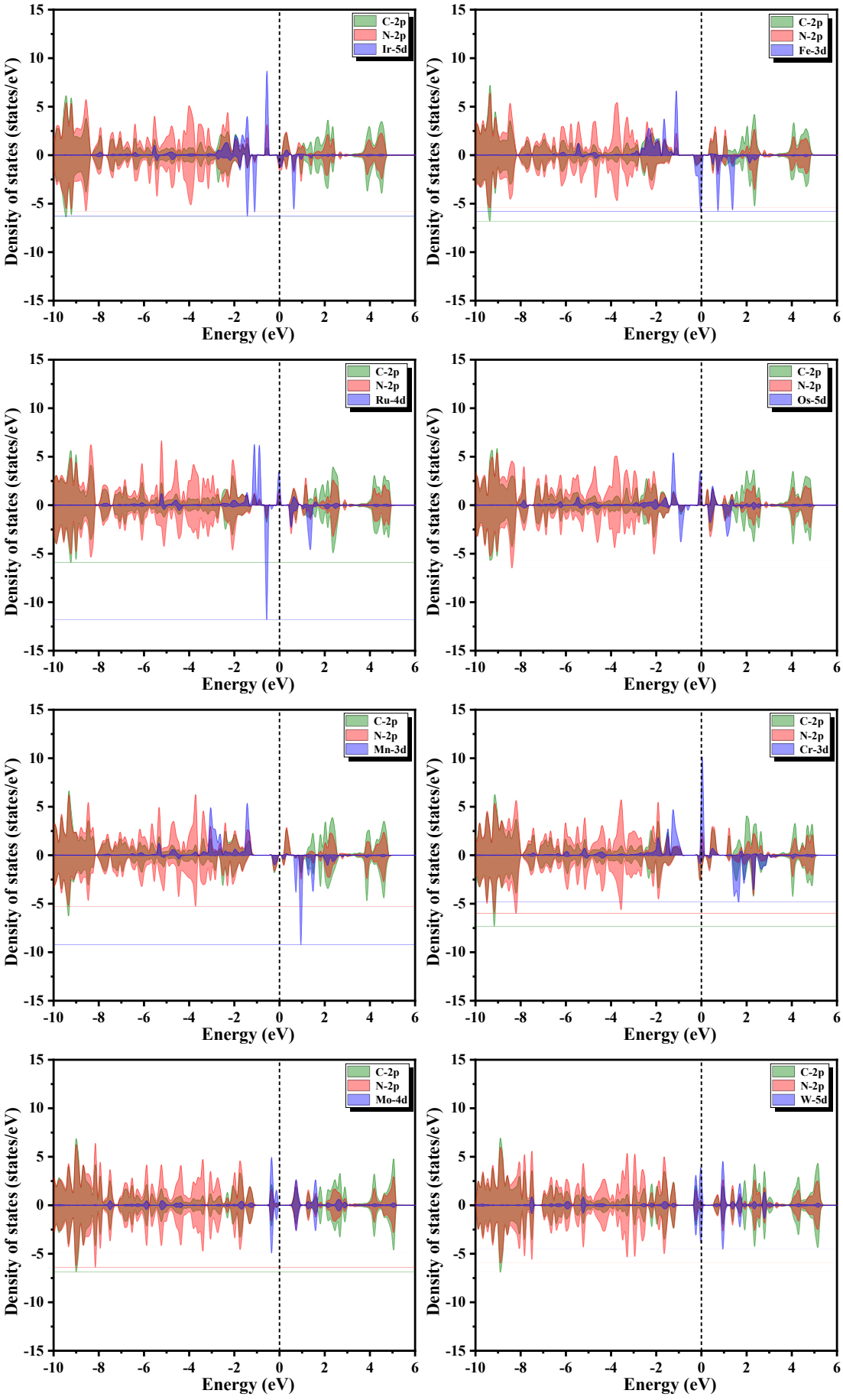


Fig. S2 Scaling relationship between the charge transfer quantity (Δq) and adsorption energy (E_{ad}) of TMs.


C-2p
N-2p
Cu-3d
Ag-4d
Au-5d
Ni-3d
Pd-4d
Pt-5d
Co-3d
Rh-4d
Density of states (states/eV)
Energy (eV)


C-2p
N-2p
Ir-5d
Fe-3d
Ru-4d
Os-5d
Mn-3d
Cr-3d
Mo-4d
W-5d
Density of states (states/eV)
Energy (eV)

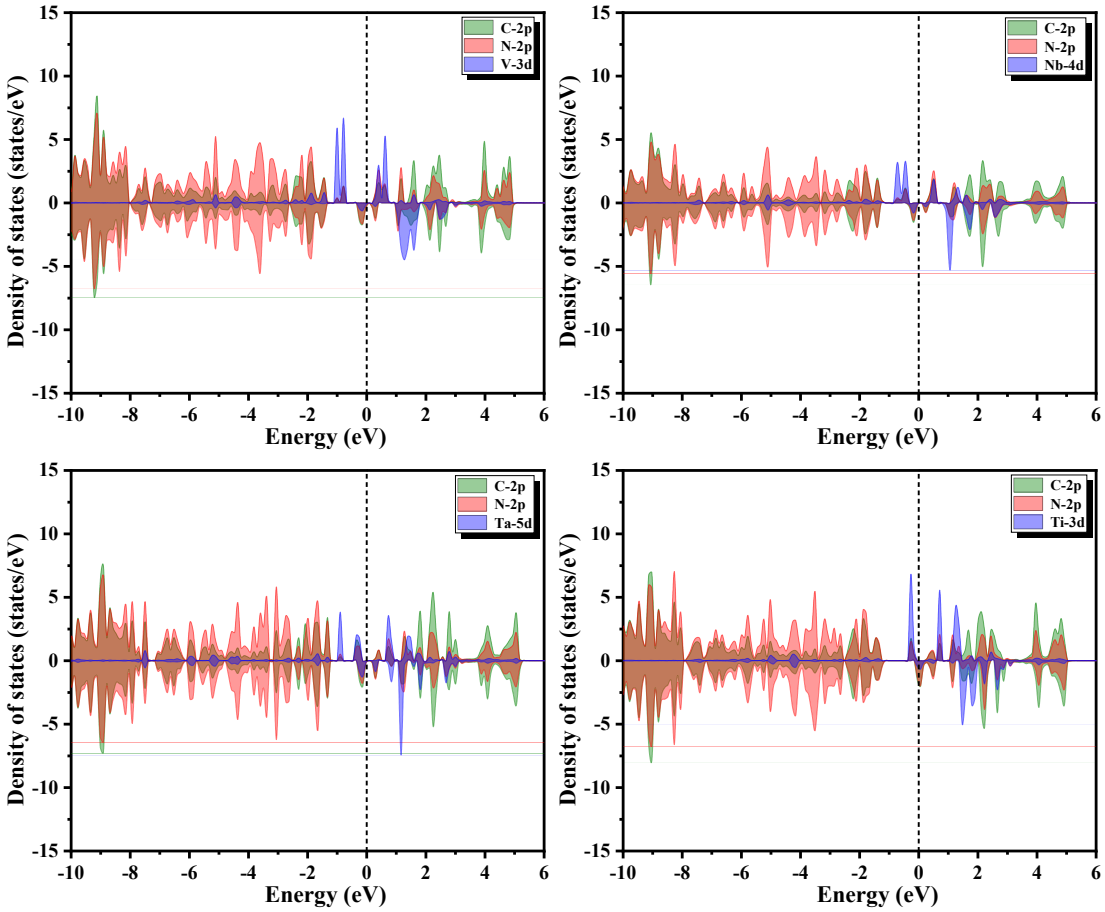


Fig. S3 Density of states of TM@C_7N_6.

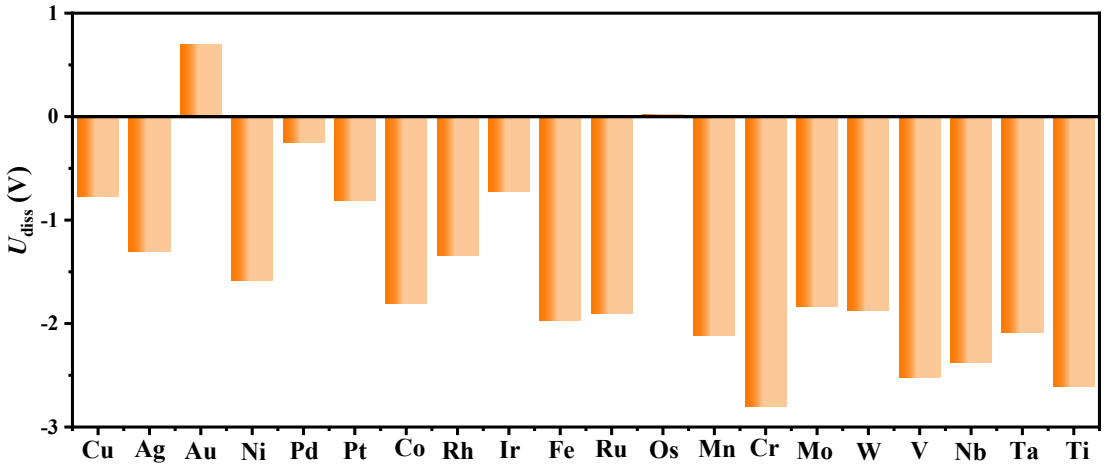


Fig. S4 Dissolution potential of TM@C_7N_6.

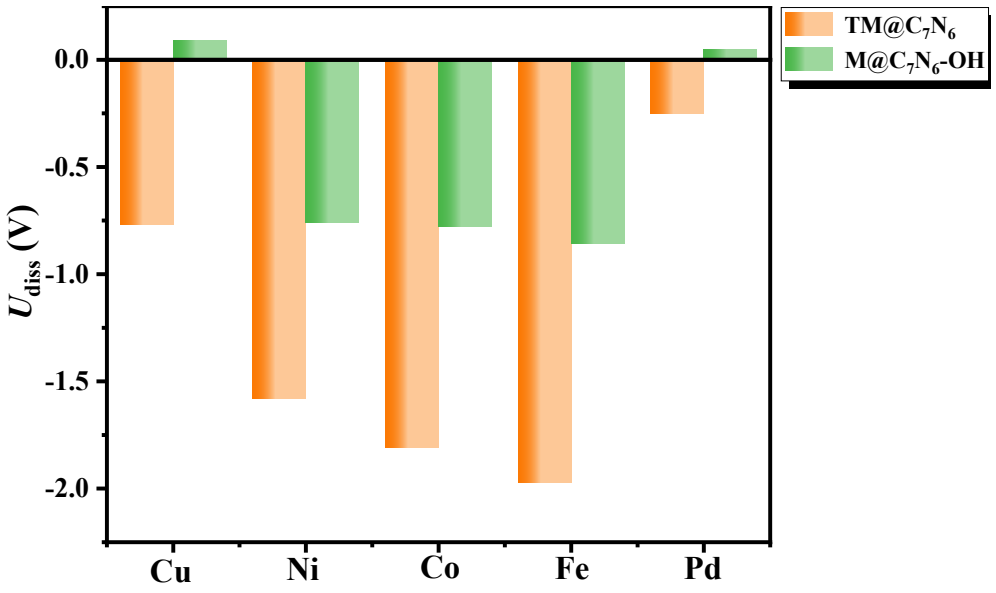
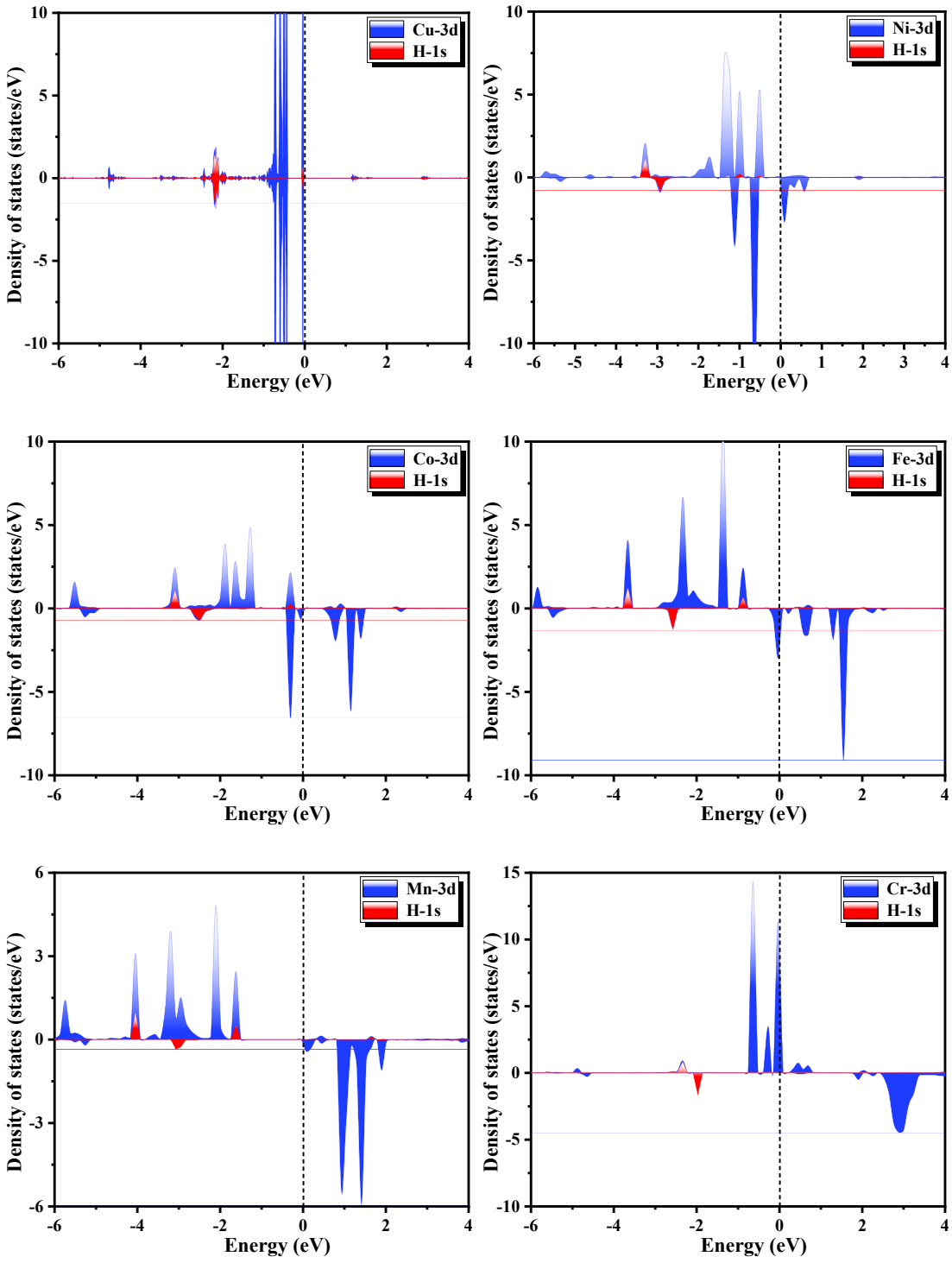


Fig. S5 Comparison of dissolution potential between TM@C_7N_6 between TM@C_7N_6-OH .


Cu-3d
H-1s
Ni-3d
H-1s
Co-3d
H-1s
Fe-3d
H-1s
Mn-3d
H-1s
Cr-3d
H-1s
Density of states (states/eV)
Energy (eV)

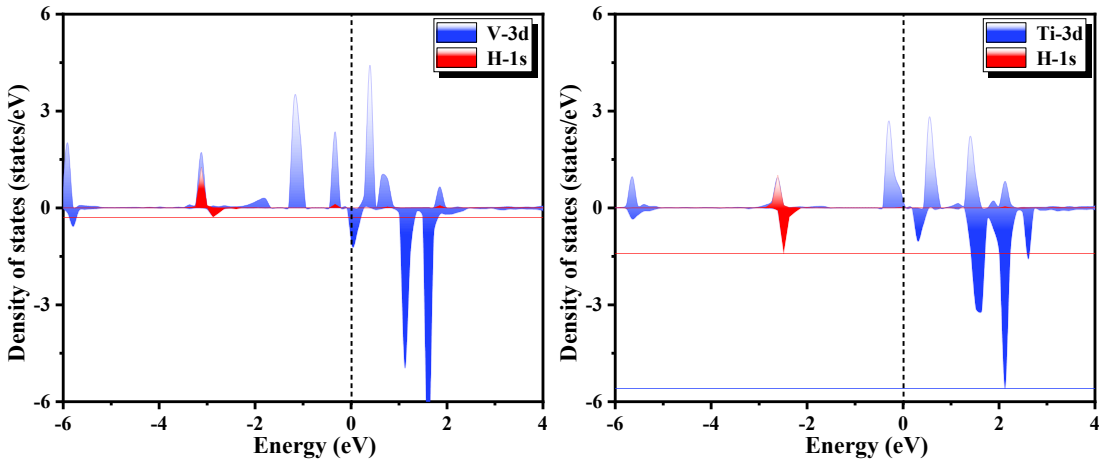
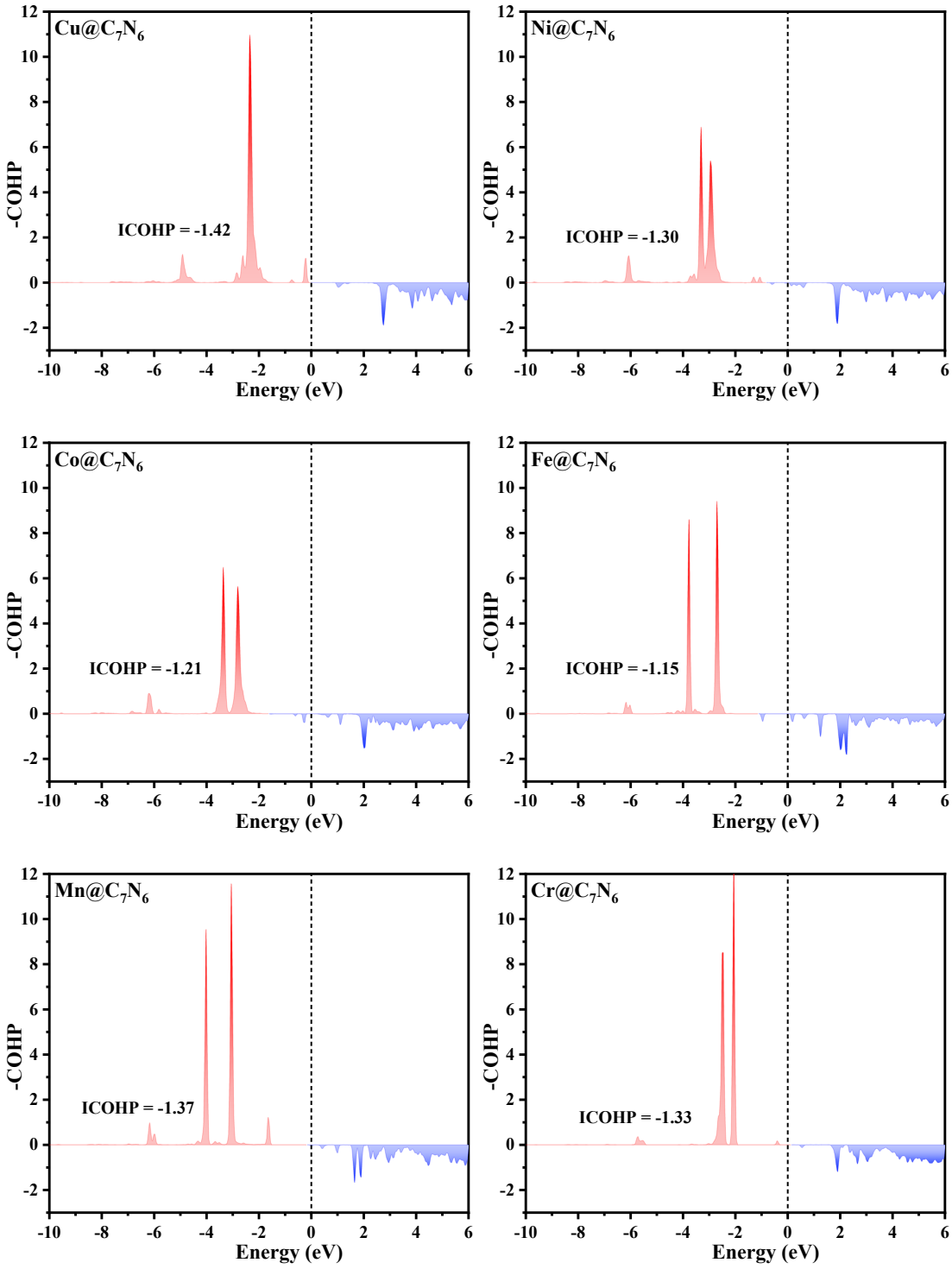


Fig. S6 Projected density of states of H adsorption on TM@C_7N_6.


Cu@C7N6
ICOHP = -1.42
Ni@C7N6
ICOHP = -1.30
Co@C7N6
ICOHP = -1.21
Fe@C7N6
ICOHP = -1.15
Mn@C7N6
ICOHP = -1.37
Cr@C7N6
ICOHP = -1.33
-COHP
Energy (eV)

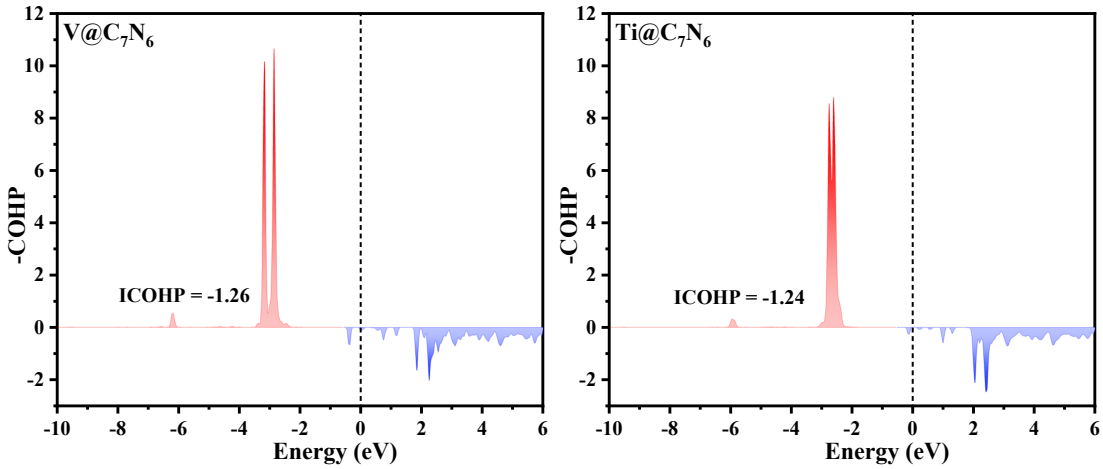
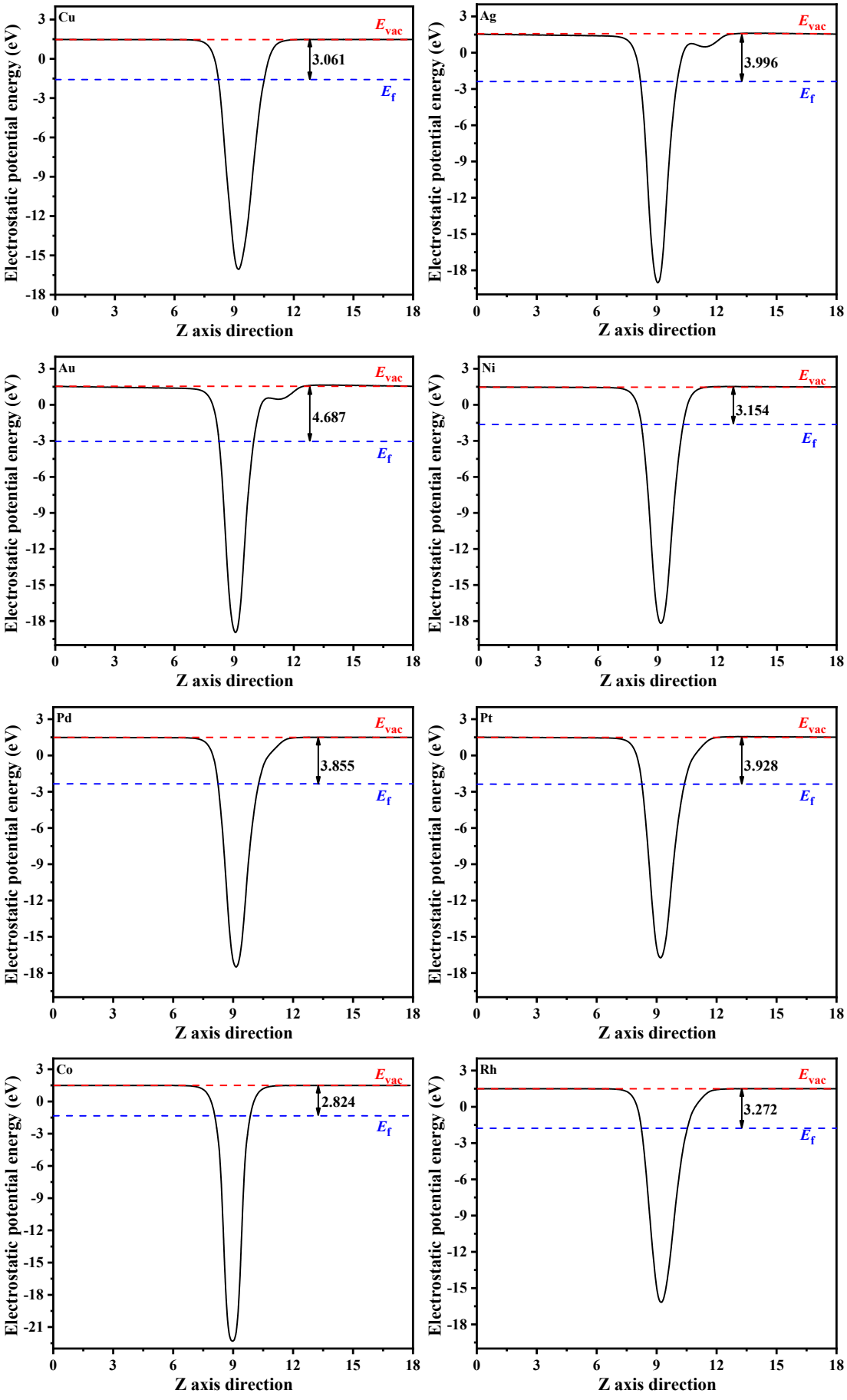
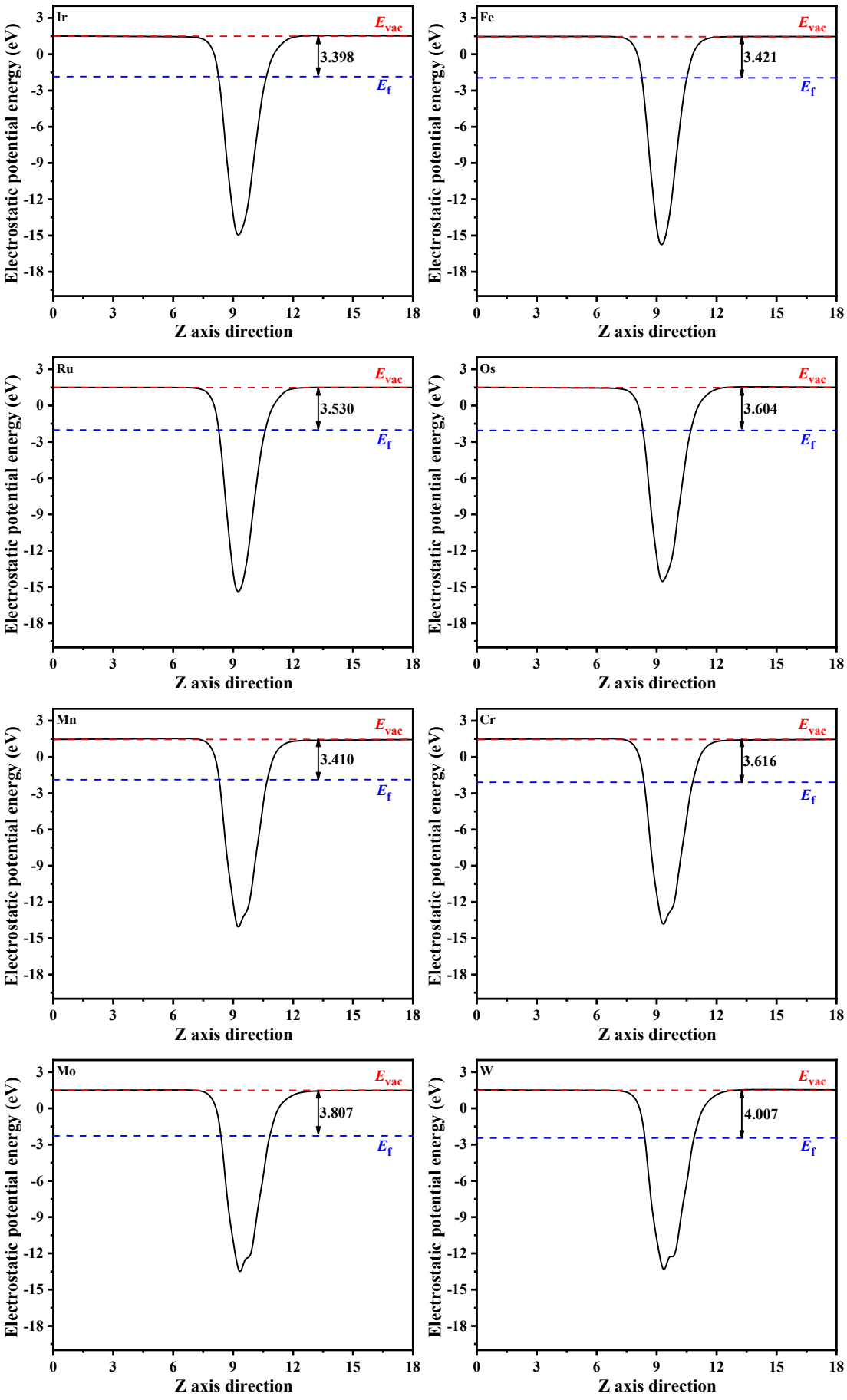


Fig. S7 Projected crystal orbital Hamilton population (pCOHP) of H adsorption on TM@C_7N_6.


Cu
E_{vac}
E_f
3.061
Ag
3.996
Au
4.687
Ni
3.154
Pd
3.855
Pt
3.928
Co
2.824
Rh
3.272
Electrostatic potential energy (eV)
Z axis direction


Ir
E_{vac}
3.398
E_f
Fe
E_{vac}
3.421
E_f
Ru
E_{vac}
3.530
E_f
Os
E_{vac}
3.604
E_f
Mn
E_{vac}
3.410
E_f
Cr
E_{vac}
3.616
E_f
Mo
E_{vac}
3.807
E_f
W
E_{vac}
4.007
E_f
Electrostatic potential energy (eV)
Z axis direction
3
0
-3
-6
-9
-12
-15
-18
0
3
6
9
12
15
18

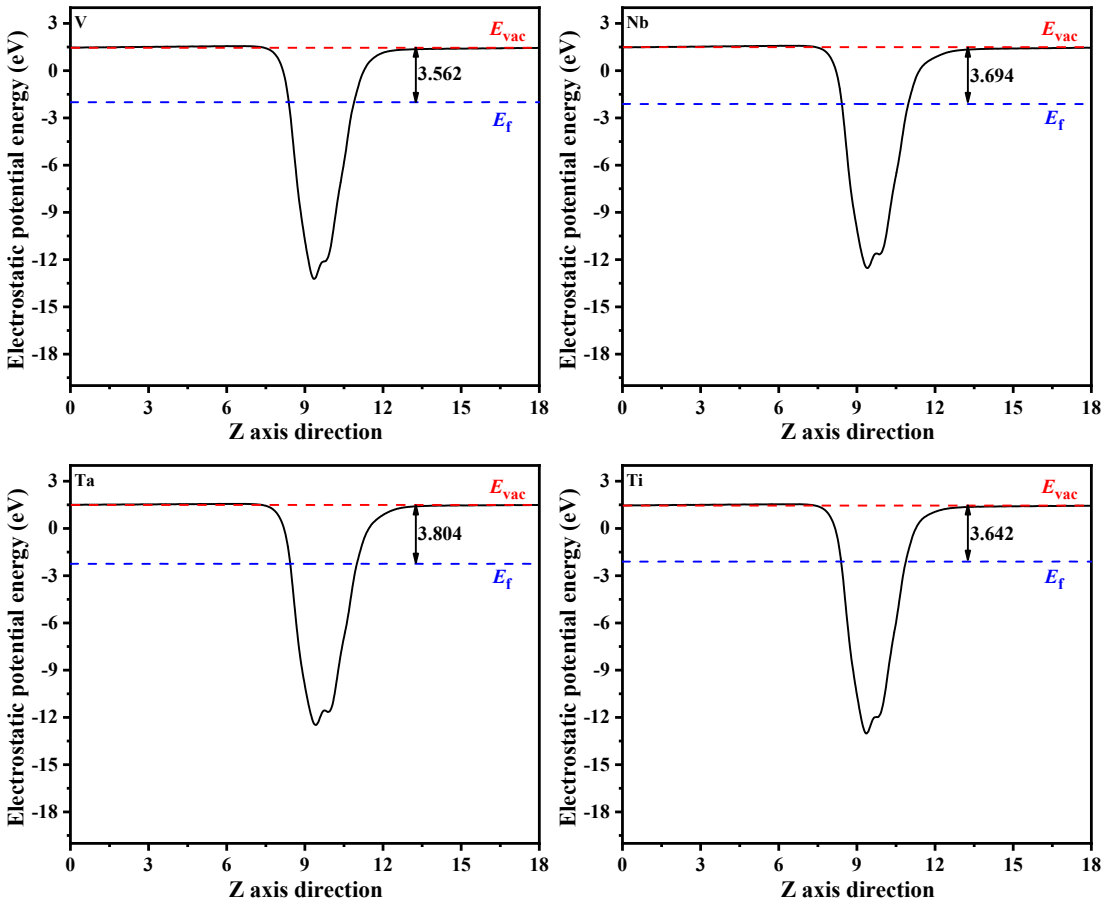


Fig. S8 Calculated work functions for TM@C_7N_6.

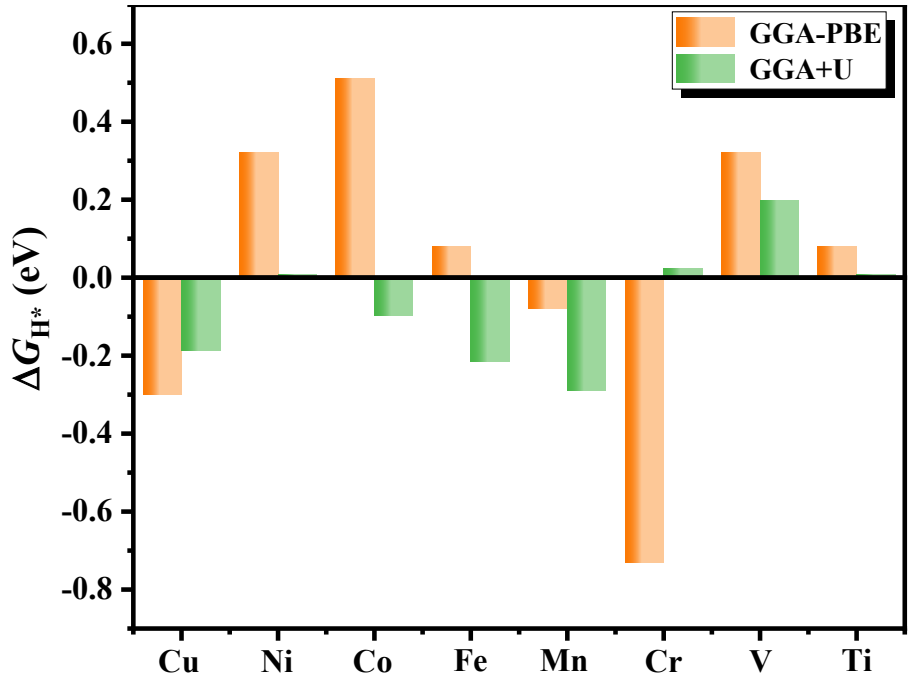


Fig. S9 Comparison of the calculated ΔG_{H*} values for TM@C_7N_6 using the GGA-PBE and GGA+U methods.

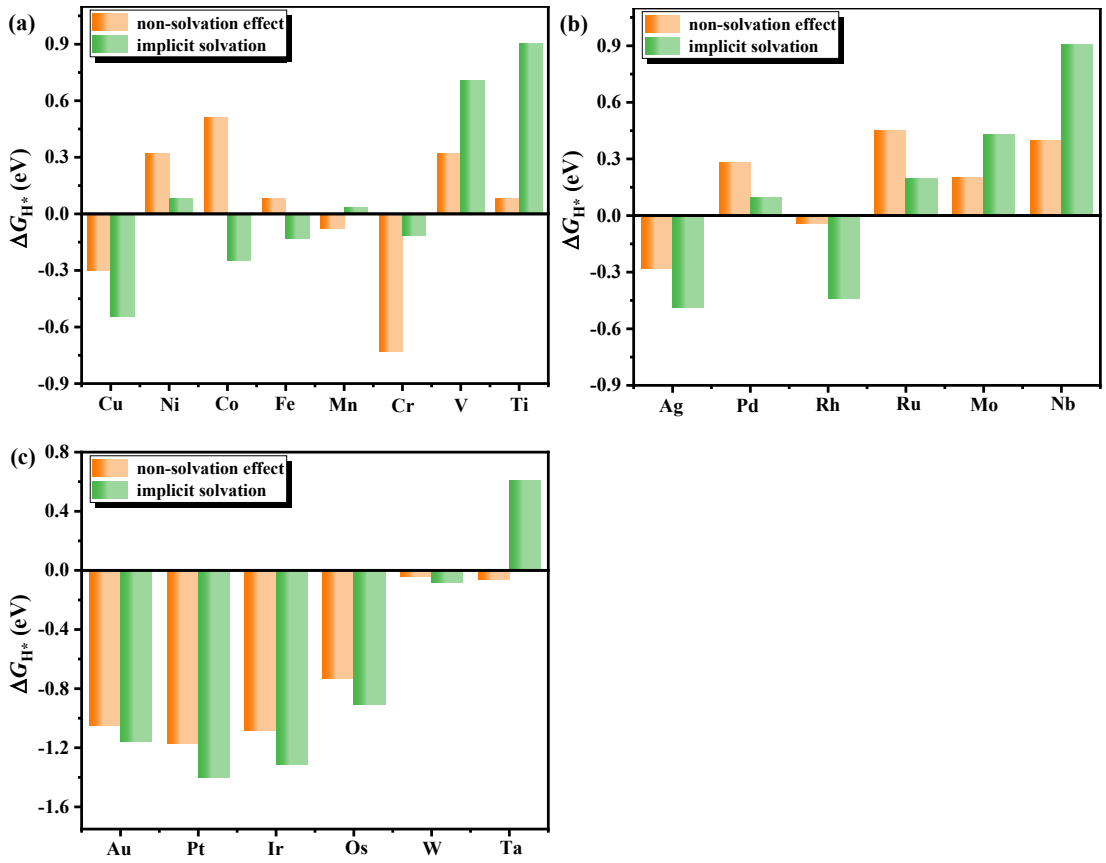


Fig. S10 Comparison of the calculated ΔG_{H^*} values for TM@C_7N_6 with and without solvation effects.