Artificial Photosynthesis at Soft Interfaces

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Abstract: The concept of artificial photosynthesis at a polarised liquid membrane is presented. It includes two photosystems, one at each interface for the hydrogen and oxygen evolution respectively. Both reactions involve proton coupled electron transfer reactions, and some ultrafast steps at the photosensitization stage.

Keywords: Artificial photosynthesis · Liquid-liquid interfaces · Proton coupled electron transfer reactions

Artificial Photosynthesis

Energy conversion and energy storage are some of the key challenges to the scientific community this century. The development of photovoltaic and other means of solar energy conversion will require ways to store this intermittent source of energy supply. There are basically two ways to store energy: Physically or chemically. Physical energy storage can be done very efficiently by retro-pumping of water to dams, or by using flywheels. From a chemical standpoint, a very efficient way to store energy is to form a chemical bond. For example, a hydrogen–hydrogen bond stores 436 kJ·mol^{-1}.

To store solar energy as chemical fuels, different strategies can be envisaged. The one being developed practically today is to couple a classical photovoltaic solar panel to an electrolyser to split water and produce hydrogen. Indeed, PEM (Polymer Electrolyte Membranes) electrolysers can operate in intermittent conditions, and many companies already offer photovoltaic-electrolysis systems to produce hydrogen that can be compressed, stored in carbon fibre re-enforced cylinders and used
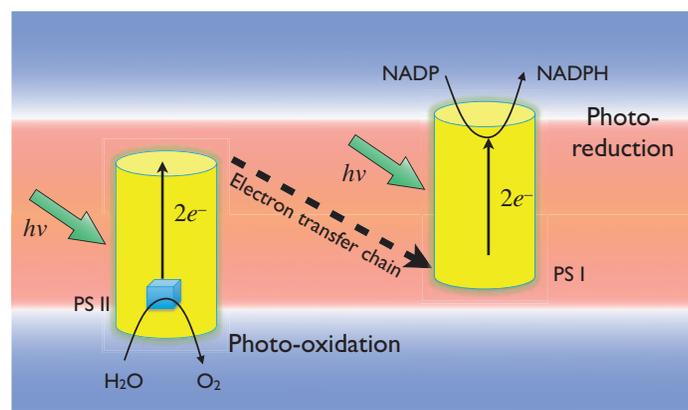

Fig. 1. Z-Scheme in natural photosynthesis with water oxidation at photosystem II (PSII) and reduction of NADP at photosystem I (PSI).

in fuel cell systems either to power cars, boats, *etc.* or to produce electricity at night.

The second strategy is to develop photo-electrochemical solar panels able to directly produce hydrogen. This route is based on the seminal work of Fujishima and Honda[1] who had shown that semiconductor electrodes made of TiO_2 could, in principle, split water. This photo-electrochemical approach is nowadays followed by the group of Prof. M Grätzel at the PECHouse, EPFL where the solar panel includes a hematite photo-anode, a dark cathode to produce hydrogen coupled to a dye-sensitised solar cell to provide a sufficient photo-voltage to split water.

A third strategy is to photolyse water directly. For many years, semi-conducting nanoparticles capped with a catalyst for Hydrogen Evolution Reaction (HER) such as platinum and with a catalyst for Oxygen Evolution Reaction (OER) such as RuO_2 have been investigated to split water.[2] Since then, many research programs are dedicated to producing 'artificial leaves' using semiconductors to perform the charge separation step.[3]

Natural photosynthesis in plants does not rely on semiconductors to absorb light and create charge-separated systems. Indeed, plants rely on molecular antennas such as chlorophyll and molecular elec-

tron relays to separate the photoproducts as shown in Fig. 1.

The fourth strategy for water-splitting currently being developed at the Laboratoire d'Electrochimie Physique et Analytique (LEPA) at EPFL is a reverse-engineering approach of natural photosynthesis using two soft interfaces to carry out an artificial Z-scheme as shown in Fig. 2. This strategy is based on photo-electrochemistry at polarised liquid–liquid interfaces.

Polarised Liquid-Liquid Interfaces

The interface between Two Immiscible Electrolyte Solutions (ITIES) can indeed be polarised. The most usual ITIES include an aqueous electrolyte and an organic electrolyte dissolved in an immiscible organic solvent such as chloroform, 1,2-dichloroethane, nitrobenzene, toluene, *etc.* or even in a hydrophobic ionic liquid. The Galvani potential difference between the two phases can be as large as –0.5 to 0.5 V and be used to drive charge transfer reactions such as:[4]

– ion transfer reactions;
– assisted ion transfer reactions where an ionophore in one phase is used to lower the solvation energy of a specific ion in that phase. Assisted ion transfer reac-

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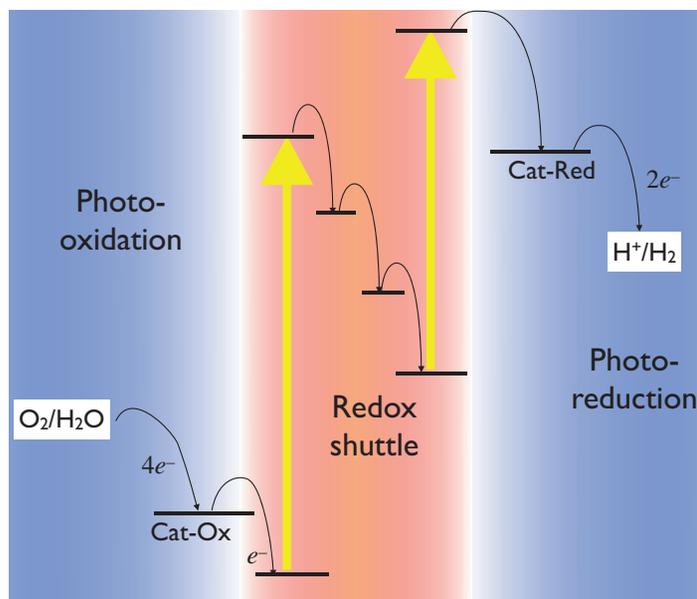CH-1015 Lausanne
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Fig. 2. Z-Scheme for artificial photosynthesis using amphiphilic catalysts at soft interfaces.

tions also include acid-base reactions, where for example a lipophilic base is used to extract protons to an organic solution;

– heterogeneous electron transfer reactions between two redox couples, each soluble in one phase only.

All these charge transfer reactions are potential dependent like a redox reaction on a solid electrode, and their kinetic is also potential dependent: the larger the overvoltage the faster the reaction.

Photo-induced charge transfer reactions include bulk photochemical reactions followed by the transfer of one of the photoproducts or by a heterogeneous redox reaction with this photoproduct. Another class of photo-induced charge transfer reactions more relevant to artificial photosynthesis includes heterogeneous photo-electron transfer reactions between a sensitizer located in one phase and a redox quencher located in the adjacent phase as illustrated in Fig. 3.

LEPA at EPFL has dedicated a lot of effort over the last two decades to develop electrochemical methodologies based on voltammetry to be able to study both the thermodynamic and the kinetic aspects of charge transfer reactions at ITIES. Considering that many types of charge transfer reactions can occur concomitantly at such soft polarised interfaces for a given interfacial polarisation, *e.g.* an ion transfer reaction and a heterogeneous electron transfer reactions taking place in parallel, we have developed over the years a range of spectro-electrochemical methods such as:

– potential modulated techniques (potential modulated reflectance,[5] potential modulated fluorescence,[6] *etc.*) to monitor by spectroscopy potential dependent charge transfer processes;

– non-linear spectroscopy techniques such as Surface Second Harmonic Generation (SSHG) to measure *in situ* the resonant UV-Vis spectra of interfa-

cial molecules as a function of the applied potential;[7]

– quasi-elastic light scattering to measure *in situ* the interfacial tension, thereby measuring the electrocapillary curves and determining the surface excess concentrations of adsorbed species, including nanoparticles.[8]

In addition to spectroscopy techniques, we have developed methods based on Scanning Electrochemical Microscopy (SECM). In this technique, a metallic microelectrode is positioned very close to the interface *e.g.* a few microns and the current associated with a given redox species in one liquid phase will be enhanced (positive feedback) or decreased (negative feedback) depending on the presence of other redox species in the adjacent liquid phase. Here, we do not use this technique to record SECM images of the interfacial reactivity as the interface is often not structured in the absence of adsorbed films but we use this methodology to measure the kinetics of the heterogeneous recycling reactions by recording approach curves.[9]

Finally, we have developed methods to study adsorbed nanoparticles at ITIES. Indeed, solid nanoparticles such as quantum dots or metallic nanoparticles such as platinum or gold nanoparticles adsorb at liquid–liquid interfaces due to a compromise between line tensions and interfacial tensions. As it happens, this adsorption process is potential dependent and we have shown for example that we can form reversibly (on-off) 'gold mirrors' of variable curvatures at liquid–liquid interfaces.[10] This opens new routes for electrovariable liquid optical devices such as the liquid–liquid zoom lens found in certain mobile phones.

All these developments have been used to address some problems specific to biphasic systems such as the determination of extraction constants of metallic species by solvent extraction, the characterization of ion selective electrodes, the elucidation of the pharmacokinetic aspects of ionic drug partition (electrochemical log$P$ measurements), *etc.* Now the time is ripe to use all this knowledge and to apply it to address chemical reactivity. In this respect, Proton Coupled Electron Transfer (PCET) reactions represent an interesting case, as it is possible to react a molecule located at the interface both with aqueous protons and with lipophilic electron donors.[11]

Hydrogen Evolution at Liquid–Liquid Interfaces

An example related to artificial photosynthesis is the reaction of metallocenes at ITIES. When a metallocene such as decamethylferrocene (DMFc) in 1,2-dichloro-
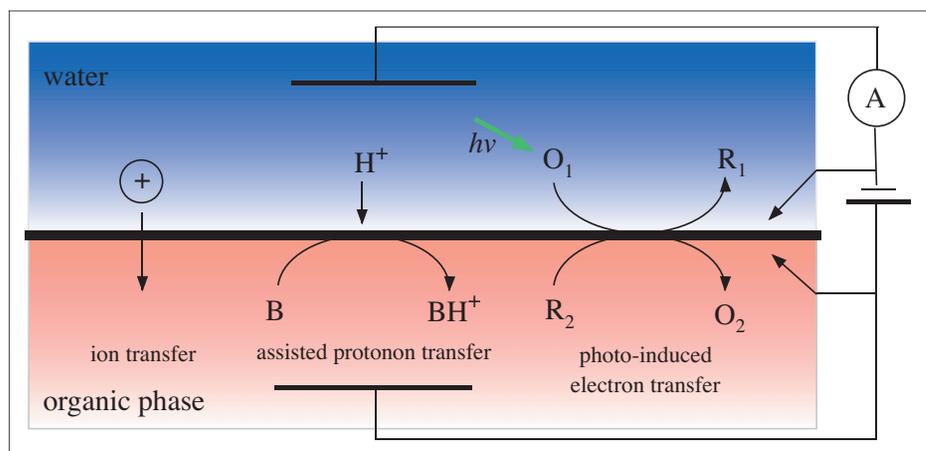

Fig. 3. Charge transfer at an electrochemical liquid-liquid interface: a) ion transfer, b) assisted proton transfer and c) heterogeneous electron transfer between an aqueous acceptor O_1 and a lipophilic donor R_2.

Fig. 4. H$_2$ bubble forming on a 1,2-DCE droplet containing DMFc in an aqueous HCl (pH = 1) solution.

ethane is placed in contact with an aqueous acidic solution, we can, by polarising the interface (water positive with respect the organic solvent), drive both the oxidation of DMFc to DMFc$^+$ in the organic phase and the reduction of aqueous protons. Mechanistic studies have shown that the first step of this process is the interfacial protonation of DMFc to form the hydride DMFc-H$^+$. In anaerobic conditions, hydrogen is produced[12] as shown in Fig. 4 whereas in aerobic conditions both hydrogen and hydrogen peroxide are formed by oxygen reduction.[13,14]

One of the objectives of LEPA in the NCCR MUST project is to investigate the role of the interface and its polarisation in the stabilisation of charge separated states in sensitizer-molecular dyads such as the one illustrated in Fig. 5.

Usually in bulk solutions, these sensitizer-catalyst dyads are inefficient at producing hydrogen. Ultrafast measurements such as transient absorption spectroscopy have shown that the lifetime of the charge-separated state (CS) is too short for the catalytic HER to take place, the charge-recombination reaction (CR) being too fast in comparison.[15] In order to follow these processes at the interface, we require a time-resolved surface-sensitive technique. As described in this issue by the group of Prof. E. Vauthey in Geneva, Time Resolved-Surface Second harmonic Generation (TR-SSHG)[16] should be suitable for carrying out these measurements at free-standing polarised water|1,2-dichloroethane interfaces. The goal of this study is to measure the potential dependence of the charge separated state, in the other words to investigate how the local electric field created upon polarisation of the interface influences the charge separation. The second objective is to measure the influence of the sacrificial electron donor (D in Fig. 5) to reduce the sensitizer and again to monitor the potential dependence of this interfacial electron transfer reaction. Final-
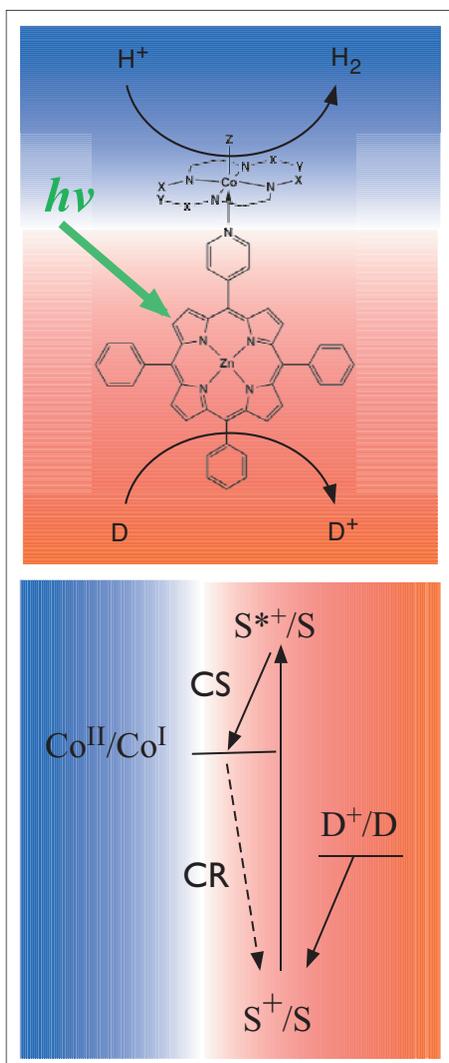

Fig. 5. Sensitizer-catalyst dyad comprising a Zn-porphyrin antenna and cobaloxime catalyst for hydrogen evolution with the corresponding Jablonski diagram.

ly, the molecular catalyst for HER being on the aqueous side of the interface, it can be operated at relatively low pH values being more favourable for HER. This work will be carried in collaboration with the group of Prof. J. Moser, Group of Photochemical Dynamics, EPFL.

In a next step, we plan to study adsorbed nanoparticle catalysts at liquid–liquid interfaces. We have already shown that adsorbed platinum and palladium nanoparticles formed *in situ* by the interfacial reduction of metallic precursor salts added to the aqueous phase by the organic electron donor DMFc can catalyse the HER illustrated in Fig. 4. The next step is to study semi-conducting nanoparticles.

Oxygen Evolution at Liquid–Liquid Interfaces

Oxygen evolution at liquid–liquid interfaces is a more difficult topic. Here, we plan to study OER using TiO$_2$ as a model system. Again, the goal of this MUST project is to measure the interfacial photodynamics in a time-resolved mode. We have already shown[17] using Intensity Modulated Photocurrent Spectroscopy (IMPS) that adsorbed TiO$_2$ nanoparticles at the water|1,2-dichloroethnae can photoreduce tetracyanoquinodimethane (TCNQ) as illustrated in the Fig. 6. The goal of the proposed study is to measure the influence of the local electric field on the timescale of the different steps.

CO$_2$ Reduction at the Water–Supercritical CO$_2$ Interface

We have recently demonstrated that most of the methodologies developed to study polarised interfaces between two immiscible electrolyte solutions can be transposed to study the water–supercritical CO$_2$ interface. sc-CO$_2$ can indeed be considered as a solvent of low polarity such as an alkane. For example, we have demonstrated that some strategies for photochemical CO$_2$ reduction such that based on the coupling the sensitizer ruthenium trisbipyridine (Ru(bpy)$_3$$^{2+}$) to the catalyst nickel cyclam (1,4,8,11-tetraazacyclotetradecane) operates much more selectively in supercritical
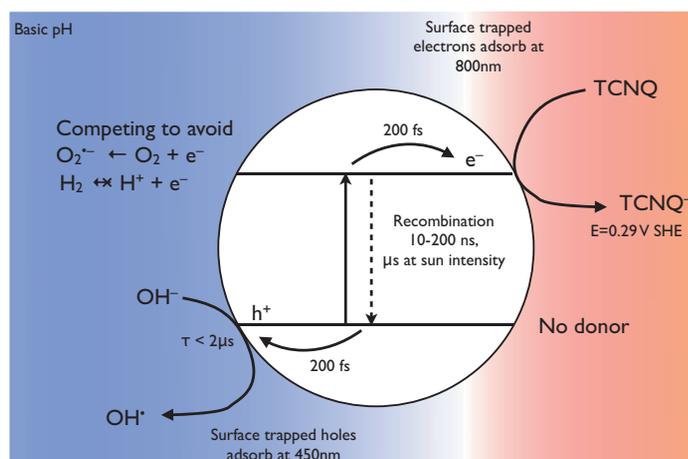

Fig. 6. OER using TiO$_2$ at an ITIES in the presence of a sacrificial acceptor.

conditions than just in bulk water saturated with CO_2.[18]

One goal of the present project is to carry out time-resolved spectroscopy under high-pressure conditions to elucidate these catalytic reaction mechanisms.

Conclusion and Outlook

Solar fuel production by direct artificial photosynthesis will only be competitive if the processes developed are cheap and can provide a relatively rapid return on investments. The photonic yield, *i.e.* the 'amount of fuel produced per photon', is by definition low and cannot exceed at best 10%.[19] Biphasic systems can meet these targets if we can identify cheap and robust HER and OER catalysts. Basic research is required to address the underlying fundamental scientific questions.

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