

Workshop Scientific Report (ESF)

Workshop: Photo- meets Electrocatalysis: United We Split (...Water)

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1.) Summary

The workshop “Photo- meets Electrocatalysis: United We Split (...Water)” was held at the Hanse-Wissenschaftskolleg (HWK) in Delmenhorst, Germany from October 4th to October 7th 2011. In total, 60 participants from Germany, USA, UK, Denmark, Japan, Poland, Sweden, Italy, France, Belgium, China and Switzerland attended the workshop.

The programme consisted of 20 invited lectures, one poster session and an excursion to allow for informal exchange. The lectures were scheduled to last 45 min, including 15 min discussion time. In addition to this extended time for discussion, the chairpersons were instructed to introduce the subject of the session and to actively participate in the discussion. This “Gordon-conference-style” was essential to guarantee a vivid discussion. The organizers ensured that well-established scientists acted as chairpersons, who in part were attending the conference only for this duty.

Concerning the poster session, we accepted only 12 posters to allow for an intense exchange of ideas at each single poster. Here, we encouraged in particular the young scientists to ask questions. The participation of PhD students was supported since the conference fee was waived in this case. Thus, no local costs emerged for young scientists.

Due to the slightly remote location of the HWK in the small city of Delmenhorst, all participants had to stay together for the whole time of the conference, which additionally enforced the scientific discussion which was mandatory since scientists from two generally separated fields, i.e. photocatalysis and electrocatalysis were attending the meeting to merge ideas and formulate a common goal, i.w. water splitting.

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II.) Scientific content and discussion

If a photochemical splitting of water by sunlight can be realized at the large-scale technical level, it will provide the basis for the hydrogen economy of the future. As in many other areas predictive-quality computational materials modelling could become a key contributor in this quest. However, at present such quantitative modelling from first principles is still faced with severe methodological challenges. In this situation substantial impulse could come from exploiting the similarities of electrochemical and photochemical processes at solid-liquid and solid-gaseous interfaces, respectively. Method development in these two areas occurs currently rather separately, pushed by two communities with little overlap. The motivation and aim of the workshop was to bring these two communities together - to explore the similarities in general and discuss possibilities of uniting the state-of-the-art approaches to the envisioned quantitative modelling of photoelectrochemical splitting of water in particular.

Furthermore, a system that can convert solar light into hydrogen is generally quite complicated. It needs to harvest the light, separate and transport the holes and electrons to the interface with water, and catalyze the water splitting reaction. All these components request different methods for atomistic modelling, and this is done traditionally in quite separate research communities. However, to understand and assist the development of photochemical water splitting, these divided research communities have to come together, as the issues regarding the different components in reality are closely linked. The main goal of the interdisciplinary workshop was to encourage interaction and information exchange between different fields. Therefore, from the broad range of experienced researchers working in these areas, we have invited exceptional individuals who have already successfully made this step across traditional boundaries, in order to allow them to share their experience during the seminar with the younger participants.

Since the subject of the workshop is so interdisciplinary, also the background and scientific communities of the lecturers and participants were quite diverse. It was therefore the aim of the workshop to familiarize the participants with different subjects, to encourage interdisciplinary interactions, and to share experience of different research fields with one another. In this way, we managed to foster the exchange of ideas and methods, to highlight the apparent and the hidden similarities of different systems and approaches, and hopefully stimulated new and fruitful collaborations across subject boundaries

The workshop combined atomistic modelling of the different components needed for photochemical water splitting, i.e.

- Solid/liquid interfaces
- Charge transfer
- Electrocatalysis
- Light harvesting

All major areas of experiment and theory with a focus on photochemical water splitting have been represented by invited talks.

The first session contained experimental teasers, presenting the main challenges of electrochemical and photoelectrochemical water splitting. Experimental aspects of catalysed hydrogen evolution were discussed. For instance, bioinspired molecular

clusters based on molybdenum and sulphur evolve hydrogen at similar rates as compared to the expensive noble metal platinum. In particular, cubane-like Mo_3S_4 clusters were demonstrated to be efficient co-catalysts when coupled to a p-type Si semiconductor for light harvesting in the red part of the solar spectrum. Further experimental insights were presented for the complex Oxygen Evolution Reaction (OER). Still a major challenge consists of a detailed understanding of the catalytic OER mechanism and the development of stable and inexpensive catalysts. This aspect will be crucial to achieve closed energy and material cycles in a sustainable environment. Interesting similarities and differences were pointed out when the artificial water oxidation was compared with its natural counterpart. Rate determining steps were discussed in functionality of the biological photosystem II enzyme and the impact of the results on future development for artificial water oxidation was discussed.

The main theme of the speakers discussing the solid/liquid interface was the modelling approaches. One new aspect was the explicit treatment of a counter electrode by periodic DFT calculations. It was also demonstrated that the water structure at the metal/water interface has a significant influence on relevant properties such as the water-induced work function change. From a materials point of view, new insight was reported on hydroxyl formation on rutile $\text{TiO}_2(110)$. The abstraction of hydrogen from an adsorbed water molecule adsorbed on Ti(4c) centre of a titania surface is often regarded as the first and possibly rate determining step in the (photo) electrolysis of water. By comparing the results of PBE and hybrid functionals such as HSE it was demonstrated that the relaxation energy due to localization of the valence band hole created by ionization is crucial in the OH bond dissociation free energy which compensates for the deprotonation energy. The solvent itself seems to play a minor role here in this respect. Other materials such as RuO_2 and anatase TiO_2 were considered as well.

The session on charge transfer covered a broad methodological range. In an experimental talk, the advantages of scanning electrochemical microscopy (SECM) were introduced while three theory talks addressed fundamental aspects of charge transfer. An atomistic modelling could be achieved by the solution of the time-dependent Schrödinger equation (TDSE) either for the electrons or the nuclei. In particular the limitations of time-dependent density functional (TDDFT) calculations were discussed in the electron dynamics simulations with a critical examination of coherent control of charge-transfer on an atomistic level. Furthermore, the applicability of parameterized Anderson-Newns-type models in combination of quantum dynamical calculations based on multi-configurational approaches was discussed in order to describe the photoinduced electron transfer process from dye molecules to semiconductor substrates. It turns out that an accurate description of the mutual influence of electron and nuclear dynamics is of crucial importance in order to obtain accurate results.

In the electrocatalysis session both molecular and solid catalysis were discussed. Molecular catalysts such as mononuclear nickel complexes with cyclic diphosphine ligands exhibit the potential to mimic enzyme functionalities. In particular the role of proton relays in H_2 oxidation was elucidated and extended to O_2 and N_2 reduction as well as water oxidation. Additionally, activity trends of catalysts of the Oxygen Evolution Reaction (OER) were predicted on the basis of simple electronic-structure descriptors based on DFT-calculations.

In the light harvesting session started with an experimental talk by Prof. Michael Grätzel to set the scene as a well-recognized experimentalist. In the subsequent presentation photo-induced surface processes were discussed. In particular photochemical reactions on wide gap oxides were investigated on the basis of periodic and embedded cluster calculation within the framework of DFT. A particularly simple reaction, laser induced desorption, was studied extensively. Later in the session, the importance of understanding the trapped states of holes and electrons and the potentially powerful possibility of computational large-through-put-screening was elucidated.

III.) Assessment of the results and impact on future direction of the field

It became apparent from the presentations and the corresponding discussions that the modelling in each component in photo-chemical water splitting is indeed very challenging. In some areas of the research field the methods and approaches have still not matured, so that intrinsic technical and conceptual problems persist. When combining various approaches it should be realized that the properties of the excited electrons may have a significant influence on electrocatalysis.

Furthermore, a faithful description of the solid liquid interface is crucial for further progress in the field. While clearly being defined as a key problem and thus being a merging field, the methodology still hasn't converged in terms of the approaches and approximations. For instance, it still is under debate at what level of theory the liquid should be modelled for understanding the aspects on the charged solid/liquid interface on conductors and semi-conductors.

In the field of charge transfer in complex systems it became apparent, that in certain cases TDDFT has to be treated with caution. Although TDDFT is a promising technique potentially applicable to complex surface photochemistry, the validity of current exchange correlation functionals is a serious issue. Here, the field should benefit from molecular quantum chemistry, where electronically excited states and photochemistry at interfaces is accessible via Complete Active Space Self Consistent Field (CASSCF), perturbation theory (CASPT-2) or Configuration Interaction (CI), respectively, at the price of extreme costly calculations and rather simple systems. Another important issue of charge transfer is the accurate description of the mutual influence of electron and nuclear dynamics for a faithful theoretical approach towards an understanding on the atomistic level. Due to the non-separability of time-scales of electronic and nuclear motion due to strong non-adiabatic effects, special effort has to be invested in the development of new ideas and methods. Again, quantum chemical approaches might be helpful in this respect.

In the field of (photo-)electrocatalysis, it became clear that even though there are fundamental differences, there are also similarities in the challenges encountered. For the time being, the two communities are quite complimentary in the sense that the main issue for molecular catalysts is the size of the rate determining step, whereas potential seems to be a larger concern for the solid electrode catalysts. In order to combine the approaches by anchoring molecular catalysts to an electrode, both issues will become important. This is a good example on the mutual benefit of interdisciplinary work.

In summary, plenty of challenges have been identified and will be addressed in the future. It is also clear that only "united" we will ever succeed in splitting water.

As it became apparent, the topic of the workshop was well suited for a workshop within the given framework, a lot of development work concerning the corresponding simulations is underway and even more is needed. A related workshop on CO₂ reduction is scheduled for next year.

October 19th 2011

The Organizers