Single-atom catalysts based on TiN for the electrocatalytic hydrogen evolution reaction: a theoretical study

Bingling He[1,2], Jiansheng Shen[1], Bin Wang[1], Zhansheng Lu[3], and Dongwei Ma[2,*]

[1]*College of Physics and Electronic Engineering, Xinxiang University, Xinxiang 453003, China*

[2]*Key Laboratory for Special Functional Materials of Ministry of Education, and School of Materials Science and Engineering, Henan University, Kaifeng 475004, China*

[3]*College of Physics, Henan Normal University, Xinxiang 453007, China*

Support Information

*Corresponding author. E-mail: madw@henu.edu.cn (Dongwei Ma).

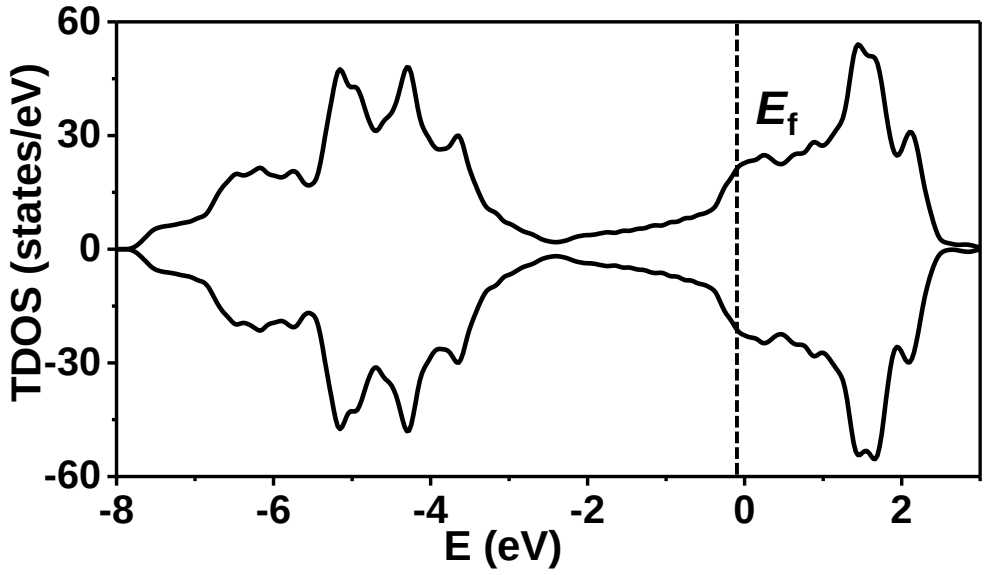

Fig. S1. The TDOS for the stoichiometric TiN (100) surface. The Fermi level (E_f) is denoted by the dashed line and set to 0 eV.

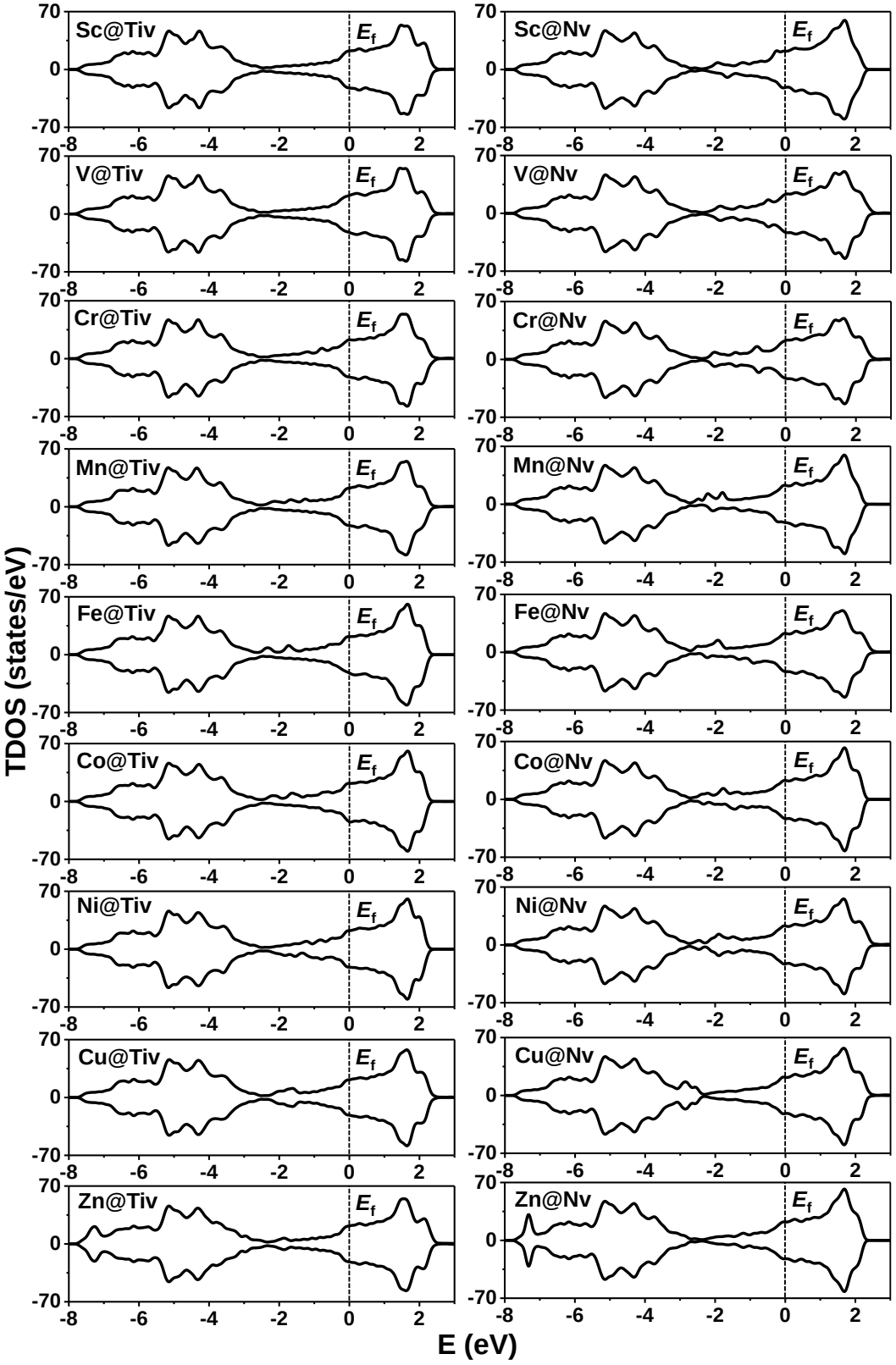

Fig. S2. The TDOS for the M@Tiv and M@Nv. M are 3*d* TM atoms for M@Tiv (left panel) and M@Nv (right panel). The E_f is denoted by the dashed line and set to 0 eV.

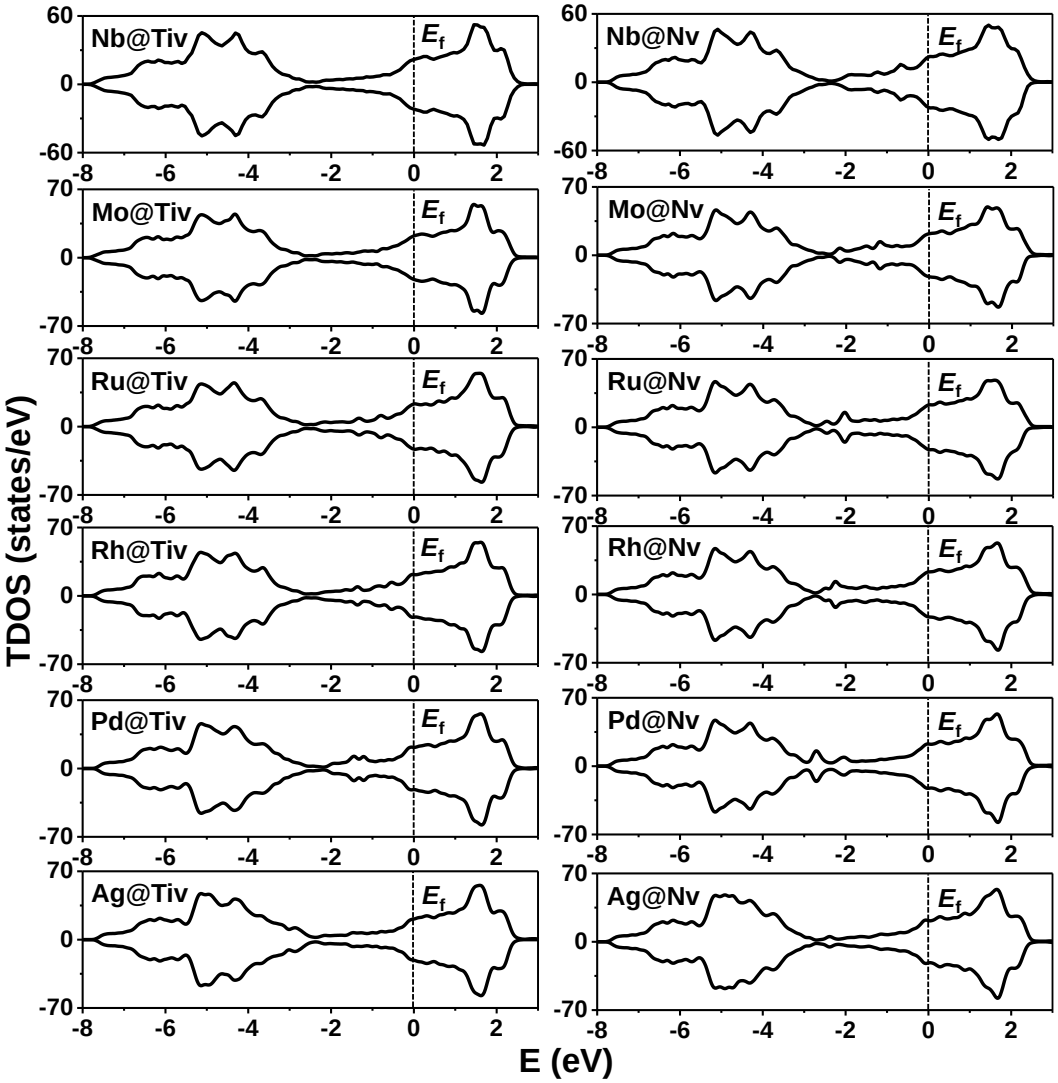

Fig. S3. Similar to Fig.2, except that M are 4*d* TM atoms. The E_f is denoted by the dashed line and set to 0 eV.

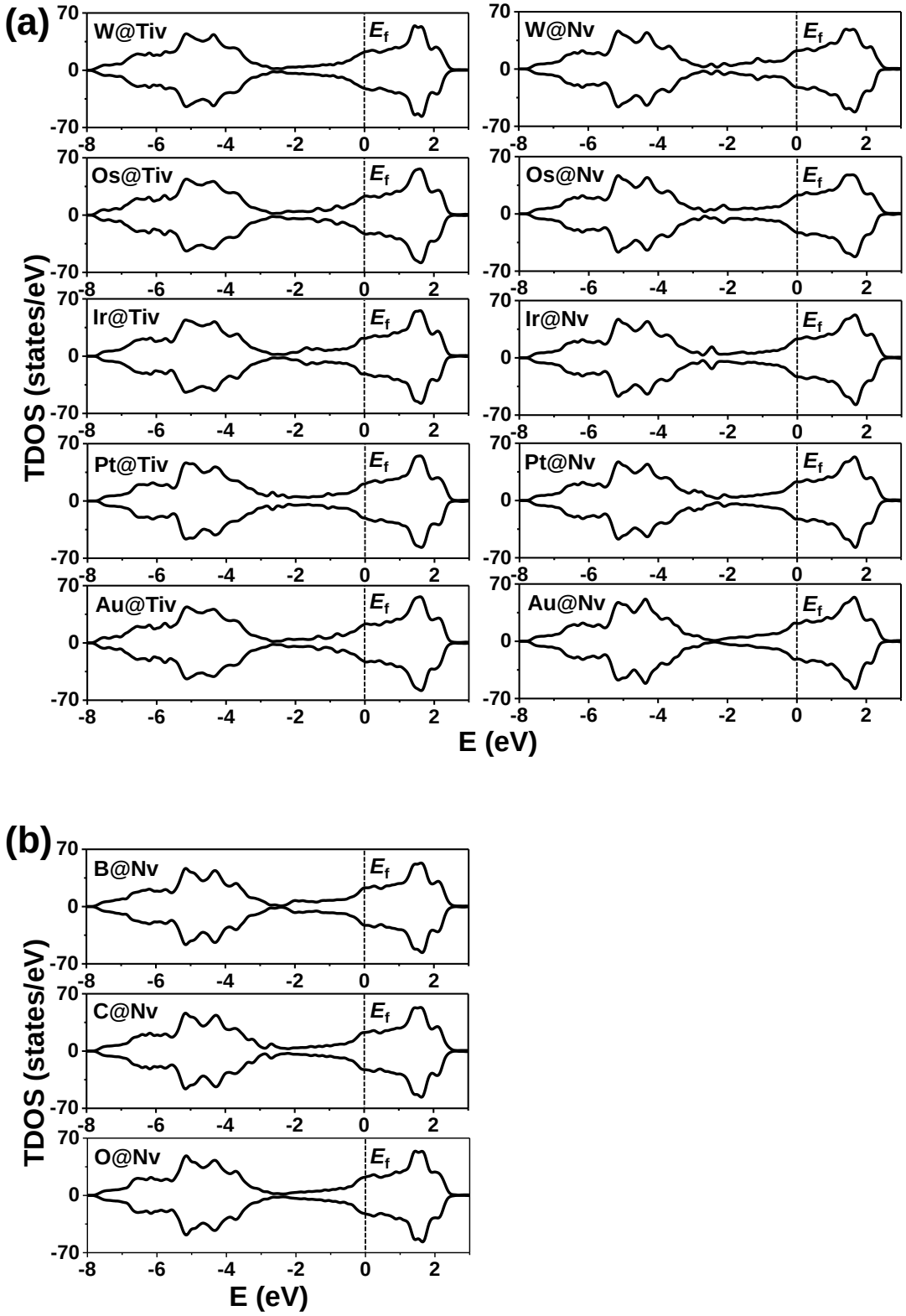

Fig. S4. Similar to Fig.2, except that M are 5*d* TM atoms (a) and B, C and O (b). The E_f is denoted by the dashed line and set to 0 eV.

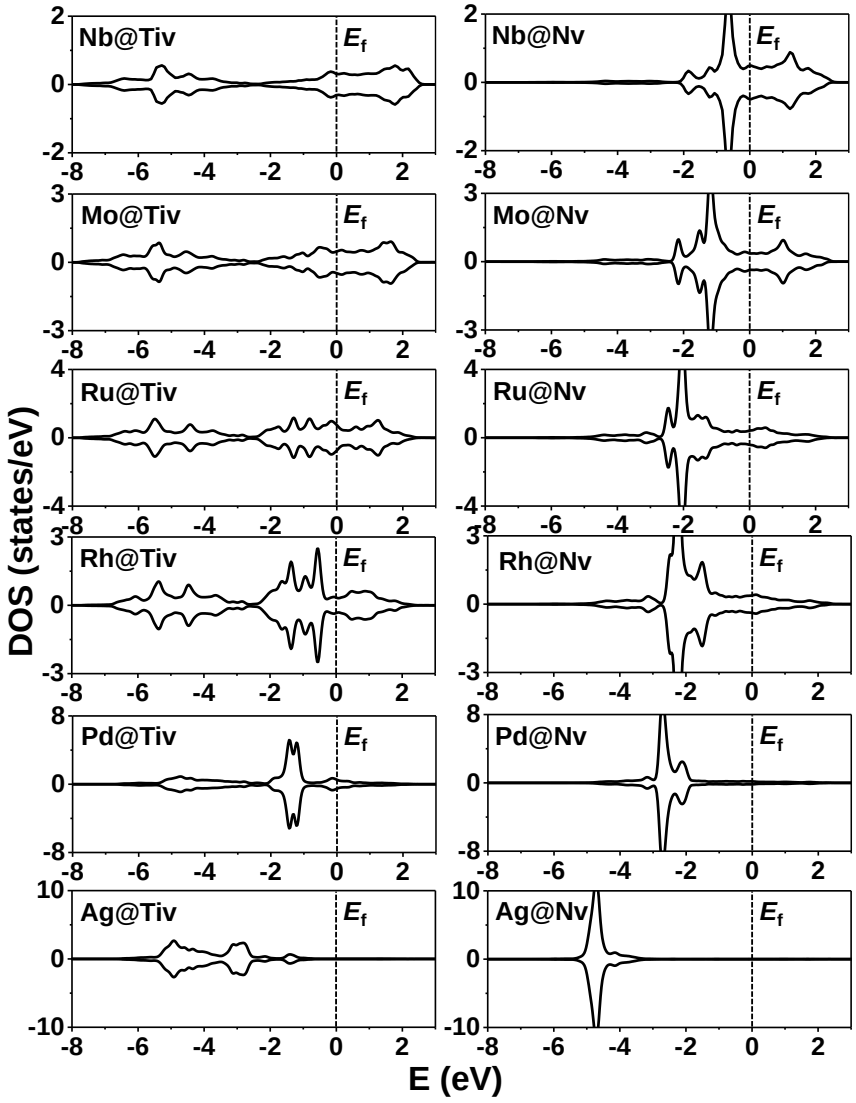

Fig. S5. The DOS for the *d* orbitals of the 4*d* TM atoms anchored by the TiN (100) surfaces with Ti vacancy (left panel) and N vacancy (right panel). The E_f is denoted by the dashed line and set to 0 eV.

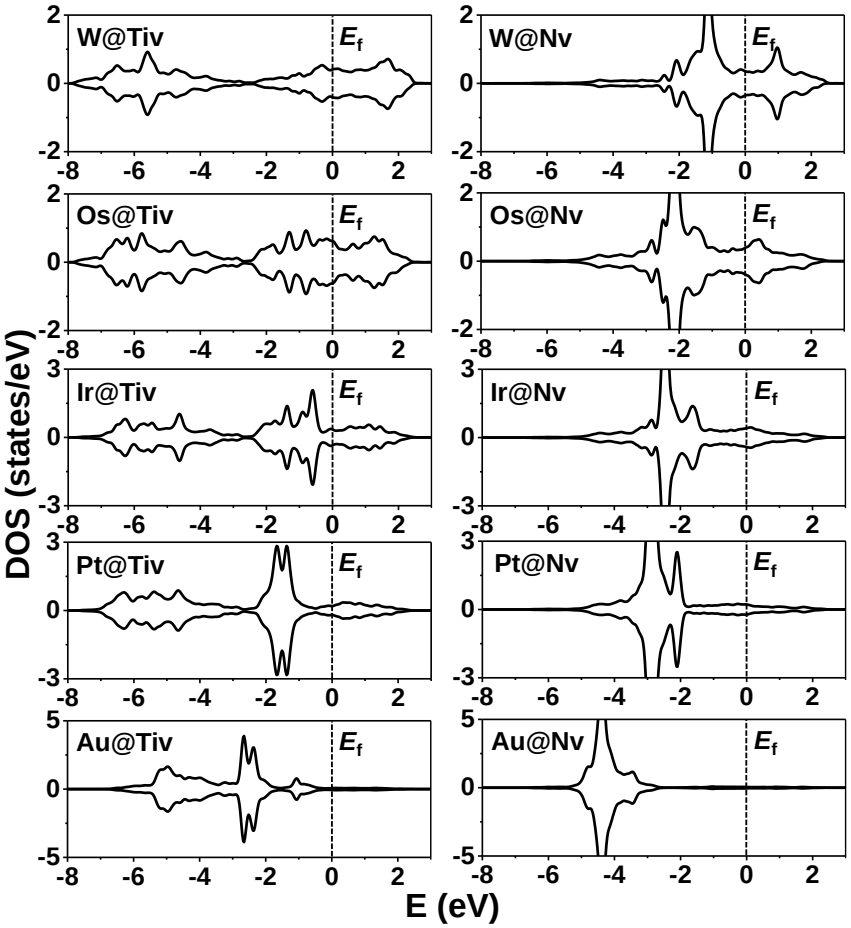

Fig. S6. Similar to Fig.4, except that M are 5*d* TM atoms. The E_f is denoted by the dashed line and set to 0 eV.

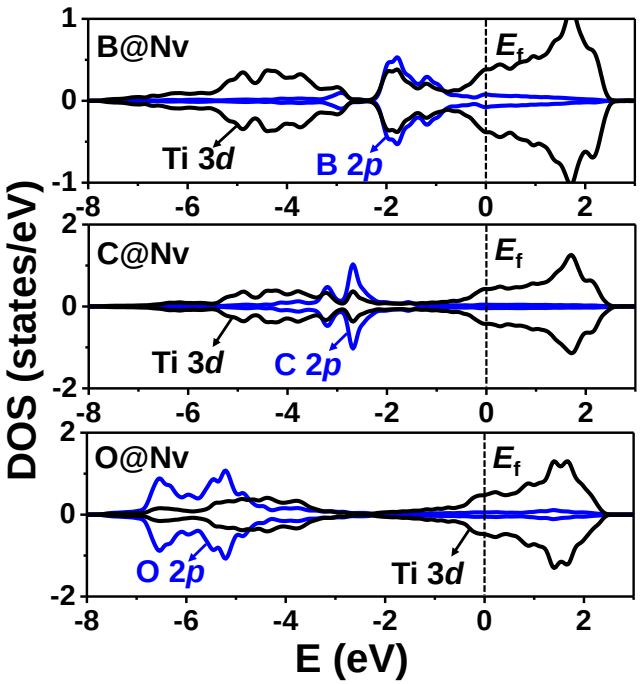

Fig. S7. The 2*p* states of the B, C and O as well as the 3*d* states of their neighboring Ti atoms for B, C, and O@Nv. The E_f is denoted by the dashed line and set to 0 eV.

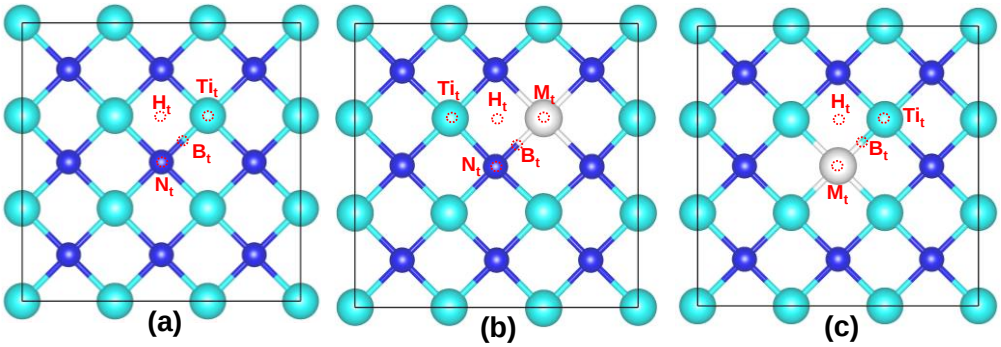

Fig. S8. The top views of the first atomic layer for the TiN (100) (a), M@Tiv (b), and M@Nv (c) surfaces with the considered adsorption sites for the atomic H.

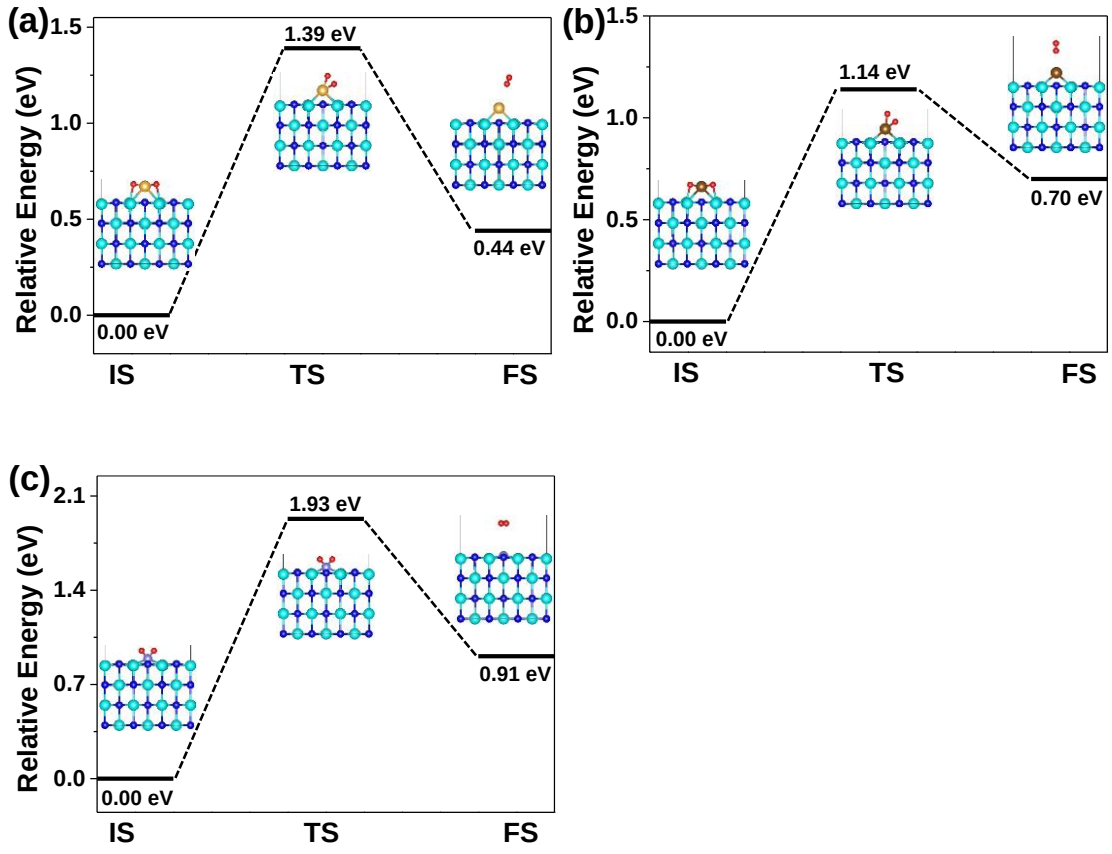

Fig. S9. Minimum-energy pathways of the HER under the Tafel mechanism for the Au@Nv (a), Pd@Nv (b) and B@Nv (c) catalysts. The energies of initial state (IS), transition state (TS), and final state (FS) are given relative to the IS, and their corresponding atomic structures are displayed as insets.

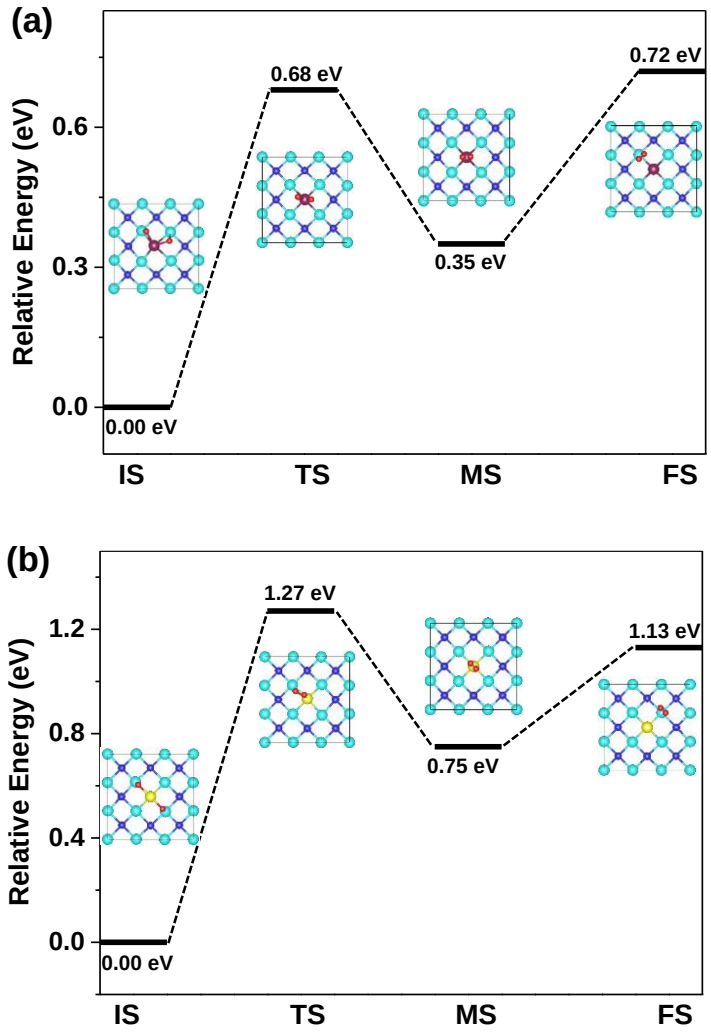

Fig. S10. Minimum-energy pathways of the HER under the Tafel mechanism for the W@Nv (a) and Mo@Nv (b). MS is the chemisorption configuration for H_2 molecule, and FS is the physisorption configuration. The energies of IS, TS, intermediate state (MS) and FS are given relative to the IS, and their corresponding atomic structures are displayed as insets.

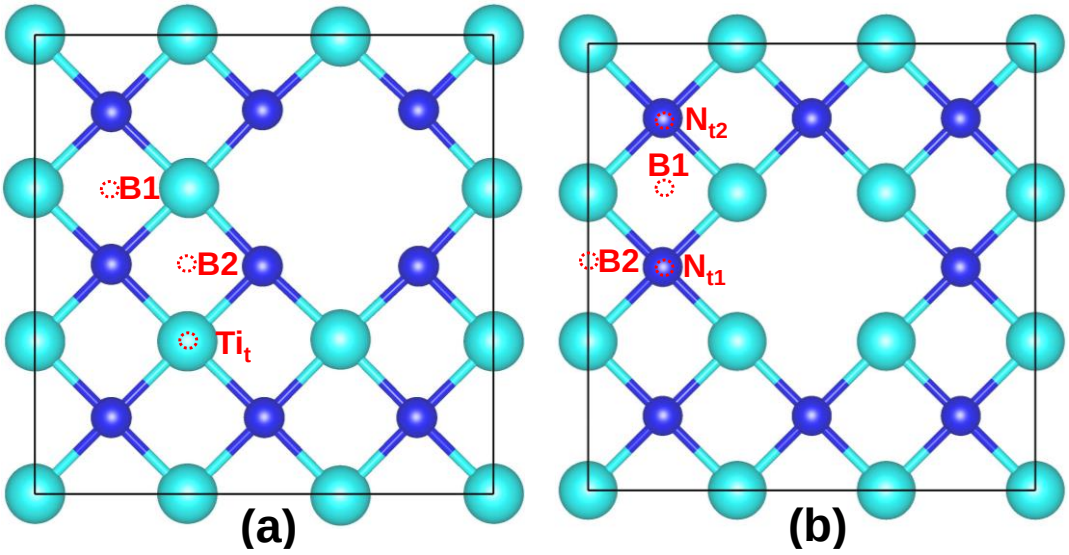

Fig. S11. The considered adsorption sites for the TM atoms on the defective TiN (100) surfaces with the Ti vacancy (a) and the N vacancy (b).

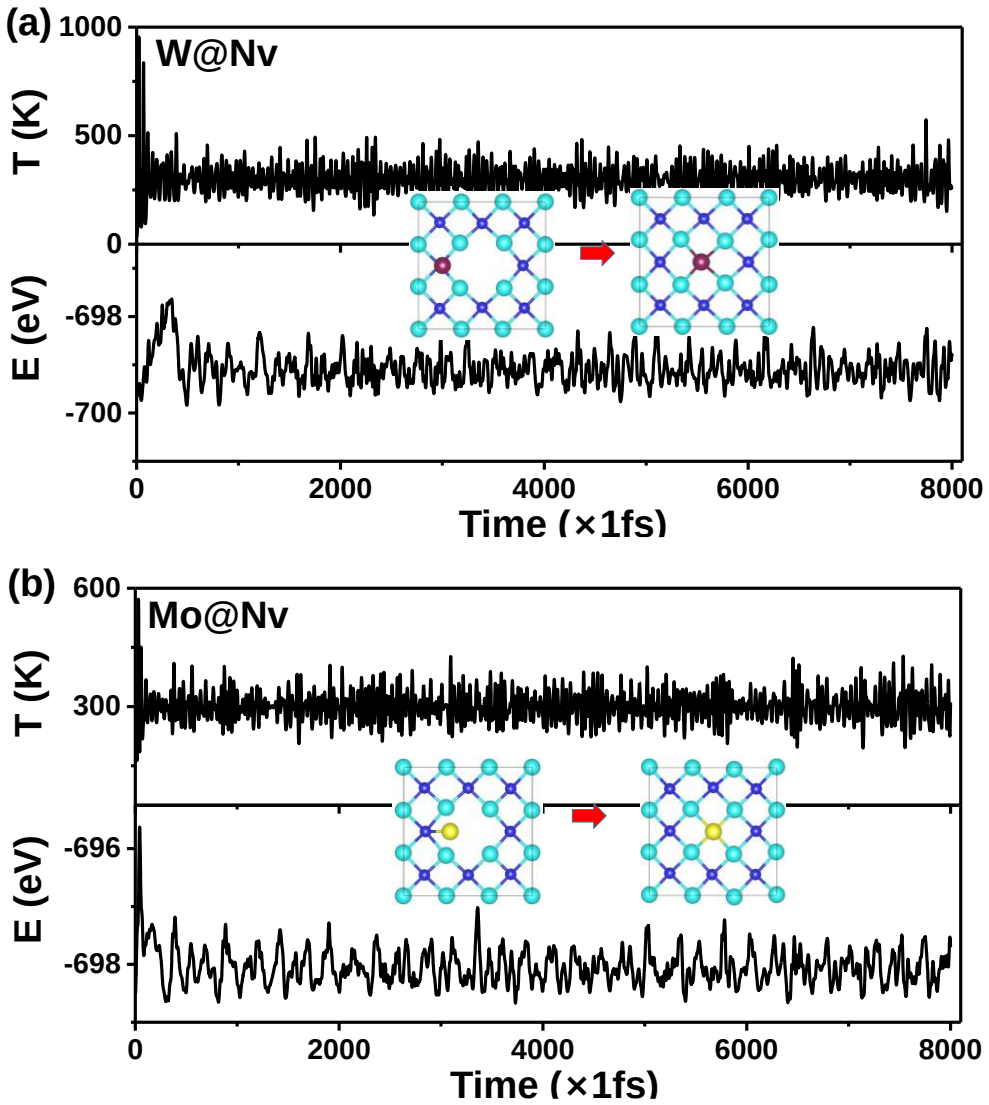

Fig. S12. The variations of total energies and temperatures during the ab initio molecular dynamics modelling for W@Nv (a) and Mo@Nv (b) at the temperature of 300 K. In (a) and (b), the top views of the initial and final atomic structures are inserted.

Table S1. Zero-point energy (E_{ZPE}, in eV) and entropy multiplied by T (T = 298.15 K and TS in eV) for adsorbed H atom.

	E_{ZPE}		TS	
	Ti Vacancy	N Vacancy	Ti Vacancy	N Vacancy
Sc	0.15	0.18	0.02	0.01
V	0.17	0.17	0.01	0.01
Cr	0.18	0.17	0.01	0.01
Mn	0.19	0.18	0.01	0.01
Fe	0.27	0.23	0.01	0.02
Co	0.27	0.15	0.01	0.03
Ni	0.27	0.16	0.01	0.02
Cu	0.27	0.17	0.01	0.01
Zn	0.16	0.17	0.03	0.01
Nb	0.16	0.17	0.02	0.01
Mo	0.19	0.17	0.01	0.02
Ru	0.21	0.18	0.01	0.02
Rh	0.21	0.17	0.01	0.02
Pd	0.25	0.15	0.01	0.03
Ag	0.15	0.16	0.03	0.01
W	0.20	0.16	0.01	0.02
Os	0.22	0.18	0.01	0.02
Ir	0.23	0.18	0.01	0.02
Pt	0.20	0.18	0.02	0.02
Au	0.20	0.15	0.02	0.01
B	---	0.19	---	0.02
C	---	0.20	---	0.04
O	---	0.15	---	0.02

Table S2. The Ti and N vacancy formation energies (E^f, in eV) on the TiN (100) surface under N-lean and N-rich conditions. The values in the brackets are taken from Ref. [1].

	Ti		**N**	
	N-lean	N-rich	N-lean	N-rich
E^f	3.77 (3.40)	-0.18 (-0.04)	-0.79 (-0.42)	2.80 (3.02)

Table S3. The H binding free energy (in eV) on the stoichiometric TiN (100) surface. The adsorption sites are shown in **Fig. S8(a)**. For the H adsorption at B_t site, it moves to N_t site after structural relaxation.

	B_t	H_t	N_t	Ti_t
ΔG_H	N_t	0.99	0.82	0.49

Table S4. The H binding free energy (in eV) for M@Tiv and M@Nv catalysts. The considered adsorption sites for the atomic H are given in **Figs. S8(b)-8(c)**.

	M@Tiv					M@Nv			
	B_t	H_t	N_t	M_t	Ti_t	B_t	H_t	M_t	Ti_t
Sc	M	Ti	0.69	0.69	0.45	-0.55	-0.29	0.21	B
V	M	M	0.64	0.36	0.54	-0.57	M	-0.21	B
Cr	M	M	0.58	0.24	0.58	-0.83	-0.17	-0.05	B
Mn	N	M	0.59	0.46	0.59	-0.41	0.03	-0.03	B
Fe	N	Ti	0.52	0.60	0.67	-0.28	M	-0.21	B
Co	N	M	0.34	0.53	0.69	-0.48	M	-0.49	B
Ni	M	Ti	0.05	0.78	0.50	-0.32	M	-0.27	B
Cu	0.65	M	0.43	0.90	0.68	-0.91	-0.58	-0.52	B
Zn	M	M	0.47	0.11	0.42	-0.49	-0.06	-0.03	B
Nb	M	M	0.74	0.08	0.47	-0.22	-0.13	0.27	B
Mo	M	M	0.58	-0.12	0.54	-0.06	-0.15	0.16	B
Ru	M	M	0.48	-0.38	0.64	-0.11	M	-0.33	B
Rh	M	M	0.47	-0.02	0.70	M	M	-0.32	M
Pd	0.66	0.66	0.39	0.82	0.72	0.04	M	0.05	B
Ag	0.43	1.12	0.28	0.53	0.47	0.28	M	0.65	B
W	M	M	0.60	-0.37	0.54	-0.16	-0.10	-0.09	B
Os	M	M	0.41	-0.73	0.65	M	M	-0.65	M
Ir	M	M	0.44	-0.49	0.72	M	M	-0.65	M
Pt	M	M	1.57	0.58	1.81	M	M	-0.32	M
Au	M	M	-0.08	-0.89	0.59	0.17	M	0.20	B
B	---	---	---	---	---	-0.15	-0.15	0.04	0.59
C	---	---	---	---	---	M	M	0.29	0.63
O	---	---	---	---	---	Ti	0.85	1.12	0.39

Table S5. The binding energies (in eV) for the M atoms near the Ti vacancy of the defective TiN (100) surface, and the energy differences (ΔE_{ad}, in eV) between the most stable configurations and the corresponding M@Tiv systems. The adsorption sites neighboring the Ti vacancy are shown in **Fig. S11(a)**.

	Ni	Zn	Nb	Mo	Rh
B1	3.48	0.54	4.53	4.43	4.53
B2	B1	0.52	4.46	4.38	B1
Ti_t	3.42	0.58	3.91	4.05	4.54
ΔE_{ad}	1.54	1.10	5.91	4.81	1.57

Table S6. Similar to **Table S5**, except that it is for the TiN (100) surface with the N vacancy. The adsorption sites neighboring the N vacancy are shown in **Fig. S11(b)**.

	Au	Mo	Pd	W	B
B1	2.80	4.02	Vac	3.50	N1
B1	2.79	4.09	2.73	3.57	3.45
N_{t1}	Vac	4.57	Vac	4.28	4.97
N_{t2}	Vac	3.78	2.94	3.78	4.67
ΔE_{ad}	1.48	0.72	1.82	1.02	1.73

References:

1. R.-Q. Zhang, T.-H. Lee, B.-D. Yu, C. Stampfl and A. Soon, *Phys. Chem. Chem. Phys.*, 2012, **14**, 16552-16557