Photocatalysis

Engineering Metal Oxides for Renewable Energy

The imminent reduction in readily available fossil fuels, primarily oil and natural gas, requires different, most likely multiple, sources of energy to ensure comfortable living standards for the human race. The pace of industrial development since the start of the industrial revolution has resulted in large scale pollution of the planet, arising from factories, transport and consumerism. In the developing world, the scale of pollution can only grow over the next few years as these nations accelerate their development to catch up with The West, thus magnifying greatly the extent of this problem. Thirdly, a shortage of fossil fuels impacts not only on energy supplies but also on raw materials used for the manufacture of the myriad of foods and goods we take for granted, such as fertilizers and plastics.

Modification of TiO₂ surfaces with metal oxide nanoclusters is a novel approach to engineering TiO₂ for visible light active photocatalysis

In confronting these challenges, solutions based on solar hydrogen production are at the forefront utilising the most widely available and abundant energy source, i.e. the sun. We use computer modelling and experiment to develop novel material systems to harness the abundant solar energy for visible light activated photocatalytic water splitting to produce hydrogen, where the hydrogen so produced is the fuel of the future.

Our work is focussed on first principles DFT simulations of rutile and anatase TiO₂ surfaces modified with metal oxide clusters, which allows us to engineer the electronic structure of the heterostructure to obtain visible light photocatalytic activity. This work is funded in the Engineering Metal Oxide Interfaces for Renewable Energy Photocatalysis (EMOIN) project under the Starting Investigator Research Grant Program by Science Foundation Ireland. See also a recent review here.

TiO₂ Nanocluster Modified Rutile TiO₂

We used DFT to model the structure and electronic properties of TiO₂ clusters on the rutile (110) surface, and have found that the formation of the heterostructure reduces the band gap compared with pristine TiO₂, which will induce a shift towards the visible region - the electronic DOS in the image shows the cluster derived electronic states in the previous TiO₂ energy gap. In addition, the type II heterostructure formed facilitates electron and hole separation upon photoexcitation, which will reduce charge recombination, thus improving activity. These findings also hold for heterostructures with cluster size up to 1.5 nm.

See here.
The top panel shows the Ti 3d projected electronic DOS and the bottom panel the O 2p projected electronic DOS for a Ti3O6 cluster adsorbed at the rutile TiO2 (110) surface. The inset shows the cluster-surface heterostructure.

Iron Oxide Nanocluster Modified Rutile TiO2
We have also extended this work to other oxides supported on TiO2. In 2011, Tada and co-workers showed that clusters of around 2 nm or smaller of iron oxide can be deposited onto TiO2 using a chemisorption and calcination cycle approach here. We modelled, in cooperation with Prof. Tada structures of small FeO and Fe2O3 clusters on rutile TiO2 (110), see figure 2 for the interface structures. The iron oxide, irrespective of oxidation state of iron, will adsorbed strongly at the rutile (110) surface. Figure 3 shows the electronic DOS of Fe2O3-TiO2, showing iron oxide derived states in the TiO2 energy gap, pushing the valence band up in energy, which leads to a band gap reduction of 0.3 eV. This is consistent with the work of Tada et al.

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Structures of (top) FeO-TiO$_2$, (middle) Fe$_2$O$_2$-TiO$_2$ and (bottom) Fe$_2$O$_4$-TiO$_2$
Modification of TiO2 with SnO2 Nanoclusters
Together with Tada, we have examined how the TiO2 crystal form, either rutile or anatase, affects the modification of the band gap when SnO2 nanoclusters are deposited. We have found, from both simulation and experiment, that with anatase, SnO2 modification has no effect but at rutile, SnO2 modification reduces the band gap.

Predicting Band Gap Modification of Rutile TiO2 with Metal Oxide Nanoclusters
In a paper in Chemical Communications we predicted that the energy gap of rutile TiO2 can be modified by nanoclusters of CrO2 and Cr2O3, as well as MoO2, by raising the valence band edge. However, HfO2 and ZrO2 modified rutile will show no change in the band gap of unmodified rutile.

In a recent paper in ACS Applied Materials and Interfaces, we further predicted that non-transition metal oxides, Ga2O3 and MgO, can be deposited as nanoclusters to enhance the photocatalytic activity of rutile. We also presented a model of the photoexcited state of modified TiO2 (inspired by recent work from di Valetin and Selloni on anatase), in which a model excited state is generated and the location of the photoexcited electron and hole is determined. In both cases, we find, as predicted from analysis of the density of states, that the hole will be localised on the nanocluster and the electron on the TiO2 surface, and the relaxation of the heterostructure in the excited state is significantly larger than the bare surface.

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