Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

How TiO_2 crystallographic surfaces influence charge injection rates from a chemisorbed dye sensitiser in dye-sensitised solar cells

Natalia Martsinovich*, Alessandro Troisi

Department of Chemistry and Centre for Scientific Computing, University of Warwick, UK

Supporting Information

1. Surface-adsorbate interatomic distances (Table ST1).
2. Calculation of the conduction band energies.

1. Surface-adsorbate interatomic distances

Table ST1 Selected surface-adsorbate interatomic distances for formic acid adsorbed on the TiO_2 anatase (101), (001), (100), (110), (103)-smooth and (103)-faceted surfaces. The final interatomic distances for bonds that were broken during optimisation are shown in brackets. The O_{surf}-H distances involving the dissociated proton not interacting with the rest of the molecule in BB and BC configurations (0.97 ± 0.02 Å) are in italics.

Structure	Interatomic distance, Å		
	Ti-O_{COO}	O_{COO}-H	O_{surf}-H
(101)			
BB	2.09, 2.11	–	*0.96*
BC→BB-asymm	2.02, 2.55	–	*0.96*
MH1	2.15	1.04	1.48
MH2	2.2	1.03	1.54
(001)			
BB1	2.07, 2.09	–	*0.97*
BB2	2.11, 2.12	–	*0.93*
BB2-H1(far)	2.08, 2.09	–	*1.01*
BB2-H2(far)	2.09, 2.10	–	*0.97*
BB2a	1.98, 1.99	–	*0.96*
BC-H(far)	2.18, 2.23	–	*0.97*
BC-H(near)	2.16, 2.18	–	*0.97*
MH	1.97	1.51	1.02
(100)			
BB-H(near)	2.07, 2.08	–	*0.97*
BB-H(far)	2.07	–	*0.97*
BC→M	1.91, (3.30)	–	*0.96*
MH	2.14	1.05	1.48
(110)			
BC-H(far)	2.11, 2.15	–	*0.97*
BC-H(near)	2.11, 2.12	–	*0.97*
MH	1.96	1.56	1.01
(103)-smooth			
BB-H(far)	2.08	–	*0.96*
BB-H(near)	2.06, 2.10	–	*0.99*
BC-H(far)	2.02, 2.44	–	*0.96*
BC-H(near)	2.02, 2.36	–	*0.98*
MH1→M1	1.98	(2.59)	*0.97*
MH2	2.13	1.01	1.77
(103)-faceted			
BB1-H1	2.08, 2.09	–	*0.97*
BB1-H2	2.05, 2.08	–	*0.97*
BB2-H1	2.07	–	*0.97*
BB2-H2	2.07, 2.11	–	*0.97*
BC1-H2→M	1.92, (3.36)	(2.52)	*0.97*
BC2-H1	2.21	–	*0.97*
BC2-H2→M'	1.95, (3.49)	(3.40)	*0.97*
MH1	2.16	1.01	1.79
MH2	2.18	0.99	1.82
MH3	1.92	1.57	1.02

2. Calculation of conduction band energies

2.1. Symmetric slabs

The energies of the conduction band minimum (CBM), E_{CBM}, for clean symmetric three-layer anatase slabs exposing the different surfaces, described in Section 2.1 of the main text, are presented in Table ST2. The absolute value of E_{CBM} can be calculated as the difference between the Kohn-Sham energy of the conduction band edge and the energy of the electron at an infinite distance from the slab (in vacuum), E_{∞}. In CRYSTAL 2D (slab) calculations, the electrostatic potential is defined in such a way that, for symmetric slabs, the electrostatic potential at infinity (and, therefore, E_{∞}) equals zero.[S1] Therefore, the conduction band energies are exactly (within the accuracy of DFT) given by the DFT calculations of symmetric slabs.

To improve the quality of E_{CBM} calculations of the symmetric slabs, we added a layer of ghost atoms at the top and bottom of the cell (i.e. a Ti_2O_4 layer at each side of the cell), following the recipe in the study of the work function of metallic surfaces.[S1] Adding the ghost atoms shifted the conduction band energies slightly, by 0.1-0.4 eV towards more negative values, but did not significantly change the ordering of the slabs' E_{CBM} or the spread of the values. In the discussion in the main text, we use the values calculated using added ghost atoms.

Adding the ghost layers also reduces the surface energies by 0.09-0.18 J m^{-2} (10-15%) compared to the values in Table 1, but does not change the ordering of the surfaces' stabilities.

Table ST2 Calculated conduction band minimum (E_{CBM}) values for clean symmetric anatase three-layer slabs and for three-layer slabs with ghost atom layers (ordered from the lowest to the highest position of the conduction band)

Slab surface	E_{CBM}, eV	
	Bare slab	Slab+ghost atoms
(101)	-3.89	-4.01
(103)-faceted	-3.79	-4.00
(100)	-3.49	-3.69
(001)	-3.41	-3.81
(110)	-3.16	-3.46
(103)-smooth	-2.00	-2.30

2.2 Slabs with adsorbates

E_{CBM} has also been calculated for constrained slabs (with a fixed bottom layer), by correcting E_{CBM} for the electrostatic potential $E_{(+\infty)}$ at infinity at the upper (unconstrained) side of the slab. However, because the lower side of these slabs was constrained, the calculated E_{CBM} of the constrained slabs was artificially different from that of the free slabs and differed by an energy δE (different for each surface orientation). We used the CBM energies of the free slabs as a common reference point. Thus, to obtain CBM energies of slabs with adsorbates, we shifted the (vacuum level-corrected) E_{CBM} of slabs with adsorbates by the value δE for each particular surface orientation. These aligned E_{CBM} energies of slabs with adsorbates were then used in the calculations of injection times.

References

[S1] K. Doll, Surface Science 600 (2006) L321–L325.