

FIG. 5: RPBE calculation of the total density of states in eV^{-1} per TiO_2 functional unit versus energy in eV for undoped (thin black solid line), boron doped (magenta dashed line) and nitrogen doped (blue thick solid line) TiO_2 (a) (2,2) nanorods, (b) (3,3) nanotubes and (c) (4,4) nanotubes, with 3.1%, 2.1%, and 1.6% doping respectively. Energies are measured from the top of the valence bands of anatase TiO_2 ϵ_{VB} , and the DOSs are shifted to align the lowest eigenstate with that for anatase TiO_2 . Occupancy is denoted by curve filling for states in the band gap.

B. DOS of 1D Nanorods and Nanotubes

We shall now discuss how boron and nitrogen doping influences the electronic structure of stable 1D nanorods and nanotubes. Although the most stable doping sites are the same as those obtained for doped TiO_2 rutile surface and bulk [5, 16, 17], the influence of dopants on the DOS is rather different.

Figure 5 shows the DFT calculated DOS and Fig. 6 the structures of the most stable boron doped and nitrogen doped TiO_2 (2,2) nanorods, (3,3) nanotubes, and (4,4) nanotubes. The highest occupied state is also shown as isosurfaces of $\pm 0.05e/\text{\AA}^3$ in the side views of the doped structures.

As with TiO_2 clusters, the influence of boron dopants on TiO_2 nanorods and nanotubes may be understood in terms of boron's weak electronegativity, especially when compared with the strongly electronegative oxygen. We find that boron prefers to occupy oxygen sites which are 2-fold coordinated to neighboring titanium atoms. However, as with the 0D clusters, boron's relatively electropositive character induces significant structural changes in the 1D structures, creating a stronger third bond to a neighboring three-fold coordinated oxygen via an oxygen dislocation, as shown in Fig. 5. This yields three occupied mid-gap states localized on the boron dopant, which overlap both the valence band O $2p_\pi$ and conduction band Ti $3d_{xy}$ states, as shown in Fig. 5. Boron dopants

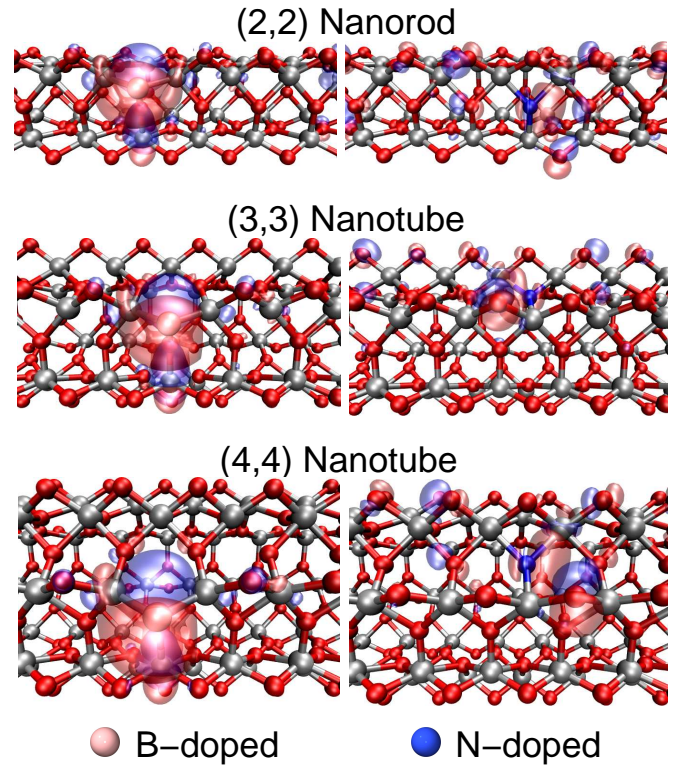


FIG. 6: Schematics of boron doped (left) and nitrogen doped (right) TiO_2 (2,2) nanorods, (3,3) nanotubes, and (4,4) nanotubes, with 3.1%, 2.1%, and 1.6% doping respectively. The highest occupied states for boron and nitrogen doped TiO_2 1D structures are depicted by isosurfaces of $\pm 0.05e/\text{\AA}^3$.

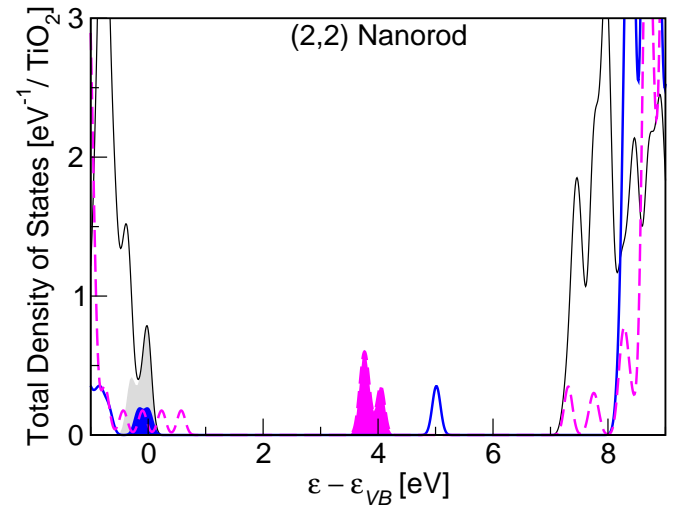


FIG. 7: GW calculation of the total density of states in eV^{-1} per TiO_2 functional unit versus energy in eV for undoped (thin black solid line), boron doped (magenta dashed line) and nitrogen doped (blue thick solid line) TiO_2 (2,2) nanorods with 3.1% doping. Energies are measured from the top of the valence bands of the undoped TiO_2 nanorod ϵ_{VB} , and the DOSs are shifted to align the lowest eigenstate with that for the undoped TiO_2 nanorod. Occupancy is denoted by curve filling for states in the band gap.