

Simulation of Mineral Speciation in Aqueous Solution

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Invited Talk

The crystallization of minerals is an important process in a wide range of contexts from industrial separation and preparation, through to biomineralization. Understanding how the precursor ions to minerals associate in aqueous fluids prior to nucleation is therefore critical in being able to exert control over such processes, leading to either promotion of desired phases or suppression of the formation of undesirable scales. Given that detection of many precursor species is challenging from an experimental perspective, it is therefore attractive to develop reliable methods of simulating such reactions in order to probe these early stages of crystallization.

As specific examples of mineral crystallization, the ion association for calcium containing phases including sulfate, phosphate and carbonate will be presented, as they represent systems of relevance to either biomineralization or industrial applications. After initially considering the ion pairing, the question of whether any larger clusters may be thermodynamically stable will be examined. A particular focus will be a critical examination of the simulation protocols currently being used to probe mineral speciation with a comparison of force field and first principles methods, highlighting the limitations of both for such problems. Future directions for improvement will also be discussed.

Order-disorder Interplay and Piezochromic Effects in Nanocrystals under Pressure

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**Physics Department, King's College London*

Invited Talk

Nanocrystals show a wealth of distinctive behaviours with respect to their bulk counterparts, which can be tuned by varying their size, shape and surface. These include the way they respond to applied pressure, transforming from the original crystalline structure to new ordered or disordered phases. Of particular technological and fundamental interest are nanocrystals of tetrahedrally coordinated materials, such as Si, Ge, CdSe, CdS and ice, which can be driven by pressure toward highly coordinated crystalline or amorphous phases. We have used a series of simulation techniques, including density functional theory, molecular dynamics and the enhanced sampling method metadynamics, to characterize the mechanisms of structural transformations in these nanocrystals, focussing on the competition between amorphization and crystallization, the effects of an implicit or explicit description of the environment and the emergence of metallic phases. Moreover, we have investigated, as a function of size and surface ligands, pressure-induced effects in the electronic and optical properties of nanocrystals, which may be exploited in the development of novel pressure sensors.

Precisely Tunable Materials with Help from Accurate Electronic Structure Theory - Where We Are and Where We Are Going

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Invited Talk

A material's properties arise at the atomic scale. For some applications, the exact details of the atomic structure do not matter so much; for other properties, however, precise control over the atomic structure is essential (semiconductors, light harvesting and light emission are among them). Having the ability to manufacture precisely tunable materials by manipulating their atomic structure would be nice; and it would be even nicer if theory could tell us which particular components to use in a material and where to place them, so as to achieve a specific, given set of properties. This talk summarizes some recent progress in our group and by a wider set of collaborators towards accurate electronic structure formalisms for understanding and predicting new complex materials that can be synthesized experimentally with the atomically precise control of single crystals. Topics covered include the all-electron electronic structure code FHI-aims (<https://aimsclub.fhi-berlin.mpg.de/>), progress towards large-scale, high-accuracy all-electron simulations using the open-source infrastructure ELSI (<https://wordpress.elsi-interchange.org/>), and progress on many-body theory of excitations (GW and BSE) using both frameworks. The "tunable" materials spaces to which these approaches will be applied include layered organic-inorganic perovskite semiconductors for optoelectronics and multinary chalcogenide semiconductors for light harvesting applications, pursued in close collaboration with the experimental group of David Mitzi (Duke University) and a broader NSF-funded consortium "Hybrid³" (<https://hybrid3.duke.edu>).

Computational Chemistry : An Industrial Perspective

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Invited Talk

The talk will give an overview of how atomistic modelling and HPC resources are being used in industry to understand the structure and activity of catalytic materials and how this understanding can be used to predict new catalysts or materials for a number of applications. Highlights of where DFT has been used to predict new alloys for the cathode of PEM fuel cells based on both activity and stability of the catalyst will be presented along with recent work on modelling large metallic nanoparticles and how these are influenced by the support. An overview of how atomistic simulations are being used to enhance our understanding of current emissions controls catalysts and to guide the design of new catalysts will also be presented.

Quantum Computing And Its Near-Term Potential Within Computational Chemistry

Dr. Matthew D. Hutchings*

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* *Quantum Technology Enterprise Centre, University of Bristol.*

Invited Talk

Richard Feynman famously described his vision of how hard problems, like those found in quantum chemistry, that are nearly intractable using classical computation platforms, might be successfully modelled using a universal quantum computer. This was hypothesized via the notion that only a controllable quantum system could efficiently simulate the quantum systems that form the building blocks of the world around us.

Computational chemistry is recognised as an important tool within the chemical industry. However, limitations in current high performance computing have made it difficult to achieve chemical accuracy in complex quantum chemistry models. Despite this, state-of-the-art computational methods have overcome a number of these limitations and have demonstrated significant value through predictive modeling. With that, they have become deeply imbedded within industry. Quantum computers have the potential to provide exponential speedup for quantum chemistry simulations. With this power, chemical accuracy in complex molecular models is achievable. Though universal quantum computing is still a number of years away, we are beginning to understand how near-term quantum computing hardware can be combined with the impressive state-of-the-art classical methods to provide valuable solutions within the chemical industry.

I will present an overview of quantum computing; from a background of historical developments, through to a discussion of the state-of-the-art systems available today through the cloud¹. I will describe how quantum algorithms harness the power of quantum mechanics to provide a speedup for hard computational problems. I will discuss how these algorithms are being advanced, through the use of hybrid quantum-classical methods, to unlock the power of near-term quantum hardware². It is hoped that open discussion like this will fuel further collaboration between the quantum and classical computational communities. It is through collaboration, that the true value of the quantum computer can be established.

1) IBM Quantum Experience, <http://www.research.ibm/quantum/>.

2) Nikolaj Moll, et al., 2018 Quantum Sci. Technol. **3** 030503 (2018).

Early Oxidation of Prismatic Surfaces of Troilite FeS

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e05-surfin-lee

Pyrrhotites $\text{Fe}(1-x)\text{S}$ ($0 < x < 0.125$), the most common iron sulfides in nature after pyrite, are minerals with promising catalytic properties. Like pyrite, pyrrhotites are very reactive towards molecular oxygen, which is easily incorporated into their surfaces. In order for the catalytic mechanisms to be properly understood, it is essential to achieve a detailed knowledge of the oxidised substrate available to the reactants. In this work, after using X-ray photoelectron spectroscopy to show that the catalytically relevant surfaces contain oxidic species, we use density functional theory to investigate the early oxidation mechanism of the prismatic surfaces of troilite FeS, i.e. the stoichiometric end-member of the pyrrhotite group. We find that atomic oxygen adsorbs in Fe-O-Fe bridging motifs which are thermodynamically stable under ambient conditions. During the first oxidation steps, the formation of the S-O bond is less favoured than Fe-O, suggesting that the sulfur oxides observed experimentally form only subsequently. Our calculations predict, moreover, the possible substitution of sulfur for oxygen and a clustering growth of the oxidic units. In agreement with experiment, the oxidation of troilite is exothermic, where the equilibrium between adsorption and substitution is influenced by the presence of Fe vacancies.

Simulating the Effect of Organic Molecules on Clustering in Calcium Carbonate and Phosphate

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e05-biomat-har

Calcium carbonate and calcium phosphate are the most important biominerals in nature but there is still no consensus on how they form. Many nucleation and growth mechanisms have been and continue to be proposed. An amorphous phase is known to precede both crystalline carbonate and phosphate phases. It is also known that both inorganic and organic additives can affect the crystallisation process, the polymorphs formed, and the physical properties of the resulting materials. Simulations have frequently been used to try to unravel the complex mechanisms involved but require considerable computer resources to reach the long timescales required.

Recent work on calcium carbonate solutions at low concentration in the presence of amino acids has shown that they exhibit behaviour typical of that expected by classical nucleation theory with free ions, ion pairs and other small clusters present. At high concentration the amino acids self-assemble into aggregates, facilitated by 'spectator' ions and usually by bicarbonate ions. Liquid-like clusters form from the remaining calcium carbonate. These are also seen at the surface of the amino acid aggregates. When simulations are performed in the presence of oligopeptides (amino acid hexamers) liquid-like networks are formed, seeming to stabilise a dense liquid phase. Calcium phosphate also forms liquid-like clusters in the presence of amines, in this case the buffer tris(hydroxymethyl)aminomethane (TRIS). The simulations suggest that TRIS favours the formation of negatively charged complexes, and we believe that these are responsible for the inhibitory effect of TRIS. More generally, the formation of charged large aggregates could explain the formation of dense liquid phases in phosphate solutions.

We discuss the implications of these results for the role of a dense liquid phase in the nucleation mechanism for calcium carbonates and phosphates, connecting with the long-established proposal by Gower of the importance of a polymer-induced liquid phase (PILP) in the nucleation of biominerals.

Carbon Nitride Materials for Photocatalytic Water Splitting

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e05-softm-cat

One of the key technological challenges of the 21st century is providing energy for a rapidly increasing population while reducing drastically the emissions of pollutant and greenhouse gas. Solar power is key to meet such an ambitious goal, and various ways to harvest and store it have been explored. This research is therefore part of a wider project involving 3 universities across the UK studying both theoretically and experimentally the catalytic, photocatalytic and electrocatalytic pathways for CO₂ capture and reduction. As a first step in this process, hydrogen is produced through photocatalytic water splitting by means of a novel oxygen-doped variant of carbon nitride. Oxygen doped carbon nitride is a novel polymeric material which is designed to offer a tunable band gap and good performance as a photocatalyst for Z-scheme photocatalytic water splitting cells. We have worked with experimentalists in UCL in order to highlight the relationship between the bulk geometrical and electronic properties of the material and its performances as the amount of oxygen precursor in the polymerization process is changed.

Control of Pickering Emulsion to Advance New Materials and Knowledges

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e05-surfin-str

The stability of nanoparticle-stabilized emulsions has attracted enormous attention because of a variety of applications including drug delivery, cosmetics, and Inkjet printing. Because nanoparticles (NPs) of different chemical and mechanical properties are used as emulsifiers, their characteristics have critical effects on the emulsions properties. To be effective in preventing droplet coalescence, the solid particles should be able to prevent fluid molecules to transfer from one droplet to the other when the droplets are not at contact. Furthermore, particles, once adsorbed, are rather difficult to displace from the interfaces. It is this property which makes that particles such a good colloidal stabilizers of emulsions and bubbles.

This talk will focus on dynamical and thermodynamic properties of specific deformation of *armored* droplets. As our aim is not to model at the atomistic scale the droplet deformation for a specific water-oil system but rather to correlate the associated mechanism of deformation with the physical properties of the NPs that stabilize this system, we consider a mesoscopic model in which the structural unit is a coarse-grained representation of a large number of molecules. We report the interplay between the evolution of droplet shape, layering of the particles, and their distribution at the interface when the volume of the droplets is deformed or reduced, as encountered in coalescence, buckling, and division mechanisms.

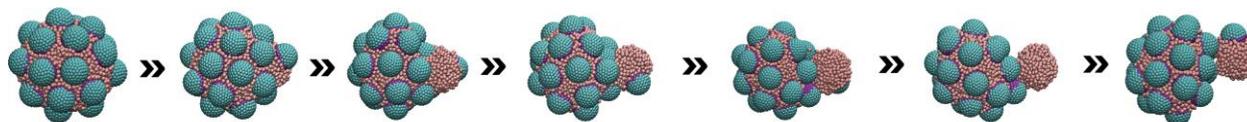


Figure 1 Sequence of simulation snapshots representing the division process of water in oil droplets armored with Janus nanoparticles.

Cluster-Assembled Nanowires based on $X_{12}Y_{12}$ ($X=\text{Zn, Ga, Al, Y}=\text{O, N}$) clusters as High Performance Gas Sensors

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e05-nandef-cat

Motivated by the recent realization of cluster-assembled nanomaterials as gas sensors, first-principles calculations are carried out to explore the stability and electronic properties of cluster-assembled nanowires based on $X_{12}Y_{12}$ ($X=\text{Zn, Ga, Al, Y}=\text{O, N}$) clusters and the adsorption behaviors of environmental gases on the $X_{12}Y_{12}$ -based nanowires. Our results indicate that the ultrathin $X_{12}Y_{12}$ cluster-assembled nanowires have semiconducting electrical properties with direct energy gaps, and are particularly thermodynamic stable at room temperature. By analyzing the adsorption energy, adsorption types (chemisorption or physisorption), charge transfer, the adsorption behavior of the target molecules comparison with other common molecules, the change of electronic properties (particularly, DOS, band structures, and electric conductivity), the recovery time before and after the adsorption, we can confirm that the $\text{Zn}_{12}\text{O}_{12}$ -based nanowire is a potential candidate for gas sensors with high sensitivity and selectivity for NO and NO_2 detection, and the $\text{Al}_{12}\text{N}_{12}$ -based nanowire should be a highly sensitive CO and NO sensor with quick response as well as short recovery time, and the $\text{Ga}_{12}\text{N}_{12}$ -based nanowire should be a promising gas sensor for CO, NO, and NO_2 detection.

First-Principles Modelling of Polaron Formation in TiO₂ Polymorphs

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e05-nandef-mck

We present a computationally efficient and predictive methodology for modelling the formation and properties of electron and hole polarons in solids [1]. Through non-empirical optimization of the fraction of Hartree-Fock exchange (α) in a hybrid functional, we ensure the generalized Koopmans' condition is satisfied and self-interaction error is minimized. Our previous work in model systems has shown that accurate densities and energies can be obtained from such an optimization [2]. The approach is applied to model polaron formation in known stable and metastable phases of TiO₂ including anatase, rutile, brookite, TiO₂(H), TiO₂(R) and TiO₂(B). Electron polarons are predicted to form in rutile, TiO₂(H) and TiO₂(R) (with trapping energies ranging from -0.02 eV to -0.35 eV). In rutile the electron localizes largely on a single Ti ion, whereas in TiO₂(H) and TiO₂(R) the electron is distributed across two neighboring Ti sites. Hole polarons are predicted to form in anatase, brookite, TiO₂(H), TiO₂(R) and TiO₂(B) (with trapping energies ranging from -0.16 eV to -0.52 eV). In anatase, brookite and TiO₂(B) holes localize on a single O ion, whereas in TiO₂(H) and TiO₂(R) holes can also be distributed across two O sites. We find that the optimized α has a degree of transferability across the phases, with $\alpha=0.115$ describing all phases well. We also note the approach yields accurate band gaps, with anatase, rutile and brookite within six percent of experimental values. We conclude our study with a comparison of the alignment of polaron charge transition levels across the different phases. Since the approach we describe is only two to three times more expensive than a standard density functional theory calculation, it is ideally suited to model charge trapping at complex defects (such as surfaces and interfaces) in a range of materials relevant for technological applications, but previously inaccessible to predictive modelling.

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Relation between Image Charge and Potential Alignment Corrections for Charged Defects in Periodic Boundary Conditions

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**Department of Physics and Astronomy, UCL*

e05-nandef-shl

Charged defects are often studied within periodic density functional theory (DFT), but this introduces strong finite-size artifacts. In spite of this challenge, accurate formation energies for charged defects are required to assist the experimental identification of defects. *Post hoc* correction methods have been developing over the last 25 years, and there are now many approaches available in the literature [1-3]. However, the many disagreements in the literature mean that the current position is rather unclear, especially for non-experts. We develop an electrostatic image interaction correction method based on direct solution of the Poisson equation for charge models constructed directly from DFT [4]. These image corrections are found to be detail-insensitive, depending almost entirely on bulk dielectric. In order to better understand this result, we explore potential alignment in detail, and introduce a novel decomposition to separate out different contributions. We find that two main sources of potential alignment are defect image interactions, and changes in the number of atoms present in the supercell. This first effect is accurately predicted by our image correction. The second contribution is unrelated to image interactions, and justifies the common observation that the magnitude of finite-size dependence can strongly vary between vacancy and interstitial defects. It can be approximately predicted using atomic radius, but is sensitive to the pseudopotential used. Combined, these developments justify known finite-size scaling rules [5]. Our results suggest that for cubic supercells, the Lany-Zunger interaction correction [2], combined with a simplified potential alignment between neutral systems, can yield accurate corrections in spite of the simplicity of the approach. Additionally, we are able to predict the relative importance of image interaction and potential alignment corrections for a particular defect.

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***Ab initio* design of Ternary Sb-containing Transparent Conducting Oxides**

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e05-nandef-dos

The existing range of transparent conducting oxide (TCO) materials has been widely deployed in display screen and photovoltaic devices, as well as energy-efficient window coatings. Goals for the development of future TCOs include reduced dependence on indium and the development of alternative band alignment options in order to enable new semiconductor devices. A consistent theme in successful materials has been the use of post-transition metals (Al, Ga, In, Sn, ...) which interact strongly with oxygen, creating wide bandgaps (i.e. optical transparency) with strongly dispersive conduction bands (i.e. low carrier effective masses.)

We have identified two rutile-derived oxides containing Sb(V) which have promising fundamental properties: ZnSb_2O_6 and GaSbO_4 . ZnSb_2O_6 has a well-defined tri-rutile structure, while elucidating the structure of GaSbO_4 has been more challenging. By *ab initio* calculations we are able to show that the supposed random cation arrangement is highly unlikely, and by identifying a low-energy ordered arrangement we are able to explain the wide measured bandgap. By computing the formation energies of charged defects using hybrid density-functional theory, we are able to examine the intrinsic defect chemistry in both materials and screen for suitable extrinsic dopants. This analysis is advising experimental work to develop new n-type TCOs.

Role of Carrier Injection and Localization in Degradation of Oxide Films

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e05-nandef-shl

Most current electronic and electrochemical devices are stacks of thin films and interfaces operating under electrical stress. Nanometre-thick oxide films play crucial role in performance of these devices. Injection of excess electrons and holes into oxide films is responsible for the mechanisms that govern the formation of conductive filaments in resistance switching memory devices, the dielectric breakdown in microelectronic devices, and the performance of photo-electrochemical and oxide fuel cells. Our theoretical modelling combined with experimental observations demonstrates that structural disorder in amorphous SiO_2 , Al_2O_3 , TiO_2 , ZnO and HfO_2 films creates precursor sites which can spontaneously trap up to two electrons or holes in deep states in the band gap. The results demonstrate that single- and bi-polaron electron and hole states can form in a- SiO_2 [1] and a- HfO_2 [2] where the effect of local disorder is amplified by polaronic relaxation of amorphous network. Only hole trapping is found in a- Al_2O_3 [3] The electron localization results in weakening of Me–O bonds, which can be broken upon thermal activation, creating an O^{2-} interstitial ion and a neutral O vacancy [4]. O^{2-} interstitial ions can easily diffuse through the oxide and in devices are guided to the positive electrode by the electric field [5]. Thus electron injection can lead to the formation of new defects and significantly alter the structure of oxide films at large injection densities. We discuss the implications of this effect for the mechanisms of electrical breakdown and resistance switching in electronic and memory devices. The creation and field-driven movement of oxygen ions causes changes in oxide structure on a much larger scale than previously thought.

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A DFT study of Copper Oxides as Photovoltaic Absorbers

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e05-surfin-lee

The expanding solar technology market has raised interest in exploring p-type semiconductors like copper oxides. Consequently, there is a need for acquiring knowledge about the electronic and optical properties of such materials in order to assess their absorbing potential and solar power conversion efficiency. However, most photovoltaic absorbers are identified using the standard Shockley-Queisser (SQ) selection principle which relies entirely on optimal band gap values. This has been proven as an insufficient criterion as many materials with appropriate values perform badly. We have employed calculations based on the density functional theory (DFT) to assess three copper oxides as potential photovoltaic materials: Cu_2O , Cu_4O_3 , and CuO . We created a unique model that describes all three copper oxides accurately. Furthermore, we have assessed their mechanical, electrical, magnetic, and optical properties and linked them to theoretical values of photovoltaic efficiencies. On top of that, we extended the standard SQ limit and answered why copper oxides miss to achieve high solar-absorbing photovoltaic efficiencies despite the fact that they have promising energy band gaps values.

Computational Studies of Porous Materials: from Defective Metal-Organic Frameworks to 2D Zeolites

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e05-surfin-lin

In this presentation, I will discuss our recent work on defects in metal-organic frameworks (MOFs) and prediction of 2D zeolites using a graph theory approach.

I will first discuss defects in MOFs. UiO-66 has emerged as one of the most promising MOF materials due to its thermal and chemical stability and its potential for catalytic applications. Typically, as-synthesised UiO-66 has a relatively high concentration of missing linker defects. The presence of these defects has been correlated with catalytic activity but characterisation of defect structure has proved elusive. We refine a recent experimental determination of defect structure using static and dynamic first principles approaches, which reveals a dynamic and labile acid centre that could be tailored for functional applications in catalysis [1].

I will then discuss a new graph-theory based approach for generating crystal surfaces and how we can use it to predict 2D zeolites [2]. We hypothesise that determining how to cut a 3D material in half (i.e., which Miller surface is formed) by severing a minimal number of bonds or a minimal amount of total bond energy per unit area can yield insight into preferred crystal faces. We answer this question by implementing a graph theory technique to mathematically formalize the enumeration of minimum cut surfaces of crystals. We have identified a simple descriptor based only on structural information that predicts whether a zeolite is likely to be synthesizable in the 2D form and correctly identifies the expressed surface in known layered 2D zeolites. This is a joint work with the groups of Dr Maciej Haranczyk and Prof Berend Smit.

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Pt-water Double Layer Structure in Realistic Solution Conditions

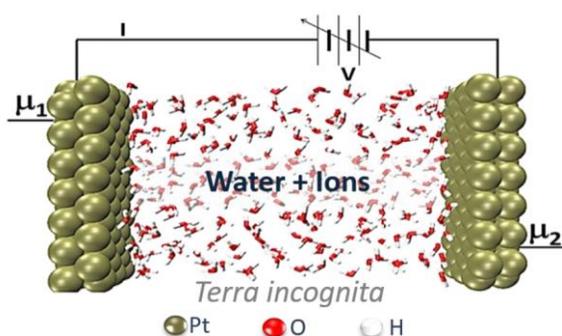
Clotilde Cucinotta *

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e05-surfin-clo

The operation of current and emerging energy devices such as water electrolysers, fuel and solar cells, batteries, supercapacitors and sensors, underpins the coupled flow of matter and charge across electrified interfaces at the nanoscale, under applied potential. Understanding the microscopic detail of these electrochemical processes is key to device optimization, enabling them to fulfil their promise for cleaner, more efficient, cheaper and safer nanotechnology. However, core challenges remain unanswered in computational electrochemistry, and the knowledge gap between theory, experimental insight and technologic applications is particularly big.

In this talk I will introduce some issues connected with the simulation of electrified interfaces at the nanoscale focusing on modelling the effect of an applied potential to a cell. I will present some recent progress in the simulation of the double layer of a prototypical Pt-water interface and its response to changes of applied potential.



I will show how surface charging is not consistent with a traditional simple capacitor model and that charge distribution as well as structure and number density of the first water layers in contact with the electrode strongly depend on the applied potential. The interfacial dipole is not merely determined by water reorientation in the first

layer but by the combination of its number density and charging. Water reorientation becomes relevant only in the second layer. This dependence of the structure of this electrified interface on the applied potential will likely affect the catalytic processes therein.

Time allowing, I will illustrate how combining the non-equilibrium Green functions formalism and DFT can lead to a more sophisticated description of EC phenomena and a deeper understanding of how currents and applied bias can affect atomic dynamics.

The Interaction of Phosphate with Cerium Dioxide Surfaces

Marco Molinari*, Adam R. Symington, Joseph M. Flitcroft, David J. Cooke, Dean C. Sayle, Stephen C. Parker

**Department of Chemistry, University of Huddersfield*

e05-surfin-mol

Cerium dioxide, CeO_2 , is considered a promising nanozymes, a metal oxide that mimics enzyme activity, and has therapeutic potential in oxidative stress and metabolic disorders. However its activity is modulated by surface charge, composition and the presence of many adsorbed species present in cellular environments.

Here, we use ab initio and classical modelling to provide insights into the interaction of phosphate, a common bodily electrolyte, with the surfaces of CeO_2 .

We define surface chemical modifications that strongly affect the complex biological activity of CeO_2 , focusing on the morphology dependent interaction with phosphate. We found that regardless of surface composition, the $\{100\}$ surfaces of CeO_2 nanocubes bind strongly to phosphates, which inhibit redox and hence nanozyme activity. On the other hand, the $\{111\}$ surfaces of CeO_2 nano-octahedra display less interaction with phosphate and may be a better choice in biological applications where phosphate may hinder nanozyme activity. We discuss this in light of experimental data.

Computational QM/MM studies of the Methanol to Hydrocarbons process on zeolites H-Y and H-ZSM-5

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e05-react-log

We use state-of-the-art molecular simulations with validation of the results against recent experimental neutron scattering studies, to gain a better understanding of the early stages of the widely studied and important methanol to hydrocarbons process (MTH).

We used Chemshell [1] as our computational environment to support the hybrid QM/MM calculations, with several codes that have been proven to allow chemical accuracy [2] to describe the QM (DFT) and MM (forcefield) regions. We employ these packages to determine different observables describing sorbate-zeolite interactions (including adsorption energy, transition barriers to the methoxylation step and vibrational frequencies) in faujasite (H-Y) and the industrially used H-ZSM-5 and by comparing our calculated values with experimental spectroscopic results [3].

To gain a better understanding of the methanol to hydrocarbons process we model the reaction pathway up to the formation of dimethyl ether in order, thereby giving insight into the conditions prior to the formation of the first C-C bond. In the initial part, we modelled using static calculations, the formation of a methoxylated framework converted from an adsorbed single methanol and then a methanol dimer at 0 K. Afterwards, we employed molecular dynamic techniques in order to have a better replica of the experimental environment by modelling the reaction temperature (300 K) and pressure (1 bar) and adsorbing up to five methanol molecules in the H-ZSM-5 catalyst and gaining a broader insight about the interactions between our feed and catalyst pores.

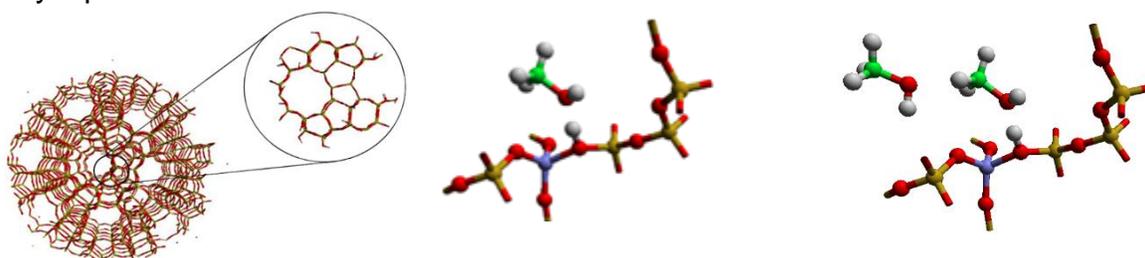


Figure 1: An example of a QM/MM setup for zeolite H-Y, describing the reaction path to adsorption of two methanol molecules, from the empty cluster (left), a section of the QM region with one adsorbed methanol (middle) and a section of the QM region with the two adsorbed methanol molecules (right).

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Theoretical Simulation of the Catalytic CO₂ Activation and Dissociation on the Major Magnetite Fe₃O₄ Surfaces

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e05-react-lee

The spinel structured iron oxide magnetite (Fe₃O₄) is an important component of industrial catalysts for both oxidation/reduction and acid/base reactions due to the mixed valence state of the octahedral cation sublattice. However, atomic-level mechanistic interpretations for many chemical processes are still unknown. Herein, we address the catalytic CO₂ activation and dissociation along with its adsorption on the Fe₃O₄(001) and (111) surfaces obtained from density functional theory (DFT) calculations.¹

We have calculated the fundamental aspects of the adsorption of CO₂ on the Fe₃O₄(001) and (111) surfaces for the different interaction modes, including the adsorption energies, structural parameters and vibrational frequencies. The electronic charge transfers were estimated between Fe₃O₄ and the CO₂ molecule. We found that the CO₂ molecule interacts more strongly with the (111) than with the (001) surface (see Figure 1) and that it gains electronic charge from Fe₃O₄ for each adsorption configuration. We have also investigated the mechanisms for the dissociation of the CO₂ molecule catalysed by the Fe₃O₄ surfaces. These findings are important in the interpretation of the catalytic properties of Fe₃O₄.

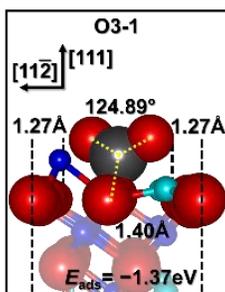


Figure 1. Side view of the CO₂ adsorption configuration that releases the largest adsorption energy on the Fe₃O₄(111) surface.

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Kinetic Control of Molecular Assembly on Insulating Surfaces

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e05-react-flo

I will illustrate, via density functional theory, the fundamental principles driving a sequence of molecular transitions on the calcite (10.4) bulk insulating surface, from molecular deposition to the formation of stable and metastable ordered molecular networks [1, 2]. The comprehensive theoretical investigation is combined with experimental data obtained from non-contact AFM microscopy [3, 5]. The quantitative analysis highlights the role of kinetics as the driving mechanism for the observed specific transition path and, importantly, as a possible new route to realize molecular architectures on insulating surfaces by kinetic control. The knowledge of reaction and diffusion mechanisms on insulators helps in identifying routes to create ordered molecular patterns (still rather challenging) with technological advantages over structures routinely obtained on metallic surfaces.

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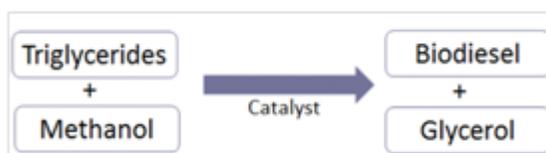
The Effect of Ceria Morphology on Gas Phase Glycerol Conversions

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e05-react-wil

Biodiesel production has increased hugely over recent years as focuses towards renewable fuels and feedstocks have intensified; biodiesel is produced through the base catalysed reaction of triglycerides and methanol.



The production of biodiesel is predicted to exceed 38 billion litres by 2024,¹ leading to a huge glycerol surplus. Currently the process requires methanol derived from non-renewable sources, thus the process is only 90 % sustainable. The conversion of aqueous glycerol to methanol has been demonstrated over ceria catalysts [2], however so far, little effort has been made to improve methanol selectivity by catalyst design.

In this project we are aiming at studying some mechanistic proposals to understand the selective pathway for the conversion of crude glycerol to methanol. Although the poster is going to focus on the computational findings, the entire project is done in collaboration with some experimental groups based at Cardiff University and they have prepared cubes, rods and polyhedral nanostructures on which the catalysis occur.

On the Computational section of the project, we have modelled the CeO_2 {100}, CeO_2 {110}, and the CeO_2 {100} which was optimized using the Periodic DFT code known as VASP; and the GGA [1] functional was used together with a plane-wave-basis set. The energetics of the various morphologies of the CeO_2 calculated will assist in determining which of the CeO_2 nanostructures is more favorable for the reaction scheme of Glycerol conversion to Methanol.

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Hazardous Compounds at the Soil-Water Interface

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e05-surfin-par

The accumulation and persistence of hazardous compounds (HCs) in surface and ground water as well as living organisms has emerged as an adverse effect of human anthropogenic behavior. A variety of HCs, from emerging contaminants found in pharmaceutical residues and personal care products to household chemicals, biocides/pesticides and manufacturing wastes have been found to persist in the environment. Some of these compounds have been shown to cause adverse effects in aquatic organism as well as promote increased risk of developing thyroid disorders, tumors and diabetes¹.

In this study, we aim to build on the foundations of our understanding of how HCs interact with the environment by applying atomistic simulation methods to determine the physicochemical factors controlling the distribution of pollutants and their metabolites in aqueous and terrestrial environments, and then apply this to identifying sustainable ways of controlling their transport and removing them from the environment.

Initial studies centered on adsorption of HCs on two model clay surfaces; sodium montmorillonite and pyrophyllite. Simulations were performed using a combination of dispersion corrected DFT and classical MD methods, to calculate the binding free energy and identify favorable sites for HC adsorption on clays in vacuum and water. Our initial investigation focused on 10 molecules including dibenzo-dioxins and two poly-chlorinated derivatives, chloro- and hexachloro-benzene, emerging contaminants amphetamine, methamphetamine, ephedrine MDA and MDMA. These compounds were chosen as they have a wide range of functional groups which will allow us to identify links between the chemical nature of the HCs and their fate and effects in the environment. This will allow for us to predict the fate of other molecular species based on their chemical nature.

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Actinyl Adsorption on Magnetite (111)

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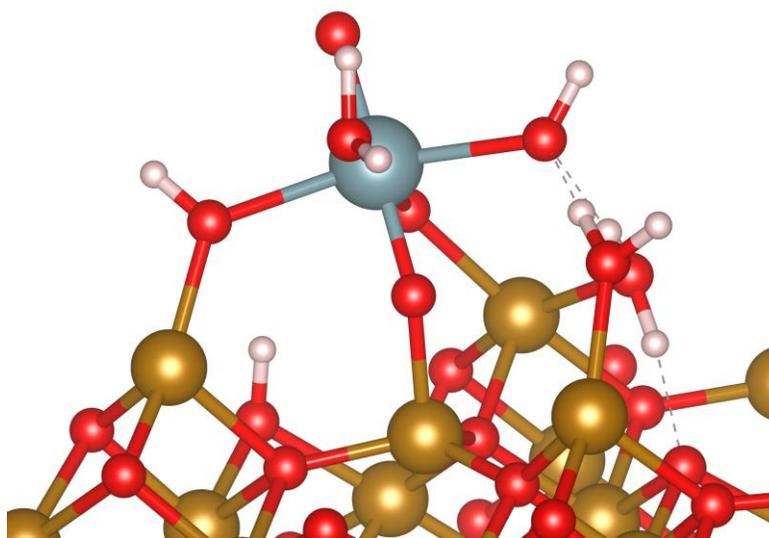
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e05-surfin-nik

Fundamental understanding of the atomic scale bonding between actinide elements and mineral surfaces is key to developing strategies to prevent and control the migration of these elements when they are released into the environment either via accident or as a result of terrorist activity. This understanding can also aid the decommissioning and storage of these materials.

We have studied, with the use of DFT in VASP, actinyl, AnO_2^{n+} ($An = U, n = 2; Np, n = 1,2; Pu; n = 1,2$) molecules adsorbed on magnetite (111) surfaces; H_2O and OH^- groups complete the actinyl equatorial coordination and ensure charge neutrality. We have subsequently employed the FEFF code to compute Fourier-transformed XAFS spectra.

We find that the surface termination has a large effect on whether the actinyl is reduced. The magnetite (111) termination Fe(III) sites at the surface shows reduction of the actinide. The uranium systems show this effect most clearly, with the U remaining in the VI oxidation state when the Fe(III) at the surface are not present but reducing to the V state with them present. Np and Pu are reduced more readily than U. The reduced actinyl complexes have the strongest adsorption energies.



Hybrid Time Dependent Density Functional Perturbation Theory in CP2K

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e05-nandef-mat

We will present results obtained using our implementation of Time Dependent Density Functional Perturbation Theory (TDDFPT) within the CP2K package.

We recently implemented a fully periodic implementation of TDDFPT that works with hybrid functionals and with the full range of optimizations and speed ups available within the CP2K code. In particular the Auxiliary Density Matrix Method for speeding up the calculation of two electron repulsion integrals has been tested and found to give accurate results at a fraction of the full cost when using diffuse basis sets.

We have applied TDDPT to a variety of defects – particularly oxygen vacancies in MgO and HfO₂. The hybrid functionals allow charge transfer excited states to be reasonably described and we can identify many of the proposed transitions associated with these well studied defects.

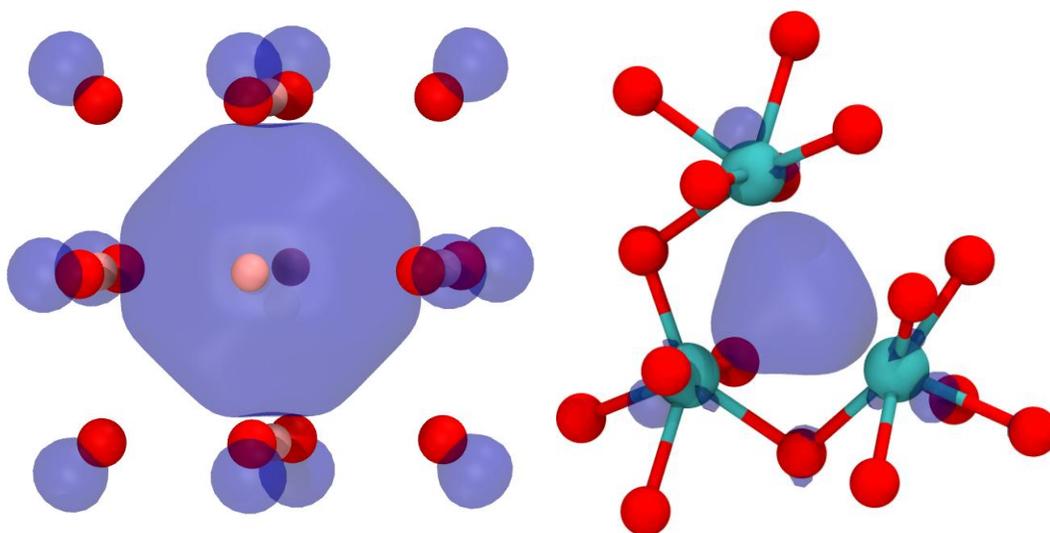


Figure 1: Kohn-Sham isosurfaces of oxygen vacancy defects in MgO and HfO₂.

Photocatalytic Interfaces of TiO₂ with Graphene and Reduced Graphene Oxide: A Computational Study

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e05-gener-nat

Photocatalysis has great potential for applications in water splitting and generation of hydrogen fuel. However, photocatalysts' efficiency is limited by inefficient harvesting of sunlight and by recombination of photogenerated electrons and holes. Composite systems of TiO₂ with carbon materials, such as reduced graphene oxide and carbon nanotubes, show improved activity compared to pure TiO₂.¹ This improvement is attributed to enhanced light absorption and photoinduced charge transfer,² but detailed understanding of the mechanisms is still lacking. Computational studies so far have focussed on idealised TiO₂/pure graphene interfaces,² ignoring the complexity of the real materials. We report our studies of realistic photocatalyst composites: TiO₂ interfaces with reduced graphene oxide (rGO) – an oxygenated form of graphene.

We use hybrid density functional theory to model the electronic properties of the ideal TiO₂ rutile (110)/graphene interface and several rutile (110)/rGO interfaces. We show that rutile (110)/graphene is a physisorbed system with weak electronic interaction: graphene's electronic structure is preserved, and the composite's highest occupied and lowest unoccupied bands are graphene-based.³ Therefore, photoelectrons are likely to decay to the lowest unoccupied band and recombine with photo-holes.

In contrast, rutile (110)/rGO interfaces can form Ti-O-C and hydrogen-bonded bridges linking the TiO₂ and rGO components, with profound effect on the electronic properties. Graphene's semimetallic electronic structure disappears and a band gap opens. The lowest unoccupied band is largely localised on the carbon-oxygen parts of rGO and is positioned below the TiO₂ conduction band, while the highest occupied band remains largely graphene-like and delocalised. Moreover, the rutile (110)/rGO composites possess an indirect band gap. We suggest that the rGO-based lowest unoccupied band acts as photoelectron trap, and the indirect band gap hinders electron-hole recombination, therefore making TiO₂/rGO composites efficient photocatalysts.

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Insights into Emerging Photovoltaic Materials through Density Functional Theory

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e05-gener-dos

The global demand for energy increases year on year as the need to satisfy modern technological desires is combined with an increasing population. This need must be met while also considering environmental and economic impact, and so an energy source of the future must be both inexpensive and sustainable. Photovoltaics (PVs) are a technology set to meet that need – as efficiencies have increased and costs have dropped, the photovoltaic market has expanded immensely, with capacity growing from 4 GW in 2000 to 227 GW in 2015. Nevertheless, the most successful materials used to harvest light in PV currently all have weaknesses – whether inefficient absorption of light by silicon, or toxic and expensive elements in CdTe or Cu(In,Ga)Se₂. Thus, there is much interest in emergent materials, such as the lead halide perovskite (CH₃NH₃)PbI₃ (MAPI) which has reached competitive device efficiencies in just 9 years of development.

In this presentation, we will discuss our efforts to explore a number of such emergent materials computationally, examining their optoelectronic properties and suitability as solar absorbers. These studies have ranged from analyzing the performance of the Cs₂AgBiX₆ family as Pb-free alternatives to MAPI, through to detailed optical and defect characterizations – in direct comparison with experimental ellipsometry and DLTS – of antimony chalcogenides, and the *ab initio* prediction of a promising solar absorber within the Pb-Bi-S family. Throughout, we will consider the accuracy and aptitude of theoretical Density Functional Theory calculations as an additional tool in the search for new photovoltaic materials.

Phonon Anharmonicity in Energy Materials

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e05-gener-par

Phonon anharmonicity is an increasingly common theme in modern materials science. Understanding the interplay between anharmonic structural dynamics and material properties is an active research area, and one that could ultimately lead to new design paradigms for functional materials. Accurate first-principles techniques such as DFT, together with modern computing capabilities, have made it possible to use first-principles lattice-dynamics calculations to explore anharmonicity at the microscopic level and make quantitative predictions of *e.g.* phonon lifetimes and lattice thermal conductivity. This talk will discuss two examples where modelling has played a leading role in linking structural dynamics to key properties.

Orthorhombic SnSe was recently shown to have record-breaking bulk thermoelectric efficiency, due in part to its “ultralow” lattice thermal conductivity. Calculations reveal the high-temperature *Cmcm* phase to be a crystallographic average over lower-symmetry *Pnma* minima, resulting in an anharmonic double-well potential and substantial softening of the phonon frequencies. By mapping the potential-energy surface along the soft modes, we have characterized the phase transition and developed an approximate renormalization scheme to quantify the effect of the soft modes on the thermal transport.

Hybrid halide perovskites such as the archetypal methylammonium lead iodide (MAPbI₃) have had a huge impact on photovoltaics research, and have raised questions on the fundamental relationship between their structural dynamics and physical properties. In conjunction with experimental measurements of the phonon frequencies and linewidths, we have applied lattice-dynamics calculations to examine the interactions between the organic cation and the perovskite cage in MAPbI₃, and to elucidate the microscopic origin of its picosecond phonon lifetimes. Our results highlight the unique structural dynamics of this class of materials compared to conventional semiconductors, and have important implications for carrier cooling and charge transport.

First-principles study of Electronic and Structural Properties of CuFeO₂ Surfaces

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e05-gener-lis

A major challenge towards a sustainable and renewable energy technology is energy storage. One potential solution is to store chemical energy in the form of hydrogen gas obtained by photoelectrolytic water splitting. However, current photoelectrochemical cells for water splitting are not sufficiently efficient for industrial applications. The efficiency of such devices depends strongly on the alignment of the photoelectrode band edge positions and the redox potentials for the oxygen and hydrogen evolution reactions.

Due to its favourable positioning of its band edges, CuFeO₂ is a very promising photoelectrode material [1]. However, despite other beneficial properties such as a large absorption coefficient, good charge carrier mobility and long charge carrier lifetimes, CuFeO₂ performs below the expected performance when used as a photocathode. Based on experimental evidence, it is speculated that the poor performance is due to detrimental surface states [2].

I will present work we have carried out to unveil the nature of the surface states of CuFeO₂. Developing a fundamental understanding of these states is crucial for identifying ways how they could be passivated. Furthermore, we studied the relative stabilities of the four different surface terminations of the (0001) surface.

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Computational studies of Cathode Materials for Mg Ion Batteries

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e05-store-cor

Mg²⁺ ion batteries are a promising alternative to Li⁺ ion technology for portable applications, and can achieve high volumetric energy densities due to the viability of Mg metal anodes. One of the most critical issues in the development of Mg-ion batteries is the discovery of cathode materials, offering suitable operating voltages, long cycle life and good kinetics. Achieving good kinetics is extremely challenging, since strong electrostatic interactions between the divalent Mg ion and the anionic framework of the cathode host results in high barriers for migration of Mg and low mobility.

Currently, experimentally known Mg intercalation hosts are limited in number compared to Li. Expansion of this range can be aided by computational screening of new materials, and improvements in performance can be driven by greater understanding of factors affecting voltage, mobility and structural changes upon Mg incorporation.

Here we present our computational studies of two possible Mg-ion battery cathode materials: V₂O₅ and anatase TiO₂.

V₂O₅ is considered one of the most promising materials for Mg ion battery cathodes, but suffers from several performance issues. Experimental results for V₂O₅ as a Li ion cathode material indicate some limitations may be overcome by doping.¹ We have investigated the location and effects of metal ion dopants in α -V₂O₅,² the factors affecting the stability of the important α - and δ - phases, and how doping can be tailored to achieve Mg mobility.

TiO₂ is an attractive sustainable material for battery applications, yet experimental capacity of Mg in anatase TiO₂ is limited. We unravel the mechanisms that contribute to this low performance and how they may be overcome using rationally designed doping strategies.

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Doubled Conductivity in Transparent Conducting In_2O_3 through Novel Dopant Design

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e05-nandef-dos

Transparent conducting oxides (TCO) are a vital component in many opto-electronic devices such as mobile devices, low-emissivity windows and photovoltaics. In_2O_3 is currently the market leader accounting for the majority of the >\$5 billion TCO market. When donor-doped with Sn (ITO), high conductivities and carrier concentrations are realisable in In_2O_3 whilst retaining the high optical transparency. Despite a drive to move away from In due to the high costs arising from its non-abundant nature, Sn-doped In_2O_3 is still unmatched in its desirable properties. Through hybrid density functional theory calculations twinned with an experimental analysis of thin films, we show that doping In_2O_3 with molybdenum (IMO) doubles the conductivity and increases the transparency. This has the effect of enabling the fabrication of thinner films resulting in a reduced cost for optoelectronic devices. Our work also outlines the novel doping mechanisms which gives rise to these effects and which can be applied to other systems.

Global Optimisation of Alkali Earth Oxide Nanoclusters and their deposition on Graphene

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e05-nandef-smw

Nanoclusters have a wide range of applications including catalysis, data storage and gas sensing. However, unless they are kept separated, nanoclusters have a tendency to come together to form larger, more stable structures. One way of keeping them separated is deposition and anchoring on a surface.

Specifically, we have looked at Group II oxide nanoclusters in this study. Magnesium oxide clusters are of interest in gas sensing applications, while barium oxide nanoclusters are particularly relevant because they can be characterised using atomic-resolution microscopy which can then be compared to theoretical results to verify them. Using interatomic potentials in GULP and DFT in FHI-aims in conjunction with a genetic algorithm in our code KLMC (Knowledge-Led Master Code) we have investigated $(MO)_n$ nanoclusters, where $n < 24$ and $M = \text{Mg, Ca, Sr and Ba}$ and will present results on these in vacuo. For a surface, we chose graphene, and have therefore used data from density functional theory to parametrise interatomic potentials to calculate the interaction of these nanoclusters with a graphene surface in order to get insight into their structure and behaviour on graphene. We have also investigated the effect of including image potential states at the graphene surface in our model, and refined results which we gained with this model as a starting point and then using FHI-aims.

All atomic configurations of our published local minima are have been uploaded into the HIVE database for nanoclusters – <http://hive.chem.ucl.ac.uk> – and, therefore, readily available to visualise and download.