

# Computational Modeling of Catalysis: Challenges and Opportunities

## Book of Abstracts



**International Meeting:** "Computational Modeling of Catalysis: Challenges and Opportunities"

**Organization:** High Performance Computing Chair (\*\*)

**Scientific Organizing Committee**

Estelina Lora da Silva, University of Porto (\*\*)

Alfredo Palace Carvalho. University of Évora, Portugal (\*\*)

Miguel Avillez, University of Évora, Portugal, & Technische Universität Berlin, Germany (\*\*)

**Book of Abstracts:** Version 1.0, 2024.11.25

**Website** <https://indico.hpc.uevora.pt/event/97>

(\*\*) The HPC Chair is a R&D infrastructure (based at the University of Évora), endorsed by Hewlett Packard Enterprise (HPE), and involving a consortium of higher education institutions, research centres, enterprises, and public/private organisations. <https://catedrahpc.uevora.pt>





# Contents

## Opening Talk

*Geert-Jan Kroes*

Best-of-both-worlds predictive approach to dissociative chemisorption on metal surfaces . . . 3

## Day 1 - Session 1

*Francesc Viñes*

MXenes for CO<sub>2</sub> Capture, Storage, and Conversion Technologies (IT) . . . . . 7

*Vikram Mahamiya*

Ambient Condition Hydrogen Release in Layered Nanomaterials Through External Pressure Regulation (CT) . . . . . 8

*Bikram Kumar Das*

Decomposition mechanisms of di-methyl carbonate on oxygen functionalized graphite anodes: a combined first-Principles and classical reactive simulation approach (CT) . . . . . 9

## Day 1 - Session 2

*Katrine Svane*

High Entropy Oxides as Electrocatalysts for the Oxygen Evolution Reaction (IT) . . . . . 13

*Natalia Martsinovich*

Mechanism of photocatalytic conversion of methane to ethane on PdCu/TiO<sub>2</sub> photocatalyst (CT) . . . . . 14

*Lars Grabow*

Opportunities for improving the accuracy of computational models in heterogeneous catalysis (IT) . . . . . 15

**Day 2 - Session 1***Mie Andersen*

Machine learning of binding energies (IT) . . . . . 19

*Kossi Kety*Amorphous MoS<sub>2</sub> from a Machine Learning Inter-atomic potential (CT) . . . . . 20*Nestor Aguirre*

Bridging Scales: Atomistic Simulations to Reactor Design in Catalysis (CT) . . . . . 21

*Albert Rimola*

Quantum Chemical Insights into the Surface Properties of Interstellar Grains (IT) . . . . . 22

**Day 2 - Session 2***Mukesh Singh*

Improving Hydrogen evolution catalytic activity of 2D carbon allotrope Biphenylene with B, N, P doping: Density Functional Theory Investigations (CT) . . . . . 25

*Valentin Diez Cabanes*Engineering MOF/Carbon Nitride Heterojunctions for Effective Dual Photocatalytic CO<sub>2</sub> Conversion and Oxygen Evolution Reactions (CT) . . . . . 26*Paul Dauenhauer*

An Introduction to Programmable Catalysis for Chemical Energy Technology (IT) . . . . . 27

# Opening Talk





## Best-of-both-worlds predictive approach to dissociative chemisorption on metal surfaces

Geert-Jan Kroes

*Leiden University, The Netherlands*

**Email:** g.j.kroes@chem.leidenuniv.nl

Heterogeneously catalyzed processes consist of several elementary reactions. Accurately calculating their rates often requires the availability of accurate barriers for transition states with a high degree of rate control. However, currently no first principles electronic structure methods can be relied upon to deliver the required accuracy. Aiming to solve this problem, we have first developed a novel implementation of the specific reaction parameter approach to density functional theory (SRP-DFT). While the original procedure was restricted to cases where the Born-Oppenheimer static surface model could be used ( $H_2$  with surfaces), we can now also use it for heavier molecules interacting with metals. For this, at first we combined SRP-DFT with Density Functional Molecular Dynamics. More recently we have started to develop potential energy surfaces also depending on the degrees of freedom associated with the surface phonons using machine learning approaches. Additionally, the effects of electron-hole pair excitation can be modeled with the local density friction approximation and with orbital dependent friction. I will describe our recently published benchmark-database that may be used to test electronic structure methods for their performance on dissociative chemisorption barriers on metal surfaces, for a selected, but restricted class of systems. We are increasingly turning to systems for which DFT at the generalized gradient approximation (GGA) and the meta-GGA level is insufficiently accurate. The example that will be discussed is  $O_2+Al(111)$ , which is infamous for how difficult this system is to model with DFT. For systems like  $O_2+Al(111)$ , we have evidence to suggest that systems characterized by low values of  $(\Phi-EA)$  (the work function of the metal surface minus the electron affinity of the molecule) can be described more accurately with screened hybrid functionals than with GGA functionals. I will also discuss quantum Monte-Carlo results for  $H_2+Al(110)$ , obtained in a collaboration with Katharina Doblhoff-Dier. These results suggest that even GGA-DFT correctly describes the energetic corrugation of the barrier heights (how they vary with impact site and orientation of the molecule), although their absolute number may be wrong. These results also suggest a way to obtain chemically accurate results for systems with  $(WF-EA) < 7$  eV: For this one can use a predictive approach we have called quantum Monte-Carlo based DFT (QMC-DFT). I will also present dynamics results comparing to results of molecular beam experiments on sticking of  $H_2$  on  $Al(110)$  using a potential energy surface based on QMC-DFT calculations that suggest QMC-DFT to be accurate to within 1.5 kcal/mol.



# **Day 1 - Session 1**



## MXenes for CO<sub>2</sub> Capture, Storage, and Conversion Technologies (IT)

Francesc Viñes

*IQTC, Unviersity of Barcelona, Barcelona, Spain*

**Email:** francesc.vines@ub.edu

The continued increase of greenhouse gases (CO<sub>2</sub> and CH<sub>4</sub>) concentration in the Earth's atmosphere is one step away from the non-return point for climate change. Consequently, the intergovernmental panel against climate change has outlined a series of strategies to fight it and adapted to it, with the ultimate goal of avoiding the mean rise in temperature of 1.5 °C compared to pre-industrial levels. Within this context, carbon capture and storage technologies are especially relevant, even more so when capturing and converting CO<sub>2</sub> into useful chemicals for industry, turning de facto CO<sub>2</sub> waste economy into a waste-to-product model. However, given that CO<sub>2</sub> is a very stable molecule, its capture, activation, and subsequent catalytic conversion requires highly active materials, which also need to feature high surface areas for a large-scale conversion. Finally, they have to be of abundant elements in the Earth's crust to be economically viable. Here we highlight the potential of MXenes for this purpose, being novel two-dimensional materials with a few atomic layers, mostly nitrides or carbides of early transition metals. Simulations based on density functional theory, complemented with thermodynamic and kinetic analyses show that these materials are viable for the CO<sub>2</sub> capture,[1] and even its conversion to CO through the reverse water gas shift reaction.[2] The theoretical predictions of CO<sub>2</sub> capture, confirmed experimentally,[3] are an order of magnitude greater than those corresponding to other porous material. Furthermore, CO<sub>2</sub> conversion is in principle feasible, with data sustaining the swing operando conditions for CO and H<sub>2</sub>O products formation.[2,3]

### References:

1. Morales-García, Á., Fernández-Fernández, A., Viñes, F., & Illas, E., *J. Mater. Chem. A* 6, 3381 (2018)
2. IPersson, I., Halim, J., & Lind, H., et al., *Adv. Mater.*, 31, 1805472 (2019)
3. Morales-Salvador, R., Gouveia, J. D., & Morales-García, Á., et al., *ACS Catal.* 11, 11248 (2021)

## Ambient Condition Hydrogen Release in Layered Nanomaterials Through External Pressure Regulation (CT)

Vikram Mahamiya

*International Centre for Theoretical Physics (ICTP), Trieste, Italy*

**Email:** vmahamiy@ictp.it

Transition-metal (TM) atom-functionalized nanomaterials are promising candidates for hydrogen storage due to their capacity to adsorb multiple hydrogen molecules through Kubas interactions. However, achieving efficient hydrogen desorption at ambient conditions remains a critical challenge for practical use. In this work, we present a novel approach to modulate the desorption temperature of hydrogen in TM-intercalated bilayer graphene (BLG) using external mechanical forces. By employing first-principles density functional theory and thermodynamic occupancy probability calculations, we demonstrate that adjusting the interlayer distance allows for precise control over the interaction energy of H<sub>2</sub>, thereby facilitating its desorption at ambient conditions. Our findings suggest that external mechanical forces can effectively bring hydrogen occupancy to zero by minimizing charge transfer from the TM d-orbitals to H<sub>2</sub> antibonding orbitals. Notably, while the total charge transferred from the TMs remains nearly constant at varying interlayer distances, its redistribution between the graphene layers and H<sub>2</sub> fine-tunes the interaction strength. This approach can be extended to interlayer distances up to 10 Å, as supported by recent experiments on graphene oxide membranes [1]. Furthermore, recent experimental advances in noble gas and alkali metal intercalation in BLG highlight the potential of this approach to overcome the long-standing challenge of high desorption temperatures in TM-functionalized layered nanomaterials.

### References:

1. Li, W., Wu, W., & Li, Z., ACS Nano, 12, 9309 (2018)

## Decomposition mechanisms of di-methyl carbonate on oxygen functionalized graphite anodes: a combined first-Principles and classical reactive simulation approach (CT)

**Bikram Kumar Das**, Henry Andres Cortes, Mauricio Bonilla, & Elena Akhmatkaya

*Basque Center for Applied Mathematics, Bilbao, Spain*

**Email:** aguirre@scm.com

The stability and efficiency of lithium-ion batteries (LIBs) are significantly influenced by the solid electrolyte interphase (SEI) layer, which forms on the anode due to electrolyte decomposition. In typical LIB electrolytes containing a 1:1 molar ratio of ethylene carbonate (EC) and dimethyl carbonate (DMC), EC has been extensively studied as the primary SEI contributor, whereas the role of DMC in SEI formation remains underexplored. This study, using the VASP code, investigates DMC decomposition on functionalized graphite anodes (O-, OH-, CHO-, and COOH-functionalized) combining ab-initio molecular dynamics (AIMD), density functional theory (DFT), and Nudged Elastic Band (NEB) methods.

Our AIMD simulations, initiated from various probable DMC decomposition configurations, identified low-energy decomposition products that include both established SEI components:  $\text{CH}_3\text{OCOOLi}$ ,  $\text{CH}_3\text{OLi}$ ,  $\text{CH}_3^*$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{C}_2\text{H}_6$  along with several uncommon or scarcely reported products such as  $\text{CH}_3\text{OC(OH)OLi}$ ,  $\text{Li}_2\text{C(OH)O}_2$ ,  $\text{LiHCO}_3$ ,  $\text{CH}_4$ ,  $\text{HCHO}$ ,  $\text{CH}_3\text{OCH}_3$ ,  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OCHO}$ . These product structures, identified as local minima, were further optimized using DFT to determine their true ground states. By calculating the difference in ground-state energy between reactants and products in both vacuum and implicit solvent, we predicted the thermodynamic spontaneity of these reactions. The CHO-functionalized surface was identified as the least reactive one. The formation of the uncommon products always involved an intra- or inter-molecule H-hopping mechanism. The direction of the inter-molecule H-hopping was highly dependent on the surface functionalization type.

Subsequent kinetic barrier calculations identified the OH-functionalized anode as the most active surface, promoting DMC reduction through both one- and two-electron pathways. Several uncommon products, such as  $\text{CH}_3\text{OCHO}$ ,  $\text{CH}_3\text{OCH}_3$ , and  $\text{LiHCO}_3$ , were found to form spontaneously, both kinetically and thermodynamically, with detailed reaction pathways established. Finally, ReaxFF-MD simulations demonstrated the long-term stability of these DMC-decomposed products within an explicit electrolyte environment, supporting a bottom-up SEI formation mechanism<sup>3</sup> on OH- and COOH-functionalized graphite anodes where the organic products were detached from the anode surface after formation and moved deep into the electrolyte. On the contrary, the Li containing DMC decomposed products on O-functionalized graphite remained attached to the anode surface due to strong attractive interaction between the surface oxygen atoms and  $\text{Li}^+$  ions. This work provides a comprehensive insight into the DMC decomposition process and highlights the significance of surface functionalization in determining SEI composition and stability in LIBs.





## **Day 1 - Session 2**



## High Entropy Oxides as Electrocatalysts for the Oxygen Evolution Reaction (IT)

Katrine Svane

*University of Copenhagen, Denmark*

**Email:** kls@chem.ku.dk

High entropy oxides (HEOs) consist of five or more metals in a single-phase solid solution with oxygen. For applications within catalysis, the many different local atomic environments of the active sites result in a range of binding energies of the catalytic intermediates, some of which may be exactly right for the reaction of interest. Here, we investigate rutile HEOs as catalysts for the oxygen evolution reaction. Using density functional theory, we calculate the adsorption energies of the catalytic intermediates for a limited number of sites, considering two different reaction pathways, and use these energies to fit a linear model capable of predicting the adsorption energies for all possible local atomic environments.[1] Our results demonstrate that the mechanism on individual sites depends on the local atomic environment. The co-existence of two reaction pathways results in an interdependency of neighbouring sites which means that the composition cannot be optimised directly. Instead an explicit model of the surface is constructed and the catalytic activity is evaluated at regular intervals throughout composition space in order to identify the optimum composition. Comparison of the theoretically based activity model with a model based on experimental data reveals areas of good agreement but also highlights the idealized nature of the theoretical model, which does not include the effect of structural changes under experimental conditions. [2]

### References:

1. Svane, K. L., & JRossmeisl, J., *Angew. Chem. Int. Ed.*, e202201146 (2022)
2. Mints, V. A., Svane, K. L., Rossmeisl, J., & Arenz, M., *ACS Catalysis*, 14, 6936 (2024)

## Mechanism of photocatalytic conversion of methane to ethane on PdCu/TiO<sub>2</sub> photocatalyst (CT)

Natalia Martsinovich

*University of Sheffield, UK*

**Email:** n.martsinovich@sheffield.ac.uk

Methane is one of the most promising energy sources and chemical feedstocks. However, the activation energy for methane's chemical conversion is high and requires harsh reaction conditions, making the process costly and environmentally unfriendly. Photocatalysis can offer a solution, using a combination of photocatalyst and co-catalyst to lower the activation barrier for C-H bond breaking to convert methane into value-added chemicals. Our experimental collaborators produced an efficient, stable and selective photocatalyst for oxidative coupling of methane to form ethane at room temperature, by depositing PdCu alloy nanoparticles on TiO<sub>2</sub>.<sup>[1]</sup> In this presentation I will describe our theoretical investigation of the mechanism of methane conversion and the role of the PdCu alloy co-catalyst in the photocatalytic process.

Density functional theory (DFT) calculations were carried out to investigate the adsorption and the mechanism for conversion of methane to ethane on TiO<sub>2</sub>, on Pd and on a PdCu alloy with the Pd:Cu ratio of 8:1. Our calculations showed that dimerization of two adsorbed methyl groups involved much lower barriers than dimerization of methane molecules on all surfaces, therefore pre-dissociation of a C-H bond in methane is essential. The activation energy of C-H bond breaking, the key process in the conversion of methane, was significantly lower for methane adsorbed on the metal co-catalysts than on TiO<sub>2</sub>. Furthermore, DFT modelling of the electronic structure of TiO<sub>2</sub>/Pd and TiO<sub>2</sub>/PdCu interfaces revealed that the metal co-catalysts gave rise to occupied states below the Fermi level; this enables Pd and PdCu co-catalysts to act as hole acceptors and promotes separation of photogenerated charges. Thus, the PdCu co-catalyst plays a dual role of catalysing C-H bond breaking and promoting charge separation, and therefore is essential for efficient operation of the TiO<sub>2</sub> photocatalyst for methane conversion.

### References:

1. Li, X., et al., Nature Commun., 14, 6343 (2023)

## Opportunities for improving the accuracy of computational models in heterogeneous catalysis (IT)

Lars Grabow

*University of Houston, Houston, USA*

**Email:** grabow@uh.edu

Surface science has made invaluable contributions to shaping our fundamental understanding of heterogeneous catalysis. In practice, however, a catalyst may be comprised of nonuniform metal alloy particles on an amorphous oxide support and exposed to a reactive environment, and the idealization of such complex system to an ideal single crystal surface in vacuum is rather crude. To close the gap between experimental reality and its computational approximation, we pursue two main ideas. Active site models used in density functional theory (DFT) calculations must be improved to better capture electronic, geometric and coverage effects under reaction conditions. One way to benchmark such DFT models could be the temporal analysis of products (TAP) reactor, which allows measuring intrinsic kinetics at constant surface coverages and oxidation states. Next, nonuniformities and changes on the catalyst surface should be accounted for in microkinetic models to improve the robustness of performance predictions. To this end, we envision machine-learning enhanced microkinetic models, which retain the interpretability of kinetic models formulated as system of ordinary differential equations but leverage modern data science tools to encode the rich kinetic information extracted from transient kinetic experiments. The convergence of both techniques would greatly improve the quantitative description of catalytic phenomena and performance, particularly for applications in dynamic or programmable catalysis.



## **Day 2 - Session 1**





## Machine learning of binding energies (IT)

Mie Andersen

*Aarhus University, Aarhus, Denmark*

**Email:** mie@phys.au.dk

Materials with a catalytic function may be found in such diverse places as the chemical industry (heterogeneous catalysts) or molecular clouds in the interstellar space (dust grains). Despite their crucial role on Earth and in interstellar space for accelerating chemical reactions, the reliable description of catalytic properties and the prediction of what materials may be even better catalysts than those we know already is still challenging. As catalysts are typically rather complex and may consist of different types of (nanostructured) materials, experiments or astronomical observations alone are often insufficient to understand the factors controlling their reactivity or to identify the “active sites” responsible for the actual catalytic effect. Predictive-quality theory and computer simulations may provide crucial input, e.g., in the form of binding energies of key atoms or molecules at different types of active site motifs of the material. While it is possible to use quantum mechanical calculations (e.g., density functional theory, DFT) to study simple reactions and simple model catalysts, the computational demands of such an approach can quickly become prohibitively large for realistic materials, i.e. interstellar dust grains or the catalytic materials that are actually present inside chemical reactors.

In this contribution, I will highlight some of our recent efforts to develop and train machine learning (ML) models that can predict catalysis-relevant properties, e.g. binding energies, at much lower cost than DFT. Examples of materials spaces targeted in our work include nanostructured Mg-rich silicates (dust grain analogue), metal alloys, oxides and metal/oxide interfaces. I will also discuss how binding energies can be used in astrochemical models or in microkinetic models of working heterogeneous catalysts.

## Amorphous MoS<sub>2</sub> from a Machine Learning Inter-atomic potential (CT)

Kossi Kety<sup>1</sup>, Huma Nawaz<sup>2</sup>, Nicola Seriani<sup>3</sup>, Samare Rostami<sup>4</sup>, & Tsogbadrakh Namsrai<sup>5</sup>

<sup>1</sup> *International Centre for Theoretical Physics - EAIIR, Rwanda, & Université Gustave Eiffel, France*

<sup>2</sup> *Texas Center for Superconductivity and Department of Physics, University of Houston, USA*

<sup>3</sup> *International Centre for Theoretical Physics, Trieste, Italy*

<sup>4</sup> *European Theoretical Spectroscopy Facility, Université Catholique de Louvain, Belgium*

<sup>5</sup> *Department of Physics, National University of Mongolia, Mongolia*

**Email:** kossi.kety2@univ-eiffel.fr

Amorphous molybdenum disulfide has shown potential as a hydrogen evolution catalyst, but the origin of its high activity is unclear, as is its atomic structure. Here, we have developed a classical inter-atomic potential using the charge equilibration neural network method, and we have employed it to generate atomic models of amorphous MoS<sub>2</sub> by melting and quenching processes. The amorphous phase contains an abundance of molybdenum and sulfur atoms in low coordination. Besides the 6-coordinated molybdenum typical of the crystalline phases, a substantial fraction displays coordinations 4 and 5. The amorphous phase is also characterized by the appearance of direct S–S bonds. Density functional theory shows that the amorphous phase is metallic, with a considerable contribution of the 4-coordinated molybdenum to the density of states at the Fermi level. S–S bonds are related to the reduction of sulfur, with the excess electrons spread over several molybdenum atoms. Moreover, S–S bond formation is associated with a distinctive broadening of the 3s states, which could be exploited for experimental characterization of the amorphous phases. The large variety of local environments and the high density of electronic states at the Fermi level may play a positive role in increasing the electrocatalytic activity of this compound.

## **Bridging Scales: Atomistic Simulations to Reactor Design in Catalysis (CT)**

Nestor Aguirre

*Software for Chemistry & Materials B.V., Amsterdam, The Netherlands*

**Email:** [aguirre@scm.com](mailto:aguirre@scm.com)

The discovery of new catalytic materials and the optimization of catalytic processes are crucial challenges in modern chemistry. Traditionally, this has been a time-consuming and expensive process, often relying on trial-and-error experimentation. However, recent advances in multiscale modeling offer a promising new approach.

Under the framework of the EU-funded ReaxPro project (<https://www.reaxpro.eu>), we have developed a multi-scale modeling workflow that combines the versatility of the Amsterdam Modeling Suite (AMS, <https://www.scm.com/doc/AMS>) for atomic-scale simulations (including density functional theory (DFT) and machine learning potentials), automated energy landscape explorations with EON (<https://theory.cm.utexas.edu/eon/>), and Zacros (<https://zacros.org>) for dynamic modeling of heterogeneous catalysis. This seamless workflow is enhanced by an intuitive graphical interface and automatic search methodologies for transition states at different levels of theory. In particular, our recent integration of Quantum Espresso (<https://www.quantum-espresso.org>) with AMS allows us to leverage its advanced DFT capabilities, enabling highly accurate energy barrier calculations.

Our strategy enables the exploration of vast chemical spaces using accurate atomistic simulations. We aim to create a user-friendly platform that provides a comprehensive multiscale modeling framework, from atomistic level to continuum modeling of catalytic materials and reactors. We will present illustrative examples of different catalytic processes and the current status of integration with the Computational Fluid Dynamics code CatalyticFoam (<https://www.catalyticfoam.polimi.it>) to bridge the gap to reactor-scale modeling.

## Quantum Chemical Insights into the Surface Properties of Interstellar Grains (IT)

Albert Rimola

*Departament de Química, Universitat Autònoma de Barcelona, Barcelona, Spain*

**Email:** albert.rimola@uab.cat

The Universe is molecularly rich [1]. Its chemical diversity and complexity are reflected by the almost 300 molecular species detected by rotational emission in the gas phase [2] and the different solid-state phases in the form of refractory dust grains usually covered by ice mantles [3]. The presence of the gas-phase molecules cannot be explained uniquely by reactions taking place in this phase state but chemical reactions occurring on the grain surfaces are essential to rationalize the interstellar chemistry. Traditionally, Astrochemistry has been sustained by combining astronomical observations with astrochemical modelling and laboratory experiments, but this interdisciplinary approach is not enough to fully unveil the grain surface chemistry due to some intrinsic limitations [4,5,6]. Quantum chemical simulations can partly alleviate these limitations as they provide reliable, quantitative atomic-scale information (structure, energetics, and dynamics) of chemical processes taking place on the surface of grains, this way allowing us to determine the actual role of the grains on them. In this contribution, different paradigmatic roles exerted by grains in different chemical reactions of astrochemical interest will be introduced [7,8,9,10], putting special emphasis on their catalytic properties [11,12].

### References:

1. Ceccarelli, C., *Faraday Disc.*, 245, 11 (2023)
2. B. A. McGuire, B. A., *Astrophys. J. Suppl. Ser.*, 259, 30 (2022)
3. McClure, M. K., et al., *Nat. Astron.*, 7, 431 (2023)
4. Caselli, P., Ceccarelli, C., *Astronomy & Astrophysics Rev.*, 20, 1 (2012)
5. Cuppen, H. M., et al., *Space Sci. Rev.*, 212, 1 (2017)
6. Potapov, A. & McCoustra, M., *Int. Rev. Phys. Chem.*, 40, 299 (2021)
7. Ferrero, S., et al, *Astrophys. J.*, 904, 11 (2020)
8. Germain, A., et al., *ACS Earth Space Chem.*, 6, 1286 (2022)
9. Ferrero J., et al., *ACS Earth Space Chem.*, 6, 496 (2022)
10. Ferrero, S., et al., *Astrophys. J.*, 944, 142 (2023)
11. Pareras, G., et al., *Astronomy & Astrophysics*, 680, A57 (2023)
12. Pareras, G., et al., *Astronomy & Astrophysics*, 687, A230 (2024)

## **Day 2 - Session 2**



## Improving Hydrogen evolution catalytic activity of 2D carbon allotrope Biphenylene with B, N, P doping: Density Functional Theory Investigations (CT)

Mukesh Singh

*Indian Institute of Technology Bombay, Bombay, India*

**Email:** mukeshphy@iitb.ac.in

Using a first principles approach, we studied the hydrogen evolution reaction (HER) activity of newly synthesized Biphenylene (BPh) and B, N, P decorated BPh sheet. HER activity of pristine BPh sheet is not encouraging, as it is similar to pristine graphene. The Gibbs free energy and overpotential of P(N) doped on BPh sheet are 0.022 (-0.092) eV and 22 (92) mV, respectively. The reported Gibbs free energy and overpotential of Pt are 0.09 eV and 90 mV. Hence doping of P(N) atom on top of BPh sheet improves HER activity much better (near to) Pt metal. We analyzed the adsorption mechanism of dopants (B, N, P) and hydrogen with Bader charge analysis and density of states (DOS) analysis. P and N-decoration on BPh sheet change its electronic structure so that one obtains improved HER activity for P and N-doped BPh sheet. Furthermore, the stability of N, P decorated BPh at room temperature with ab-initio molecular dynamics and formation energy near that of BPh indicate experimental feasibility. We have compared all our best HER activity results in the reaction coordinate and volcano plots of pristine, B, N, and P-doped BPh sheets. They indicate that P-doped BPh is a metal-free, powerful catalyst for HER activities.

### References:

1. Singh, M., Shukla, A., & Chakraborty, B., International Journal of Hydrogen Energy, 48, 37834 (2023)

## Engineering MOF/Carbon Nitride Heterojunctions for Effective Dual Photocatalytic CO<sub>2</sub> Conversion and Oxygen Evolution Reactions (CT)

Valentin Diez Cabanes<sup>1,2</sup> Kevin Granados-Tavera<sup>3</sup>, Inderdip Shere<sup>2</sup>, Gloria Cárdenas-Jirón<sup>3</sup>, & Guillaume Maurin<sup>2</sup>

<sup>1</sup> *Institut Charles Gerhardt Montpellier, CNRS, France*

<sup>2</sup> *ICCRAM, University of Burgos, Spain*

<sup>3</sup> *Laboratory of Theoretical Chemistry, Faculty of Chemistry and Biology, University of Santiago de Chile, Chile*

**Email:** vdcabanes@ubu.es

Photocatalysis appears as one of the most promising avenues to shift towards sustainable sources of energy, owing to its ability to transform solar light into chemical energy, e.g. production of chemical fuels via oxygen evolution (OER) and CO<sub>2</sub> reduction (CO<sub>2</sub>RR) reactions. Ti metal-organic frameworks (MOFs) and graphitic carbon nitride derivatives, i.e. poly-heptazine imides (PHI) are appealing CO<sub>2</sub>RR and OER photo-catalysts respectively. Engineering of an innovative Z-scheme heterojunction by assembling Ti-MOFs and PHI offers an unparalleled opportunity to mimic an artificial photosynthesis device for dual CO<sub>2</sub>RR/OER catalysis. Along this path, understanding of the photophysical processes controlling the MOF/PHI interfacial charge recombination is vital to fine tune the electronic and chemical features of the two components and devise the optimum heterojunction. To address this challenge, we developed a modelling approach integrating force field Molecular Dynamics (MD), Time-Dependent Density Functional Theory (TD-DFT) and Non-Equilibrium Green Function DFT (NEGF-DFT) tools with the aim to systematically explore the structuring, the opto-electronic and transport properties of MOF/PHI heterojunctions conformed by two types of representative 3-D Ti-based MOFs (i.e. MIP-177 and MIL-125-NH<sub>2</sub>). We revealed that the nature of the MOF/PHI interactions, the interfacial charge transfer directionality and the absorption energy windows of the resulting heterojunctions can be finely tuned by incorporating Cu species in the MOF and/or doping PHI with mono- or divalent cations. Interestingly, we demonstrated that the interfacial charge transfer can be further boosted by engineering MOF/PHI device junctions and application of negative bias. Overall, our generalizable computational methodology unraveled that the performance of CO<sub>2</sub>RR/OER photoreactors can be optimized by chemical and electronic tuning of the components but also by device design based on reliable structure-property rules, paving the way towards practical exploitation.



## **An Introduction to Programmable Catalysis for Chemical Energy Technology (IT)**

Paul Dauenhauer

*University of Minnesota, USA*

**Email:** hauer@umn.edu

Economic viability of wind and solar power in the last decade absent concomitant energy storage has left the world with a half-solved problem of sustainable energy integration. The major chemical reactions important for converting electrical power to chemical energy remain slow or unselective using expensive catalysts, including the electrolysis of water for H<sub>2</sub>, the synthesis of ammonia, or the conversion of CO<sub>2</sub> to chemicals. To address this, a new class of programmable catalytic materials have been created that oscillate in electronic state at the natural frequencies of elementary reactions and catalytic cycles using external perturbation (i.e., a program). By manipulating the charge of the active site for chemistry, it becomes possible to dynamically change the chemical energy landscape, leading to faster and more controllable reactions. Surface electronic oscillations in devices such as a ‘catalytic condenser’ can accelerate reactions at resonance conditions leading to thousand-fold rate enhancement, even beyond the Sabatier catalytic rate limit. Experimental and computational results are presented to introduce the concepts of programmable chemistry, the design of experimental catalytic devices, and the principles associated with this emerging field of chemistry.

**Biosketch.** Paul Dauenhauer is a Distinguished McKnight University Professor at the University of Minnesota and the Zsolt Romy Innovation Chair and MacArthur Fellow in the Department of Chemical Engineering and Materials Science. He is the Director of the Center for Programmable Energy Catalysis, a U.S. Department of Energy, Energy Frontier Research Center. His work has been highlighted with the NSF CAREER award, the DOE Early Career Award, the Camille Dreyfus Teacher-Scholar award, and the AIChE CRE Young Investigator award. He has co-founded three companies, and his patents serve as the scientific foundation of five startup companies including Sironix Renewables, Lakril Technologies, Carba, Activated Research Company, and enVerde, LLC.