Supporting information

Water on Graphene-Coated TiO_2: Role of Atomic Vacancies

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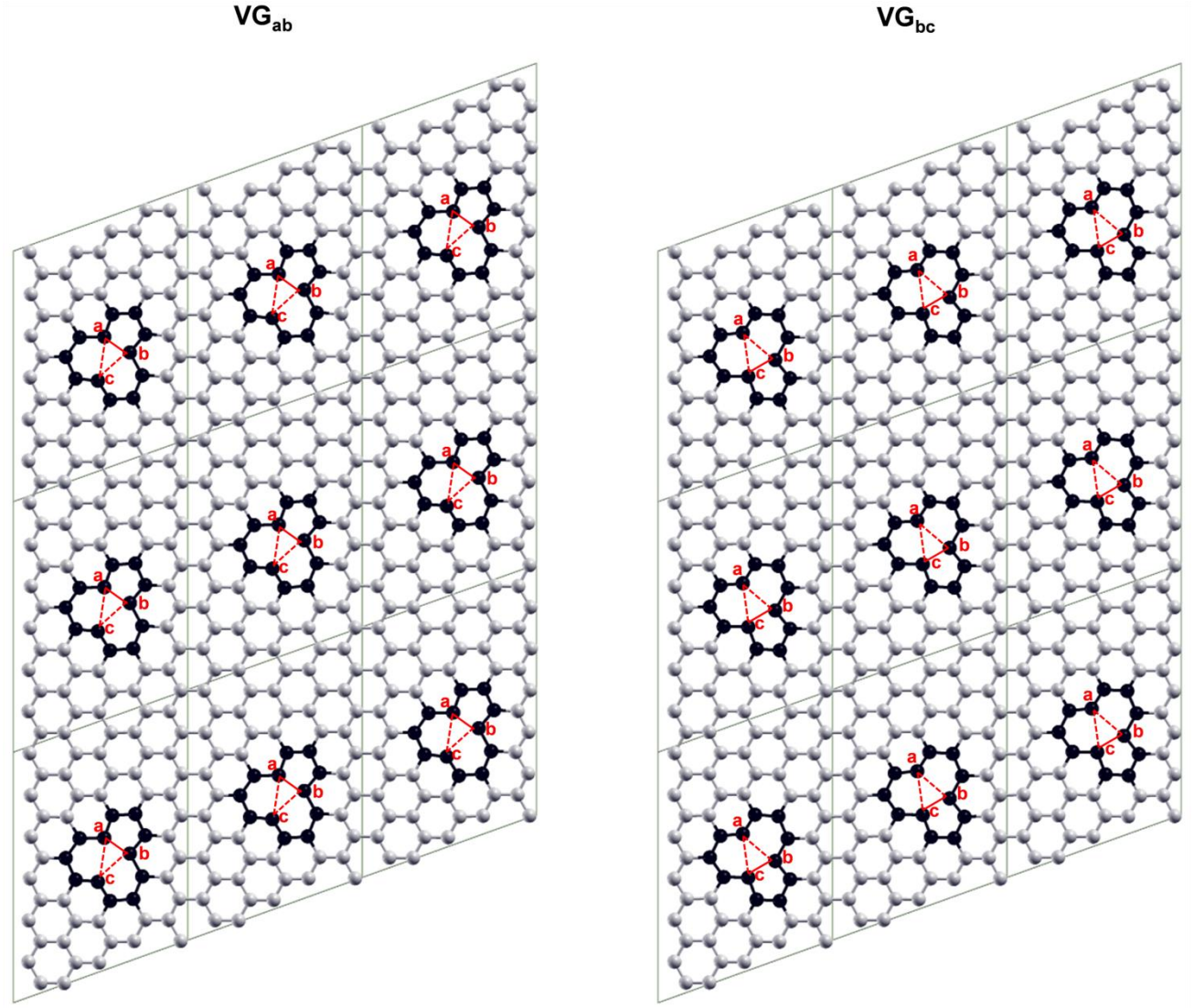

Figure S1. Top views of vacancy patterns in VG_{ab} (on the left) and VG_{bc} (on the right) due to the repetition of the supercell. The red triangles indicate the vacancy defect. The solid red lines represent elongated C-C bonds and the dotted lines indicate no C-C bond. The three C atoms at the vacancy are marked with a, b and c. The C atoms at the vacancy are highlighted in black and the other C atoms are shown in light gray.

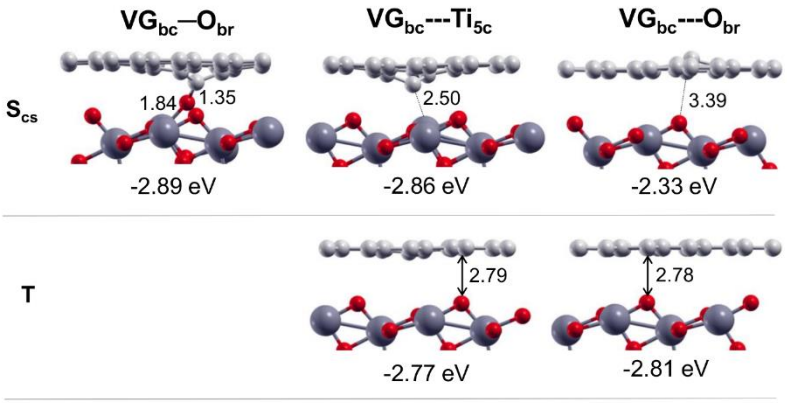

Figure S2. Side views of selected configurations of VG_{bc}/TiO_2 interfaces in the singlet close shell (S_{cs}) (top line) and in the triplet solutions (bottom line). For labels see Computational methods (section 2) and Figure 1 in the manuscript. Adhesion energies per supercell calculated according to equation (1) in the manuscript are listed below each configuration. Small red and light gray balls represent O atoms and C atoms. Big dark gray balls represent Ti atoms. Distances are in Å.

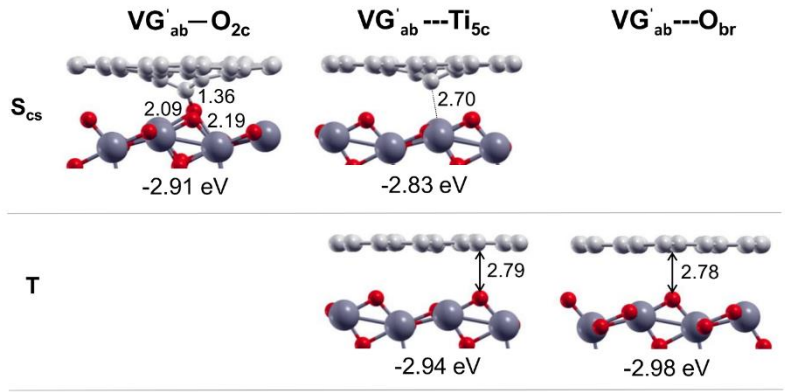

Figure S3. Side views of selected configurations of VG_{ab}'/TiO_2 interfaces (VG_{ab}/TiO_2 interfaces with a mirror flipping of graphene) in the singlet close shell (S_{cs}) (top line) and in the triplet solutions (bottom line). For labels see Computational methods (section 2) and Figure 1 in the manuscript. Adhesion energies per supercell calculated according to equation (1) in the manuscript are listed below each configuration. Small red and light gray balls represent O atoms and C atoms. Big dark gray balls represent Ti atoms. Distances are in Å.

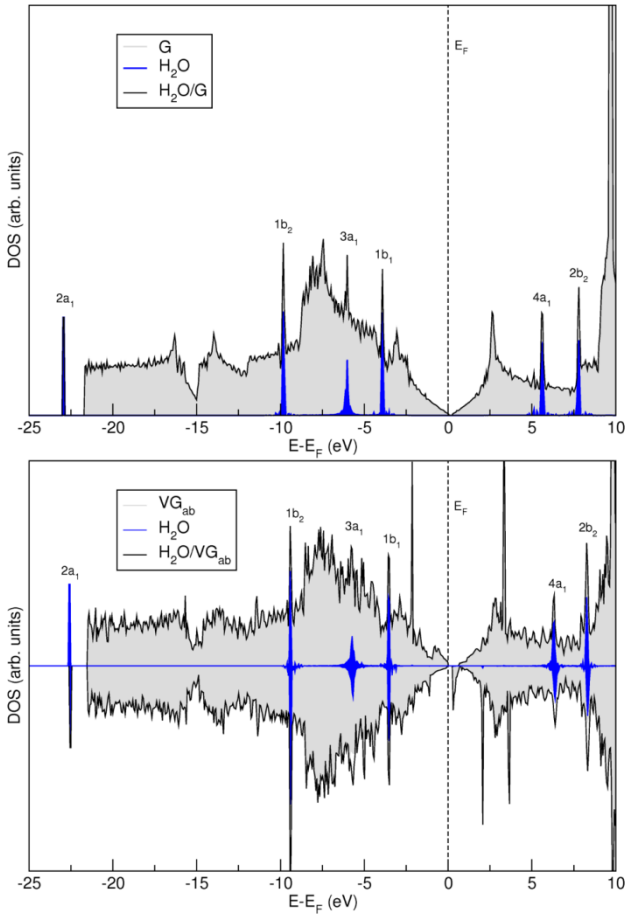

Figure S4. Total and projected DOS for the physical adsorption of water on free standing graphene with (lower part) and without (upper part) vacancy. The black line is the total DOS, filled gray area represents the DOS projected on graphene with vacancy (VG_{ab}) or without vacancy (G) and filled blue areas are DOS projected on H_2O. States from the four highest occupied molecular orbital and the two lowest unoccupied molecular orbitals of water molecule are marked. Fermi energy (E_F) is set at the top of the occupied states. For labels see Computational methods (section 2) and Figure 1 in the manuscript.

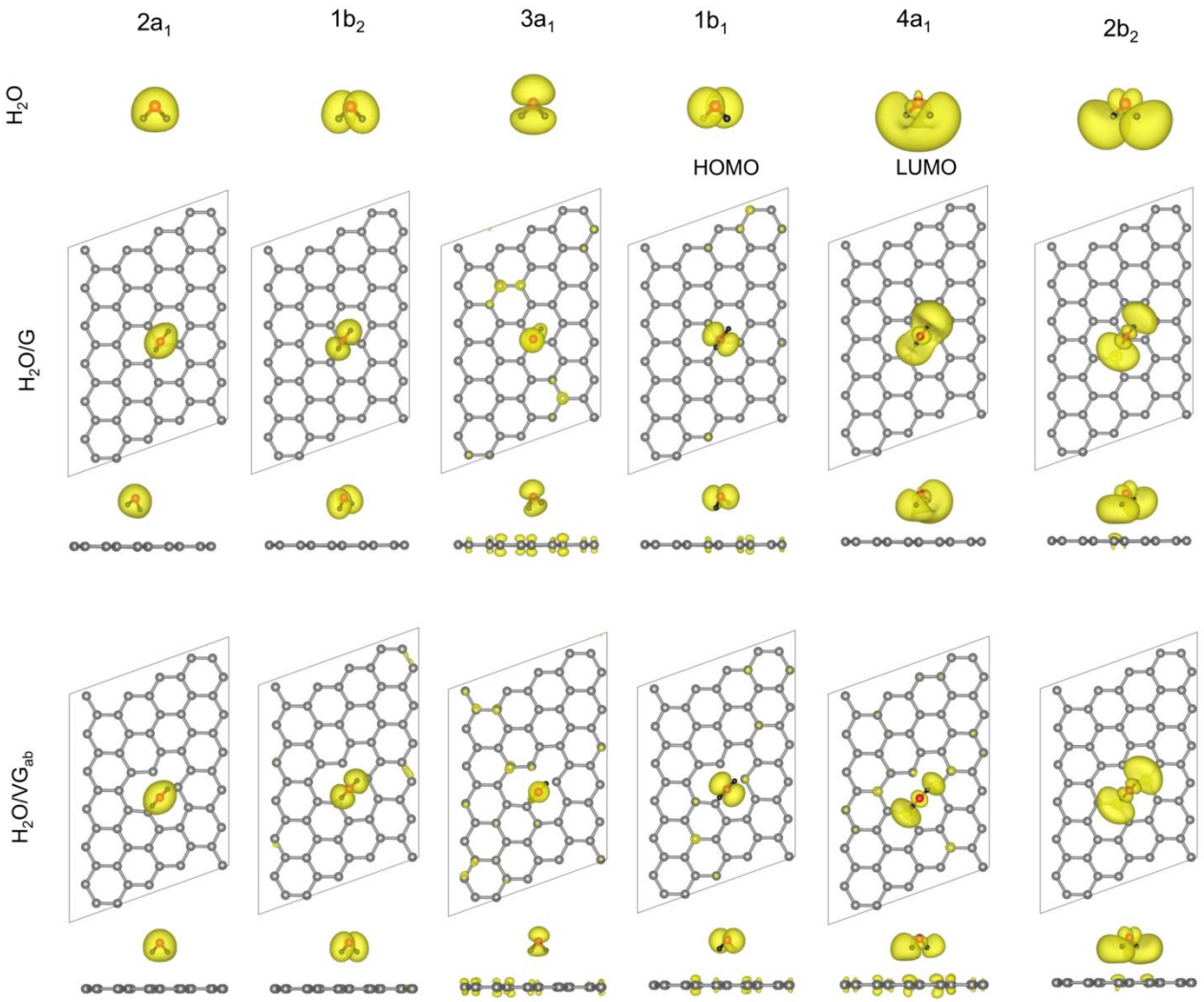

Figure S5. In the upper part, the four highest occupied molecular orbital and the two lowest unoccupied molecular orbitals of isolated water molecule. Above the structures the labels of the molecular orbitals according to their symmetry. In the middle and in the bottom, charge density of four highest occupied bands and two lowest unoccupied bands marked in Figure S4 for H_2O/G and H_2O/VG_{ab} respectively. The isosurface level is 0.005 electron/bohr^3. Red, light gray and black balls represent O atoms, C atoms and H atoms, respectively. For labels see Computational methods (section 2) and Figure 1 in the manuscript.

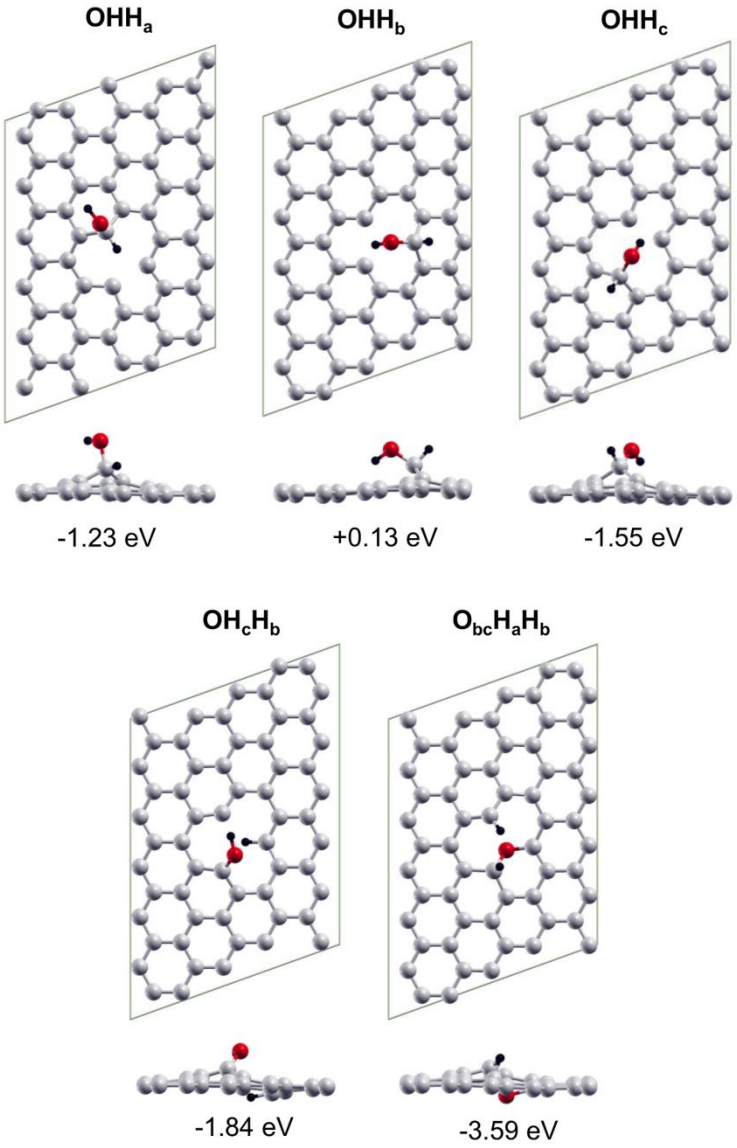

Figure S6. Top views and side views of the partially and fully dissociated products of water (OH + H and O + H + H respectively) on free-standing VG. Labels and dissociation energies are reported above and below each configuration, respectively, and defined in section 2 of Computational methods in the manuscript. Red, light gray and black balls represent O atoms, C atoms and H atoms, respectively.

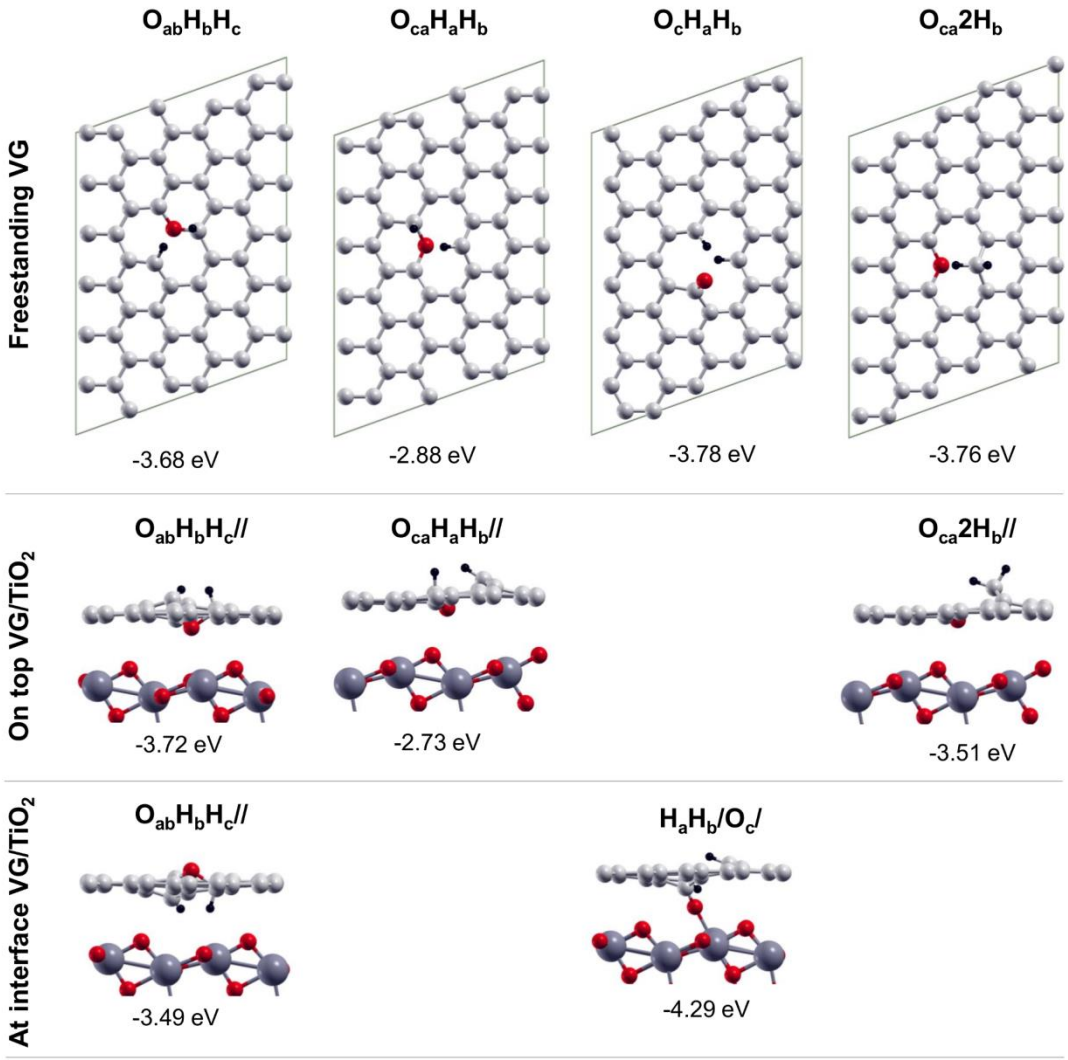

Figure S7. Top views of the fully dissociated products of water (O + H + H) on free-standing VG (top line); side views of the fully dissociated products of water on top of the interface VG/TiO_2 (middle line) and at the interface VG/TiO_2 (bottom line). Labels and dissociation energies are reported above and below each configuration, respectively, and defined in section 2 of Computational methods in the manuscript. Small red, black and light gray balls represent O atoms, H atoms and C atoms, respectively. Big dark gray balls represent Ti atoms.

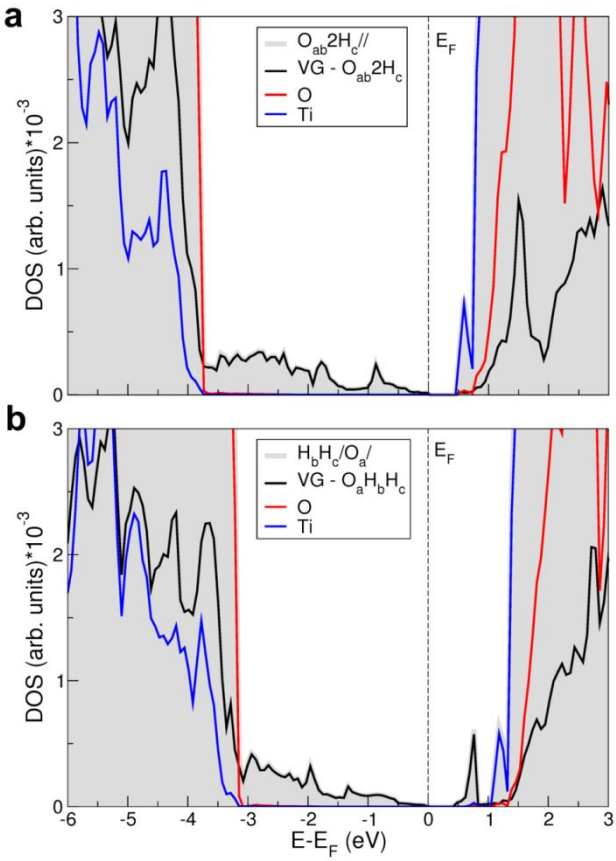

Figure S8. Total and projected DOS for $O_{ab}2H_c$// (a) and H_bH_c/O_a/ (b). In the DOS, the filled gray area represents the total DOS, the black lines are DOS projected on graphene (G or VG) together with the fragment coming from water dissociation (O + H + H). The red and blue lines are DOS projected on all O atoms and all Ti atoms in the TiO_2 slab, respectively. The structures of $O_{ab}2H_c$// and H_bH_c/O_a/ can be seen in Figures 9 in the manuscript. Fermi energy (E_F) is set at the top of the occupied states.