

Hydrogen Goes Green - Model Experiments for Artificial Photosynthesis

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Abstract Photocatalytic hydrogen production without the bypass via photovoltaics and electrolysis has been realized using a versatile photocatalytic system with only three components: the redox mediator ethyl viologen, the photocatalyst proflavin and the sacrificial donor EDTA. By adding a reduction catalyst made of nano-platinum on alumina to the aqueous solution of these three chemicals, hydrogen can be produced by irradiation with sunlight.

Keywords: photocatalyst, redox mediator, sacrificial donor, reduction catalyst, energy conversion, energy carrier, artificial photosynthesis, sustainable development goals SDGs

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1. Introduction

Hydrogen from Sunshine: The opening, newly developed experiment reported on in this article concerns with the photocatalytic production of hydrogen powered either by sunlight or by blue light from LEDs.

Not only the simplicity of the experimental setups shown in [Figure 1](#), but also the following additional features make the experiment recommendable for teaching purposes:

- A yellow, magnetically stirred suspension turns blue within 1-2 minutes when exposed to sunshine or irradiated with blue light emitting LEDs. Then the evolution of hydrogen begins. During irradiation, the solution remains blue.
- 5 - 8 mL of hydrogen are obtained within 30 - 50 min starting from 50 mL of reaction mixture. This consists of only 50 mg of a solid catalyst containing nano-platinum suspended in a very diluted aqueous solution of a homogenous photocatalytic system (see chemicals in [Figure 3](#)).
- The hydrogen produced can be unequivocally proven proofed and applied, e.g. by the hydrogen-oxygen explosion test, by gas chromatographic analysis, by the glow up on a platinum-containing catalyst, or by powering a fuel cell car (see [Figure 2](#)).
- All chemicals needed for the experiment, i.e. the components of the photocatalytic Photo-Blue-Bottle PBB-solution are shown in [Figure 3](#), and the reduction nano-platinum catalyst indicated in [Figure 2](#) are commercially available, most of them

even in school chemical storage. They are non-toxic, harmless from the safety point of view, cost effective, and recyclable.

- *Sources of supply:* Merck/Sigma-Aldrich 6381-92-6 (EDTA), 53721-12-3 (ethyl viologen), 1811-28-5 (proflavin), 205974 (5% Nano-Platinum on Al₂O₃ powder), and SCS GmbH, Article 44020 (5% Nano-Platinum on Al₂O₃ Fibres).
- The basic experiment shown in [Figure 1](#) is suitable for demonstrations in lectures, but the setups can also be used as starting devices for investigations by the students in the classroom or even outdoors in the sunlight. They can determine the influence of different parameters, e.g. the volume of the PBB-solution, the amount of the reduction catalyst, the power of the LEDs or the intensity of the solar radiation, and other parameters.

Concerning teaching approaches in science education, the following aphorism by A. Einstein, already mentioned in this journal [1], is always our guideline "a pretty experiment quite often is more precious than twenty equations bred in the thinking reort". Following this, our investigations in the research of this experiment during the last two years were focused on the production of really "green" hydrogen, i.e. without the use of electric energy but completely by irradiation with visible light instead. Actually, we wanted to show a possible way out of rapidly progressing global warming caused by humans, a development against which young people around the world have demonstrated again and again in the *fridays for future* since 2019. However, the current version of the experiment shown in [Figure 1](#) has several precursors and needs further development. This will be discussed in section 2.



Figure 1. Setups for the photocatalytic production of hydrogen by irradiation with sunlight, and with blue light from LED. The reaction mixture is stirred magnetically, and the evolving hydrogen is pneumatically collected in a flexible tube of silicone

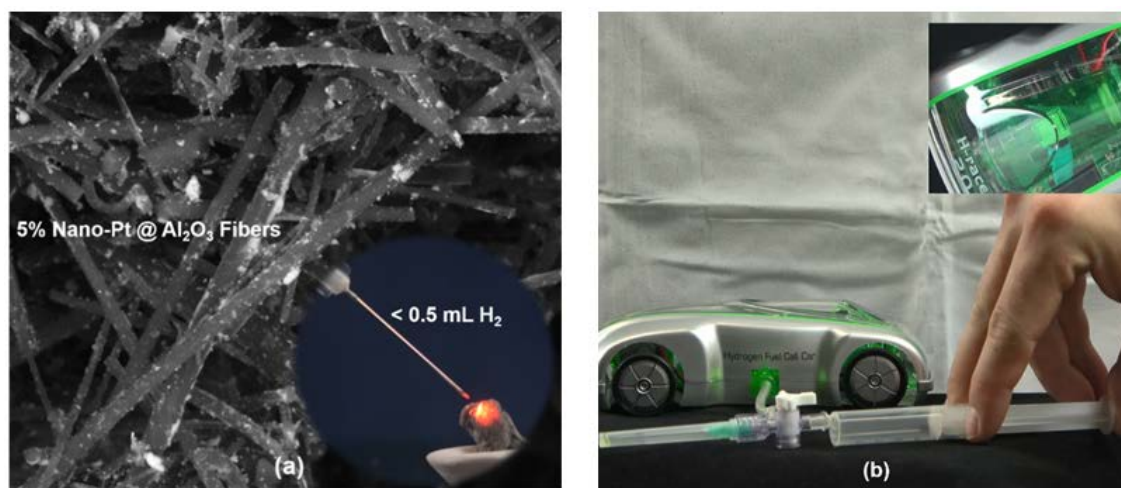


Figure 2. a) SEM-photograph of the catalyst with excerpt showing the detection of very small amounts of H_2 by the glow up, and b) fueling of the fuel cell car with approx. 5 mL of hydrogen

2. History and Theoretical Background

One of us has been working for over 25 years on the Photo-Blue-Bottle system, which provides the photocatalytic system exploited in the experiment described above [2]. The basic version of the PBB experiment and the concentration cell version were already reported on in 2001 [3]. These two PBB versions provide several didactically concise observations, namely repeatable colour cycles yellow-blue-yellow and the emergence of an electrical voltage in the concentration cell. The teaching application of these observations results

in the comparison of the similarities between the cycle of substances and the energy conversions in the natural photosynthesis and respiration, and the cycle of the substrate in the PBB experiment. However, these first versions of the PBB experiment contained some decisive disadvantages for use in the classroom: i) The reactions were carried out in a relatively large water-cooled immersion-lamp reactor with approx. 450 mL of PBB-solution per batch, ii) a medium-pressure 150 W mercury lamp was used as irradiation source and iii) the toxic chemical methyl viologen was used as the substrate in the PBB solution.

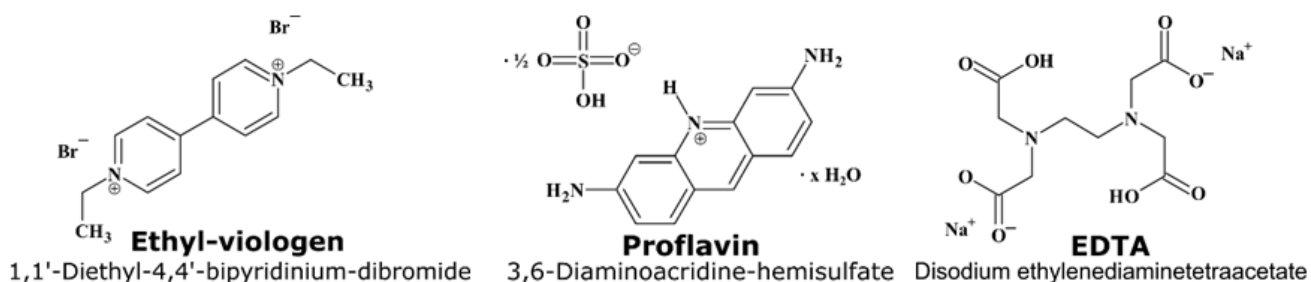


Figure 3. Chemicals for the photocatalytic PBB-solution: redox mediator ethyl-viologen, photocatalyst proflavin, and sacrificial donor EDTA

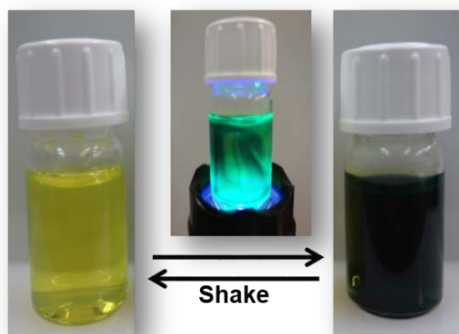


Figure 4. Basic PBB experiment in microscale version showing the colour cycles yellow-blue-yellow



Figure 5. Concentration cell with PBB-solution in microscale version showing the occurrence of an electrical voltage by irradiation of one half cell

During the last 8 years we have succeeded in developing PBB microscale versions with 3-5 mL of PBB-solution (see Figure 4 – Figure 5), using exclusively LEDs as artificial light sources, and replacing the toxic

methyl viologen by non-toxic ethyl-viologen [4,5,6,7]. Further details on the “Metamorphosis” of the PBB experiment are given in [8].

Leaving the history of the PBB experiment behind, we now turn to give some technical details of different PBB versions and explain their theoretical background. Teaching recommendations will follow in section 5.

The “new” PBB-solution: The solution required for all versions of the PBB experiments is prepared simply by dissolving 1 g of EDTA, 561 mg of ethylviologene, and 12 mg of proflavine (see formula in Figure 3) in 500 mL of distilled water. The solution should be stored in the dark in a glass flask. It can be used over several months in several learning groups.

Artificial light sources for irradiation: The central experiment of this paper (Figure 1) works with an LED module of the type *Sahlmann Photochemical Solutions*. It consists of 3 LEDs for blue light, $\lambda = 450$ nm, power per LED: 910 mW; price on request from the manufacturer; e-mail: bs@sahlmann-ps.de. For irradiation of the PBB-solution in the microscale vials shown in Figure 5 and Figure 6, blue light emitting LEDs available via internet, are suitable.

Colour cycles yellow-blue-yellow: This impressive phenomenon can be produced and investigated even by children. For this, they can work in sunlight or with blue light emitting LED torches. If they carry out the experiment with 3 mL of PBB- solution in closed 5 mL screw cap vials, the cycle indicated in Figure 6 can be repeated more than 20 times. The less air there is above the solution, the fewer cycles can be performed. When fresh air is admitted by opening the vial for a couple of seconds, colour cycles can be repeated again.

While the yellow colour of the non-irradiated PBB solution is caused by the proflavin absorbing in the blue spectral region ($\lambda_{\text{max}} = 444$ nm), the irradiated solution appears blue because the reduced species EV^+ additionally absorbs in the region of longer wavelengths showing an absorption maximum at 602 nm (see Figure 6).

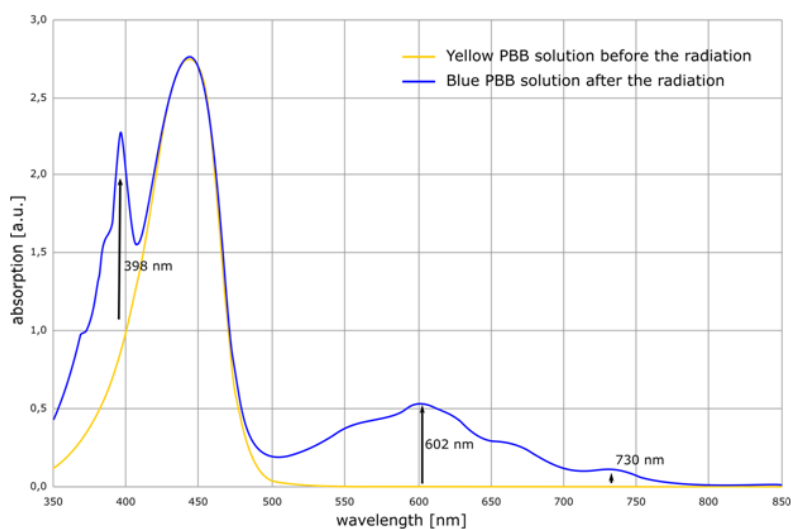
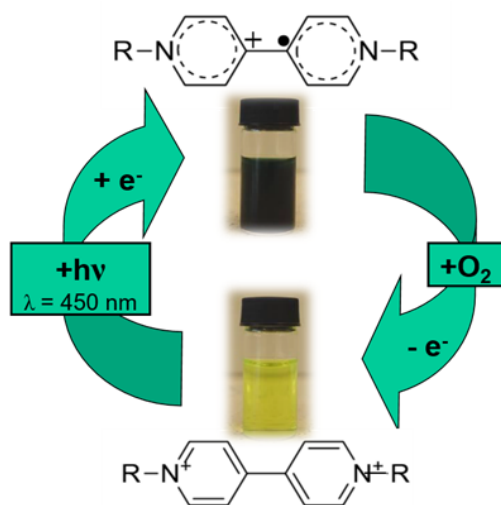


Figure 6. Redox cycles of ethyl viologen, and absorption spectra of the PBB-solution

Molecular structure and color of EV^{++} and EV^+ : The chemical structure of the two viologen species shown in Figure 6 differ essentially in the torsion angle between the planes of the two aromatic pyridinium units. For viologen di-cations of the type EV^{++} , torsion angles of 50° - 60° are mentioned in the literature [10,11]. In contrast, for mono-cation radicals of the type EV^+ , torsion angles of only 0.1° - 1° have been calculated, and experimentally verified [10,11,12,13]. In the ethyl-viologen mono-cation, which we simplify denoted as EV^+ , the two pyridine units are therefore almost coplanar. Thus, while the bond delocalization in di-cation EV^{++} is limited to one pyridine unit, in mono-cation EV^+ it extends over both rings. This causes a strong bathochromic shift in the light absorption of the mono-cation EV^+ (see Figure 6). In this sense, the system of EV^{++} and EV^+ is a textbook example of the relationship between molecular structure - light absorption - color.

Energetics of light-driven endergonic redox reactions: At molecular level, every light-driven process begins with the absorption of a photon. This generates an electronically excited state of the absorbing molecule, that is considered as "the heart of all photoprocesses" [9]. In the terms of the molecular orbital model, electronic excitation corresponds to the transition of an electron from the HOMO into the LUMO (Figure 7). In the case of proflavin, this occurs by the absorption of a photon from the blue spectral region of visible light. It should be mentioned that the redox behaviour of the excited states is completely different from those of the ground state.

With the relative positions of the energy levels shown in Figure 7, a photoelectron transfer PET from the LUMO of proflavine to the ethylviologene dication EV^{++} becomes energetically possible. Note, that's not the case from the HOMO of proflavin. Furthermore, the photoelectron transfer is kinetically preferred over the competing deactivation via fluorescence, due to the large excess of ethyl-viologen in the PBB-solution, (the concentration of ethyl-viologen is in the range of 10^{-3} mol/L and the concentration of proflavin is about 100 times smaller). From the energetic point of view, the reduction of EV^{++} to EV^+ arises at the expense of the photon absorbed by proflavin. The photon's energy is partially converted into chemical energy and stored in the reduced species EV^+ . It is stable in the absence of oxygen in the solution, but it is immediately oxidized back to EV^{++} when the vial shown

in Figure 4 is shaken, and oxygen from the air is introduced into the solution. Therefore, the reduced substrate in the form of the di-cation species EV^{++} is a very unstable energy storing system.

However, as the reduced species of the redox pair EV^{++}/EV^+ , it can serve as an electron donor to other chemical species, e.g. to H^+ ions. For this reason, in the following text we no longer refer to the pair EV^{++}/EV^+ as "substrate", but as "mediator".

Redox potentials and reactions in the PBB-system:

The mechanism of photocatalytic hydrogen production in the central experiment of this report is in Figure 8. The seven consecutive steps are shown in the diagram with redox potentials of the redox pairs involved (left side), as well as in the related coupled elementary processes (right side). The first step (1) is the electronic excitation of a proflavin mono-cation $PF^+ \rightarrow PF^{+*}$. As explained in the previous chapter, the redox properties in the excited state are completely different from those in the ground state. In this case the redox potential of the proflavin changes dramatically by 1.7 V from $E^\circ[PF^+/PF^{++}] = +1.1$ V to $E^\circ[(PF^{+*})/PF^{++}] = -0.6$ V, so that the reaction sequence can be triggered until the production of molecular hydrogen [14,15]. After the excitation (1), the photoelectron transfer shown in Figure 7 occurs in the coupled redox reaction of the oxidation (2) and the reduction (3). This involves an electron transfer from the excited proflavin mono-cation PF^{+*} to the di-cation of the mediator EV^{++} . As a result, the reduced species EV^+ of the mediator is generated, and the initial mono-cation of the photocatalyst PF^+ gets oxidized to the di-cation PF^{++} . This is called an oxidative quenching of the excited state PF^{+*} [16]. The oxidation (4) and the reduction (5) from Figure 8 complete the cycle of the photocatalyst proflavin. In this process, the so-called sacrificial donor EDTA is irreversibly oxidized. Finally, the combination of the oxidation (6) and the reduction (7) leads to the target product hydrogen and the completion of the reaction cycle of the mediator ethyl-viologen. However, for the electron transfer in steps (6) and (7), three preconditions are necessary: 1) a sufficient concentration of H^+ ions in the PBB solution, 2) matching redox potentials of the involved redox pairs, i.e. the redox potential be more negative than that of $H_2/2H^+$, and 3) a suitable reduction catalyst which facilitates the electron transfer and the evolution of gaseous hydrogen.

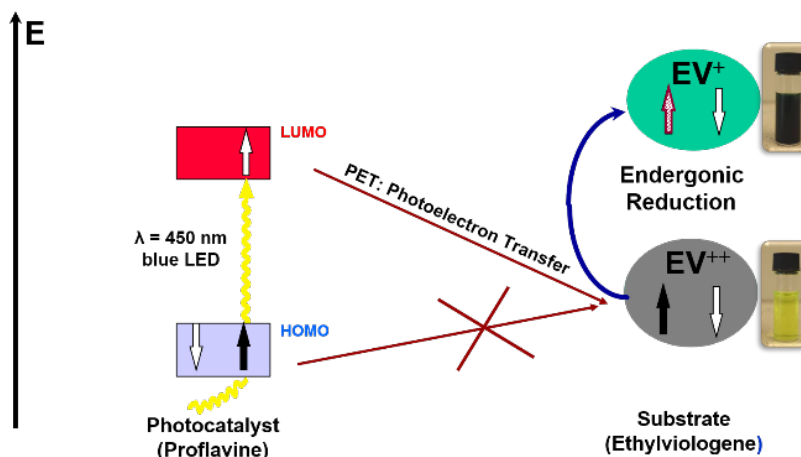


Figure 7. Electronic excitation and photoelectron transfer PET in the PBB system

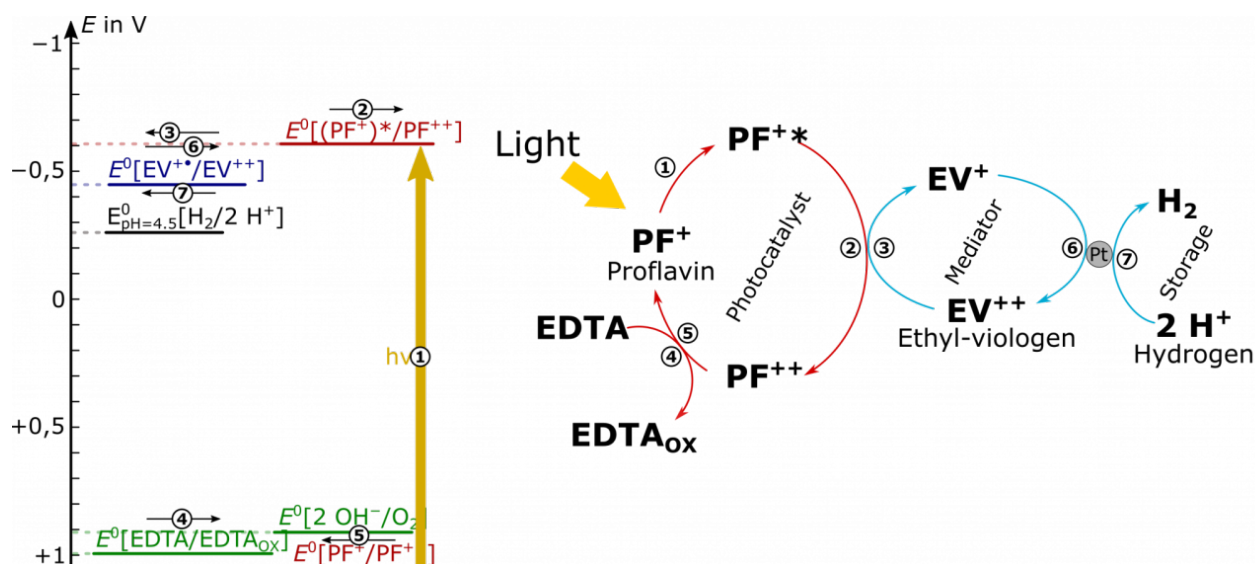


Figure 8. Redox potentials and sequence of the elementary redox processes in the photocatalytic 1-pot-cell with the PBB system

In our central experiment these three conditions are fulfilled as follows:

- 1) Due to the buffer effect of EDTA ($\text{pH} \approx 4.5$), the PBB-solution offers H^+ ions in a sufficient concentration as electron acceptors.
- 2) At $\text{pH} = 4.5$ the redox potential of the system $\text{H}_2/2\text{H}^+$ calculated using the Nernst equation is $E^\circ = -0.265 \text{ V}$. Since the redox pair $\text{EV}^+/\text{EV}^{++}$ has a pH-independent redox potential of $E^\circ = -0.449 \text{ V}$ [17], the redox reaction according to the coupled steps (6) and (7) is electrochemically permitted.
- 3) 5% Nano-Pt@ Al_2O_3 Fibers indicated in Figure 2 proves to be catalytically very effective for hydrogen evolution.

Contrary to expectations, this catalyst is inexpensive. It can be purchased in small packages for approx. 15 Euro per gram at the school chemical service SCS (see above). Only about 50 mg of this catalyst is needed for a reaction batch as shown in Figure 1 and it is recyclable. It can be regenerated by filtering off the PBB-solution, treating with sulfuric acid, $c = 1 \text{ mol/L}$, and hydrogen peroxide solution, $w = 30 \%$, re-filtration and rinsing with water. Alternatively, it can be regenerated simply by strong heating for 1 minute. Finally, with this catalyst, the smallest amounts of hydrogen can be detected quickly, safely and impressively (see Figure 2).

Hydrogen production in the photogalvanic 2-pot cell:

This version of the experiment works without the reduction catalyst.

Therefore, the electrons must take a circuitous route on the way from the reduced mediator EV^+ to the H^+ ions. Actually, the electron transfer is conducted via a low cost graphite-foil electrode and a metallic conductor to a platinum electrode immersed in hydrochloric acid. The two half-cells are connected by a salt bridge containing potassium chloride solution. The resulting 2-pot cell shown in Figure 9 can be powered just like our 1-pot cell from Figure 1 with sunshine or with blue LEDs.

We have to concede that the efficiency of hydrogen production in the 2-pot cell is significantly lower than in the 1-pot cell. It takes about 90 minutes to produce 0.6 mL

of hydrogen in the 2-pot cell (cf. the data from section 1 for the 1-pot cell). However, there are didactic reasons that justify the use of this experimental version:

- The experimental set-up is analogous to the classical galvanic cells, e.g. the Daniell element, and the photogalvanic 2-pot-cell for converting light into electrical energy [18,19].
- The generation of the hydrogen bubbles and their drip off from the platinum electrode can be observed very well.
- Similarities and differences to the galvanic and photogalvanic cells mentioned above can be discussed.
- Hypotheses for the efficiency limiting parameters can be formulated, and experimentally verified (note: important parameters are the surface of the graphite foil and the salt bridge between the half cells).

However, there is also a reason of scientific interest to deal with the 2-pot-cell type. This cell allows to measure the current in the outer circuit continuously during the irradiation (note that is not possible in the 1-pot-cell). Doing so, one gets curves as in Figure 10, i.e. after an increase to a certain value, the current intensity remains constant over a long period of time.

This corresponds to the setting of a *photosteady state* (*photostationarity*) in the photocatalytic PBB system from the irradiated half-cell. In the photosteady state, the formation of the reduced form of the mediator EV^+ and its oxidation to EV^{++} with the release of electrons to the graphite electrode proceed at the same rates. In our experiments, we can neither see nor measure how quickly EV^+ forms and disappears, but we can see that the PBB-solution turns blue when irradiated with light and remains permanently blue during the irradiation. However, from the constant time course of the current (see Figure 10) it can be concluded that there is a constant rate of electron transfer from the PBB system to the graphite electrode, and as a consequence a constant current flow is achieved over time. The measurable constant current is therefore an indirect proof of the setting of the photosteady state.



Figure 9. Photogalvanic 2-pot-cell for photocatalytic production of hydrogen, and removal of hydrogen from a sealed platinum electrode commonly used in schools

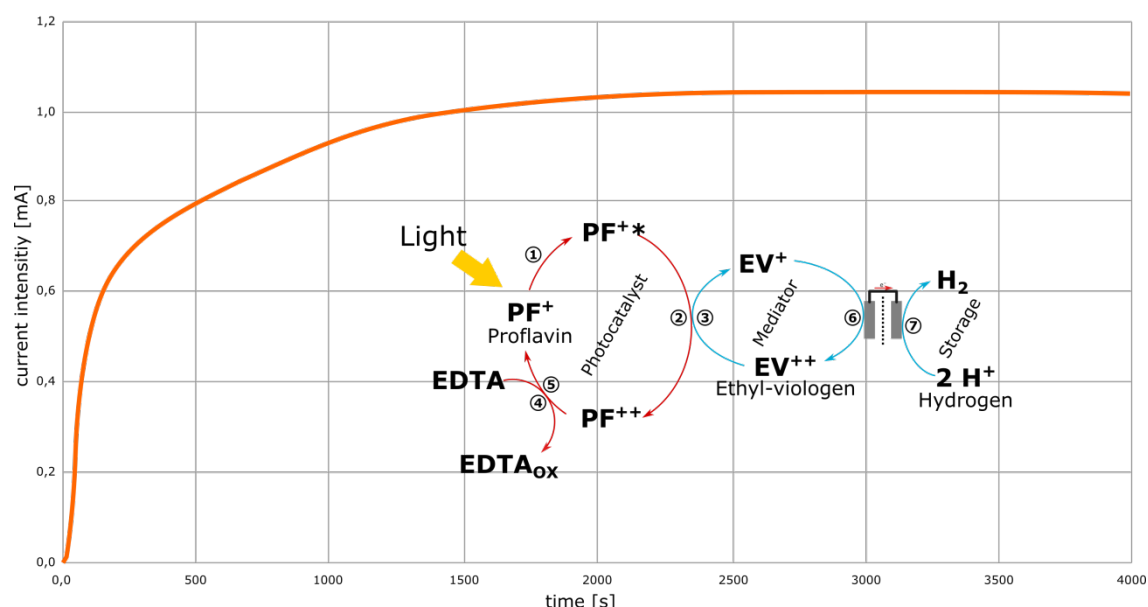


Figure 10. Temporal change of the current intensity in the photogalvanic 2-pot-cell, and underlying elementary processes in the photocatalytic PBB system

In order to accentuate the difference to the *chemical (thermodynamic) equilibrium*, it should be emphasized that photosteady state can be achieved and maintained only by irradiation, and it can not only be set in a closed system, but also in an open system. In fact, the PBB system in both the 2-pot cell and the 1-pot cell from our experiments is an open system, because the reaction product hydrogen escapes from it.

3. Artificial Photosynthesis - Principle and Perspectives

According to the report of German Academies of Sciences [20], “Artificial photosynthesis is used for

the production of chemical energy carriers and valuable substances using sunlight as the only energy source”, and “For this purpose, a central principle of the biological model is imitated: the coupling of light-induced charge separation with catalytic processes for the production of energy-rich compounds.” The report [20] emphasizes that science journalism can help to increase the social acceptance of such research and development.

We are deeply convinced that communicating the possibilities and opportunities as well as the problems still to be solved in connection with artificial photosynthesis is also of eminent importance, especially for the upcoming generation. Therefore, these topics also have to be taught in schools, mainly in chemistry classes.

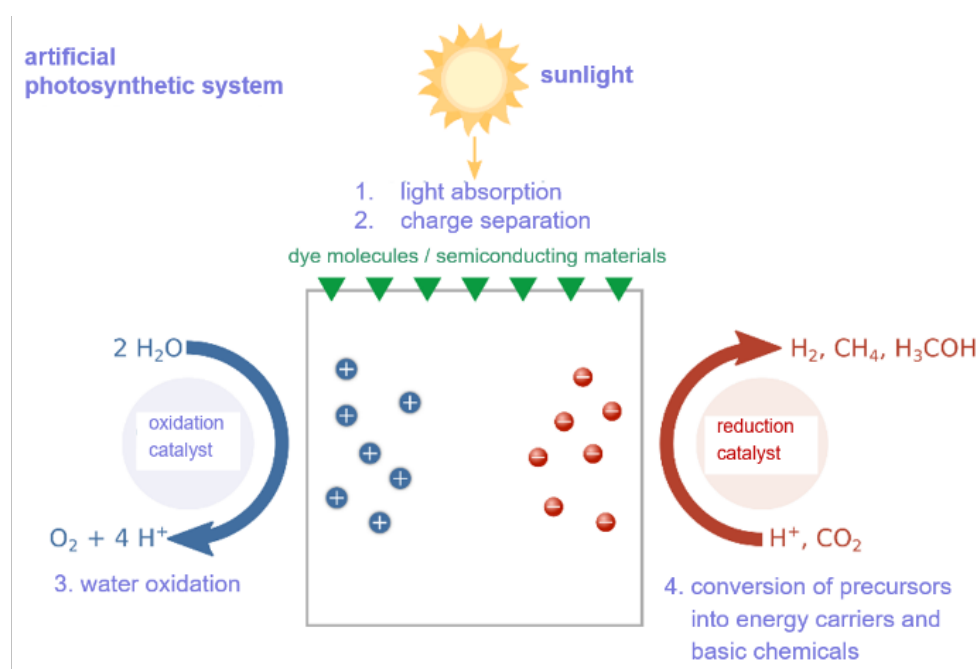


Figure 11. Principle and sub-processes of artificial photosynthesis according to [20]

In addition to the above-mentioned unique use of solar light as an energy source, the basic principle of artificial photosynthesis also includes the exclusive use of water and carbon dioxide as material resources. The principle of artificial photosynthesis can be represented as shown in Figure 11. Basically, it is neither necessary nor advantageous to aim for a 1:1 copy of the processes occurring in natural photosynthesis in green plants. Rather, the research focuses on the *four sub-processes* shown in Figure 11, i.e. 1) light absorption, 2) charge separation, 3) water oxidation, and 4) conversion of precursors from 1)-3), i.e. H^+ and CO_2 , into energy carriers and basic chemicals.

In our model experiments, three of the four sub-processes from Figure 11 are realised. Only the sub-process 3), the water oxidation, does not occur, instead the sacrificial donor EDTA is irreversibly oxidised. Most publications on the photocatalytic production of hydrogen with visible light also include sacrificial donors which, as in our experiments, are necessary to complete the catalytic cycles of the light absorbing species. At this point it should be mentioned that "... whenever hydrogen is generated from water/photocatalyst dispersions in the presence of a sacrificial electron donor (for example, alcohols or similar electron donor systems) then the process is definitely not water splitting and cannot be claimed to be so" [21].

In this sense, we do not yet claim the title "hydrogen from water with sunlight" for our experiments, but we do claim "hydrogen goes green". This label is well-justified because the experiments realise three essential sub-processes of the artificial photosynthesis (see Figure 11), and are therefore a far-reaching experimental approach towards artificial photosynthesis. Furthermore, the practical and theoretical work with these experiments motivate teachers and learners to inform themselves about the possibilities and the state of the art in research concerning the photocatalytic production of hydrogen by overall water splitting as well as production of synthetic fuels and

organic chemicals by capture of carbon dioxide from air and subsequent reduction [22-27]. In this way, (photo)chemical education can and should provide a substantial contribution to the realisation of the *Sustainable Development Goals SDGs* from the Agenda 2030 of the United Nations [28].

4. Digital Materials

Not as a substitute, but as an additional support to the experiments, we offer *videos* on our internet portal "Chemistry with Light" [29]. The videos can be used equally in face-to-face, distance and hybrid teaching. Since each video shows the *procedure* and the *results* of particular experiments, the videos provide precise working instructions on how to carry out the experiments, i.g. the central experiment of this report (Figure 12). Selected scenes from these videos are suitable for exercises, e.g. *verbalizing* the observed phenomena, and *criticizing* deficits in the presentation.

One of the two *video tutorials* "Photosynthesis - A Case for Two" (Figure 13) with *narration in English* presents and comments the model experiments from Figures 4 and 5, and the second one contains further experiments and explanations on the cooperation of chlorophylls and carotenoids in the light reaction part of photosynthesis.

This provides the opportunity to discuss the explanations and the terminology from the tutorial videos with or among the learners. During the Covid pandemic, four *very short videos* were produced to enhance the tutorial video indicated in Figure 13. They show in particular the Basic PBB experiment, as well as the influence of the following three parameters: i) color of the irradiating light, ii) temperature, and iii) presence of air above the PBB-solution. In this way, even students from lower secondary education can correctly interpret the observations on the phenomena level and correlate them with the natural photosynthesis/respiration cycle without

the formulae of the substances and without concepts such as photon, excited state, redox potential, electron transfer etc.



Figure 12. Screenshot from the video “Photocatalytic hydrogen with PBB” [29]



Figure 13. Screenshot from the tutorial video “Photosynthesis – A Case for Two”, (Part 1 of 2) [29]

5. Core Concepts in (Photo)-Chemical Education

There are some *core concepts* in chemical education that can be used to structure and connect the most important content of chemistry taught in schools.

“Big five” of them are shown in Figure 14.

Each of the experiments in this article provides *content* and *key terms* that can be more or less assigned to all five of these core concepts.

Regarding the *energetics* of chemical reactions, all the experiments presented above emphasize light as energy able to drive endergonic reductions (c.f. Figure 6 and Figure 7).

Redox reactions are also omnipresent in all the experiments covered in this article (c.f. Figure 8).

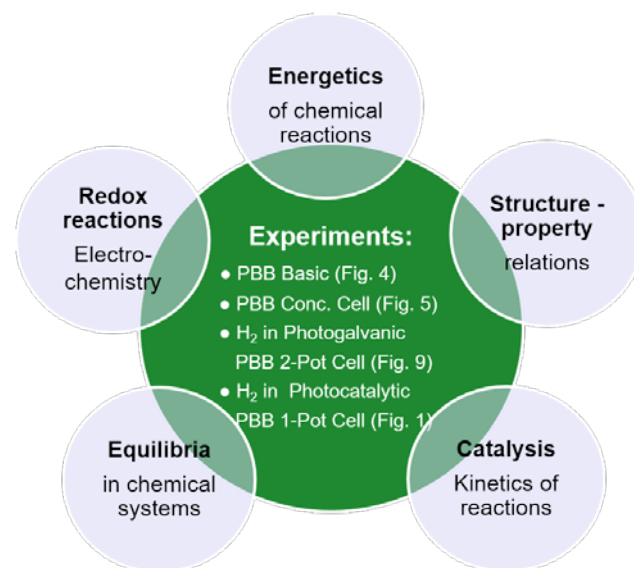


Figure 14. Core concepts of chemical education addressed in the presented experiments

Concerning the *relation structure-properties*, for color changes in the PBB system the relation between the molecular structure, the absorption of light and the perceived color is in the center of attention. However, the water solubility of the three organic chemicals in the PBB-solution can and should also be explained with the relation structure-properties. All three chemicals are dissolved from their soluble salts as cations (ethylviologene and proflavine) or anions (EDTA).

In the experiments considered in this paper, the *catalysis* and the *equilibria* are of a special kind, which is conceptually specified by the prefix “photo”. It is photocatalysis, or photosteady state, respectively. Actually, these two terms and a series of other key terms and concepts of photochemistry are suitable for *higher secondary education* at high schools and for *tertiary education* at universities as well as in teacher training - however, less so for lower secondary education (Figure 15).

Nevertheless, even at the *lower secondary level*, photochemical content should in future be integrated more extensively than at present into chemistry education, with experiments and evaluations at the phenomenal level. Kids will be able to learn how chemical reactions can be driven by light by carrying out experiments with the PBB basic version and the variation of the parameters mentioned in section 6. They will be trained to distinguish between oxidation and reduction, low and high energy substances, and energy conversion and storage (Figure 15). Recognizing that these experiments simulate the natural cycle of photosynthesis/breathing will motivate them to look for other opportunities to use solar energy following the nature's example. In this sense, recommendations and material for a *ready-to-teach* unit according to the 5E model (Explore - Explain - Elaborate - Evaluate) has been presented in this Journal [6]. There one can find *what* and *how* can be taught with the mentioned experiments.

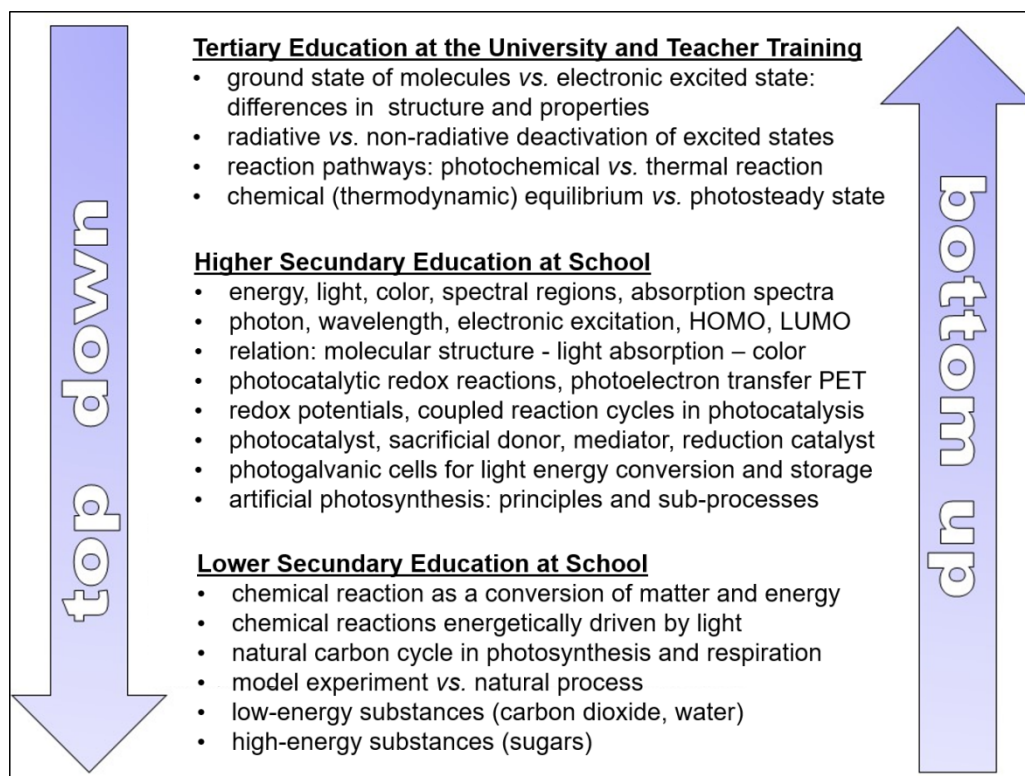


Figure 15. Key terms of photochemistry and teaching content addressed in the article

6. More Light in Chemical Education!

This is an *imperative* since, in times of climate change and transition to renewable energies, the use of sunlight, the cleanest, most sustainable, free and most abundant energy available on our planet, must be at the cutting edge of innovative technologies. Chemical education can contribute substantially to Education for Sustainable Development if a paradigm transition from thermal- and electro-chemistry to thermal-, electro-chemistry *and* photo-chemistry is achieved in the didactics of chemistry. In chemical education, light must become a *core concept* with *cross-disciplinary* links, i.e. a guiding idea that opens up access to a large field of innovative knowledge, supports its structuring and facilitates its teaching. Photochemical experiments and content are very well accepted by both students and teachers. This has been an emerging trend in the evaluation of numerous teacher training courses and was confirmed by the results of an exploratory study with 478 students and 30 teachers from 18 high schools in Germany [30].

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