Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary Materials for

First-Principles Study on the Double-Side Decorated Boron-Nitrogen Co-doped Graphene by Vanadium for Enhanced Low-Temperature Reversible Hydrogen Storage

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Note 1. Electric Field

The upward external electric field was applied along the Z direction as proposed by Neugebauer and Scheffler,[1] which considers an artificial dipole sheet in the center of the vacuum layer. This dipole sheet polarizes the top and bottom BNDG surfaces with opposite charges and thus creates a desired uniform electric field. This requires a large enough vacuum thickness to avoid the overlap between the charge density of the BNDG slab and the artificial dipole sheet. But, if the vacuum space is too wide, a strong electric field will pull out the electrons at the Fermi level of the BNDG slab and lead to field emissions in the vacuum.[2]

When the field is absent, the charge density decays roughly expressed as $exp(-\sqrt{\Phi}z)$, where Φ is the work function and z is the distance from the slab. The work function is one of the most important electronic properties of a metal surface, which measures the minimum energy required to remove an electron from the inside of bulk solid to the outside (i.e., in the vacuum). It is defined as, $\Phi = E_{vacuum} - E_f$, where E_{vacuum} and E_f are the vacuum potential and Fermi levels of Ti_3 atoms decorated on the BNDG sheet, respectively. For Ti_3 atoms decorated on the BNDG sheet, the calculated value of Φ is 4.44 eV; therefore, the charge density drops by order of magnitude per 1.00 Å. In view of the field emission issue, if the distance is over $\sim \Phi/F$ (F is the electric field), an electron can emerge into the vacuum due to tunneling effects. As the Φ for Ti_3 atoms decorated on the BNDG sheet is 4.44 eV, the maximum width between the surface and the artificial dipole sheet under the electric field should be around 7 Å; we therefore used a vacuum space of 14 Å.

Note 2: Electron Density Difference:

To understand the effects of double side decoration of BNDG sheet, we plot the two-dimensional electron density differences for both single side and double side decorated BNDG sheet using the following formulas'

For single side: $\Delta Q = Q_{Total} - (Q_{BNDG} + Q_{V_3})$

where Q_{Total}, Q_{BNDG} and Q_{V_3} are the electron densities of total system, pure BNDG sheet and V_3, respectively. (The obtained plot is shown in Figure 8a of manuscript).

For double side:

1. $\Delta Q = Q_{Total} - (Q_{V_3/BNDG} + Q_{V_3})$

   where Q_{Total}, $Q_{V_3/BNDG}$ and Q_{V_3} are the electron densities of total system (i.e., V_3 decorated on both sides of BNDG), V_3 decorated on a single side of BNDG sheet, and V_3, respectively. (The obtained plot is shown in Figure 8b of manuscript).

2. $\Delta Q = Q_{Total} - (Q_{BNDG} + 2Q_{V_3})$

   where Q_{Total}, Q_{BNDG} and Q_{V_3} are the electron densities of total system(i.e., V_3 decorated on both sides of BNDG), pure BNDG sheet and V_3, respectively. (The obtained plot is shown in Figure 8c of manuscript).

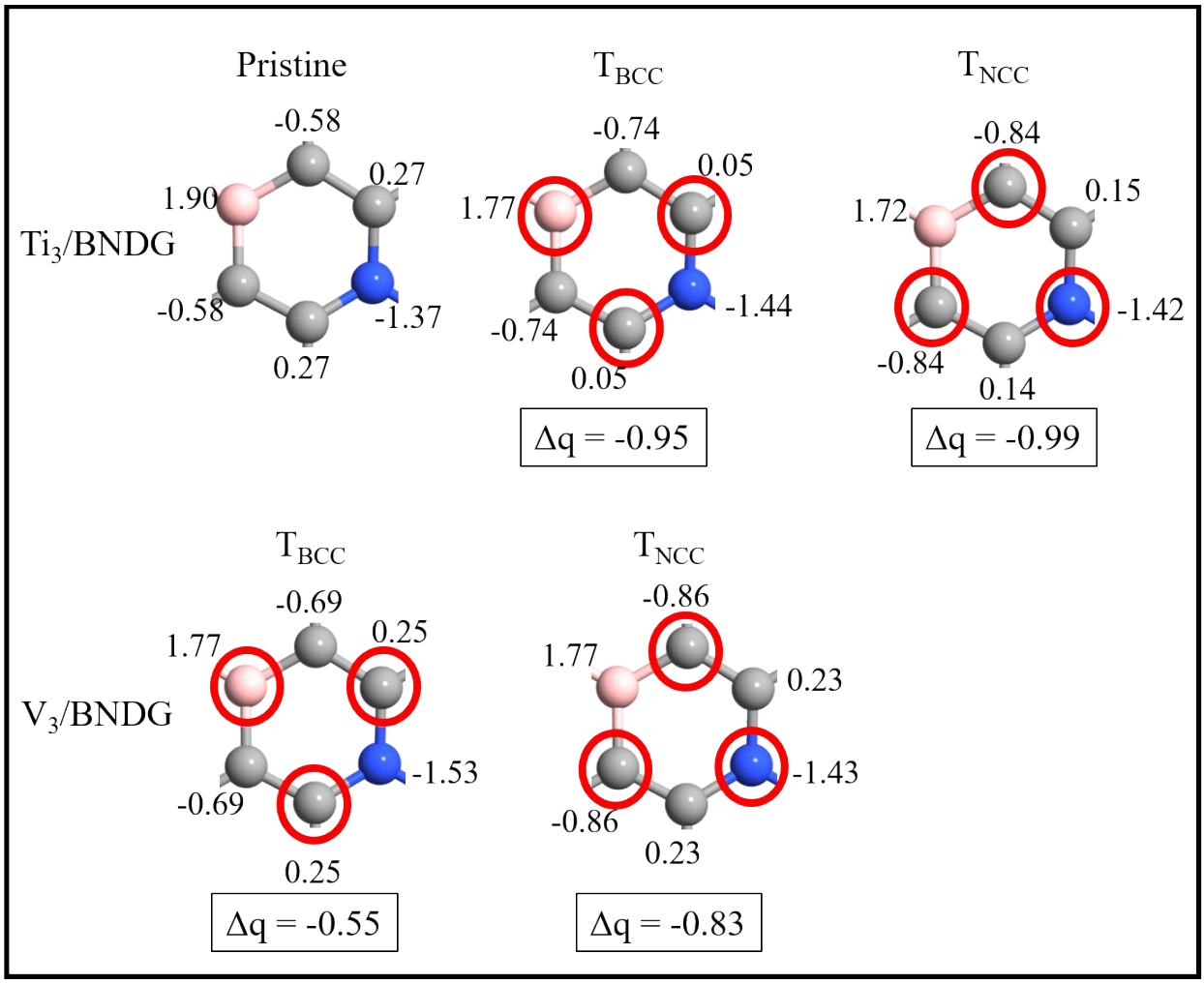

Figure 1S. The Bader charges around the one unit of the six-membered ring for Ti_3 and V_3 atoms adsorbed on both the T_{NCC} and T_{BCC} sites of the BNDG sheet. (Red circle denotes where the metal atoms are adsorbed and Δq represents the charge difference between before (pristine) and after metal adsorption).

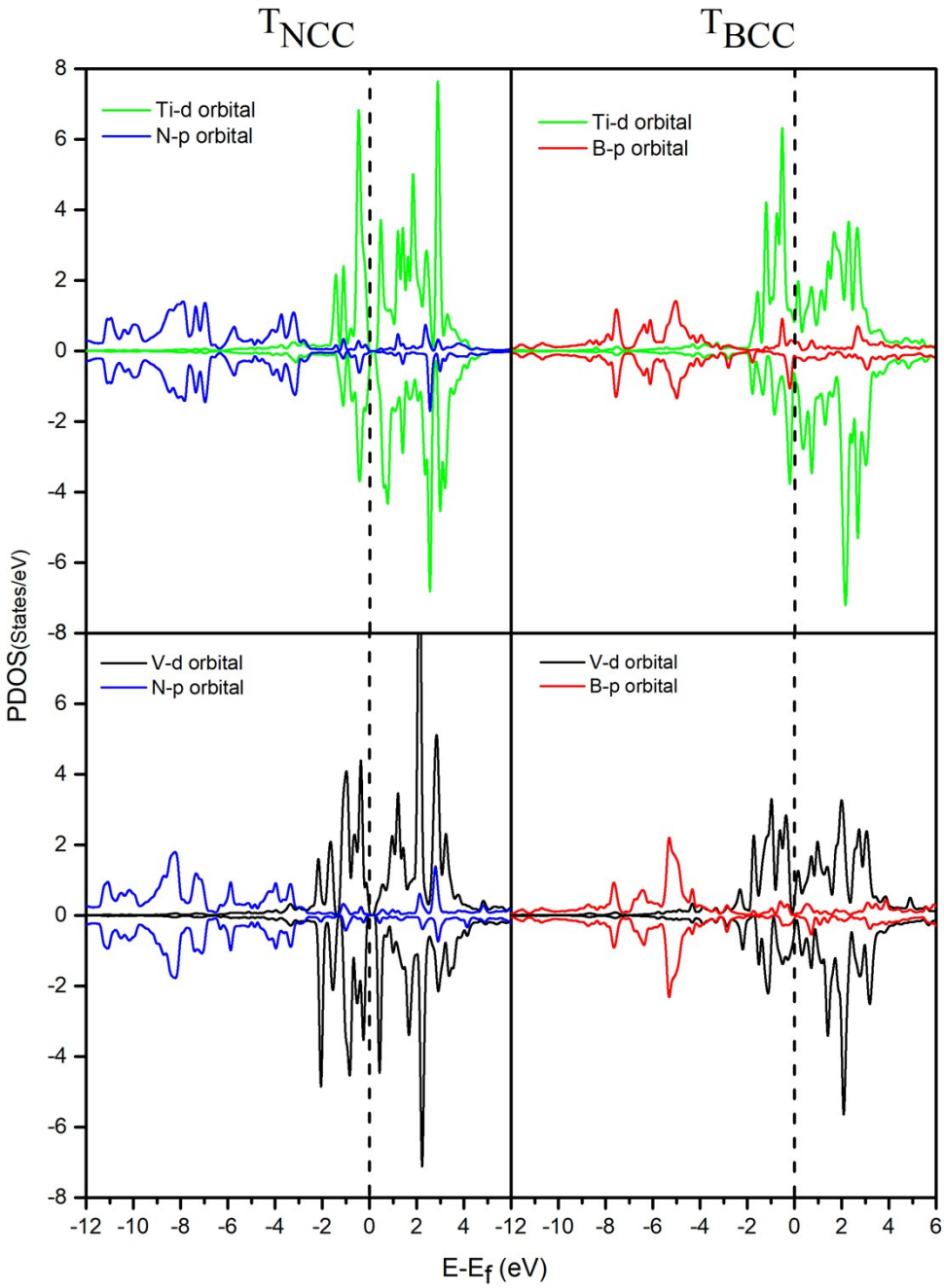

Figure 2S. The projected density of states for the *d* orbitals of Ti_3 and V_3 and *p* orbitals of N and B atoms upon Ti_3 and V_3 adsorption on the BNDG sheet. The dotted line denotes the Fermi level. (The intensities of p orbitals are multiplied by 5)

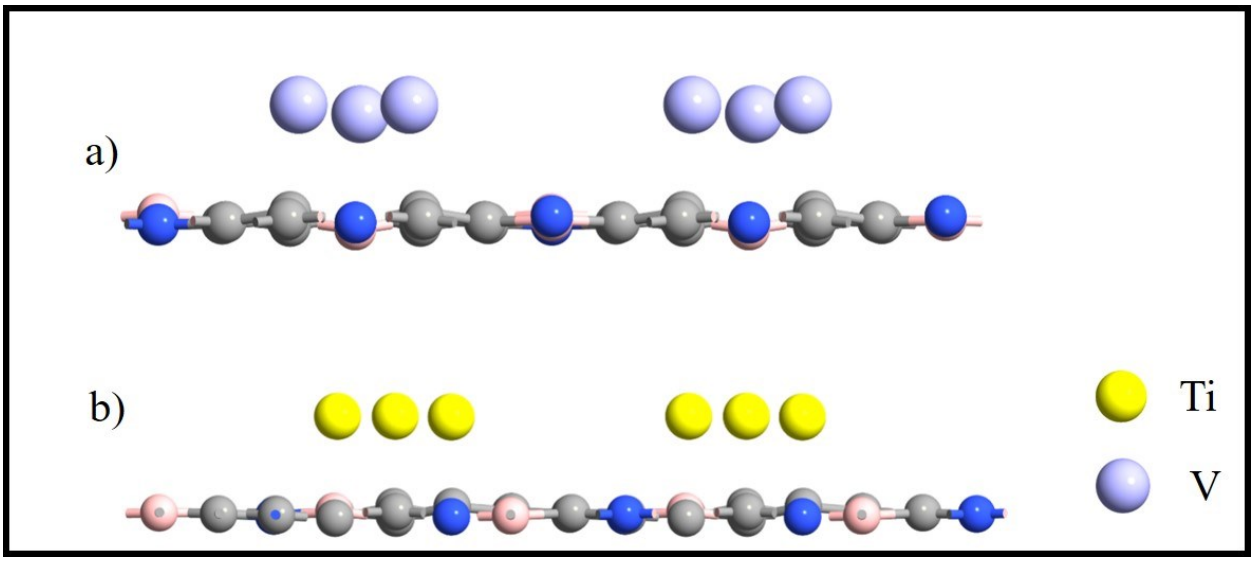

Figure 3S. The 6×3 supercell of 2 sets of V_3 (a) and Ti_3 (b) decorated Boron-Nitrogen co-doped graphene (BNDG) sheet.

Table 1S. The calculated different metal trimer binding energy (E^{M-G}_{b} in eV) on the BNDG sheet, the metal-metal binding energy (E^{M-M}_{b} in eV), and the distance between the metal to graphene (d_{M-G} in Å) and metal –metal (d_{M-M} in Å)

Metal Trimers	E^{M-G}_{b}	d_{M-G}[a]	d_{M-M}[b]
Vanadium (V)	-2.54	2.143	2.104
Manganese (Mn)	-2.14	2.065	2.467
Iron (Fe)	-2.12	2.057	2.222
Cobalt (Co)	-1.91	2.026	2.214
Nickel (Ni)	-2.47	2.015	2.249
Copper (Cu)	-2.11	2.076	2.343
Titanium (Ti)	-3.38	2.168	2.430

[a] The vertical distance of metal atom to nearest Carbon atom
[b] The horizontal distance between the two metals atoms

Table 2S. The calculated Binding energy of Ti_3 (E_b^{M-G} in eV) on the BNDG sheet with respect to different electric field strengths.

Electric Field (V/Å)	E_b^{M-G} **(in eV)**
0.60	-3.22
0.40	-3.63
0.20	-3.69
0.00	-3.38
-0.20	-3.79
-0.40	-3.83
-0.60	-3.86

Table 3S. The calculated average H_2 adsorption energy (E_{ad} in eV), stepwise energy (E_{step} in eV) of the hydrogen molecules adsorbed on V_3 single side decorated BNDG sheet in the presence of electric field (0.4 V/Å).

No. of H_2	E_{ad}	E_{step}
8	-0.49 (-0.49)	-0.069(-0.068)
9	-0.45 (-0.44)	-0.094 (-0.084)

Values in the parenthesis are those in the absence of electric field.

References:

1. J. Neugebauer and M. Scheffler, *Phys.Rev. B*, 1992, **46**, 16067-16080.
2. P. J. Feibelman, *Phys.Rev. B*, 2001, **64**, 125403.