

Contents

Acknowledgements	i
Abstract (English/Français)	iii
1 Introduction	1
1.1 Defect study in amorphous oxides	2
1.2 Motivation for investigating defects in am- Al_2O_3	3
1.3 Motivation for investigating hole transport in am- TiO_2	4
1.4 Water-splitting photocatalysts	4
1.5 Current research status of band alignment at semiconductor-water interfaces	6
1.6 Outline of the thesis	7
2 Methodology	11
2.1 Hybrid density functional theory	11
2.1.1 PBE0 functional	12
2.1.2 HSE functional	12
2.2 Defect study	13
2.2.1 Defect formation energy	13
2.2.2 Finite-size corrections	14
2.3 Thermodynamic integration	15
2.4 Computational standard hydrogen electrode	16
2.4.1 Free energy of formation of solutes	16
2.4.2 Standard hydrogen electrode (SHE)	17
2.5 Computational details	19
2.5.1 Molecular dynamics simulations of semiconductor-water interfaces	19
3 Defects in amorphous Al_2O_3	21
3.1 Model generation	21
3.2 Intrinsic defects in amorphous Al_2O_3	22
3.2.1 Oxygen vacancy	22
3.2.2 Interstitial oxygen	24
3.3 Extrinsic impurities in amorphous Al_2O_3	27
3.3.1 Hydrogen	27
3.3.2 Carbon	29

3.3.3 Nitrogen	35
3.4 Alignment to semiconductor band edges	37
3.5 Conclusion	38
4 Transport of holes in amorphous TiO₂	41
4.1 Model of amorphous TiO ₂	41
4.2 Intrinsic defects in amorphous TiO ₂	44
4.2.1 Oxygen vacancy	44
4.2.2 Double hole polaron	45
4.3 Hopping of holes in amorphous TiO ₂	48
4.4 Conclusion	49
5 Alignment of energy levels at semiconductor-water interfaces	51
5.1 Methods	52
5.1.1 Electronic-structure calculations	52
5.1.2 Band alignment at semiconductor-water interfaces	57
5.2 Absolute energy levels of liquid water	59
5.3 Electronic properties of semiconductors	62
5.4 Interface models	66
5.4.1 Generation protocol	66
5.4.2 Structural properties of semiconductor-water interfaces	68
5.5 Band alignment	70
5.5.1 Assignment of semiconductor-water interfaces	71
5.5.2 Experimental reference values	73
5.5.3 Benchmark of electronic-structure methods	75
5.5.4 Comparison with previous work	78
5.6 Conclusion	80
6 Evaluation of photocatalysts for water splitting through combined analysis of surface coverage and energy-level alignment	83
6.1 General motivation	84
6.2 Theoretical formulation	85
6.3 Method	92
6.3.1 Calculation of deprotonation energy	92
6.3.2 Electrostatic finite-size corrections	93
6.3.3 Energy of zero-point motion	94
6.4 Comparison of pH_{PZC} and $\text{p}K_{\text{a}}$ achieved with semilocal and hybrid functionals	95
6.5 Acid-Base properties	98
6.5.1 Acidity of semiconductor surfaces	98
6.5.2 Surface concentration of adsorbates vs. pH	100
6.6 Band alignment vs. pH	102
6.7 Discussion and conclusion	107

7 Conclusion	109
A An appendix	113
Bibliography	141
Curriculum Vitae	143