

Supplementary Information for Carrier doping of Bi₂Se₃ surface by chemical adsorption – a DFT study

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DENSITY OF STATES AND DETERMINATION OF ENERGY ZERO

Figure S1 shows the density of states (DOS) of all studied systems. The DOS of adsorbed systems is shown as red solid lines. The black solid line is the DOS of the pristine Bi₂O₃ surface (6 QL slab), whose Fermi-level is zero by definition. The DOS of the adsorbed systems (red) were shifted in energy such as to align the energy of the lowest valence band (Se 4s-like band at $E \approx -13$ eV) with that of the pristine surface (black).

SLAB THICKNESS DEPENDENCE OF OH/Bi₂Se₃(1×1) BAND STRUCTURE

In Fig. S2 the band structure of OH/Bi₂Se₃ with one molecule per 1×1 surface cell is shown for the 4-QL slab (a) and the 6-QL slab (b). The band dispersion of the OH-induced bands differ somewhat, but the Fermi-level shift due to OH-adsorption is comparable (+0.27 eV for 4-QL and +0.19 eV for 6-QL). Therefore the 4-QL slab used in this work is sufficient for investigating the surface doping by chemiadsorbed species.

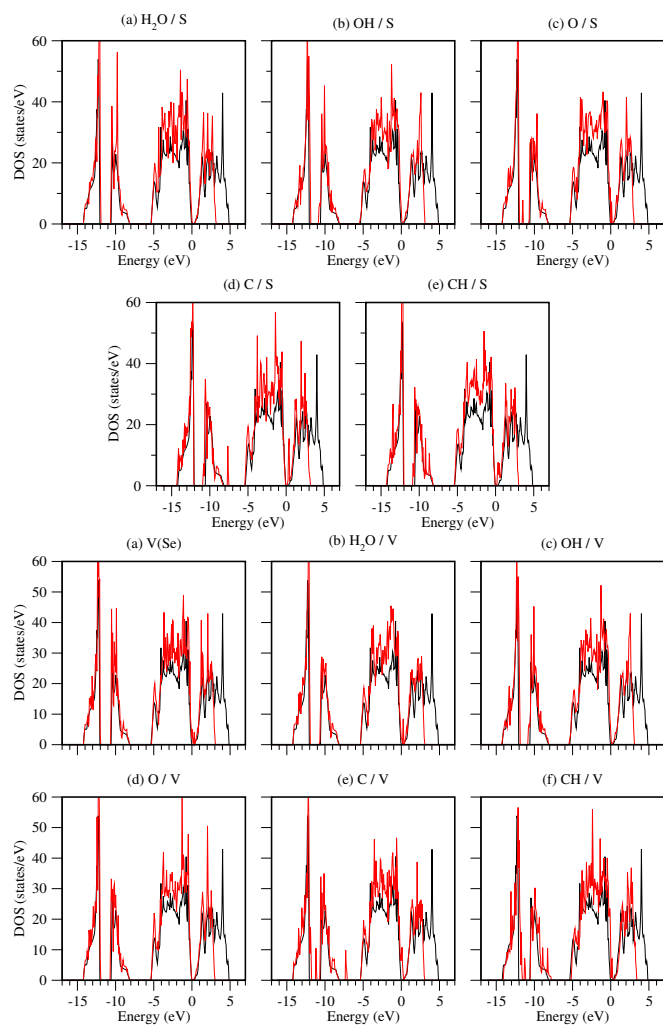
ESTIMATION OF O-1s LEVEL CHEMICAL SHIFTS

In order to assign the experimentally observed O-1s XPS peaks [1], we have computed the O-1s core-level

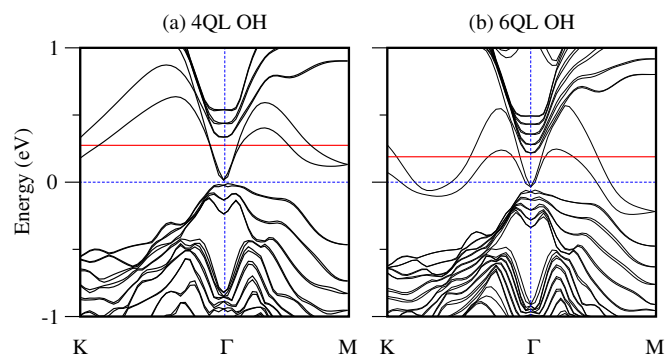
binding energy (E_B) using the final state approximation as implemented in VASP (ICORELEVEL=2) with a full core-hole. The calculated binding energies are, in eV: 570.1 (H₂O/S), 569.5 (OH/V) and 569.2 (O/S). These values differ by about 7% from the experimental values. Such large errors for the *absolute* core-level binding energy are quite common for this simple model of core-excitation energies based on single-electron Kohn-Sham levels. While the error may be reduced in various ways such as tuning the core-hole charge or considering some many-electron Δ SCF scheme, we are only interested in the relative chemical shift in order to interpret the experimental findings. The important conclusion is that the binding energies decrease in the sequence $E_B(\text{H}_2\text{O/S}) > E_B(\text{OH/V}) > E_B(\text{O/V})$. This order is also suggested on simple chemical grounds. Firstly, H is more electronegative than Bi, so the Bi-O bond is more ionic than O-H. Second, in OH/V and O/V, the oxygen atom makes three bonds to Bi so the ionicity is further increased. From these arguments, the oxygen ion is expected to have the largest negative charge in O/V and thus the smallest O-1s binding energy, the OH/V case is intermediate, and in H₂O/S, the oxygen ion has the smallest negative charge, and so the O-1s binding energy is largest.

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[1] K. Sakamoto et al. Nano Letters **21**, 4415-4422 (2021)



Supplemental Material, Figure S1. Density of states (DOS) per Bi_2Se_3 formula unit, corresponding to the band structures in Figs 4, 6 in the main text (red lines). The energy was shifted to align the DOS of the lowest energy band with that of the clean surface (black lines, corresponding to Fig. 2 e of the main text).



Supplemental Material, Figure S2. Band dispersion of one OH molecule in the 1×1 surface cell of Bi_2Se_3 , obtained with a 4-QL slab (a) and a 6-QL slab (b). The Fermi level is indicated by the red line.