

# *Talks*



## Disorder?

Neil Allan\*

\* *School of Chemistry, University of Bristol*

TBA

## Predicting the Atomic Structures of Nanoclusters for Compounds with 1:3 Stoichiometry

Dong-Gi Kang\*, Alexey A Sokol, Alin-Marin Elena, Scott M Woodley

\*Department of Chemistry, UCL

e05-nano-smw

Aluminium halides and hydrides are important compounds in multiple areas of materials chemistry. Our interest is in predicting the atomic structure of their stoichiometric, non-charged clusters. However, the study of nanoclusters, using molecular dynamics (MD) or Monte Carlo (MC) simulations of largish sized particles composed of many atoms, is limited by the exponentially increasing computer cost as each configuration to evaluate and the number of possible configurations increases rapidly. Consequently, a cheaper method to evaluate the configurations along with developing clever optimization methods for generating them are required. Here, we concentrate on the former and explore whether interatomic potentials (IP) and/or machine learning (ML) potentials can be developed and employed to model compounds/systems of interest and thus address some of the challenges of structure prediction of nanoclusters. Note that we employ an initial search over the IP/ML energy landscape for plausible structures can be refined at a later stage using an appropriate electronic structure approach.

In the first part of this talk, results for developing suitable IPs for ionic materials that have a high stoichiometric ratio, viz.  $Ti_3N_4$ ,  $Mg_xSi_yO_z$ ,  $AlX_3$  ( $X=H, F, Cl$ ), will be presented.

The second half will be about the trend in the structural characteristics analysed as a function of size (number of stoichiometric units) for the predicted ground state atomic configurations (PBEsol local minima, LM) of  $XF_3$  clusters. Results are obtained using the KLMC genetic algorithm developed in our group. For more challenging compounds to model, we are training ML potentials.

1. S. M. Woodley, *J. Phys. Chem. C* 2013, 117, 45, 24003–24014;
2. T. Krahl, E. Kemnitz *Catal. Sci. Technol.*, 2017, 7, 773-796
3. A. M. Escatllar, T. Lazaukas, S. M. Woodley, S. T. Bromely, *ACS Earth Space Chem.* 2019, 3, 2390–2403
4. V. S. Bhadram, H. Liu, T. Li, Vitali. B. Prakapenka, R. Hrubiak, S. Lany, T. A. Strobel., *Phys. Rev. Materials* 2, 011602(R)
5. V. L. Deringer, A. P. Bartók, N. Bernstein, D. M. Wilkins, M. Ceriotti, and G. Csányi, *Chem. Rev.* 2021, 121, 16, 10073–10141.

## Multiscale modelling of the electrical conductivity of carbon nanotube films

Thomas R. Durrant\*, Yvelin Giret, David Z. Gao, Alexander L. Shluger

\**Department of Physics and Astronomy, UCL*

*e05-nano-shl*

Carbon nanotubes (CNTs) are a fascinating low dimensional material with very high electrical conductivity. CNTs hold significant technological promise due to their extremely high electrical conductivities. This is because metallic CNTs behave as ballistic conductors, which enables highly energy efficient electrical devices to be constructed from them. In many practical applications, CNTs are deposited in a disorganized film. One such example application is the use of a CNT film as resistance changing element in non-volatile computer memory. In order to model the electrical conductivity of such films, models of the electrical conductivity of individual CNT junctions must be combined with larger-scale models of their geometric structure.

In this project, a multiscale model of the electrical conductivity of CNT films was developed through the following steps: **(a)** A large library of CNT-CNT junction structures was simulated using density functional tight binding (DFTB) in combination with the nonequilibrium Green's function (NEFG) approach. The intrinsic electrical conductivity of individual CNTs is high and the primary source of electrical resistance within CNT films is anticipated to occur at CNT-CNT junctions where electrons must tunnel from one CNT to another. The results were used to generate an atomistic conductivity model. **(b)** Mesoscopic models of nanoscale CNT films were generated using course-grained molecular dynamics (CGMD). A library of CNT films was generated. **(c)** The atomistic conductivity model developed in (a) was used in combination with larger-scale molecular dynamics (MD) calculations in order to parameterize electrical conductivities between the mesoscopic segments employed in (b). **(d)** The structural models generated in (b) were then combined with the electrical parameters established in (c) in order to produce a large-scale electrical model of the conductivity of a nanoscale CNT film, using the method of nodal analysis.

Using this approach, the electrical conductivity of realistic CNT films can be evaluated. Our results demonstrate that depositing CNT films in layers is one approach that can be used to tailor the conductivity of the resultant films.

# **ONETEP, with some exemplar applications thrown in**

Chris Skylaris

*University of Southampton*

TBA

# Current Challenges in Catalytic Science

Graham Hutchings

*University of Cardiff*

TBA

## Mechanism of NH<sub>3</sub> Synthesis on Fe<sub>3</sub>Mo<sub>3</sub>N

M. D. Higham<sup>\*</sup>, Constantinos D. Zeinalipour-Yazdi, Justin S. J. Hargreaves, C. Richard A. Catlow

<sup>\*</sup>*Department of Chemistry, University College London*

*e05-react-cat*

Plane-wave Density Functional Theory (DFT) techniques are applied to investigate two distinct reaction mechanisms for ammonia (NH<sub>3</sub>) synthesis over a thin-film model Fe<sub>3</sub>Mo<sub>3</sub>N(111) surface, namely an associative Mars van Krevelen mechanism and the conventional, dissociative, Langmuir Hinshelwood mechanism. The η-carbide structured Fe<sub>3</sub>Mo<sub>3</sub>N is experimentally reported to be highly active for NH<sub>3</sub> synthesis, in common with the isostructural Co<sub>3</sub>Mo<sub>3</sub>N. Experimental studies revealed that lattice N is much more active and easily removed in Co<sub>3</sub>Mo<sub>3</sub>N, in contrast to Fe<sub>3</sub>Mo<sub>3</sub>N, and computational studies showed that the presence of surface lattice N vacancies can enhance N<sub>2</sub> activation and NH<sub>3</sub> synthesis over Co<sub>3</sub>Mo<sub>3</sub>N. Hence, the present work aims to provide a detailed complementary investigation of the Fe<sub>3</sub>Mo<sub>3</sub>N system in order to elucidate the similarities and differences between the Fe and Co systems in terms of N vacancy formation behaviour and surface reaction mechanism.

Plane-wave DFT as implemented within the VASP code was applied to obtain N vacancy formation energies and obtain optimised geometries for all intermediates involved in the MvK and LH mechanisms, and to identify transition states for all elementary processes. The revised PBE functional was used throughout, along with a 650 eV plane-wave cut-off and a Monkhorst-Pack k-point sampling mesh of density (4×4×1). All structures were optimised until atomic forces were converged to within 0.01 eVÅ<sup>-1</sup>. Transition states were identified using the CI-NEB and Dimer methods, and were confirmed via vibrational analysis.

The calculations reveal that whilst surface N vacancy formation is more energy-demanding for Fe<sub>3</sub>Mo<sub>3</sub>N compared to Co<sub>3</sub>Mo<sub>3</sub>N, the vacancy formation energies are comparable, implying that it is highly likely that surface lattice N vacancies are present on Fe<sub>3</sub>Mo<sub>3</sub>N, and that loss of lattice N is limited by bulk N diffusion. It was also found that N<sub>2</sub> activation was enhanced on the Fe<sub>3</sub>Mo<sub>3</sub>N surface compared to Co<sub>3</sub>Mo<sub>3</sub>N. The calculations will inform future studies considering Cr promotion of Fe<sub>3</sub>Mo<sub>3</sub>N and the development of quaternary Fe<sub>3-x</sub>Co<sub>x</sub>Mo<sub>3</sub>N catalysts with an optimal Fe:Co ratio.



## The Electronic Structure and Catalytic Activity of a Ru<sub>3</sub> Cluster Embedded on Nitrogen-doped Graphene

Yao Zhao\*, John E. McGrady

\*Department of Chemistry, University of Oxford

e05-react-mcg

Pyrolysis has been a popular synthetic technique in producing single-atom catalysts (SACs) embedded on graphene-based materials. A slight variation, triple-atom catalysts composed of three Ru atoms embedded on N-doped graphene was synthesised in a confined pyrolysis of Ru<sub>3</sub>(CO)<sub>12</sub> and reported to catalyse alcohol oxidation 10 times more efficiently compared to its SAC analogue.<sup>1</sup> Here, we build the models of Ru<sub>3</sub>/N-graphene and analyse their electronic structures and orbital interactions between the cluster and N-graphene. Significant orbital interactions with localised p defect states on the N-graphene model led to the transfer of two electrons from the cluster to the conduction band of the surface. The surface therefore acts as a buffer, removing and restoring electrons to the active site during the catalytic cycle. Our initial exploration of the cycle indicates a potential role for Ru=O species in the C-H bond cleavage step of alcohol oxidation.

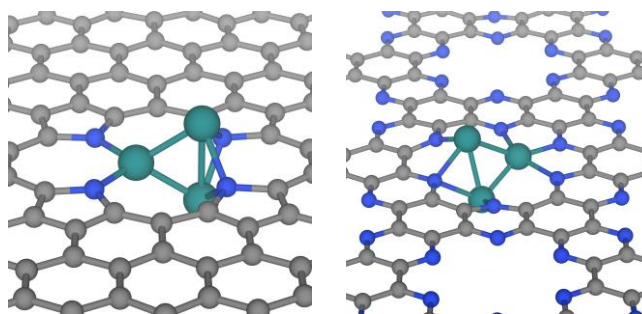


Figure 1: Ru<sub>3</sub> cluster embedded on (a) N-graphene and (b) g-C<sub>2</sub>N

1 *J. Am. Chem. Soc.* 2017, 139, 29, 9795–9798

## Computational investigation of NiOOH, from bulk to catalysis

Ruotao Yang\*, Alexey A. Sokol, C. Richard A. Catlow

*\*Department of Chemistry, University College London*

*e05-react-cat*

Mitigating environmental and ecological damage caused by human emissions are amongst the grand challenges of the 21<sup>st</sup> century. Therefore, the transition from conventional fossil energy to renewable energy, including solar and wind energy is an increasingly important topic. Power-to-gas (P2G), a process of converting renewable energy into hydrogen gas via electrolyser, is considered to be promising due to its carbon-free nature. However, to produce green hydrogen, the sluggish anodic reaction becomes the bottleneck, which reduces the efficiency of the electrolyser. To address such issues, a cheaper and more stable catalyst is desired. NiOOH (nickel oxyhydroxide) shows high suitability as an anode material for several electrocatalytic oxidation reactions. In addition, NiOOH is considered a promising electrode material for rechargeable batteries due to its proton-exchange capacity. However, limited knowledge of the bulk and surface structures of NiOOH, due to the lack of experimental evidence, caused by the complexity of the electrochemical environment, hinders a deeper understanding of its structure and reactivity.

To gain a deeper insight into the NiOOH bulk structure, we employ Ab Initio Molecular Dynamics (AIMD) based on density functional theory (DFT) to simulate its bulk structure. The initial configuration was obtained by removing a layer of protons in bulk Ni(OH)<sub>2</sub> to mimic the deprotonation process. The MD calculation showed a noticeable proton transfer, in which the proton layer immigrated to the neighbouring oxygen layer. The structure generated by AIMD was then optimized by DFT using with PBE+U functional. The as-obtained structure has a lower energy level, indicating that a mixture of Ni(OH)<sub>2</sub> and NiO<sub>2</sub> layer in the bulk system is favoured over a stoichiometric NiOOH layer. Furthermore, the electrostatic analysis suggested such proton transfer was caused by strong O-H interaction between the oxygen and hydrogen layers. Based on these results, we further cleaved its surface to investigate its catalytic activity in heterogeneous catalysis. We introduced the SO<sub>4</sub><sup>2-</sup> anions on its surface as an adsorbate and a Ni-bulk system beneath the NiOOH surface to generate an SO<sub>4</sub><sup>2-</sup>-NiOOH@Ni heterostructure. We show that the Ni-bulk system can stabilize the adsorbate and further promote the reactivity, which agrees with the experimental data.

# Amorphous ZnO: Structure, Stability and Charge Trapping

David Mora Fonz

*HTU, Mexico*

TBA

## Ab-Initio Molecular Dynamics Simulations of Substoichiometric Amorphous Alumina

J. Strand\*, A. Shluger

\**Department of Physics and Astronomy, University College London*

*e05-bulk-shl*

Oxygen vacancies play an important role in the application of oxides in technology. The notion of a vacancy is well defined in the case of crystals, where a defect is simply any break from crystallographic order. In amorphous materials, where there is no long-range order, defects are less well defined. Amorphous oxides are widely used in technology, yet there has not been a great deal of focus on this ambiguity. Often, vacancies are modelled by deleting oxygen atoms from a stoichiometric amorphous model, previously produced using the melt-and-quench technique, and then relaxing the system geometry ('post-quench' method). However, this may not be the appropriate way to model substoichiometry in amorphous oxides. Here, we use an alternative approach where we produce substoichiometric amorphous oxide models by quenching from an oxygen-deficient melt ('in-melt' method). We use ab-initio molecular dynamics (AIMD) with a hybrid DFT functional to investigate the structure of substoichiometric alumina. The models produced are periodic and pseudo-amorphous, with 357 atoms in the unit cell. We find that there are vacancy-like point defects in the amorphous oxide, characterized by undercoordinated Al ions and formation of Al-Al dimers. In subsequent simulations, we take post-quench vacancies and anneal them with ab-initio MD at 1000K. The resulting configurations are similar to those produced with the in-melt method, suggesting that use of ab-initio MD allows for a fuller exploration of configuration space and therefore more stable 'vacancy' structures.

Overall, the results suggest that, while vacancies may be ill-defined in amorphous oxides, oxygen deficiency leads to the formation of point-defects with similar properties to crystallographic vacancies. Further, it is possible that AIMD is necessary to find the most stable configurations of these defects.

## Unravelling Hydrogen Bonding Behaviours and their Impact on Proton Conductivity in Supramolecular Cages

Lei Lei, Sanliang Ling\*

\*Advanced Materials Research Group, Faculty of Engineering,  
University of Nottingham

e05-bulk-lin

Proton-exchange membrane (PEM) fuel cells hold promise as a solution for achieving a zero-emission economy. Recently, molecular cages have emerged as potential PEM candidates for stable and efficient fuel cells through structural design. However, due to their complex structures, understanding the proton transport dynamics and mechanisms using experimental or simulation methods has proven challenging. In this study, we employed *ab initio* molecular dynamics simulations to investigate these complex systems over extended timescales, spanning hundreds of picoseconds, to unravel these intricate systems. Additionally, we developed efficient python code to analyse the vast trajectory data generated. Our results highlight a significant disparity in the interaction of water with two molecular cages composed of the same functional groups, attributed to their distinct geometries. Notably, Cage 1, characterized by a spacious cavity, exhibits an average reduction of one hydrogen bond per water molecule. Consequently, Cage 1 displays faster water dynamics, a higher diffusion coefficient, and significantly diminished diffusion anisotropy. Our investigation underscores the critical role of hydrogen bonding behaviours between water molecules and functional groups within supramolecular cages, influencing water diffusion mechanisms and dynamics. Furthermore, we emphasize that precise control of hydrogen bonding behaviour through rational arrangement and passivation of strong electronegative atoms can further enhance proton conductivity within supramolecular cages.

## Investigation of unintentional aggregation of impurity-related defects within 4H-SiC.

N. Smith\*, A. Shluger

\*Department of Physics and Astronomy, UCL

e05-bulk-shl

To create p-doped regions within 4H-SiC MOSFET devices, 4H-SiC is bombarded with high energy  $\text{Al}^+$  ions from gaseous  $\text{AlH}_3$ , during ion implantation. However, recent experimental studies have found shallow electron and hole donor states affecting channel mobility, whose densities are directly proportional to the Al-implantation dose even after post oxidation anneal in NO atmospheres. This suggests that Al-related defects present after the creation of the  $(11\bar{2}0)$ -4H-SiC/ $\text{SiO}_2$  interface could be unintentionally interacting via aggregation with N- and O-related passivation defects at the interface.

We investigate the possibility of Al-O and Al-N complex formation within SiC devices, as well as whether such complexes can be correlated with the experimentally found mobility reducing states. In accordance with the charge compensation and site-competition theories, the  $\text{Al}_{\text{Si}}\text{N}_{\text{C}}\text{Al}_{\text{Si}}$  and  $\text{Al}_{\text{Si}}\text{O}_{\text{C}}\text{Al}_{\text{Si}}$  complexes have been examined using density functional theory (DFT) calculations. For each complex, four different geometry configurations corresponding to impurity substitution at different hexagonal (HEX) and cubic (CUB) lattice sites, derived using the Site-Occupancy Disorder package, were studied. Incorporation and binding energies, and charge transition levels (CTL) of these complexes in four different charge states were calculated in bulk 4H-SiC using DFT with the PBE0 functional.

Within bulk 4H-SiC, negative binding energies were obtained for all configurations, indicating that, if  $\text{Al}_{\text{Si}}$  and  $\text{N}_{\text{C}}/\text{O}_{\text{C}}$  are separately present within 4H-SiC, it is more energetically favourable for them to form aggregates. Negative incorporation energies were also obtained for all eight configurations when the impurity chemical potential sources were taken to be  $\text{AlH}_3$ ,  $\text{NH}_3$ , and NO, in correspondence to the device creation process. Within the 4H-SiC bandgap, the -1/0 charge transition is found to be the only stable transition for both complexes. The -1/0 charge transition levels of three out of four  $\text{Al}_{\text{Si}}\text{N}_{\text{C}}\text{Al}_{\text{Si}}$  geometry configurations were found to occur within the activation range of the  $\text{I}_{\text{D}}$ -DLTS identified trap state. Using  $\text{NH}_3$ , rather than NO, for the chemical potential of N resulted in even lower incorporation energies for the  $\text{Al}_{\text{Si}}\text{N}_{\text{C}}\text{Al}_{\text{Si}}$  configurations, implying the formation of the  $\text{Al}_{\text{Si}}\text{N}_{\text{C}}\text{Al}_{\text{Si}}$  complex is easier under anneal in  $\text{NH}_3$ . This aligns extremely well with experimental measurements which find the density of the shallow hole donor interface state to be higher after annealing with  $\text{NH}_3$  than with NO. For the  $\text{Al}_{\text{Si}}\text{O}_{\text{C}}\text{Al}_{\text{Si}}$  complex, the total and incorporation energies of each charge state were found to be lowest for the  $\text{Al}_{\text{Si}(\text{HEX})}\text{O}_{\text{C}(\text{HEX})}\text{Al}_{\text{Si}(\text{CUB})}$  configuration. The -1/0 transition level of this configuration was found to be at  $E_{\text{c}}-0.004$  eV, within the activation energy range of the shallow electron donor state observed experimentally. These results demonstrate how Al-O and Al-N complexes, can be responsible for channel mobility degradation in SiC devices.

## Simulation of correlation driven metal-insulator transitions in real solids using deep neural networks.

H. Sutterud\*, G. Cassella, W. T. Lou, D. Pfau, J. Spencer, W. M. C. Foulkes,

\**Physics, Imperial College London*

*e05-bulk-fou*

The use of deep neural networks (DNNs) for representing fermionic wavefunctions is gaining popularity. DNNs have demonstrated impressive results in systems such as molecules and nuclear systems as well as periodic systems such as the homogeneous electron gas and solids.

One favourable trait is the inherent flexibility of neural networks. Standard ab initio methods for solid systems often rely on uncontrollable approximations, such as the choice of a functional in density-functional theory or the form of the Slater-Jastrow trial wavefunction in quantum Monte Carlo methods. DNN ansätze, on the other hand, are built from multilayer perceptrons, which are universal approximators. The network weights and biases that define a DNN Ansatz are efficiently optimized using variational Monte Carlo methods and beyond-first-order optimizers. This produces results of consistent quality across highly diverse systems, and makes it possible to discover quantum phase transitions without prior knowledge of their existence.

In this talk, we investigate the interaction-driven Mott transition between metallic and insulating states of solids. Although Mott's first paper on the subject was published in 1949, some aspects of the transition are still not fully understood. Using the fermionic DNN architecture FermiNet to represent a supercell of bulk lithium, a metal-insulator transition with the characteristics of a Mott transition occurs spontaneously as the density of the system is adjusted. We will present our findings and discuss the nature of the transition in light of these results.

## The effect of ceria surface composition on scavenging reactive oxygen species

Khoa Minh Ta\*, David J. Cooke, Lisa J. Gillie, Roger M. Phillips, Marco Molinari

\*Department of Chemistry, University of Huddersfield

e05-surfin-mol

Cellular activities produce reactive oxygen species (ROS), such as hydrogen peroxide, superoxide anions, and hydroxyl radicals, which can accumulate and produce oxidative stress. This is linked to many degenerative diseases and cancer. Ceria nanoparticles (CeNPs) have been reported to perform enzyme mimetic activities to scavenge ROS. Here, we study the effect of surface composition on the energetic of the adsorption of such ROS. We use the most stable surfaces of ceria, i.e. {100}, {110}, and {111} surfaces, which are present in many active CeNPs, with surface compositions that include bare stoichiometric, hydroxylated, oxygen deficient and hydroxylated / oxygen deficient surfaces. We found that the three low Miller index ceria surfaces can perform both catalytic (where surface composition remains unchanged) and chemical (where surface composition changed) pathways for the scavenging. Our results suggest that hydroxylated surfaces would have limited scavenging activity compared to oxygen deficient surfaces. However, oxygen deficient surfaces may deteriorate over time due to the irreversible healing of surface oxygen vacancies.



## Modelling the effect of H in the formation, stabilisation and evolution of voids in polycrystalline Cu

Vasileios Fotopoulos\*, Alexander L. Shluger\*

*Physics and Astronomy, University College London*

*e05-surfin-shl*

Cu is used in a wide variety of applications ranging from power generation to microelectronics. Stress-induced voiding is amongst the most commonly reported defects in Cu.<sup>[1]</sup> Hydrogen plays a crucial role in Cu embrittlement and can be detrimental to the performance of electronic devices.<sup>[2,3]</sup> However, the correlation between hydrogen embrittlement and vacancy formation and aggregation leading to voiding in polycrystalline Cu is not yet fully understood. Furthermore, since measuring experimentally the amount of incorporated H in metals remains challenging, a theoretical approach is needed.

In this work, to efficiently describe the effects of H on the mechanical properties of Cu, we combine density functional theory (DFT) with bond order molecular dynamics (BO-MD). Our MD simulations Cu vacancies and H complexes in grain boundaries (GBs) demonstrate that they can withstand temperatures up to 700 K without dissociating.<sup>[4]</sup> Thus, H increases the stability of vacancy clusters in GBs during annealing. Under uniaxial strain, H at concentrations higher than 10 mass ppm facilitates the formation of partial dislocations close to the GBs, leading to a reduction of the yield strength of the crystal. Using statistical mechanics and inputs from DFT simulations, we determine equilibrium concentrations of vacancy clusters in Cu at different temperatures and study synergy effects between H and Cu vacancies. The H concentration for up to 100 bar partial pressure values and close to the melting point of Cu was orders of magnitude lower than the estimated concentration of Cu vacancies.<sup>[5]</sup> At this low H concentration, the interaction between H and Cu vacancies is negligible and becomes significant only for H partial pressures of 1 GPa or above. Therefore, the amount of H in Cu is sufficient to play a role in the initiation of voids only under extreme H pressure conditions. These results put thermodynamic limits on the hydrogen-induced vacancy clustering and void formation in bulk Cu.

[1] Wu, Z. et al. 2008. *Microelectronics Reliability*, 48(4), pp.578-583.

[2] Zarnas, P.D. et al. 2021. *International Journal of Solids and Structures*, 213, pp.103-110.

[3] Djukic, M.B. et al. 2019. *Engineering Fracture Mechanics*, 216, p.106528.

[4] Fotopoulos, V. et al. 2023. *TMS 2023 152nd Annual Meeting & Exhibition Supplemental Proceedings*, pp. 1001-1010. Cham: Springer Nature Switzerland.

[5] Fotopoulos V. et al. 2023. *Physical Chemistry Chemical Physics*. 2023. 25, pp.9168–9175.

## Simulating Hydrogenation in Magnesium Through the Application of Machine Learning Models

Oliver M. Morrison, Sanliang Ling, David Grant and Gavin Walker

\* *Advanced Materials Research Group, University of Nottingham*

*e05-surfin-lin*

In this contribution, we simulate magnesium hydride systems through the application of machine learning (ML) models, with the goal of identifying the rate limiting steps of the hydrogenation process. If metal hydride systems are to reach their full potential, it is vital that we develop a detailed fundamental understanding of how these systems evolve. Experimentally, it is difficult to pinpoint the factors that contribute to the differences between metal hydride systems, e.g differences in the kinetics of the hydrogenation and dehydrogenation reactions. Accurate molecular dynamics (MD) simulations of metal hydride systems could shed light on the rate limiting steps of the hydrogenation and dehydrogenation reactions, but traditional approaches to approximating the potential energy surface, such as classical force fields and density functional theory (DFT), are either lacking in accuracy or computational efficiency. Accurate large size, long-timescale MD simulations are therefore infeasible via these methods. ML has been applied to an abundance of problems, to assign simple functions to complicated patterns. A generic many-parameter model is designed, and parameter values are tuned to fit the model to specific examples. We apply the same concepts to produce a model that approximates the potential energy surface, mimicking the predictions of DFT with a less complicated, less computationally intensive model. This enables the simulation of large-scale atomic systems for longer time scales. The nature of ML incurs the risk of transferability issues; the model may extrapolate from our examples incorrectly when it encounters a particularly unfamiliar atomic structure. In such an event, we perform DFT on these structures and add them to set of examples used to train the model. Through repeated improvement of the ML model, we hope to identify the rate limiting steps of the hydrogenation process in magnesium, and consequently, potential improvements to the development of new catalysts to accelerate the reaction kinetics of metal hydride systems.

## Study of Hydroxyl Nests in Zeolites

Alec Desmoutier

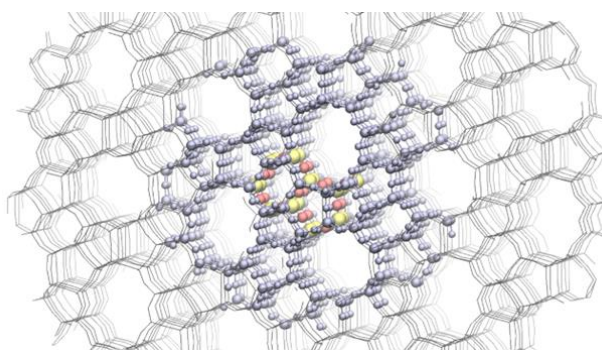
\* *University College London*

*surfin-cat*

For a long time, zeolites have been utilised as a material for various experiments in the petrochemical industry as a catalyst, however, the mechanism in which these zeolites interact has remained a mystery. The current theory is that hydroxyl nests are generated as an intermediate step in reaction within zeolites but haven't been tested computationally.<sup>1</sup>

A hybrid QM/MM approach using the ChemShell software was employed to study CHA/ZSM-5/Alpha Quartz defects. The model comprises a quantum mechanical description of a cluster of ~200 atoms around the reaction site near the porous channels, embedded in a much larger cluster modeled using a classical molecular mechanic's forcefield.<sup>2, 3</sup>

In this study, we have shown the results for the creation of hydroxyl nests as well as the aggregation of these defects to generate larger pores. Our results show the comparison of generating these defects from a point of origin outwards vs the removal of the key ring from the zeolitic framework. The formation of various mesopores that is found in the literature is a key aspect that is being aimed to emulate and recreate. Study into the introduction of metals (in this case Platinum) into the framework of the hydroxyl nest as an anchoring site for larger metal clusters to form around.



*Cluster of ZSM-5 generated, the QM region (yellow and red atoms), and the active region (grey atoms) are highlighted.*

## Bulk and Surface Contributions to Ionisation Potentials of Metal Oxides

Xingfan Zhang\*, Alexey A. Sokol, C. Richard A. Catlow

*\*Department of Chemistry, University College London*

*e05-power-sok*

Obtaining absolute band edge positions in solid materials remains an inherently complex task from both experiment and theory, and indeed there is considerable confusion in the literature. Our work shows clearly that the ionisation potential (IP) and electron affinity (EA) of metal oxides emerge as surface-related parameters, exhibiting high sensitivity to various factors, such as material morphologies and processing histories. A particularly intriguing example that exemplifies this complexity is provided by ceria ( $\text{CeO}_2$ ), where experimental measurements have yielded several electron volts of discrepancies in its IP. Therefore, developing a comprehensive understanding of how the bulk and surface contribute to the IP of metal oxides would shed light on the experimental discrepancies and our understanding of the band alignment between different materials, thereby greatly benefitting the development of novel advanced photocatalysts and photovoltaic cells.

We have employed a combination of theoretical approaches, from classical electrostatics to quantum mechanics, to elucidate the bulk and surface contributions to the IP of metal oxides. By carrying out electrostatic analyses supported by interatomic potential techniques, we discern and quantify the various sources of intrinsic surface effects contributing to energy-level shifting in metal oxides. By employing a specially designed hybrid QM/MM embedded-cluster model that excludes all surface effects, we have determined a theoretical bulk IP for  $\text{CeO}_2$  of only 5.38 eV. Changing surface orientation results in intrinsic IP variations from 4.2 eV to 8.2 eV, as revealed by plane-wave DFT calculations with slab models. Such low bulk contributions to IPs (5.4-6.1 eV) and high degree of tunability from surfaces were also found in  $\text{ZrO}_2$  and  $\text{HfO}_2$ , in which surface polarisation plays a crucial role. Our analysis, in addition to rationalising the observed broad range of experimental results, provides a firm basis for future interpretations of experimental and computational studies of oxide band structures. Rational exploitation of these relationships could benefit the design of novel photovoltaic and electronic devices towards higher efficiencies.

## Bismuth oxychalcogenide materials for thermoelectric applications

Joseph M. Flitcroft,\* Adel Althubiani, Jonathan M. Skelton

\*Department of Chemistry, University of Manchester

e05-power-ske

In order to effectively combat climate change a wide range of approaches are required. One route is to increase the efficiency of energy-intensive process to reduce the associated CO<sub>2</sub> emissions. A 2014 study showed that in the UK alone 48 TWh yr<sup>-1</sup> of energy is wasted as heat,<sup>1</sup> meaning that recovering 1 % would equate to a reduction of >250,000 Tonnes yr<sup>-1</sup> of CO<sub>2</sub> emissions.<sup>2</sup>

Oxychalcogenides are a class of prospective high-performance thermoelectric materials that combine the favorable properties of oxides, *viz.* earth abundance and thermal stability with the desirable electrical properties and low thermal conductivity of chalcogenide materials, the latter of which have some of the largest reported *ZT* values e.g. SnSe (*ZT* = 2.9).

We have applied a fully *ab initio* modelling protocol to predict the *ZT* of the bismuth oxychalcogenides Bi<sub>2</sub>OCh<sub>2</sub> (Ch = S, Se or Te) as prospective p- and n-type thermoelectrics. Lattice-dynamics calculations were performed to model the phonon spectra and lattice thermal conductivity, and electronic structures calculated using hybrid density functional theory were to model the Seebeck coefficient, electrical conductivity and electronic thermal conductivity.

All three oxychalcogenides are predicted to show low lattice thermal conductivities of < 3 W m<sup>-1</sup> K<sup>-1</sup> at 300 K. However, in most cases the high electrical thermal conductivity hampers the overall *ZT* except for p type Bi<sub>2</sub>OS<sub>2</sub> and Bi<sub>2</sub>OSe<sub>2</sub>, for which we predict maximum *ZT* values of 2.82 and 2.99, respectively.

[1] J. Besseling; H. Pershad. *Potential for Recovering and Using Surplus Heat from Industry Final Report*, London, 2014. <https://www.gov.uk/government/publications/the-potential-for-recovering-and-using-surplus-heat-from-industry> (accessed 30/05/2023).

[2] DEFRA. *Act on CO<sub>2</sub> Calculator: Public Trial Version Data, Methodology and Assumptions Paper*, 2007. <https://www.carbonindependent.org/files/actonco2-calc-methodology.pdf> (accessed 30/05/2023).

## Relating the formation energies for oxygen vacancies defects to the structural properties of tungsten oxides

R. Kerr\*, Dr. S Murphy, Dr. M. Gilbert

\*Department of Engineering, University of Lancaster

e05-power-mur

To address the growing demand for low carbon energy, the UK government has recently committed to building the world's first nuclear fusion power plant by 2040, the Spherical Tokamak for Energy Production (STEP). One of the challenges faced by the STEP project concerns the oxidation of the reactor's tungsten-based first wall, which may occur during a loss of coolant accident or during remote handling during maintenance.

The oxidation of tungsten is a complex process, starting with the formation of a protective  $WO_{2.72}$  layer. This layer then cracks leading to rapid oxygen transport to the oxide/metal interface and the formation of columnar  $WO_{2.9}$ . The abundance of vacancies in  $WO_{2.9}$  leads to rapid growth of the oxide layer and progressive transformation to  $WO_3$ .  $WO_3$  is permeable to oxygen, and its formation rate depends on oxygen ion transport to the  $WO_3/WO_{2.72}$  interface. Therefore, in this work we use density functional theory to study the physical properties of all oxide phases involved in the oxidation process. From the DFT simulations we show how key features of the electronic structure of the  $WO_x$  materials change as the metal-oxygen ratio evolves. Then we calculate the formation energies for oxygen vacancies and activation energies for their diffusion allowing an assessment of their mobility in the different tungsten oxide phases. Our results provide a new level of understanding of the sub-stoichiometric Magnéli phases that are observed during the oxidation of tungsten.

## Controlling the heat transport in thermoelectric materials

Jonathan M. Skelton\*

\**Department of Chemistry, University of Manchester*

*e05-power-ske*

Around 60 % of the energy used globally is wasted as heat, with clear implications for climate change. Thermoelectric (TE) power can address this by recycling waste heat to electricity, harnessing the Seebeck effect in a thermoelectric material to extract energy from a temperature gradient. Thermoelectric generators (TEGs) are established in the aerospace industry and have potential applications from IoT devices, to automobile engines, to repurposing decommissioned oil rigs as geothermal power plants.

An ideal thermoelectric material requires a high Seebeck coefficient and electrical conductivity and a low thermal conductivity. However, compared to the electrical properties the heat transport through the lattice vibrations (phonons) is less well understood, and less is known about how to control it.

The lattice thermal conductivity can be modelled using techniques such as the single-mode relaxation-time approximation, and theoretical calculations have proven valuable for understanding the low thermal conductivity in flagship TEs such as PbTe and SnSe. This talk will build on these success to discuss how insight from modelling studies can be used to suggest structural modifications to control the heat transport in thermoelectric materials.

The constant relaxation-time approximation (CRTA) analysis allows differences in thermal conductivity to be attributed quantitatively to the phonon group velocities, which depend on the atomic masses and the chemical bond strength, and the phonon lifetimes, which depend on anharmonic phonon-phonon interactions. In materials with large group velocities the thermal transport can be suppressed by alloying, as in e.g.  $\text{Sn}(\text{S}_{1-x}\text{Se}_x)$ , or by chemical substitution with "discordant" dopants. In materials with long lifetimes, introducing loosely-bound "rattler" ions, such as in  $\text{CoSb}_3$ , can reduce the thermal conductivity through "resonant scattering" of the heat-carrying modes. While this has yet to be explored in depth, calculations on the hybrid perovskite  $(\text{CH}_3\text{NH}_3)\text{PbI}_3$  suggest that small-molecule rattlers may be particularly effective.

## **The Baskerville Tier-2 Service**

Jon Wakelin

*University of Birmingham*

TBA



## **The GW4 Tier-2 Service**

Steven Chapman

*University of Bristol*

TBA

## Oxygen-functionalised graphene: structure, properties and potential for phosphate sensing

Negar Mansouriboroujeni, Xue Yong, Natalia Martsinovich\*

\*Department of Chemistry, University of Sheffield

e05-enviro-nat

Graphene is an outstanding material thanks to its excellent electronic and optical properties. Graphene is also a promising sensor material, which has been used in sensors for volatile gas molecules and as an electrode in electrochemical measurements. Thus, graphene already enables high-sensitivity measurements; however, selectivity is a problem, which may be addressed by functionalizing graphene with various functional groups. In this project we collaborated with experimental partners to develop graphene-based electrodes to detect phosphate, an essential plant nutrient, in water and in soil. In particular, we used theoretical modelling to investigate how the nature of oxygen functionalization affects electronic properties of graphene and its interaction with adsorbed phosphate.

Density-functional theory calculations were used to model flat and curved graphene sheets containing epoxide and hydroxyl groups and substitutional oxygen at different concentrations (1-12% oxygen). Curvature was found to have little effect on the electronic properties of graphene: curved graphenes remained semimetallic, and their optical absorption spectra were similar to graphene. However, oxygenation had significant effect on the properties, with new states at the Fermi level for graphenes containing substitutional oxygen, and gap opening in functionalised graphenes with oxygen content above 6%. Moreover, additional peaks appeared in the simulated optical absorption spectra of oxygen-containing graphenes. These results show that oxygenation significantly changes these materials' optical and electronic properties, potentially leading to new applications in electronics and sensors. Following this, we investigated how different phosphate species ( $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{H}_3\text{PO}_4$ ) can adsorb on pure and oxygenated graphene. All the considered phosphates were physisorbed, with hydroxyl-containing graphene offering the strongest adsorption. Significant changes in electrical conductivities before and after adsorbing phosphate species on these pristine or functionalized graphene sheets were found, suggesting that oxygenated graphene is a good candidate for soil phosphorus sensor material.

## An Efficient Model for sp-Lone Pair Cations

Woongkyu Jee\*, Scott M. Woodley, Alexey A. Sokol

University College London, Department of Chemistry

*e05-algor-smw*

A large class of material both of fundamental and applied interest is made by compounds of lone pair cations, notably, Sn(II), Pb(II) and Bi(III), with localised off-centre lone-pair lobes. In materials, the lone pairs remain chemically inert but are highly polarisable, which results in the stabilisation of distorted crystal structures and a wide range of complex physicochemical phenomena.

We propose a novel type of the force field, based on embedded atomic orbitals centred on lone pair cations to provide an efficient method for the study of this class of material.

To account for the formation of the lone pair lobes on cations, we focus on the hybridisation of s and p type cation valence orbitals and represent them as localised atomic orbitals. In this presentation, we will provide the theoretical basis of the lone pair model, including the full details of energy and derivatives of lone pairs interacting with atoms described in turn with traditional interatomic potentials. We will demonstrate the success of the model on application to nanoclusters of lead monoxide and difluoride. The results show that the lone pair model is efficient and accurate in predicting and reproducing the nanocluster atomic configurations obtained using density functional theory.

## Fundamental Principles of a Virtual Tokamak Fusion Reactor

S.L. Dudarev, M. Boleininger, P.-W. Ma, D.R. Mason, L. Reali, A.R. Warwick

*UK Atomic Energy Authority, CCFE, Oxfordshire OX14 3DB, UK*

The ambitious timescale of the international fusion reactor development programme implies the increasing emphasis on virtual engineering, in turn creating a strong drive towards the exploration of digital twins and advanced computer models for materials compatible with virtual engineering, to enable the assessment of a variety of expected operating conditions. This presentation examines the fundamental principles and applications of self-consistent multiscale materials modelling for predicting the gradual evolution of deformations and stresses at the reactor component scale, resulting from the continuous exposure of a mechanically loaded reactor structure to neutron irradiation – a fundamentally atomic scale microscopic phenomenon. The topics addressed in the presentation include the eigenstrain method for evaluating macroscopic deformations from the density of microscopic defect volume tensors, which can now be derived from *ab initio* density functional theory and larger scale atomistic simulations. There are now new dynamic atomic-scale simulation algorithms for treating non-linear high dose effects, predicting the power law statistics of defect structures, also discovered in the recent dedicated experimental observations of complex evolving defect microstructures.

# Optimisation of decision sequences from selection of elements to chemical formulae of functional materials

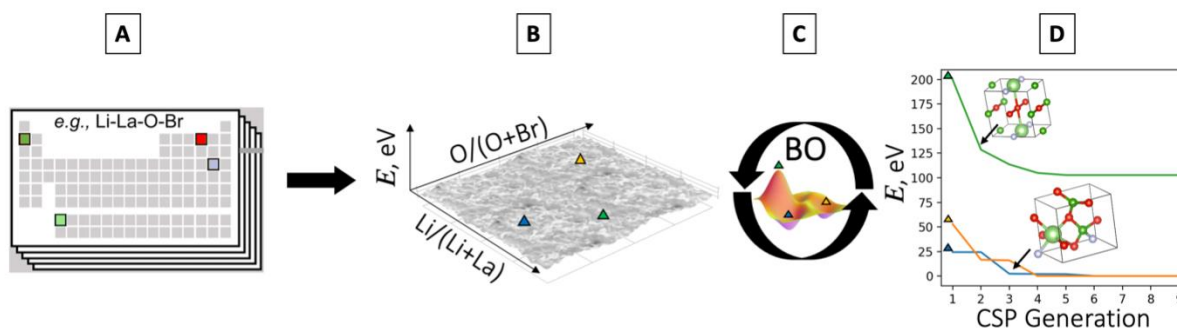
A. Vasylenko<sup>1</sup>, D. Antypov<sup>1</sup>, V. Gusev<sup>1</sup>, G. Darling<sup>1</sup>, M. S. Dyer<sup>1</sup>, M. J. Rosseinsky<sup>1</sup>

\*Department of Chemistry, University of Liverpool

e05-discov-dar

The workflow for materials discovery – from selection of chemical elements to combine (Fig 1a) to identification of functional high-performing candidates (Fig 1b) to establishing experimentally accessible formulae (Fig 1d) – presents a complex hierarchy of consequential decisions. Development of quantitative guides is thus imperative to aid decision-making, increase the success rate and accelerate the discovery workflow. Recent advances in learning the patterns of properties-materials relationships from historical data have enabled a range of powerful techniques for prediction of functional performance for materials. Applied at the level of the periodic table, these techniques have enabled ranking of elemental combinations regarding the likelihood of forming new materials<sup>1</sup>.

In this talk, I will present new capabilities for learning from materials data at two stages of the discovery workflow: phase field selection (PhaseSelect<sup>5</sup>) and stoichiometry optimisation (PhaseBO<sup>6</sup>). PhaseSelect learns from data about chemical elements themselves and discovers their contributions to functional properties of materials, e.g., such as superconductivity or magnetism; then it identifies the promising elemental combinations for new materials in terms of their functional performance. PhaseBO accelerates the exploration of all possible combinations of selected elements and increases the probability of the discovery of practically accessible new materials.



**Figure 1. Workflow of materials discovery: from selection of elements for function to identification of practically accessible new materials**

## References

1. Vasylenko, A. *et al.* Element selection for crystalline inorganic solid discovery guided by unsupervised machine learning of experimentally explored chemistry. *Nat. Commun.* **12**, 5561 (2021).
2. Vasylenko, A. *et al.* Element selection for functional materials discovery by integrated machine learning of atomic contributions to properties. *arXiv:2202.01051 [cond-mat]* (2022).
3. Vasylenko, A. *et al.*, Exploring energy-composition relationships with Bayesian optimization for accelerated discovery of inorganic materials. *arXiv:2302.00710 [cond-mat.mtrl-sci]* (2023).

# Computational Modelling of Wide Band Gap Transparent Conducting Oxide $\text{Sb}_2\text{O}_5$

Ke Li<sup>ab</sup>, Joe Willis<sup>ab</sup>, David O. Scanlon<sup>ab</sup>

<sup>a</sup>Department of Chemistry, University College London

e05-discov-dos

<sup>b</sup>Thomas Young Centre, University College London

Transparent conducting oxides (TCOs) combine optical transparency and electrical conductivity, making them indispensable in the fields of optoelectronics. However, the limited number of post-transition metal TCOs restricts the range of devices they can support. Recently, Ga-doped  $\text{ZnSb}_2\text{O}_6$ , an Sb(V)-based oxide with unique band alignment, has been computationally and experimentally examined, offering much-needed diversity to the field.<sup>1</sup> Inspired by this success, an underexplored post-transition binary Sb(V)-based system,  $\text{Sb}_2\text{O}_5$  is considered a promising candidate due to its wide band gap and comparable electronic structures to the other successful TCOs.

In this work, we use hybrid density functional theory to investigate the electronic structure of  $\text{Sb}_2\text{O}_5$ , where wide fundamental and optical band gaps are found, enabling transparency. Furthermore, we apply the Phonopy to prove the dynamic stability of  $\text{Sb}_2\text{O}_5$  by analyzing its phonon dispersion.<sup>2</sup> We simulate charge transport properties using the AMSET code.<sup>3</sup> We demonstrate the band alignment using surfaxe,<sup>4</sup> in which  $\text{Sb}_2\text{O}_5$  has the largest ionization potential and electron affinity among the existing TCOs. A large thermodynamic stability region can be seen by comparing  $\text{Sb}_2\text{O}_5$  with its competing phases. Lastly, we conduct an in-depth investigation of the intrinsic defect chemistry of  $\text{Sb}_2\text{O}_5$  where a large dopability window is present. To facilitate this study, we use ShakeNBreak to generate the defective supercells, with subsequent defect analysis carried out using the DOPED code.<sup>5</sup>

<sup>1</sup> Jackson, A. J. et al., *ACS Energy Lett.*, 2022, **7**, 3807-3816

<sup>2</sup> Togo, A. et al., *Scripta Materialia*, 2015, **108**, 1-5.

<sup>3</sup> Ganose, A. M. et al., *Nat. Comms.*, 2021, **12**, 2222.

<sup>4</sup> Brlec, K. et al., *J. Open Source Softw.*, 2021, **6**, 3171

<sup>5</sup> Mosquera-Lois, I., et al., *J. Open Source Softw.*, 2022, **7**, 4817.

# A computational study characterising the intrinsic and extrinsic doping profile of ZnS

Savyasanchi Aggarwal<sup>\*</sup>, Seán R. Kavanagh, David O. Scanlon

<sup>\*</sup>*Department of Chemistry, University College London*

*e05-discov-dos*

Zinc Sulfide (ZnS) is a widely synthesised material, largely due to its potential in luminescence devices and optoelectronics (sensors, LEDs and photovoltaics, among others) stemming from a wide and direct bandgap of 3.6 eV, alongside an inexpensive manufacturing cost and an environmentally benign nature. Despite this, there have been few studies investigating the electronic and optical properties of the material, and even fewer attempts to form a connection between the two. A noteworthy experimental paper by Hoshina et al. [1] suggested interesting excitonic behaviour dependent on n/p-type co-dopant proximity, and recent advances in computational modelling tools provide an opportunity to investigate this and other metastable states with more certainty.

The aim of this study is to construct a first-principles assessment of intrinsic and extrinsic defects in zinc-blende ZnS, using the VASP [2] density functional theory code to identify the relaxed electronic structures and corresponding optical properties. The hybrid functional HSE06 was used to accurately identify the energies of ZnS and its defect structures, along with competing phases.

This study also uses the *ShakeNBreak* [3] structure searching algorithm to scope the energy landscape and identify the global minimum structure, separating it from local minima that might lead to inaccurate excitation mechanisms. This is performed for intrinsic (antisites, vacancies and interstitials) and extrinsic (n/p- doped) point defects, as well as donor-acceptor defect complexes within ZnS, with appropriate defects generated using the *DOPED* [4] software tool. Following an analysis of the formation energies and spin-dependent charge localisation in each system, we relate each structure to a configuration coordinate diagram, identifying the excitation mechanism and optical properties associated with different dopants. This study will undoubtedly prove useful when assessing the capability of similar structures in optoelectronic applications.

## References

- [1] Hoshina, T. & Kawai, H. *Jap. Journ. Appl. Phys.*, 1980,**19**(2),267.
- [2] Hafner J., *J. Comp. Chem.* 2008, **29**(13), 2044-78.
- [3] Mosquera-Lois I, et al., *J. Open Source Softw.* 2022, **7**(80), 4817.
- [4] Kavanagh, S.R., *SMTG-UCL/doped*, *GitHub*. Available at: <https://github.com/SMTG-UCL/doped> (Accessed: April 24, 2023).

## Organosulfide-Halide Perovskites incorporating Zwitterions

Santanu Saha<sup>1,\*</sup>, Jiayi Li<sup>2</sup>, Hemamala I. Karunadasa<sup>2,3</sup>, Marina R. Filip<sup>1</sup>

<sup>1</sup>*Department of Physics, University of Oxford, Clarendon Laboratory, Oxford OX1 3PU, United Kingdom*

e05-discov-**fil**

<sup>2</sup>*Department of Chemistry, Stanford University, Stanford, CA 94305, United States*

<sup>3</sup>*Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, United States*

Halide perovskites have been the leading contender for low-cost and efficient solar cell materials, stimulating efforts to design of novel semiconductors with tunable bandgap in the visible range. Cation and/or halide mixing is a popular strategy to achieve this. However, these give rise to other undesirable effects such as halide segregation. Additionally, chalcogenide perovskites such as BaZrS<sub>3</sub> and SrZrS<sub>3</sub> also have bandgaps in the visible range with robust stability under ambient conditions. These materials, however, require high temperature for synthesis (800-1000 °C). A common characteristic of these materials is that the band edges primarily consist of B-site cations and anions contributions.

The new class of chalco(S)-halide(Cl,Br) perovskites have been synthesised at low temperature (150 °C) [1]. In these compounds, the chalcogen S was introduced via the zwitterion cysteamine (<sup>+</sup>H<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>S<sup>-</sup>), where the S occupies 1/3 of the anionic sites and the long organic chain acts as the A-site cation, stabilising these compounds. In this study, we used first principles DFT calculations to compute the electronic properties of this new materials class. We found that these new perovskites are also direct band gap semiconductors, with band gaps in the visible range, tunable by the halogen composition. In this talk, I will present our first principles study of the electronic properties of this new material family in comparison with lead halide perovskites.

We acknowledge funding support from EPSRC (EP/V010840/1), ARCHER2 Supercomputing Service and Brown Science Foundation.

[1] J. Li *et al.*, J. Am. Chem. Soc. 144 (49), 22403, 2022



## Prediction of critical micelle concentrations in surfactant mixtures by DPD simulations

Guadalupe Jiménez-Serratos<sup>1,\*</sup>, Annalaura del Regno<sup>1</sup>, Patrick B. Warren<sup>1</sup>, David J. Bray<sup>1</sup>, Scott Singleton<sup>2</sup>, and Richard L. Anderson<sup>1</sup>

<sup>1</sup>STFC Hartree Centre, Scitech Daresbury, Warrington WA4 4AD, U.K.; **Invited Talk**

<sup>2</sup>Unilever Research Colworth, Colworth House, Sharnbrook, Bedford MK44 1LQ, UK

The critical micelle concentration (CMC) has become a key design target in detergent formulation since the CMC correlates with relevant physicochemical properties. Most of applications feature surfactant mixtures, due to design or to the polydisperse nature of certain surfactants. Hence the motivation on modelling and predicting the behavior of surfactant mixtures and blends.

In this presentation, we follow the methodology presented by del Regno et al. [A. del Regno, J. Phys. Chem. B 125, 5983-5990 (2021).], where the pseudo-phase separation model (PSM) is applied to predict CMC of binary mixtures. The methodology consists on running dissipative particle dynamics (DPD) simulations of high-concentration surfactant mixtures. The molar fractions of every compound in both pseudo-phases is obtained and related to the non-ideal mixing parameters via the theory. Finally, in the limit of low concentrations, the mixture CMC is predicted as a function of the composition. The approach is applied to sodium laureth sulfate (SLES) surfactants with polydispersity in the ethoxylate spacer.

## Structural and dynamic properties of poly(styrene-co-maleic anhydride) at the interface of conjugated polymers

Christian D. Lorenz, Robert M. Ziolek & Alejandro Santana-Bonilla

*\*Department of Physics, King's College London*

*e05-biosoft-lor*

Conjugated polymers are employed in a variety of application areas due to their bright fluorescence and strong biocompatibility. For these applications, readily fabricated conjugated polymer nanoparticles (CPNs) are formed using capping agents to provide stable and soluble conjugated polymer formulations. Post-assembly functional modification and chemical doping can be used to further tune CPN properties for target applications.

The nanoscale structure of conjugated polymer materials emerges from interactions between different molecules, and holds significant control over their much-prized optical properties. Reliably controlling the optical properties of conjugated polymers upon aggregation and assembly remains a challenge. The structural properties of the interface between the capping agents and the conjugated polymer play a key role in the ability to then functionalise the surface of the conjugated polymer formulation with any specific molecules required for tuning the delivery of a CPN to a desired target. In this presentation, I will present the results of a series of all-atom molecular dynamics simulations that we have conducted in order to provide a molecular scale understanding of the structural and dynamic properties of poly(styrene-co-maleic anhydride) (PSMA), which is a common capping agents for CPNs, on the interface of the conjugated polymer, poly(9,9-di-n-octylfluorene-alt-benzothiadiazole) (F8BT). I will compare the properties of the PSMA capped interface with those which are found when using another commonly used capping agent, Brij O10. Finally I will discuss the effect of the difference in the interfaces formed on the functionalisation of these polymer interfaces.

## Iron-sulfur peptides for an efficient electron transfer to the hydrogenase enzyme

Umberto Terranova\*

\*Faculty of Medicine and Health Sciences, University of Buckingham

e05-react-ter

In the green alga *Chlamydomonas reinhardtii*, the hydrogenase HydA1 catalyses at an iron-sulfur site the conversion of protons and photosynthetic electrons to H<sub>2</sub>. The electron transfer to HydA1 is mediated by the iron-sulfur unit of ferredoxin PetF. However, PetF does not efficiently donate its electrons to HydA1, thus limiting the yield of H<sub>2</sub> [1]. In this presentation, I will investigate the replacement of PetF with two small iron-sulfur peptides (PM1 and FM1 hereafter) that hold potential for an improved electron transfer to HydA1 [2]. Using an energy-based scoring function, I will show that FM1 and PM1 bind to two different surface regions of HydA1. The distance between the two iron-sulfur clusters in FM1/HydA1 is shorter compared to PM1/HydA1, ensuring a more efficient electron transfer. This finding is in line with the reported higher H<sub>2</sub> production rates for FM1/HydA1 in vitro. I will also show that the redox potential of the peptides, and therefore their electron transfer properties, can be changed by single-residue mutations in the secondary coordination sphere of the iron-sulfur cluster. In particular, taking advantage of molecular dynamics, I have designed a PM1 variant with a bulkier side chain that is able to disrupt the hydrogen-bonding network with water. The resulting redox potential, calculated within the linear response approximation [3], is shifted by about -60 mV compared to the original peptide. These results will guide experiments aimed at replacing PetF with novel peptides that enhance the photosynthetic H<sub>2</sub> production in the alga.

[1] Rumpel *et al.*, *Energy Environ. Sci.*, 2014, 7, 3296

[2] Gunzel *et al.*, *JBIC*, 2022, 27:631-640

[3] Blumberger *et al.*, *J. Am. Chem. Soc.* 2006, 128, 13854-13867

# How bulk and surface properties of $\text{Ti}_4\text{SiC}_3$ , $\text{V}_4\text{SiC}_3$ , $\text{Nb}_4\text{SiC}_3$ and $\text{Zr}_4\text{SiC}_3$ tune reactivity: A computational study

Matthew G. Quesne\*, Nora H. de Leeuw, C. Richard A. Catlow

\* School of Chemistry, Cardiff University

e05-react-cat

The “MAX”-phase of over 100 ternary carbides/nitrides was first identified in the 1960s.<sup>1</sup> They display a very novel combination of properties including high conductivity and extreme resistance to oxidation or heating, which has led to these materials being labeled as “metallic ceramics”.<sup>2</sup> Structurally, the surfaces of these materials strongly resemble the pristine (111) facets of early transition metal carbides (TMCs), which have themselves been shown to be efficient catalysts for the hydrogenation of  $\text{CO}_2$ . Our group has previously undertaken a detailed in silico study into the catalytic activity of the equivalent TMCs to the MAX-phase material under investigation in this work and found the metal terminated (111) facets to be extremely active for  $\text{CO}_2$  reduction.<sup>3</sup> The choice of the transition metal components was partly informed by this study and partly by a systematic screening of the bulk and surface properties of a diverse array of carbides.<sup>4</sup> This talk will focus on results published as part of a recent Faraday Discussion will present the results from a computational study into the bulk and catalytic properties of  $\text{Ti}_4\text{SiC}_3$ ,  $\text{V}_4\text{SiC}_3$ ,  $\text{Nb}_4\text{SiC}_3$  &  $\text{Zr}_4\text{SiC}_3$  and compare these properties to those already obtained for  $\text{TiC}$ ,  $\text{VC}$ ,  $\text{NbC}$  &  $\text{ZrC}$ .<sup>5</sup> We will show that the addition of an interstitial silicon layer into the bulk of these material increases the lattice parameters beyond those observed for the corresponding carbides. We also show that the pristine surfaces of the MAX-phase materials are much more active towards  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$  and  $\text{OH}$ . However, our results demonstrate that pristine surfaces are not likely to be present in an oxygenating environment. Instead, the modelling predicts all surfaces will oxidise and barriers for  $\text{CO}_2$  reduction will increase in the presence of  $\text{H}_2\text{O}$ ,  $\text{O}_2$  or  $\text{OH}$ . Current work supported by the MCC is looking into the activity of these oxidized surfaces.

## References

- [1] W. Jeitschko, H. Nowotny and F. Benesovsky, *Monatshefte für Chemie*, 1963, **94**, 672–676.
- [2] Z. M. Sun, H. Hashimoto, Z. F. Zhang, S. L. Yang and S. Tada, *Mater. Trans.*, 2006, **47**, 170–174.
- [3] M. G. Quesne, A. Roldan, N. H. de Leeuw and C. R. A. Catlow, *Phys. Chem. Chem. Phys.*, 2019, **21**, 10750–10760.
- [4] M. G. Quesne, A. Roldan, N. H. De Leeuw and C. R. A. Catlow, *Phys. Chem. Chem. Phys.*, 2018, **20**, 6905–6916.
- [5] M. G. Quesne, C. R. A. Catlow and N. H. De Leeuw, *Faraday Discussions*, **230**, 87–99.