



Hydrogen evolution reaction: Optimizing a Didactically Reconstructed System with Variable Control Strategies

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Abstract

The production of hydrogen with sunlight is becoming increasingly important and is a central building block for a sustainable energy supply. One approach in current research is to embed a light-driven catalytic molecule within a hierarchically structured soft matter matrix to use solar radiation for driving a chemical reaction for photocatalytic water splitting. The reconstruction of innovative research fields with high didactic potential for schools represents an important contribution in the context of science communication. Beyond the learning opportunities, the associated experiments additionally offer the possibility to introduce scientific working methods to the students, such as variable control strategies. These will be applied in this article to optimize a didactically reconstructed experiment on the sustainable evolution of hydrogen with sunlight. For this purpose, the students are to vary the concentrations of the different components in independent planning and execution and to observe the resulting effects spectroscopically. Furthermore, the experiment offers a first insight into the development of a future generation of photosystems, which represent an approach for sustainable hydrogen development through sunlight. The subject area also offers numerous links to classical school contents (i.e., catalysis, energy conversion, redox reactions, polymers) as well as to basic concepts of chemistry (energy, structure-property relationships). Lastly, the link between photochemistry with an Education for Sustainable Development can be taken up synergistically.

Keywords: photocatalysis, hydrogen evolution reaction, photochemistry, spectroscopy, water splitting

1. Introduction

The generation of hydrogen with sunlight is becoming increasingly important and is a central building block for a sustainable energy supply. One approach in current research is to embed a light-driven catalytic molecule within a hierarchically structured soft matter matrix to use solar radiation within a chemical reaction for photocatalytic water splitting [1]. In previous work, a first proposal for the didactic reconstruction of this research area for the school chemistry education and student laboratories was already presented [2]. Besides the high didactic potential of current cutting-edge scientific research on sustainability itself, the experiments can be used to familiarize students with basic scientific research methods. The guidelines established for the Federal Republic of Germany within the educational standards for K-12 chemistry include strengthening the understanding of scientific working methods and the associated promotion of the competence area "knowledge acquisition" [3]. For this purpose, the approach of the control-of-variables strategy (CVS) is used, in which only one variable of an experiment is changed at a time and the resulting effects on the system are investigated.

2. Control-of-variables Strategy in Chemistry Education

The use of CVS for the fostering of competencies in experiments is an well-established procedure, which has already been described in detail, i.e. in physics education [4], and the use in chemistry lessons outlined here is based on this procedure. The common starting point is the observation that experiments in the classroom are often characterized by the central objective of imparting knowledge. In the process, independent experimentation is pushed into the background by the provision of detailed experimental instructions [5]. Promoting competencies in the area of independent knowledge acquisi-



tion therefore appears to be difficult to implement, since the students must be offered various decision-making options. By enabling different decisions for the further planning of an experiment, the students can independently experience and acquire this central feature of scientific working methods, the variation of a single variable with simultaneous constancy of the other components [6]. Only through this examination or experimental exploration of the individual components and their different influences is it possible for them to establish a cause-effect relationship. Pupils who have been trained by this method show an increase in the area of independent planning and execution of experiments in the further course of their schooling [7]. The control of possible variables is a challenge for students. For example, difficulties arise in inferring causal relationships by changing multiple variables simultaneously or not systematically examining different individual variables [8]. Consequently, the use of CVS offers a great potential for the students to gain a deeper scientific understanding and is a basis for university studies as well as scientific work.

In the following, we will outline how CVS can be used in the context of an experiment for the sustainable generation of hydrogen. The experiment was developed within the Collaborative Research Center/Transregio 234 "CataLight" in the framework of a cooperation between chemistry and chemistry education workgroups and is described in detail here [2]. However, the scientific background will be explained in the following, before the experimental setting is presented.

3. Scientific Background

The photocatalytically active system consists of three essential components. The **sacrificial electron donor** (triethanolamine, TEOA) provides electrons needed for reducing protons to molecular hydrogen. This reduction is facilitated by a light-excited **photosensitizer** eosin Y (PS) and the proton reduction **catalyst** TiO_2 (CAT), a system well-known from literature [9,10]. However, TiO_2 nanoparticles alone are able to perform photocatalytic hydrogen evolution upon UV-light irradiation acting as light harvesting unit and catalyst at the same time [11]. Therefore, excited electrons are generated through UV-light absorption and are available for proton reduction. To shift needed light energy into the visible region broadening the use of the solar spectrum the usage of a suitable photosensitizer provides TiO_2 with these necessary electrons. Thus, the excited PS enables the transfer of electrons from TEOA onto the CAT, which in turn is able to reduce protons to molecular hydrogen (Figure 1).

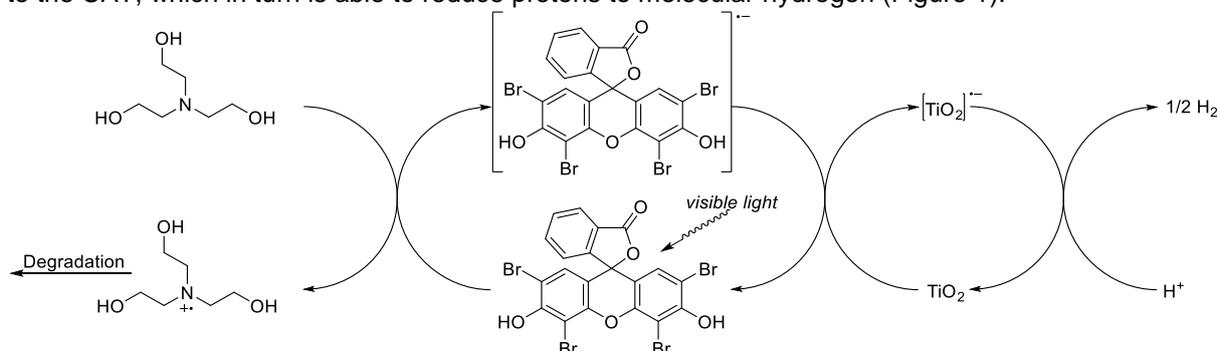


Figure 1: Reaction scheme for visible light-induced hydrogen evolution catalysis using TEOA as sacrificial electron donor, eosin Y as photosensitizer and TiO_2 as catalyst.

It is noteworthy at this point, that possible degradation pathways of TEOA after oxidation are beneficial for photocatalysis as a counterproductive electron back transfer is hindered and even stronger reductive species are formed [12]. While in sum TEOA and protons are consumed, PS and CAT can perform each cycle multiple times before both or one component degrade or are deactivated by side reactions. In the past, it was shown that core-shell hybrid materials based on a TiO_2 core and a polyampholytic shell can tremendously boost the activity of such systems [13]. The authors demonstrated that photocatalytically active molecular component interactions were increased and electron as well as proton transfer are facilitated. In this manner the degradation of the PS (eosin Y) was prevented, a crucial factor for a sustained and durable photocatalytic reaction. In this work a combination of commercially available polymers forming polyampholytic complexes is used to mimic the unique stabilizing properties of a tailor-made graft-copolymer from the latter literature example. In this context, numerous reports exploit the ability of poly(acrylic acid) ("PAA") and poly(diallyldimethylammonium chloride) ("PDADMAC") to form pH and ionic strength dependently complexes in solution [14–18]. With this polyelectrolyte combination we target a suitable soft matter matrix to perform photocatalytic investigations.



4. Experimental Setting

After carrying out and evaluating the underlying experiment [2], the students are given the opportunity to plan and carry out a series of experiments independently. Prior to beginning, the teacher needs to set a goal for the investigations. In the given example, the influence of different **concentration changes** of the components (donor, PS, CAT, PAA & PDADMAC) on the degradation rate of PS is to be investigated. The assumption is that with an accelerated degradation the reactivity of eosin Y is increased. The rate of degradation can be easily monitored by determining the eosin Y concentration with a spectrometer; alternatively, low-cost devices also are available [19].

To avoid a possible overload of the students during planning, other experimental components such as exposure time, UV filter foil, exposure distance, time in the ultrasonic bath or light source are kept constant throughout. However, these can also be included for interested learning groups or as part of seminar papers and student research projects.

Procedure: The stock solutions are prepared as described in the literature [2]. For further experiments, an inexpensive light source (e.g., OSRAM Ultra-Vitalux, 300 W), a UV-impermeable cuvette (e.g., Brand, 12.5 x 12.5 x 45 mm), a commercially available 430 nm light filter (light exclusion up to 430 nm: 98.5 %) and a UV/vis-spectrometer (e.g., VWR UV-3100PC) are required. The composition of the individual components already used in the experiment is defined as the starting material for the envisaged variations of the concentrations. For the spectroscopic investigation, the solutions must be diluted with water in a ratio of 1:7 after treatment in the ultrasonic bath and 3 mL must be filled into a UV-impermeable cuvette. Upon investigating changes in eosin Y concentration, a dilution of the sample is required to ensure analyzability with UV/vis spectroscopy (targeted concentration $c \approx 0.02 \mu\text{M}$). Measurements were performed before and in 5 min steps until 60 min under irradiation. However, significant results can be achieved in a much shorter time. The distance of sample and light source was set to 20 cm with additionally light filter foil in between.

In this work, exclusively the investigation of the influence in polymer concentration changes of the individual components is presented. Therefore, the concentration was doubled or tripled compared to the initial concentration. The corresponding time dependent UV/vis spectra are shown in Figure 2. Variation in initial absorbance between different approaches is the result of imprecisions in sample preparations.

For sample A ($c(\text{PAA}) = 0.17 \mu\text{M}$, $c(\text{PDADMAC}) = 0.23 \mu\text{M}$), a noticeable degradation of eosin Y is observed after an illumination time of 15 min. The band maximum at $\lambda = 523 \text{ nm}$ ($A = 1.06$) is shifted to $\lambda = 512 \text{ nm}$ ($A = 0.78$) after 20 min and gradually to $\lambda = 497 \text{ nm}$ ($A = 0.47$) in the course of 30 min. For sample B with double polymer concentration ($c(\text{PAA}) = 0.34 \mu\text{M}$, $c(\text{PDADMAC}) = 0.46 \mu\text{M}$) a degradation of eosin Y can be observed after 15 min irradiation. In contrast, the band maximum at $\lambda = 523 \text{ nm}$ ($A = 1.03$) is shifted to $\lambda = 509 \text{ nm}$ ($A = 0.59$) after 20 min and eventually to $\lambda = 498 \text{ nm}$ ($A = 0.47$) after 25 min. Sample C with tripled polymer concentration ($c(\text{PAA}) = 0.51 \mu\text{M}$, $c(\text{PDADMAC}) = 0.69 \mu\text{M}$) shows a shift in the band maximum $\lambda = 523 \text{ nm}$ ($A = 1.26$) to $\lambda = 522 \text{ nm}$ ($A = 1.05$) after 5 min, already. The band maximum appears further weakened at $\lambda = 504 \text{ nm}$ ($A = 0.58$) after 25 min and finally shifted to $\lambda = 502 \text{ nm}$ ($A = 0.54$) after 30 min. The acceleration of the degradation of eosin Y while increasing the polymer concentration, most prominently visible upon comparing the absorption spectrum before and after irradiating for 20 min, can be attributed to an improved dispersing effect and increasing electrostatic interactions of the components introduced by the polymers used. Literature has shown for a rather similar system consisting of eosin Y and rhodamine B (as potential electron donor) that already the addition of TiO_2 increases the rate of photodegradation dramatically [20]. We assume an enhanced spatial proximity of PS and CAT molecules in the system mediated by the polymer mixture and thus an even more efficient transfer of electrons. However, from the UV/vis spectra analogous photodegradation pathways according to several reports cannot be assumed at this point [20-23]. We observe on the one hand both a hypsochromic and hypochromic shift of the band maxima and on the other hand no significant further band change after 25-30 min of irradiation. From Figure 2D the influence of TEOA is clearly visible as the degradation proceeds slower and without any hypsochromic shift in the investigated time frame. As shown elsewhere, TEOA substantially causes the spectral change observed for Sample A-C [24]. Nevertheless, photobleaching to an extent shown in the latter literature example is not observed, rather a hindrance of further degradation after certain time. We assume that the potential polymer matrix incorporation slows down or even prevents further decomposition. In subsequent investigations detailed insights into this process are



necessary to acquire a deeper understanding of how the presence of different amounts of polymer matrix influences the system.

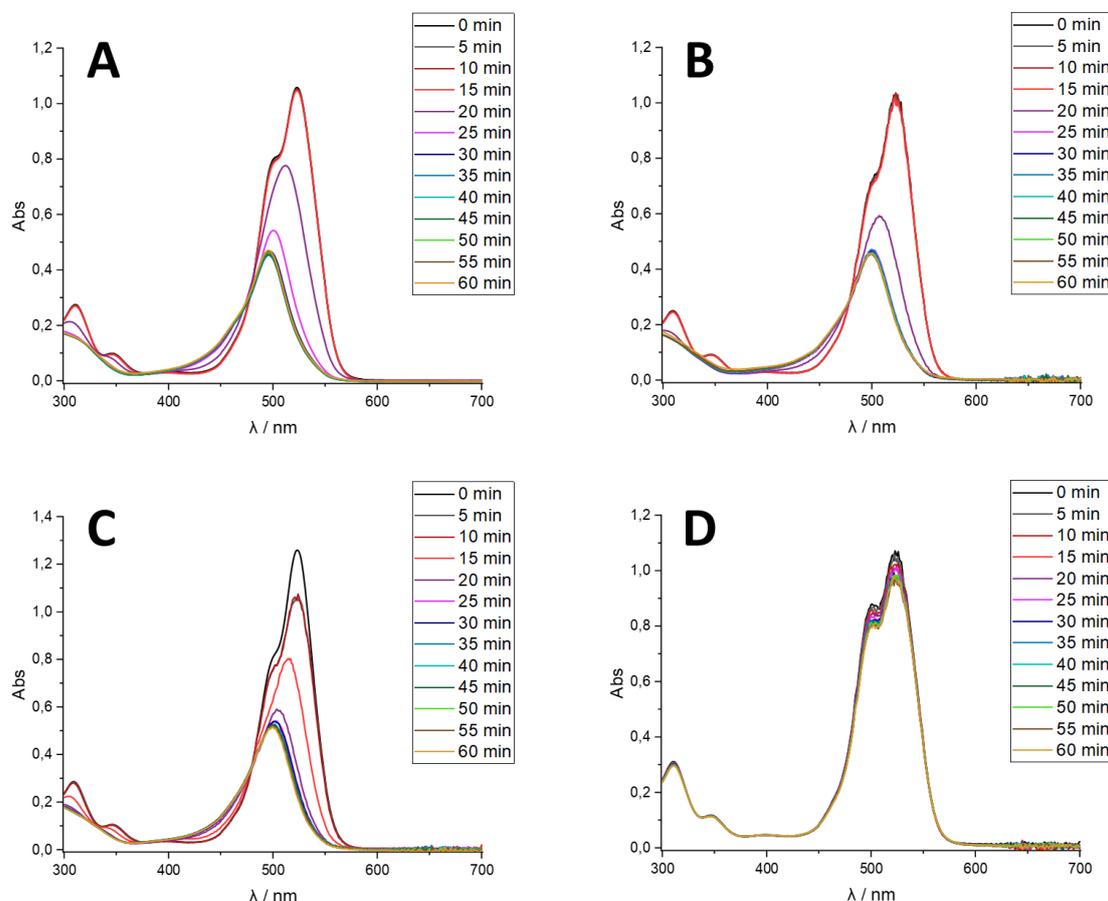


Figure 2: UV/vis spectra of different kinetic investigations, $c(\text{eosin Y}) = 22.2 \mu\text{M}$, $c(\text{TiO}_2) = 83.4 \mu\text{M}$, $c(\text{TEOA}) = 83.3 \text{mM}$. **(A):** Sample A ($c(\text{PAA}) = 0.17 \mu\text{M}$, $c(\text{PDADMAC}) = 0.23 \mu\text{M}$), **(B):** Sample B ($c(\text{PAA}) = 0.34 \mu\text{M}$, $c(\text{PDADMAC}) = 0.46 \mu\text{M}$), **(C):** Sample C ($c(\text{PAA}) = c(\text{PAA}) = 0.51 \mu\text{M}$, $c(\text{PDADMAC}) = 0.69 \mu\text{M}$), **(D):** Sample A without TEOA.

5. Conclusion & Outlook

The series of experiments presented here outlines a proposal for how an experiment can be adapted by CVS to promote students' knowledge acquisition competencies. Due to the complexity of the experiment, it is particularly suitable for projects and seminar works or for treatment in a student laboratory. In further work, the influence of all components on the system will be investigated in greater depth. In addition, the spectroscopic measurements are to be accompanied by gas chromatographic investigation to give quantitative statements on hydrogen production. For this purpose, the low-cost hydrogen sensor and the spectrometer [2,19], which are currently under development for the low-cost LabPi measuring station, are to be used for better feasibility in schools.

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