

## **Workshop scientific report**

**Title:** Interface processes in photochemical water splitting: Theory meets experiment

**Location:** CECAM-HQ-EPFL, Lausanne, Switzerland

**Webpage:** <http://www.cecama.org/workshop-0-1303.html>

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### **Introduction**

The direct conversion of solar energy into chemical energy is among the most important scientific and technological grand challenges. Despite the recent success achieved in thin film photovoltaics, solar fuel production via photocatalytic water splitting remains a difficult task, with the record efficiency of ~12%, obtained by integrating two perovskite solar cells in series with an electrolyzed.

Efficient photocatalytic water splitting requires the simultaneous optimization of i) the band-gap of the light absorber so as to maximize visible light harvesting, ii) the efficiency/cost ratio of specific electrocatalysts, and iii) the interface processes both between photoelectrodes and catalysts and between photoelectrocatalyst and environment. While in the past years, materials' band-gap and catalysis have been the subject of extensive numbers of studies (and of several past CECAM workshops), interfaces in photoelectrochemical processes received much less attention.

This CECAM workshop on interface processes in water oxidation (WOX) aims at filling this gap. This field is growing and evolving very rapidly, and it is the subject of an ever-increasing number of studies. The challenge stems from the complexity of the interfaces (structure, composition, defects), of their electronic processes (charge transfer (CT), electron-level alignment, dynamics of excited states), of their chemical processes/conditions (stability of intermediates, effect of pH), and, most notably, from the coupling between all these factors with both the photon absorption and the reaction mechanism.

### **Major outcomes**

The workshop was a meeting opportunity for chemical and physical communities that address similar challenges from different perspectives, ranging from experimental synthesis/characterization, to theory and simulation. These communities agreed that an important breakthrough in photochemical efficiencies requires strategies to optimally connect research on fundamental processes (light absorption, charge separation, electron transport, ...) to research on new working materials, up to the engineering device. A key issue is

identifying well-characterized MODEL SYSTEMS, where theory and experiment can be efficiently combined.

This tight theory/experiment interaction fostered during the last 5-10 years an exponential increase in the performance of transition metal based catalysts for water oxidation, triggered by new complexes that abandoned the traditional mu-oxo architecture. Single-site catalysts are at the moment the most efficient. The spectacular progress in efficiency was not accompanied by substantial progress in stability, which is currently the major limitation for these systems. Theoretical simulations had a significant impact in elucidating the mechanism at play also in the natural catalyst for water oxidation. A new approach based on spectroscopic fingerprinting of catalyst "states" during the catalytic cycle was presented. We remark again that these achievements stem from tight interaction between theory and experiments on well characterized systems.

Concerning solid-state heterogeneous catalytic interfaces, the request for well defined model systems where theory and experiment can be efficiently combined is more critical. The emerging strategies for designing the next generation of devices may involve exploiting both the nanoscale and mesoscale. For example growing functional oxide overlayers on hematite ( $\text{Fe}_2\text{O}_3$ ) has a significant effect on the onset potential ( $\sim 200$  meV cathodic shift). These overlayers do not necessarily act as catalyst: Possible roles include facilitating electron hole separation, saturation of surface states that might act as recombination centers, electrostatic effects leading to higher concentration of holes in regions not coated with the overlayers. Another strategy involves electron-energy engineering at interfaces, for example by exploiting local electric fields, external bias or tandem systems, In the latter, photocatalysts for the anodic reaction like hematite are coupled with photoabsorbers like perovskites (whose function is to increase the chemical potential of the electrons), mitigating the known problem of a conduction band with insufficient redox potential to reduce protons to molecular hydrogen. From the mechanistic point of view, recent experiments show that under illumination the surface concentration of holes is very high, and a third-order reaction rate w.r.t. hole concentration was reported. This suggests a rate-limiting step that requires the accumulation of multiple holes at the reaction site.

The ability of ab-initio theory approaches to accurately predict electron-level alignment at photocatalytic interfaces is still debated. Significant progress involved simulations combining first-principles molecular dynamics of electrode/electrolyte interfaces and new approaches to compute redox potentials of reference electrodes. The higher performances of hybrid functionals were highlighted by several speakers. Departing from electron energy levels towards charge-transfer rates and to currents at interfaces is a key future challenge. Main limitations include the lack of model systems where to benchmark and validate theory approximations, and new theories for excited state dynamics.

### **Community needs**

Close interaction between theory and experiments was advocated by all participants. Several speakers presented clear evidence that collaborative

projects can lead to substantial new insights. One outcome of our discussions is that to improve the effectiveness of this collaborative approach we need benchmarking on model systems.

Theory cannot yet tackle the full complexity of realistic photoelectrochemical systems. To test the validity of current and emerging theoretical approaches and to improve the predictive power of theory, simulations need to be benchmarked against well characterized systems. While there is clearly a strong incentive for experimentalists towards designing and characterizing new systems with improved performance, this field suffers from lack of fundamental studies devoted to improve our understanding of the basic principles governing the functioning of photoelectrochemical devices. Here theory can have a remarkable role, but validation against experiments on model systems is critical. Many participants advocated for more funding and more collaborative (theory/experiments) projects aimed at filling this gap.

In this workshop we decided to mix theoretical and experimental talks. All participants gave us positive feedback on this. They stressed the need to make sure the whole community understands what theory can/cannot simulate, and what is the predictive power of current approaches. At the same time, grasping the complexity of realistic systems, the different interpretations of well established experiments, can stimulate a productive interaction between theory and experiments.

Two issues where significant progress is needed is obtaining a realistic model of the atomic structure electric double layer and of the effect of pH. Large scale simulations are needed in this case, calling for improved algorithms to tackle both size and time scale limitations of current approaches. Access to large scale HPC infrastructure is critical in this field.

### **Funding**

The field of photocatalysis is the object of consistent national funding in US and in many EU countries. There are already networking actions that address either the chemical community active on molecular photo catalysts or the physical/chemical community focusing on surfaces and heterogeneous (photo)catalysis. The positive feedback received during this workshop suggest that there could be space for proposing a COST action on photocatalytic interfaces, that could bring together the EU communities of chemists, physicists and materials scientists working on molecular and solid-state systems.

### **Program, list of participants and abstracts**

These information can be found at the Workshop website:

<https://www.cecam.org/workshop-0-1303.html>