

# QM/MM investigations of the structural, electronic, and catalytic properties of TiO<sub>2</sub> surfaces

Harry Jenkins<sup>1</sup>, Andrew Logsdail<sup>1</sup>

<sup>1</sup> *Cardiff Catalysis Institute, Cardiff University, CF10 3AT*

Titania (TiO<sub>2</sub>) is a photocatalytic material that has garnered favourability due to its high chemical and thermal stability under reaction conditions. In particular, recent interest has grown for surface-supported nanoparticles and their role in catalytic applications [1]. Computational studies of bulk, mixed-phase TiO<sub>2</sub> have been undertaken [2]; however, the surface chemistry, specifically the role of surface defects in surface-support interactions and catalytic applications, remains a topic of debate.

In this work, we present our progress in building and testing QM/MM models for the low-energy surfaces of titania, which we will use to study the stability of charged defects, surface adsorbates, and their combined role in photocatalysis. This work will expand on previous studies of water-splitting intermediates [3], oxygen vacancies [4], and the inability of a pristine surface to photoelectrically split water [5].

To set up this model, we will use high-accuracy embedded-cluster QM/MM, as realised in the Chemshell software package. FHI-aims [6] and NWChem [7] will be used to perform DFT calculations, using high-level exchange-correlation functionals to ensure the validity of our results. We compare the performance of the software packages, and their associated differing basis sets, to better understand accuracy, reproducibility, and reliability in different QM/MM techniques.

We hope that our findings will bring clarity to the current deficits of the QM/MM methodology, and areas for future software development, specifically in the context of the embedding environment. We also envisage that our calculations will offer insight into the range of current experimental results; in the future, we will broaden our investigation towards surface-supported precious metal nanoparticles.

[1] Su et al. ACS Nano, 2014, 8 (4), pp 3490–3497 (2014)

[2] Scanlon et al. Nature Materials 12, 798–801 (2013)

[3] Berger et al. J. Chem. Phys. 141, 024105 (2014)

[4] Berger et al. Phys. Rev. B 92, 075308 (2015)

[5] Oberhofer et al. Phys. Rev. Lett. 117, 276001 (2016)

[6] Blum et al. Computer Physics Communications 180, 2175–2196 (2009)

[7] Bylaska et al. Computer Physics Communications 181, 1477 (2010)