Supplementary Information for:

Surface Oxidation for enhancing the hydrogen evolution reaction of metal nitrides: A theoretical study on VN

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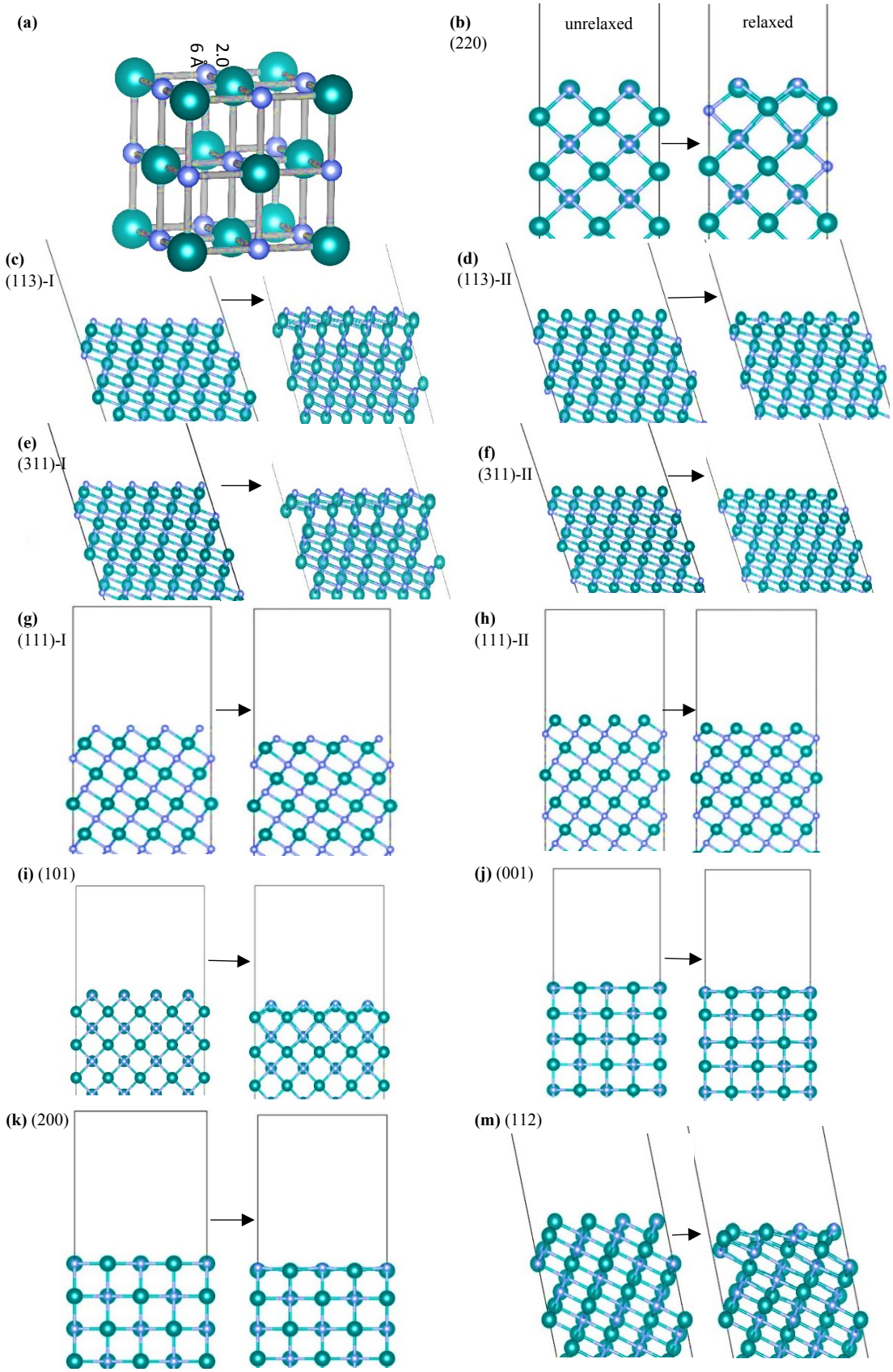

Fig. S1 DFT optimized configuration of (a) bulk VN, the lateral view of VN (b) (220), (c), (d) (113), (e), (f) (311) (g), (h) (111), (i) (101), (j) (001), (k) (200) and (m) (112) surfaces, before (left) and after (right) the structural relaxations.

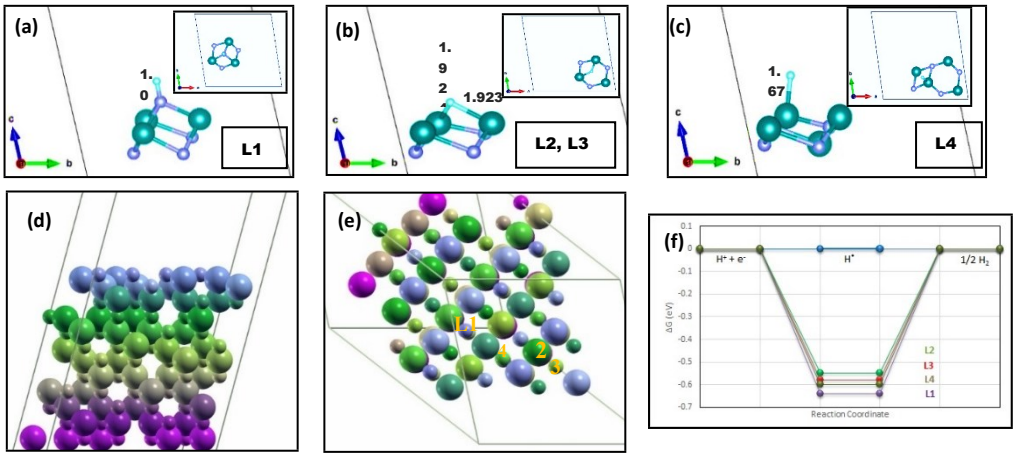

Fig. S2 The optimized local configuration of the VN (112) after the H adsorption on L1-L4 sites shown in (a)-(c), where the numbers are marked on figure (e). L1 and L4 are on-top-N sites, L2 is an on-top-V site and L3 is a bridge site. A variation of the colors is used in (d) lateral view and (e) top view of the slab, to show this is a really open surface. (f) chart the corresponding Gibbs free energies, for an easy comparison between the reported numbers in Table 1.

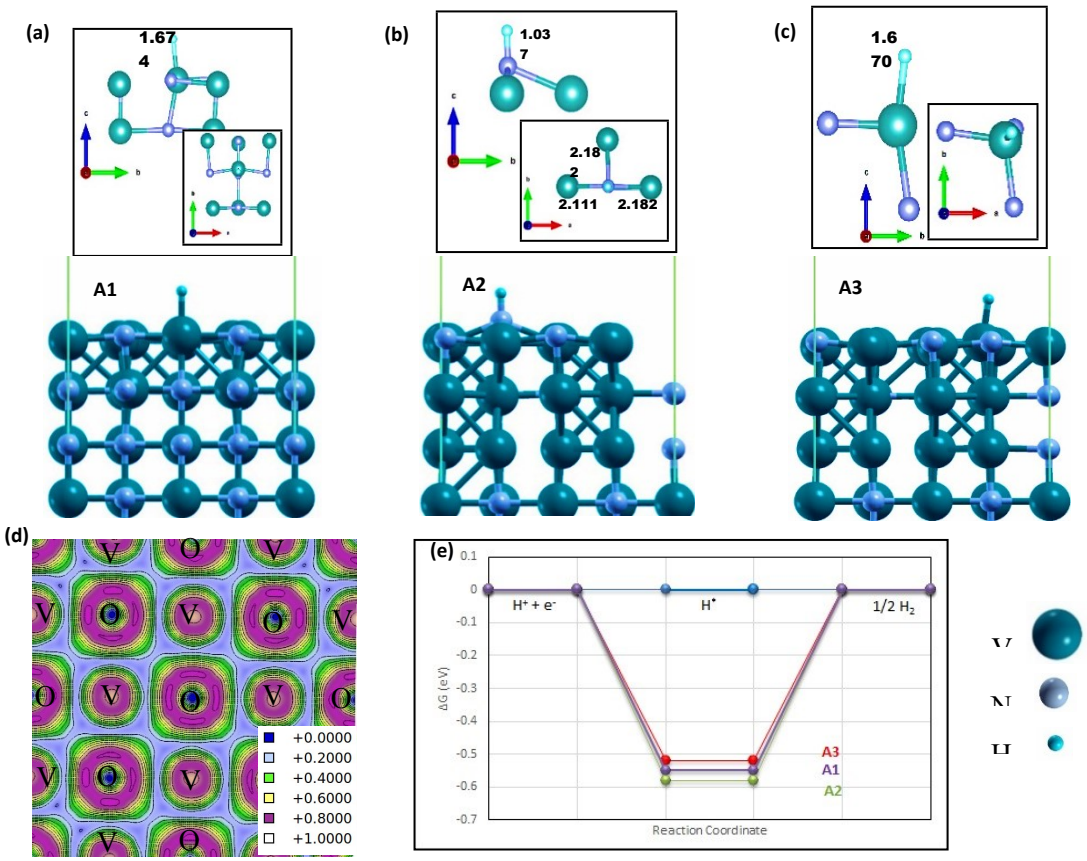

Fig. S3 Top and lateral view of hydrogen adsorption on clean VN(200) surface on top of (a) V atom, (b) N atom, and (c) bridge site. V, N, and H atoms are represented by big turquoise color, medium grey color, and small blue color balls, respectively. (e) shows The electron localization function (ELF) plot of clean VN(200) surface. A comparison between H adsorption free energies is represented in figure (e).

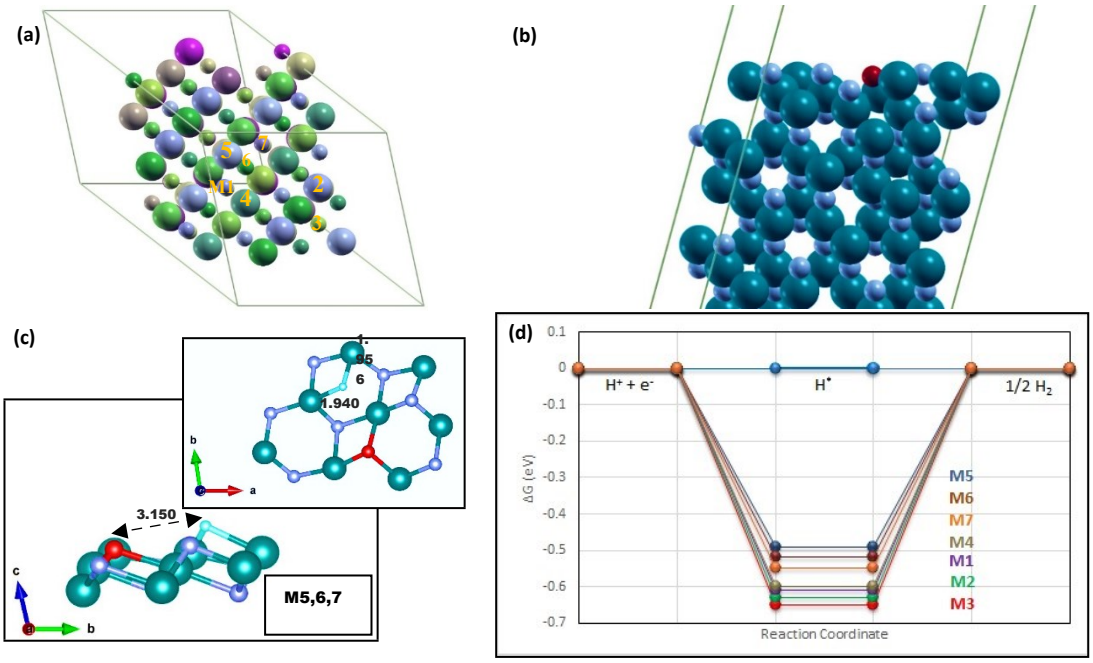

Fig. S4 Top (a) and lateral (b) view of the O-doped VN (112) surface. The variety of colors is similar to the pure surface and shows the difference in the height of the atoms relative to the vacuum space. The considered adsorption sites are marked by orange colors and will be referred to as M1~M7, in which M1 is an N-on-top site, M2, M4 and M5 are V-on-top sites, M3 and M6 are hollow-sites, while M7 is an O-on-top site. The most active adsorption site is the V atom in the direct vicinity of the dopant and all M5-7 considerations will end up to one final configuration shown in (c). (d) is a schematic view of the corresponding free energies.

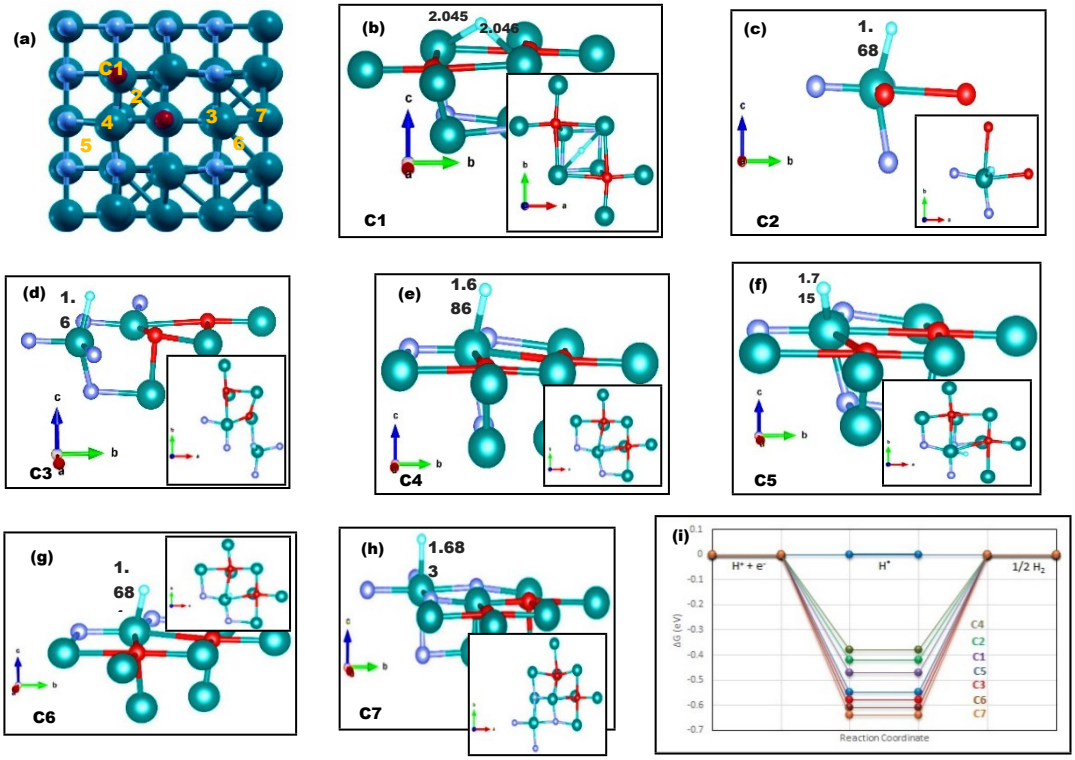

Fig. S5 DFT optimized structure of H adsorbed on VN (200) surface, doped with two O atoms, where (a) shows the sites, marked as C1-7 by orange color, (b)-(h) show the local configurations around the C1-C7 sites, respectively, and (i) represents a comparison between their corresponding free energies.

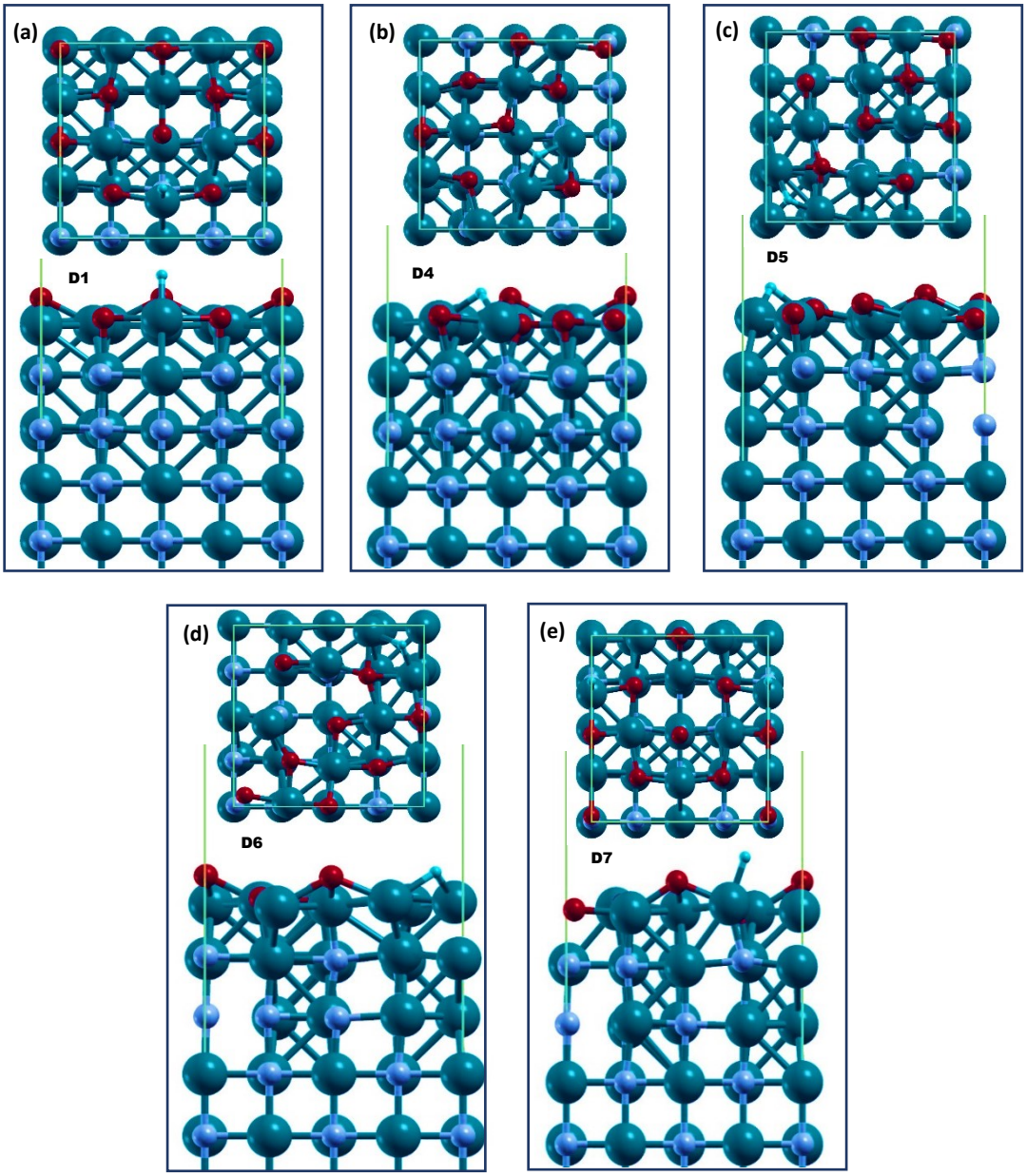

Fig. S6 Top and lateral view of VO/VN configuration after H adsorption, where all the N atoms on the topmost layer are replaced with O atoms. The local structure of adsorbed hydrogen on top of the surface is shown in Fig. 2(a)-(e), while D1-D7 sites are marked in Fig. 2(h).

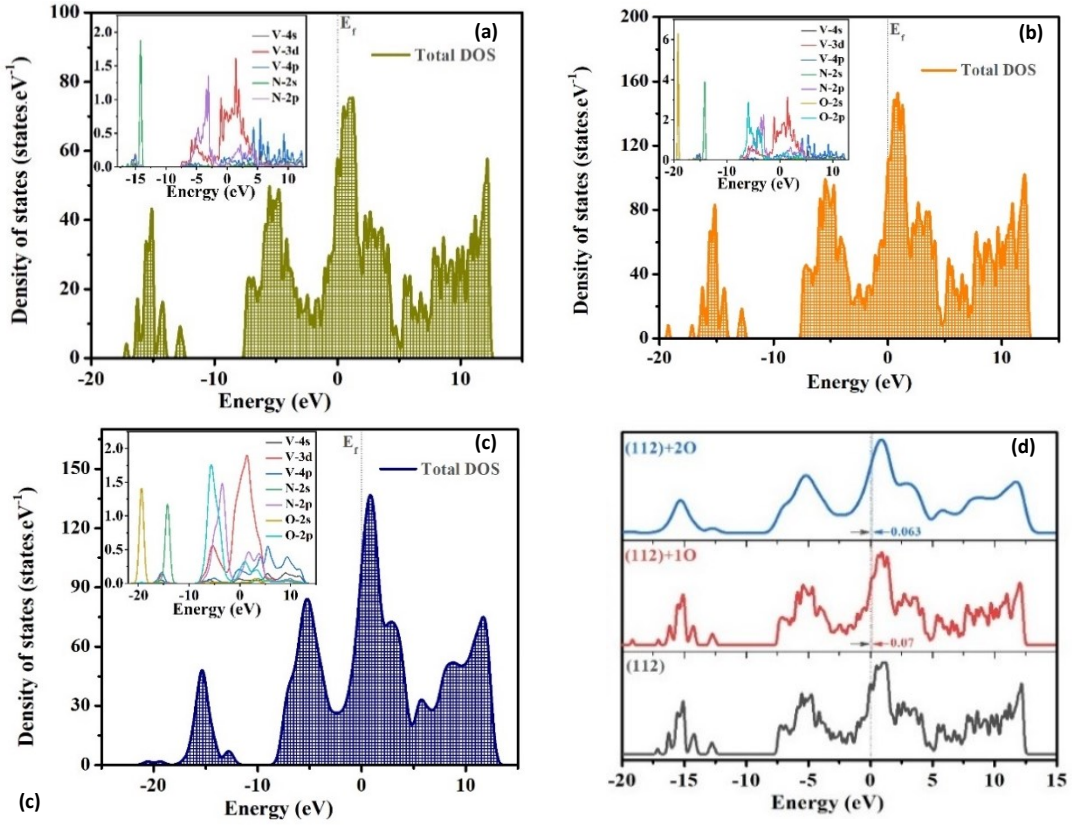

Fig. S7 Density of States plot for (a) clean, (b) one O-doped, and (c) double O-doped VN (112) surfaces. The insets represent the Partial DOS plots and the Fermi level is put on zero. Figure (d) represents a comparison between TDOS of these surfaces.

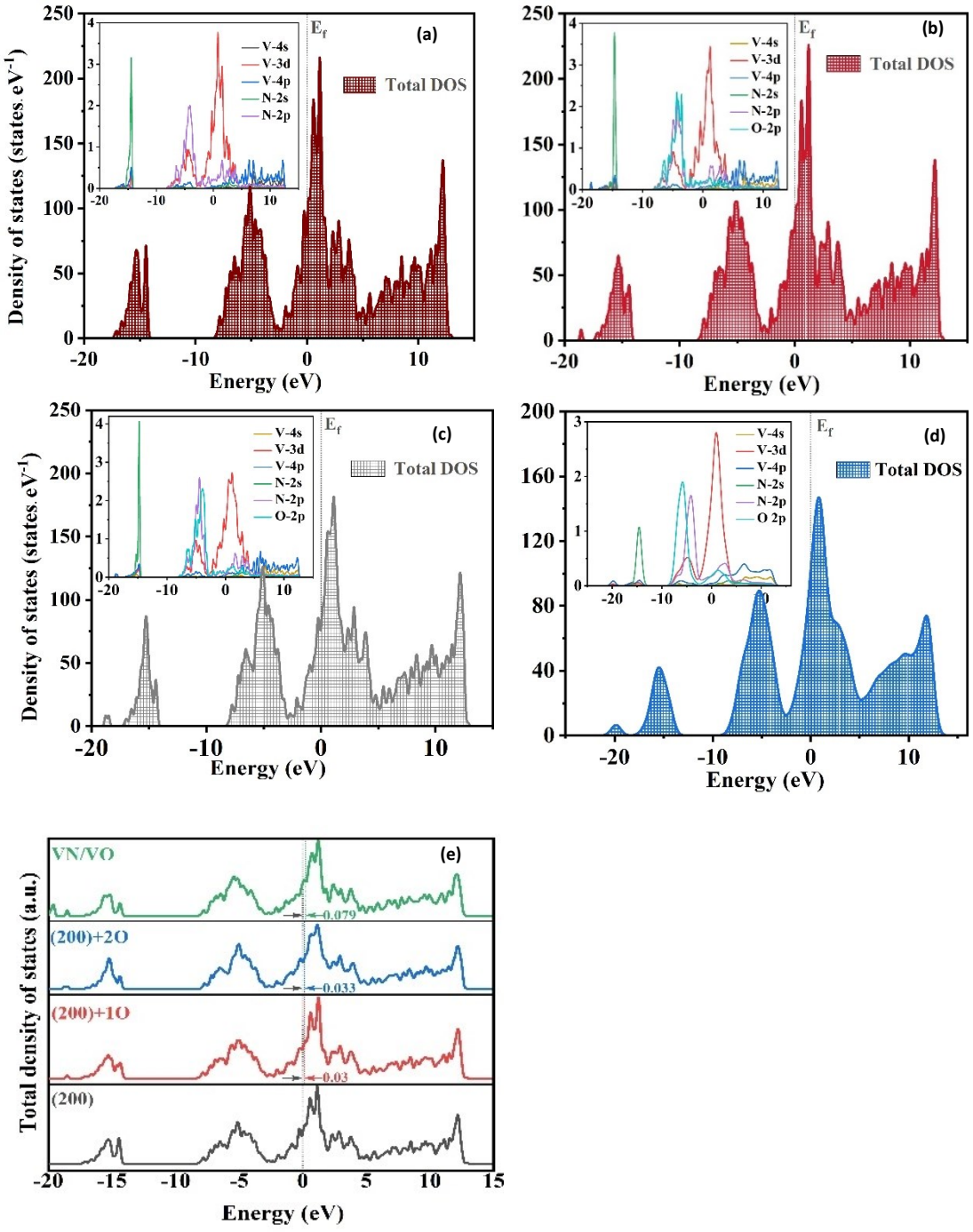

Fig. S8 The density of States plots for (a) clean, (b) one, (c) double and (d) four oxygen atoms, doped on VN (200) surface, while (e) is a comparison between Total DOSs related to the clean and O-doped (200) surfaces. The insets represent Partial DOS plots and the Fermi level is put on zero.

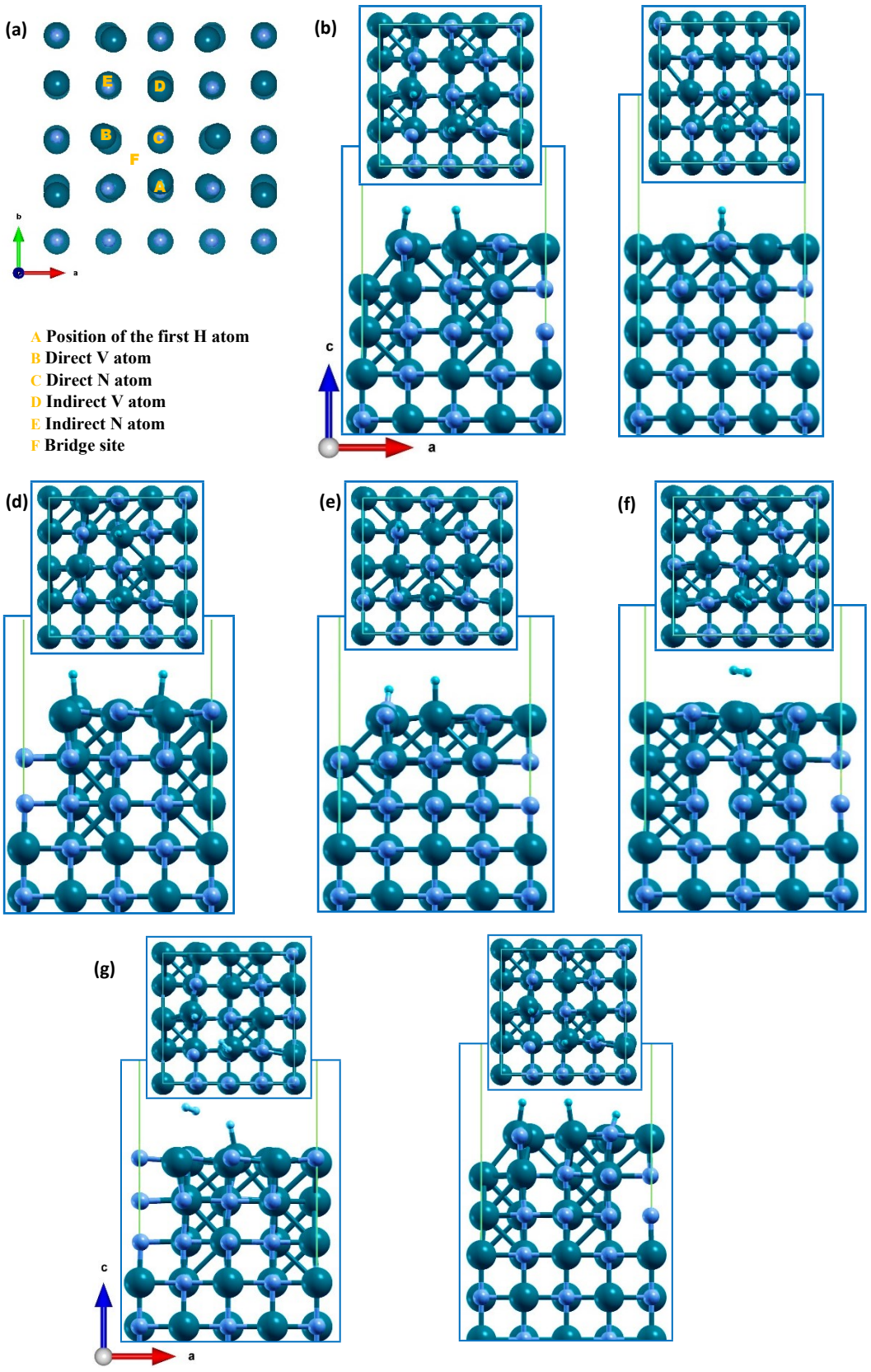

Fig. S9 Hydrogen adsorption on clean VN (200) surface at low H convergence. The second H is initially located 4 Å above the surface in different positions, where (a) shows the considered positions, and (b)-(f) show the relaxed structures, respectively. (g) and (h) represent the 3/8ML hydrogen coverage of the surface, where the next H atoms either releases the hydrogen attached to the V or stays on the surface due to the strong bonding with the nitrogen, respectively.

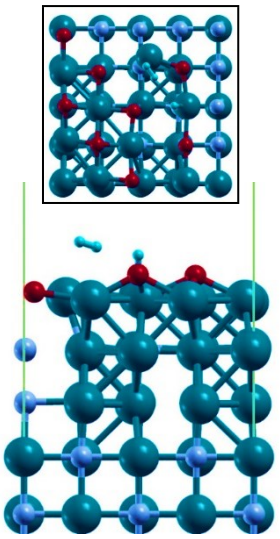

Fig. S10 Optimized configuration of three H atoms adsorbed orderly on VO/VN surface. The third H atom was put initially near the first and second ones. The formation of H_2 molecules on the surface is obvious.

Table S1 The DFT calculated surface energies (J/m^2) for eight low and high index surfaces of vanadium nitride.

VN facet	**(001)**	**(220)**	**(113)-I**
Surface Energy	1.464	1.104	1.213
VN facet	**(113)-II**	**(311)-I**	**(311)-II**
Surface Energy	1.019	1.112	1.015
VN facet	**(111)-I**	**(111)-II**	**(101)**
Surface Energy	1.028	1.015	1.019
VN facet	**(200)**	**(112)**	
Surface Energy	0.932	0.929	

Table S2. D-band center of pure and oxygen polluted VN surfaces. In the first row, (112)+1O denotes VN(112) surface with one doped O atom on top. The same procedure is kept for the others.

surface	**(200)**	**(200)+1O**	**(200)+2O**	**VO/VN**	**(112)**	**(112)+1O**	**(112)+2O**
d-band center (eV)	-1.187	-1.179	-1.167	-1.042	-1.057	-0.956	-1.003

Table S3. Bader Charge of H* on top of the VO/VN surfaces with different H coverages. The numbers are marked in Fig. 4 (a) and (b), respectively.

Site No.	**5**	**6**	**7**	**8**	**9**
Electric charge	-0.24	-0.28	-	-	-
Electric charge	-	-	-0.42	-0.32	+0.36