Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

NP monolayer supported transition-metal single atoms for electrochemical water splitting: a theoretical study

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Gibbs Free Energy Computations (OER processes)

The Gibbs free energy changes of four elementary steps for OER processes can be described as: $\Delta G_1 = \Delta G_{OH^*}$, $\Delta G_2 = \Delta G_{O^*} - \Delta G_{OH^*}$, $\Delta G_3 = \Delta G_{OOH^*} - \Delta G_{O^*}$, $\Delta G_4 = 4.92 - \Delta G_{OOH^*}$. Under electrode potential U = 0 V, the ΔG for all the four elementary steps (OER processes) can be calculated by:

(1) $\Delta G_1 = G(OH^*) + 0.5G(H_2) - G(H_2O) - G(*)$

(2) $\Delta G_2 = G(O^*) + 0.5G(H_2) - G(OH^*)$

(3) $\Delta G_3 = G(OOH^*) + 0.5G(H_2) - G(H_2O) - G(O^*)$

(4) $\Delta G_4 = 4.92 + 2G(H_2O) - 2G(H_2) + 0.5\,G(H_2) - G(OOH^*)$

With Spin vs. Without Spin

On the one hand, we examine the effects of spin polarization to the system for the HER and the results show that there is almost no difference with and without spin treatment in Table S4. On the other hand, Pt@NP shows the lowest η^{OER} of only 0.495 V, which is superior to the current best OER catalysts IrO_2. Thus we also examine the effects of spin polarization on Pt@NP for OER, as shown in Table S5.

To sum up, different spin states only have small and negligible effects on the relative energy difference. Thus, we neglect the effects of spin polarization on the systems and it will not influence our conclusion.

Table S1. Comparison of lattice constants (all in Å) of the studied NP monolayer between the reported simulations and our calculation.

	Our calculation		Reference[1]		Reference[2]	
	a	*b*	*a*	*b*	*a*	*b*
NP monolayer	3.611	2.733	3.611	2.733	3.61	2.73

Table S2. Adsorption free energies of OH, O, OOH and H (eV) on single TM supported on NP monolayer.

Single TM atom	ΔG_{OH}*	ΔG_{O}*	ΔG_{OOH}*	ΔG_{H}*
Sc	-1.672	-0.193	1.573	0.083
Ti	-1.614	-1.469	1.967	-0.004
V	-1.515	-1.710	1.791	-0.051
Cr	-0.539	-0.682	2.406	0.712
Mn	0.195	0.145	3.145	0.628
Fe	0.563	0.789	3.683	0.400
Co	0.067	1.260	3.088	0.565
Ni	0.536	2.544	3.574	0.559
Cu	0.822	3.426	3.989	0.861
Nb	-2.065	-2.455	1.261	-0.368
Mo	-0.549	-1.616	2.017	0.221
Tc	0.345	0.295	3.356	0.588
Ru	0.611	0.709	3.689	0.134
Rh	0.713	1.536	3.314	0.549
Pd	1.146	3.338	3.942	0.889
Ag	1.223	4.128	4.260	0.805
Ta	-2.473	-2.765	0.967	-0.811
Re	-0.046	-0.453	2.838	0.321
Os	0.079	0.234	3.493	-0.172
Ir	0.931	0.793	4.040	0.017
Pt	1.507	2.849	4.574	0.446
Au	0.374	2.868	3.618	-0.331

Table S3. Reaction free energy (eV vs RHE) of elementary step for OER at U = 0V on single TM atom supported on NP monolayer.

Single TM atom	ΔG_1	ΔG_2	ΔG_3	ΔG_4
Sc	-1.672	1.479	1.766	3.347
Ti	-1.614	0.145	3.436	2.953
V	-1.515	-0.195	3.501	3.129
Cr	-0.539	-0.143	3.088	2.514
Mn	0.195	-0.050	3.000	1.775
Fe	0.563	0.226	2.894	1.237
Co	0.067	1.193	1.828	1.832
Ni	0.536	2.008	1.030	1.346
Cu	0.822	2.604	0.563	0.931
Nb	-2.065	-0.390	3.716	3.659
Mo	-0.549	-1.067	3.633	2.903
Tc	0.345	-0.050	3.061	1.564
Ru	0.611	0.098	2.980	1.231
Rh	0.713	0.823	1.778	1.606
Pd	1.146	2.192	0.604	0.978
Ag	1.223	2.905	0.132	0.660
Ta	-2.473	-0.292	3.732	3.953
Re	-0.046	-0.407	3.291	2.082
Os	0.079	0.155	3.259	1.427
Ir	0.931	-0.138	3.247	0.880
Pt	1.507	1.342	1.725	0.346
Au	0.374	2.494	0.750	1.302

Table S4. Comparisons of HER activities of various SACs with and without spin treatment.

Single TM atom	Without spin		With spin	
	ΔG_{H^*} (eV)	Magnetic moment (μB)	ΔG_{H^*} (eV)	Magnetic moment (μB)
Sc	0.083	/	0.084	0
Ti	-0.004	/	0.061	1.25
V	-0.051	/	0.218	1.61
Cr	0.712	/	0.885	2.02
Mn	0.628	/	0.402	1.13
Fe	0.400	/	0.415	0.52
Co	0.565	/	0.558	0.74
Ni	0.559	/	0.607	0.70
Cu	0.861	/	0.857	0.33
Nb	-0.368	/	-0.387	1.39
Mo	0.221	/	0.275	0
Tc	0.588	/	0.586	0.02
Ru	0.134		0.131	0
Rh	0.549	/	0.508	0.59
Pd	0.889	/	0.893	0
Ag	0.805	/	0.808	0
Ta	-0.811	/	-0.724	0.72
Re	0.321	/	0.327	0
Os	-0.172	/	-0.166	0
Ir	0.017	/	0.012	0
Pt	0.446	/	0.439	0
Au	-0.331	/	-0.327	0

Table S5. Comparison of OER activity of Pt@NP with and without spin treatment.

System	Without spin				With spin			
	ΔG_1	ΔG_2	ΔG_3	ΔG_4	ΔG_1	ΔG_2	ΔG_3	ΔG_4
Pt@NP	1.507	1.342	1.725	0.346	1.507	1.297	1.770	0.346

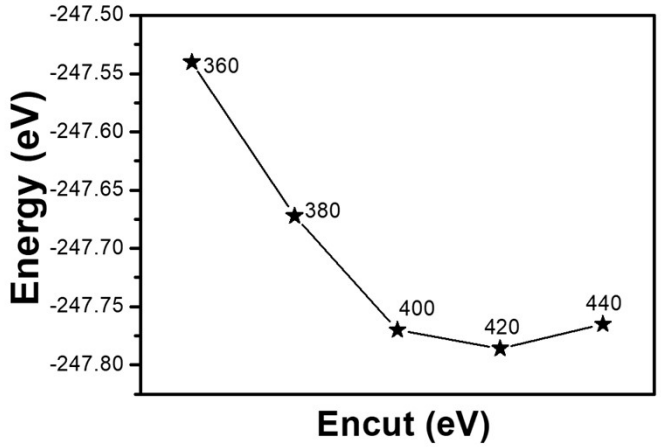

Fig. S1. The energies of NP monolayer calculated with different cut-off.

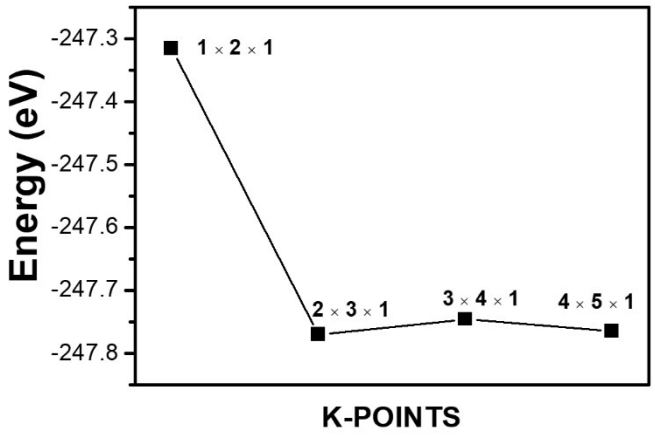

Fig. S2. The energies of NP monolayer calculated with different *k*-points.

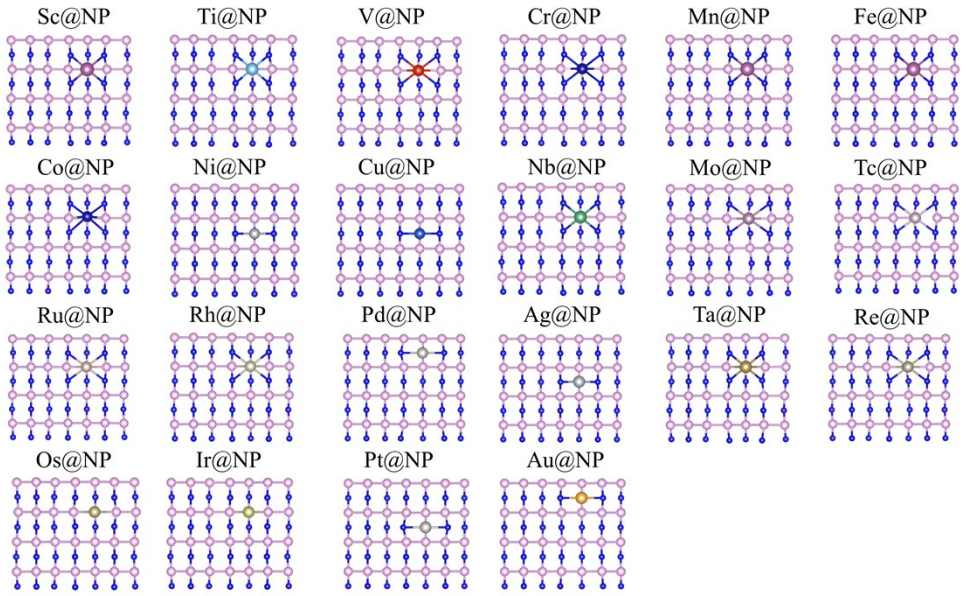

Fig. S3. The optimized configurations of metal anchored on NP monolayer.

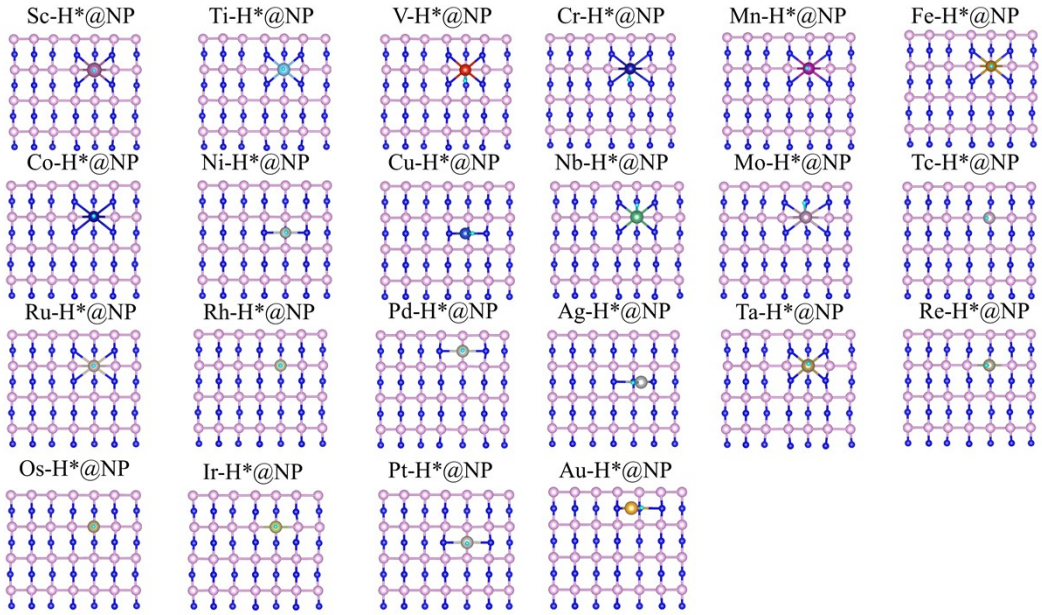

Fig. S4. Configurations of species (H) on single TM atom supported on NP monolayer.

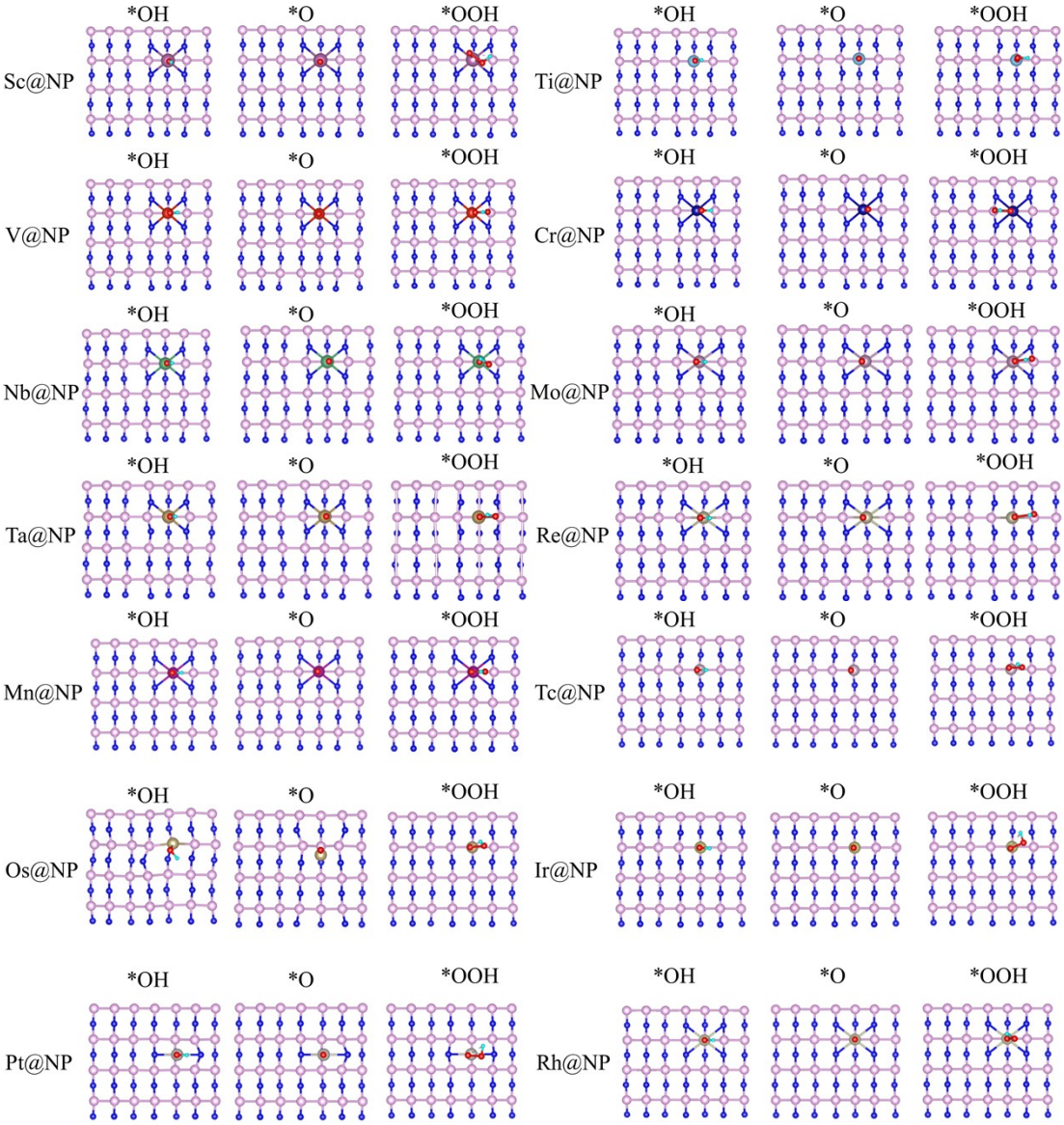

Fig. S5. Configurations of adsorbates (OH, O, OOH) on single TM atom supported on NP monolayer.

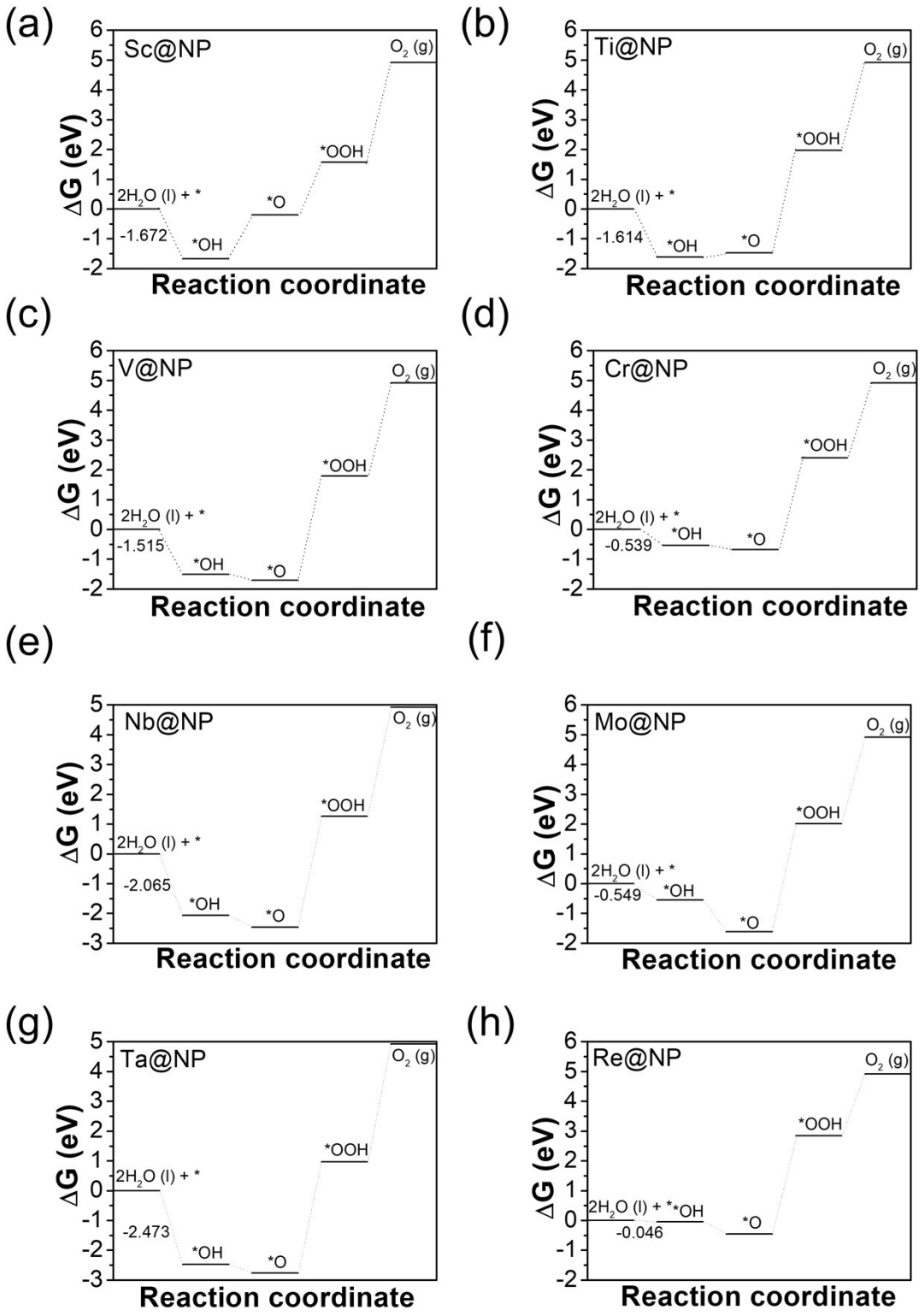

Fig. S6. The calculated free energy diagram of the OER of TM@NP SACs at the zero potential (U = 0 V). (a) Sc@NP. (b) Ti@NP. (c) V@NP. (d) Cr@NP. (e) Nb@NP. (f) Mo@NP. (g) Ta@NP. (h) Re@NP.

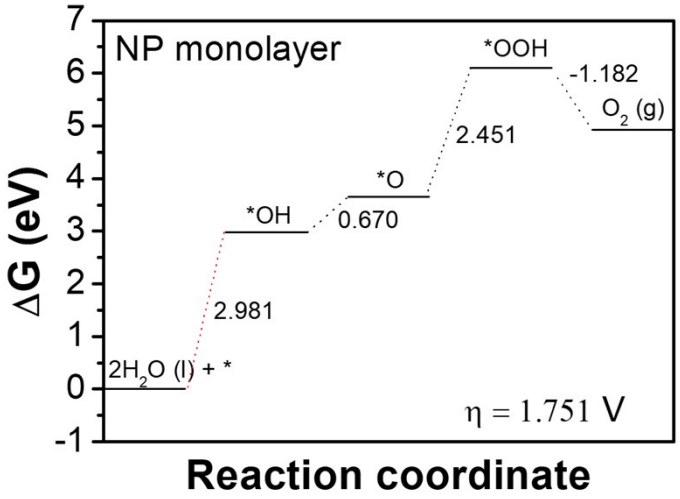

Fig. S7. The calculated free energy diagram of the OER of NP monolayer at the zero potential (U = 0 V), where the potential-determining step of the elementary reaction was marked in red.

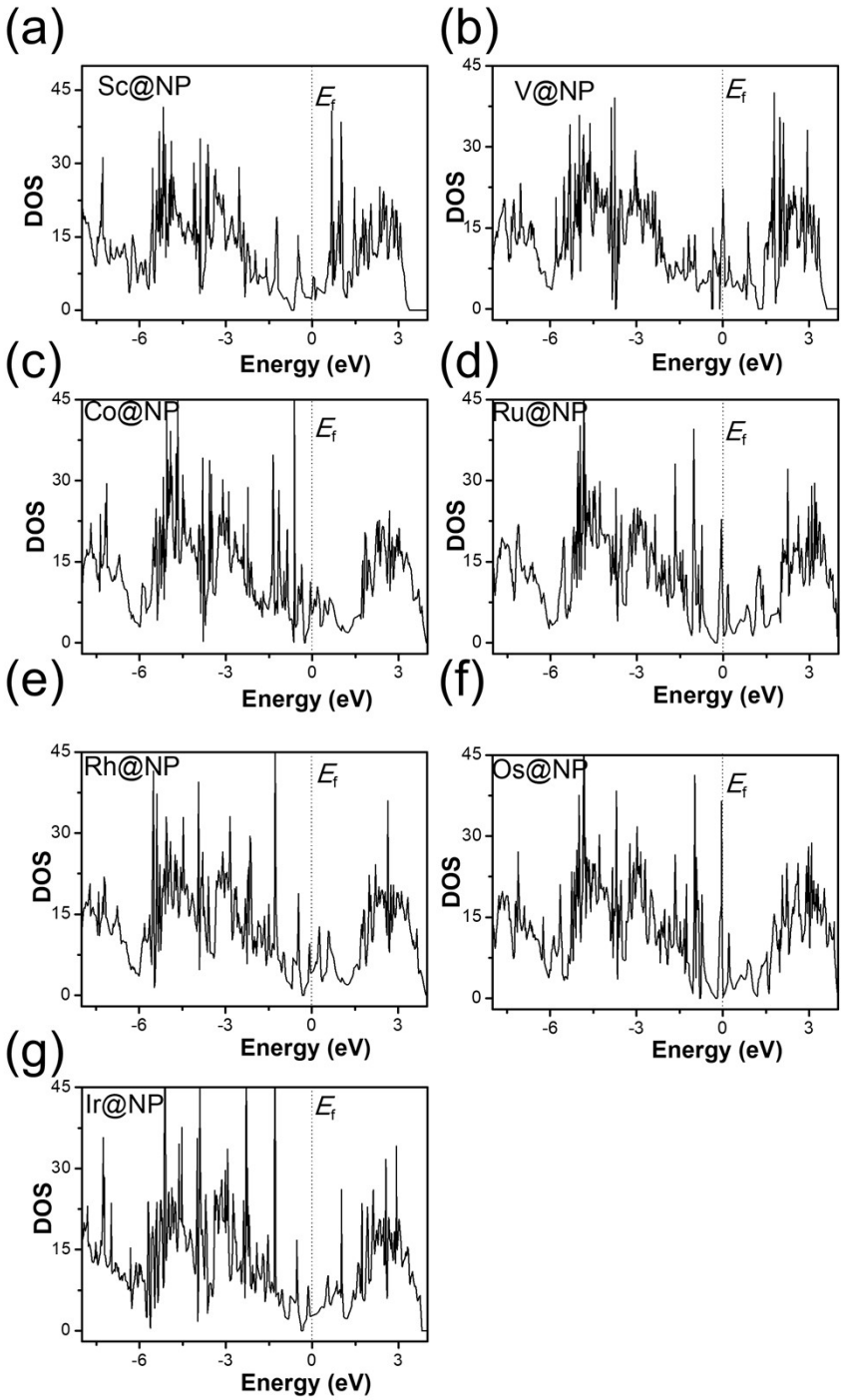

Fig. S8. The calculated DOS of the (a) Sc@NP. (b) V@NP. (c) Co@NP. (d) Ru@NP. (e) Rh@NP. (f) Os@NP. (g) Ir@NP. The Fermi level was set at the zero energy and marked by the black dash line.

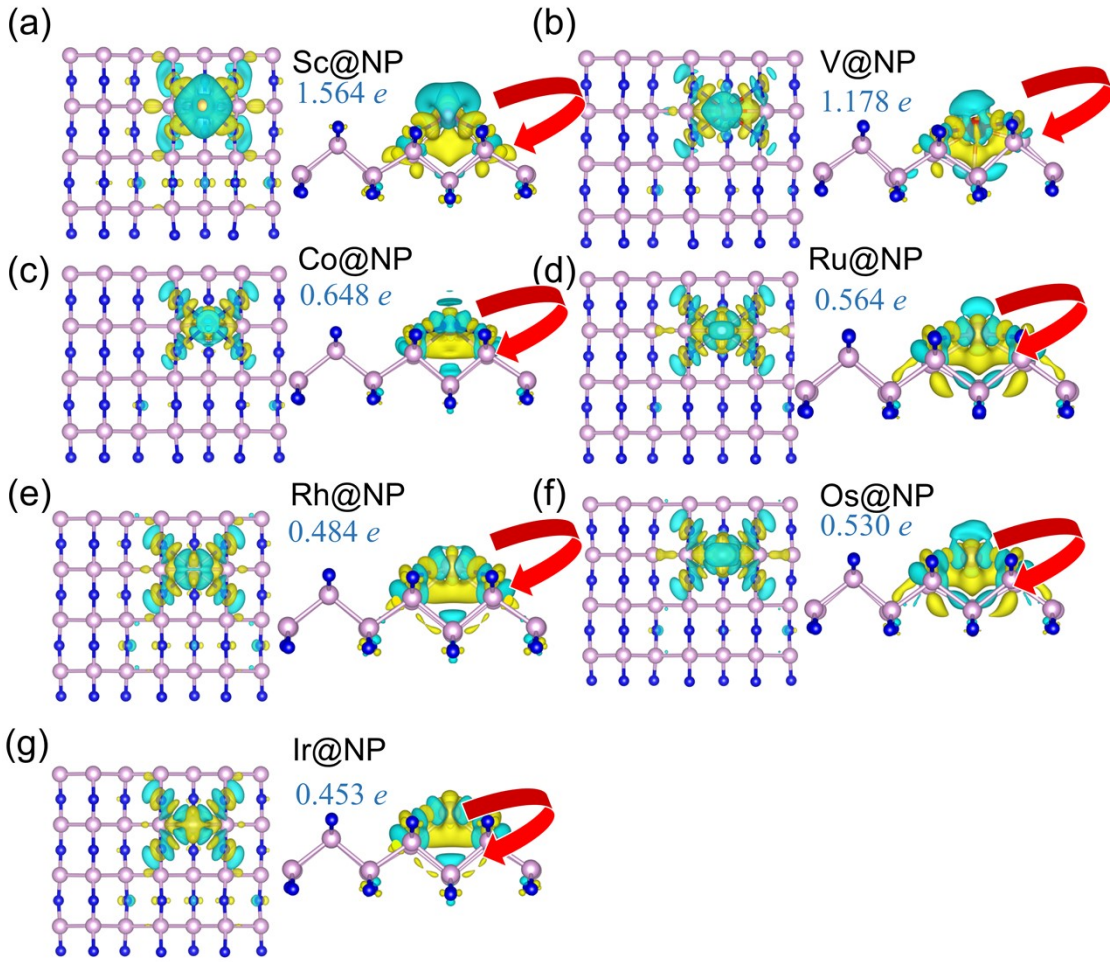

Fig. S9. The charge density difference as well as the amounts of charge transfer of (a) Sc@NP. (b) V@NP. (c) Co@NP. (d) Ru@NP. (e) Rh@NP. (f) Os@NP. (g) Ir@NP.

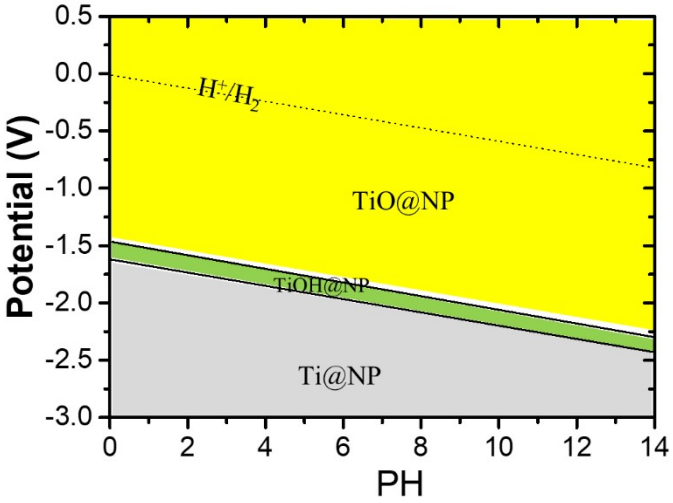

Fig. S10. The calculated Pourbaix diagram of Ti@NP.

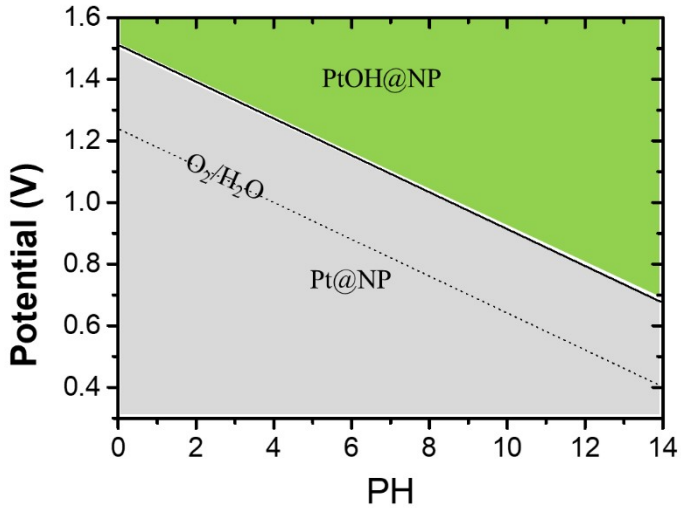

Fig. S11. The calculated Pourbaix diagram of Pt@NP.

References

1. Y. Nie, J. Zhang, W. Chen, Q. Xia, X. Wang and G.-h. Guo, *Phys Rev B*, 2020, **101**.
2. Z. Cheng, X. Zhang, H. Zhang, J. Gao, H. Liu, X. Yu, X. Dai, G. Liu and G. Chen, *Applied Surface Science*, 2021, **547**.