

Supplementary Material

Quantum Confinement Effect on Defect Level of Hydrogen Doped rutile VO₂ Nanowires

Manoj Dey¹, Suman Chowdhury¹, Sonu Kumar¹, and Abhishek K. Singh^{*†}

[†]Materials Research Centre, Indian Institute of Science, Bangalore-560012, India

*abhishek@iisc.ac.in

Surface Configurations

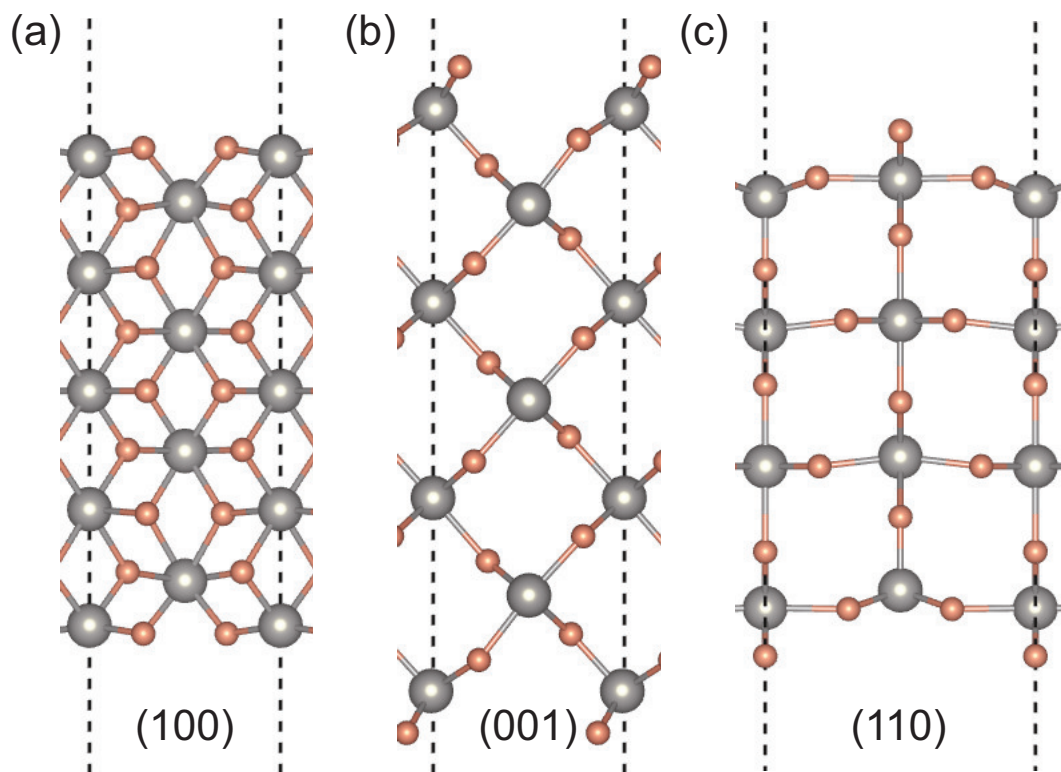


Figure S1: Relaxed structures of stoichiometric low-indexed surfaces (a) (100), (b) (001), and (c) (110) of $\text{VO}_2(\text{R})$.

Nanowire Structures : Side View

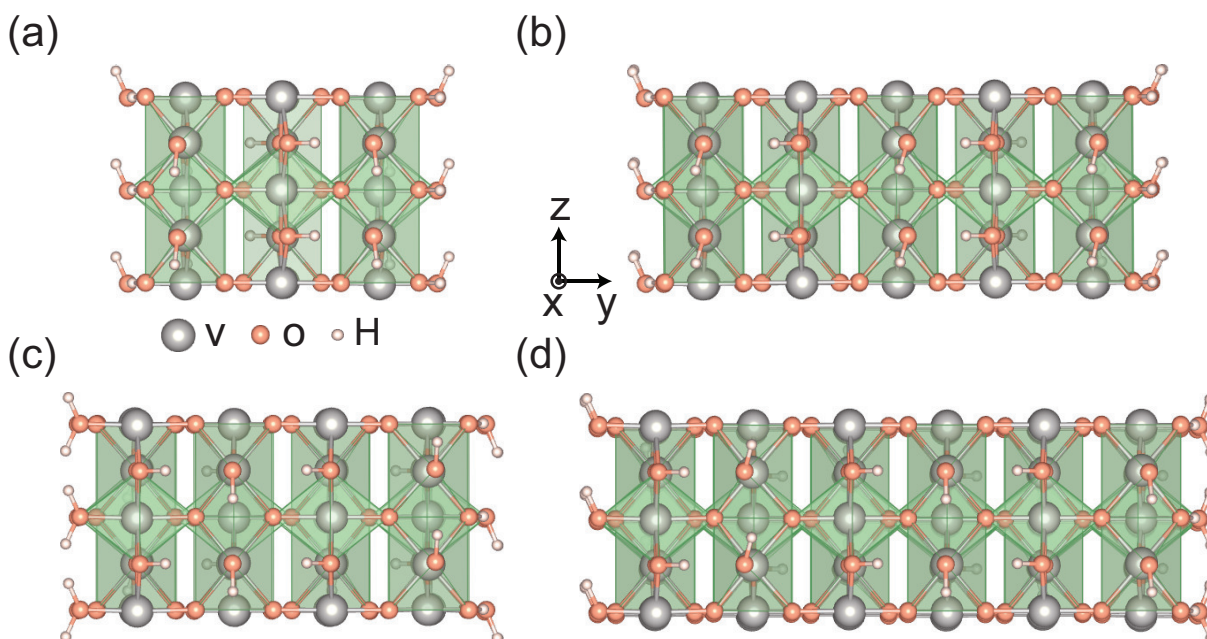


Figure S2: The side view of relaxed structures of (a) NW9, (b) NW16, (c) NW25, and (d) NW36. The V octahedral are shown in green.

Band-Decomposed Charge Density of Band-edges

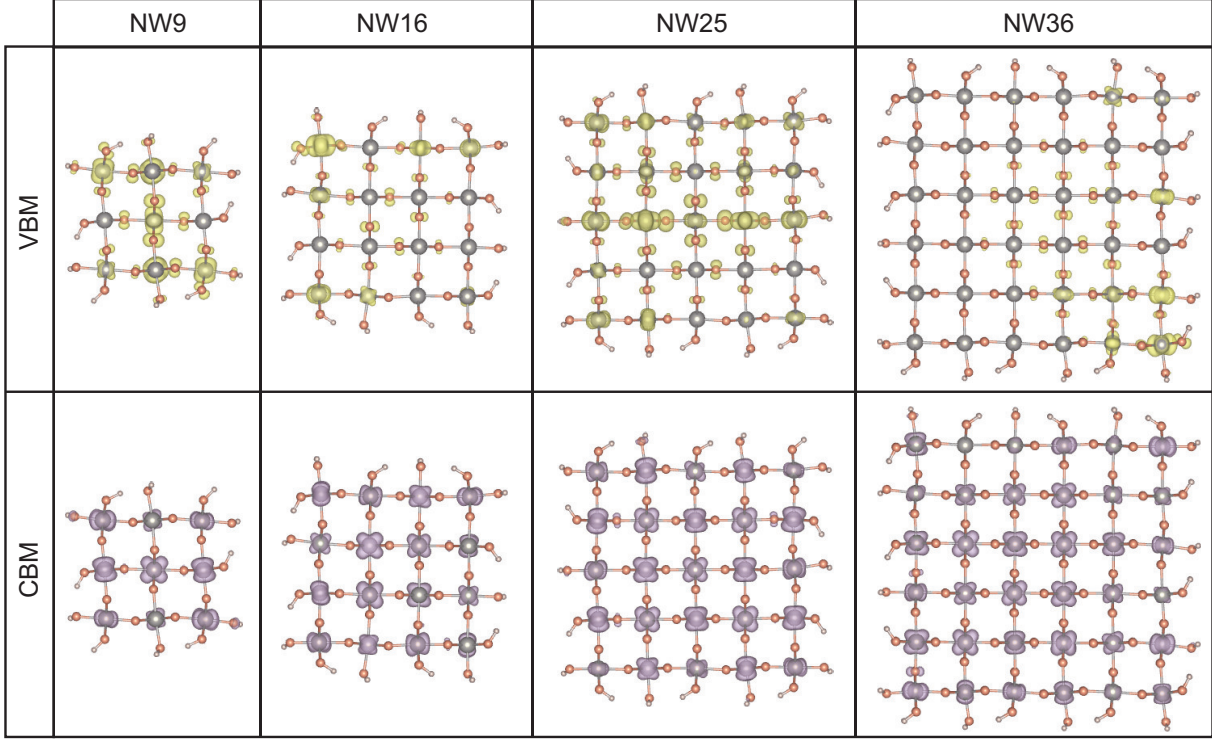


Figure S3: Band-decomposed charge density of valence band maximum and conduction band minimum of all the nanowires. Isosurface value is set to 10% of maximum.

We have calculated the band decomposed charge density of band edges of corresponding nanowires as shown in Figure S3. This clearly shows that the valence band maximum (VBM) is composed of V-d and O-p hybridized orbital spatially localized in nanowire diameter. However, the conduction band minimum (CBM) consists of only V-d orbitals.

Fitting of Band Gaps

We have calculated several goodness-of-fit parameters to determine the best fit of E_g versus d . The coefficient of determination (R^2) is calculated as,

$$R^2 = 1 - \frac{SS_{res}}{SS_{tot}} \quad (S1)$$

where, SS_{res} and SS_{tot} are the sum of squares of residuals and the total sum of squares, respectively. The root-mean-square-error (RMSE) is the standard deviation of the residuals. The best power-law fit ($d^{-0.48}$) has the highest R^2 (0.96) and lowest RMSE (0.04) values among the curves.

Table S1: Band gap fitting parameters.

Expression	a	b	R^2	RMSE (eV)
$a d^b$	1.64	-0.48	0.96	0.04
$a \exp^{bd}$	2.00	-0.26	0.93	0.06
$a d^b$	1.48	-0.3	0.82	0.08
$a d^b$	1.94	-0.8	0.59	0.12

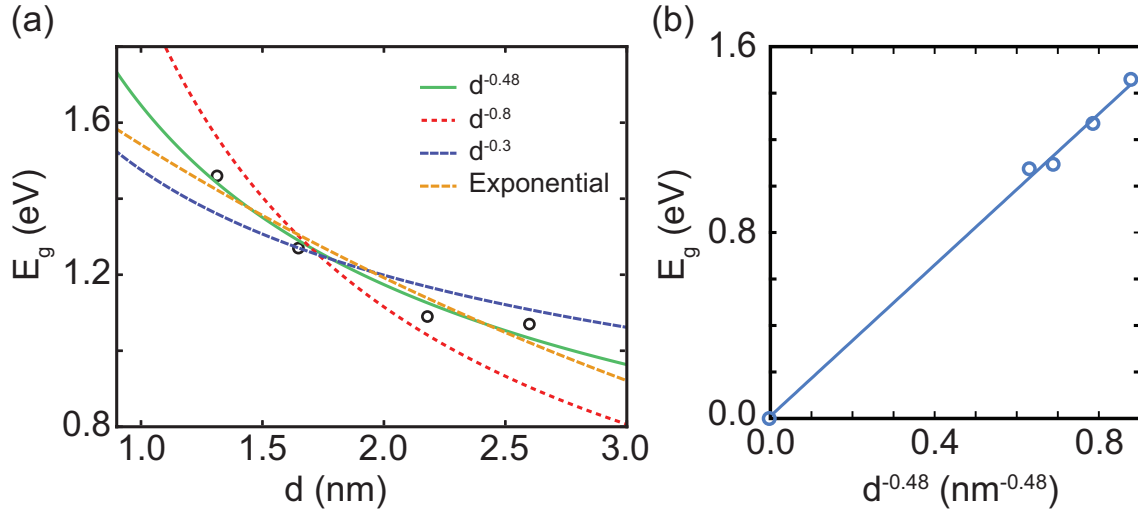


Figure S4: (a) Inverse power and exponential fitting plot of band gap with NW diameter. (b) The linear fitting of E_g versus $d^{-0.48}$ contains the zero band gap of metallic bulk $\text{VO}_2(\text{R})$.

Workfunction of Nanowires

In order to calculate the work function of all the NWs, we first determine the vacuum potentials (ϕ). We have taken sufficiently large vacuum spacing for all the configurations such that the planar averaged electrostatic potential converges to a constant value, as shown in Figure S5. The work function (W) is then calculated with reference to this converged value as,

$$W = \phi - \epsilon_F \quad (\text{S2})$$

where, ϵ_F is the Fermi level of corresponding nanowires. The calculated values of work functions are 6.09 eV, 6.30 eV, 6.00 eV, and 6.18 eV for NW9, NW16, NW25 and NW36, respectively.

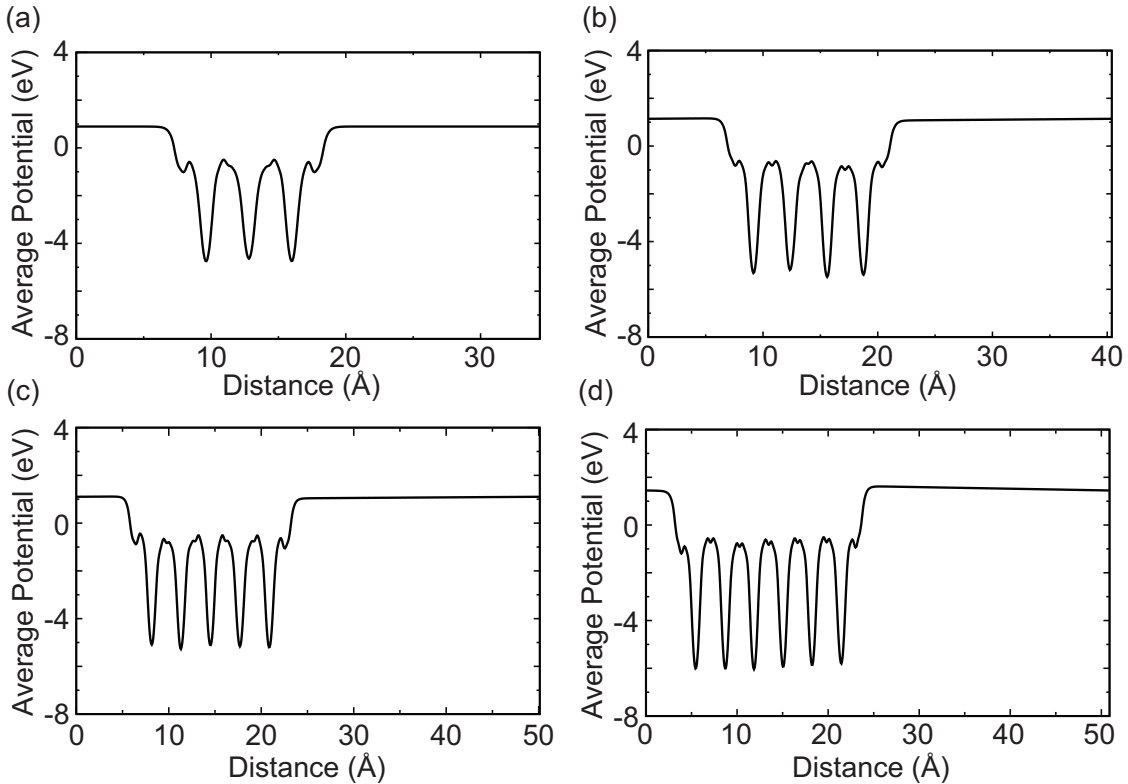


Figure S5: Planar averaged potential along x direction of (a) NW9, (b) NW16, (c) NW25, (d) NW36 nanowires.

Defect Formation Energy

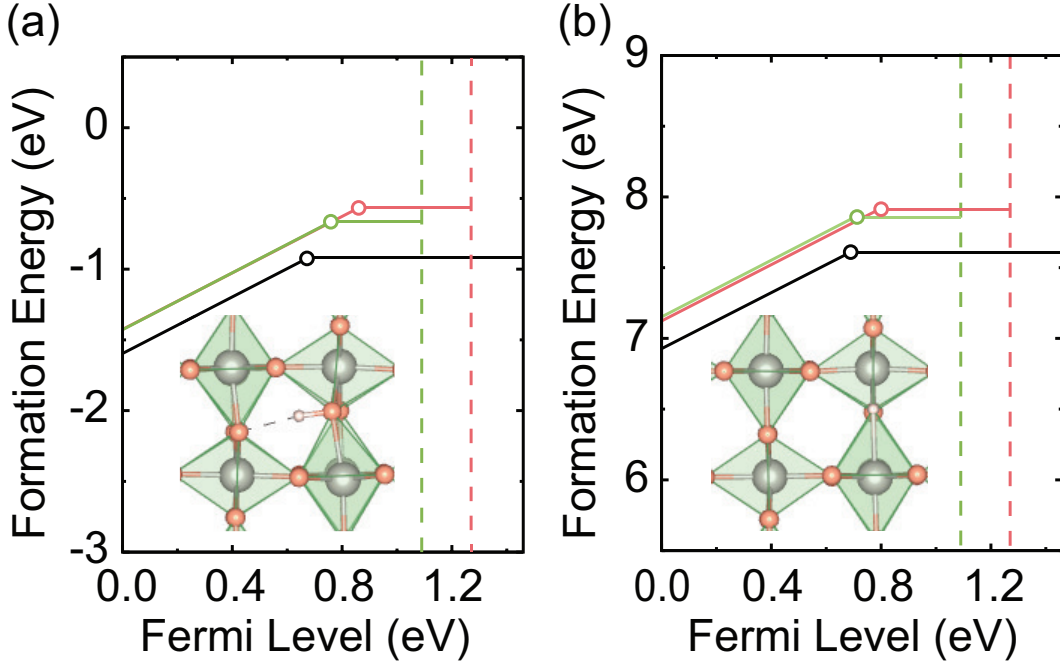


Figure S6: Formation energy and charge transition levels for (a) H_i, and (b) H_O defects in oxygen rich growth condition. The black (NW9), red (NW16), and green (NW25) lines denote the variation of formation energies with Fermi level. The position of donor level $\epsilon(+1/0)$ is shown by hollow circle.

In order to study the correlation between the H doping and size effect, we have compared the formation energies of H related defects in NWs with the bulk VO₂ as a function of growth conditions. We note that the bulk VO₂ in rutile phase shows metallic behaviour. Therefore, we have calculated the defect formation energies of both H_i and H_O in neutral charge states in bulk VO₂ and compared them with the same in NWs. The formation energy of hydrogen related neutral defects ($q=0$) defects (H_i and H_O) in NW is,

$$E_f(D^0) = E(D^0) - E(NW) + n_i\mu_i \quad (S3)$$

The formation energy is the comparison between the total energy $E(D^0)$ of the system containing H defect (NW+H system) in charge state 0 with the total energy of NW $E(NW)$ without H doping. The n_i represents the number of atoms removed or added having chemical potential μ_i . Similarly, the formation energies of H defects in bulk VO₂ are calculated as,

$$E_f(D^0) = E'(D^0) - E(BulkVO_2) + n_i\mu_i \quad (S4)$$

where, the total energy $E'(D^0)$ of bulk VO₂ containing H defect is compared with the total energy $E(\text{bulk VO}_2)$ of pristine bulk VO₂ supercell. The thermodynamic defect formation energy of H_i is independent of the growth condition (See Figure S7(a)), whereas it increases for H_O in O-rich condition (See Figure S7(b)). Both H_i and H_O defect incorporation are more favourable in the lowest diameter NW, as the formation energies are low in NW9. The formation energies of neutral defects in large diameter NWs (in NW16 and NW25) converge to the bulk VO₂ as shown in Figure S7.

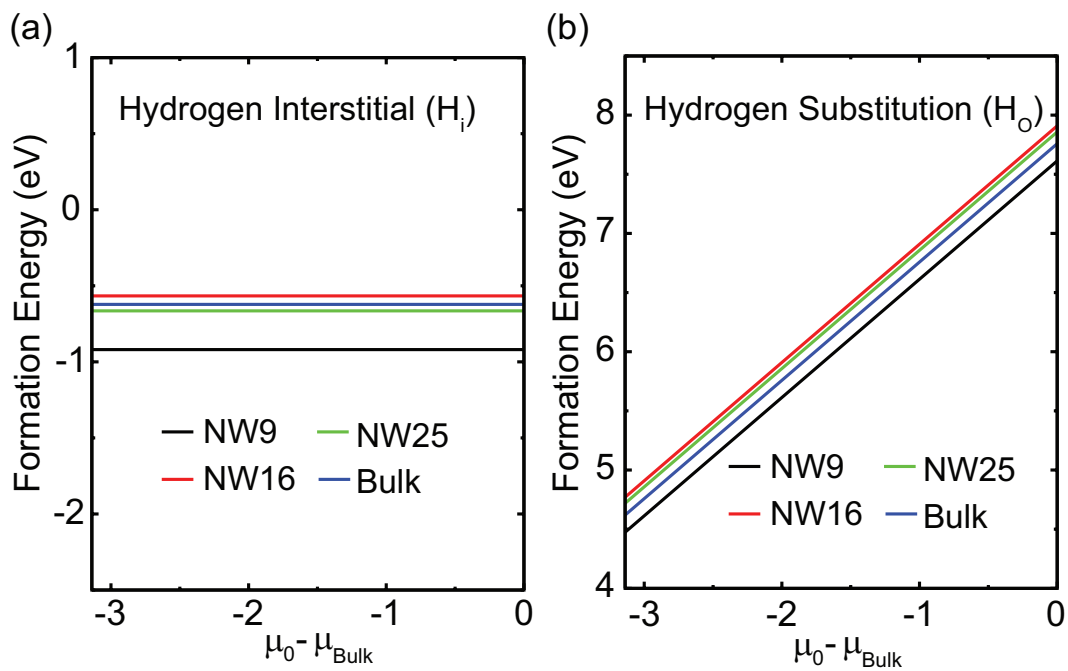


Figure S7: Calculated formation energies for (a) hydrogen interstitial (H_i), (b) hydrogen substitution (H_O) defects in nanowires (NW9: black; NW16: red; NW25: green) and bulk (blue) $\text{VO}_2(\text{R})$ as a function of O chemical potentials.