

Accurate modelling of n-type doped TiO₂ polymorphs using DFT+U with occupation matrix control

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TiO₂ is a key component in enabling technologies for the transition to Net-Zero 2050. This includes catalysis, where TiO₂ acts as a non-inert catalyst support able to enhance the reactivity of supported metal nanoparticles; as well as electronics, where TiO₂-based materials are promising transparent conducting oxide materials for photovoltaics [1]. To overcome limitations in the catalytic and electrical performance of TiO₂, substitutional dopants such as Nb and W can be introduced in order to modify its physical and chemical properties (e.g. band gap and electrical conductivity) [2]. This is highly sensitive to the TiO₂ polymorph, as has been reported experimentally where Nb and W substitutionally doped anatase and rutile exhibit varying degrees of excess electron localisation resulting in the formation of deep defect states in rutile and shallow defect states in anatase [3]. There are conflicting theoretical rationalisations for this discrepancy, due to the well-known challenge of modelling charge localisation in strongly correlated metal oxides using density functional theory. This limits any atomic-level understanding of the nature of the defect states in both polymorphs and the ability to develop accurate structure-property models. In this work, both Nb and W doped anatase and rutile TiO₂ are modelled using Hubbard corrected density functional theory (DFT+U) using the FHI-aims software. Control of the DFT+U occupation matrix allows accurate modelling of the formation of localised excess electron(s) and provides a theoretical rationalisation for experimentally observed differences in the defect states in anatase and rutile. These calculations also remain computationally inexpensive (compared to hybrid functionals) demonstrating their applicability for large systems with hundreds of atoms.

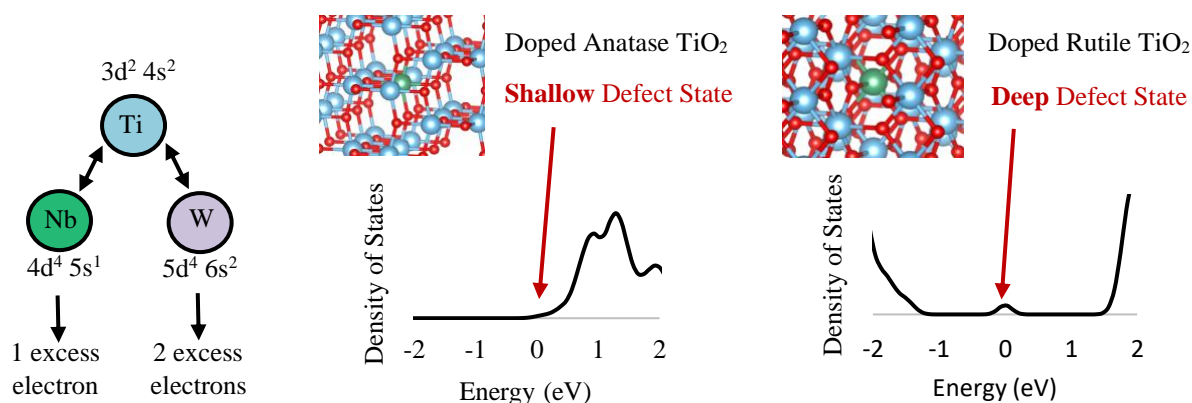


Figure 1: Comparing the polaronic defect states in Nb and W doped TiO₂ polymorphs

Acknowledgments

This work is part of a Prosperity Partnership project funded by the UK Engineering and Physical Sciences Research Council (EPSRC), bp through the bp International Centre for Advanced Materials (bp-ICAM) and Johnson Matthey plc in collaboration with Cardiff University and The University of Manchester (EPSRC grant number EP/V056565/1).

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