Hydrogen evolution reaction: Optimizing a didactically reconstructed system with variable control strategies

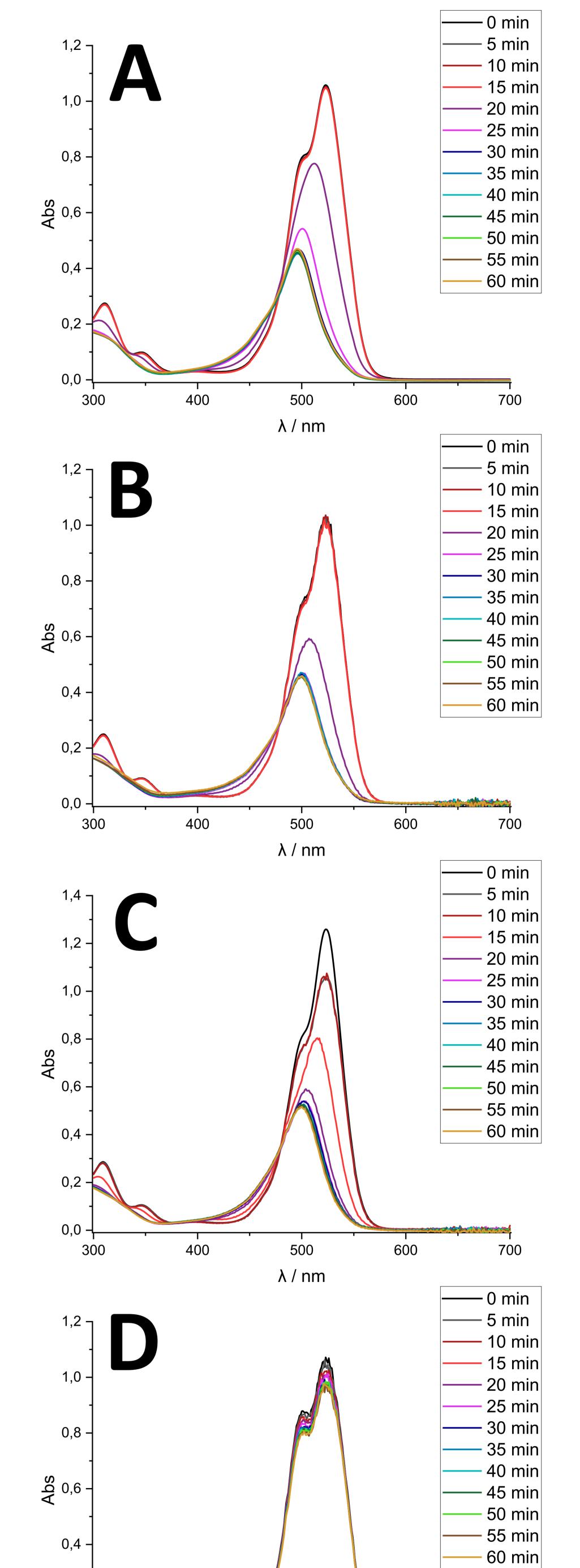
Malte Petersen[†], Jonas Eichhorn[†], Felix H. Schacher, Timm Wilke^{*}

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. In previous work, a first proposal for the didactic reconstruction of this research area was already presented (Fig. 1) [1]. 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.

Control-of-variables Strategy

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 [4]. By enabling different decisions for the further planning of an experiment, the students can independently experience and acquire the central feature of scientific working methods, the variation of a single variable with simultaneous constancy of the other components. Only through this experimental exploration of the individual components and their different influences is it possible for them to establish a cause-effect relationship.



CATALIGHT	Ru(II) dppz Photo- sensitizer	TiO₂ Photo- catalyst	[Mo ₃ S ₁₃] ²⁻ Co- Catalyst	Polyampholytic Graft Copolymers Matrix	TEOA Sacrificial donor	Methanol Inert gas atmosphere
	¥		¥			\checkmark
CATALIG H ₂ T EDUCATION	Eosin Y Photo- sensitizer	TiO₂ Photo- catalyst	[Mo ₃ S ₁₃] ²⁻ Co- catalyst	PAA / PDADMAC Matrix	TEOA:H ₂ O Sacrificial donor	Ethanol (optional) stable

optional use, commercially available, diliuted solution, non-toxic, easy included in cheap, related to every- easy to handle, day life no fume hood gas required gas required

Fig. 1: Development of a simple system for photocatalytic water splitting for student laboratories. The changes compared to the system which is used for CATALIGHT research are marked in orange.

Scientific Background

cheap, non-

toxic, included

in material set

cheaper, stable

related to every-

day life

Experiment & Results

The photocatalytically active system consists of three essential components. The **catalyst** TiO_2 (CAT) nanoparticles alone are able to perform photocatalytic hydrogen evolution upon UV-light irradiation acting as light harvesting unit and catalyst at the same time [2]. To shift needed light energy into the visible region broadening the use of the solar spectrum the usage of a suitable **photosensitizer** eosin Y (PS) provides TiO_2 with these necessary electrons. Thus, the excited PS enables the transfer of electrons from the **sacrificial electron donor** triethanolamine (TEOA), provides electrons needed for reducing protons to molecular hydrogen, onto the CAT, which in turn is able to reduce protons to molecular hydrogen (Fig. 2). In the presented example, the influence of different concentration changes of the polymermatrix on the degradation rate of PS is to be investigated. The corresponding time dependent UV/vis spectra are shown in Fig. 4. The assumption is that with an accelerated degradation the reactivity of eosin Y is increased. 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.

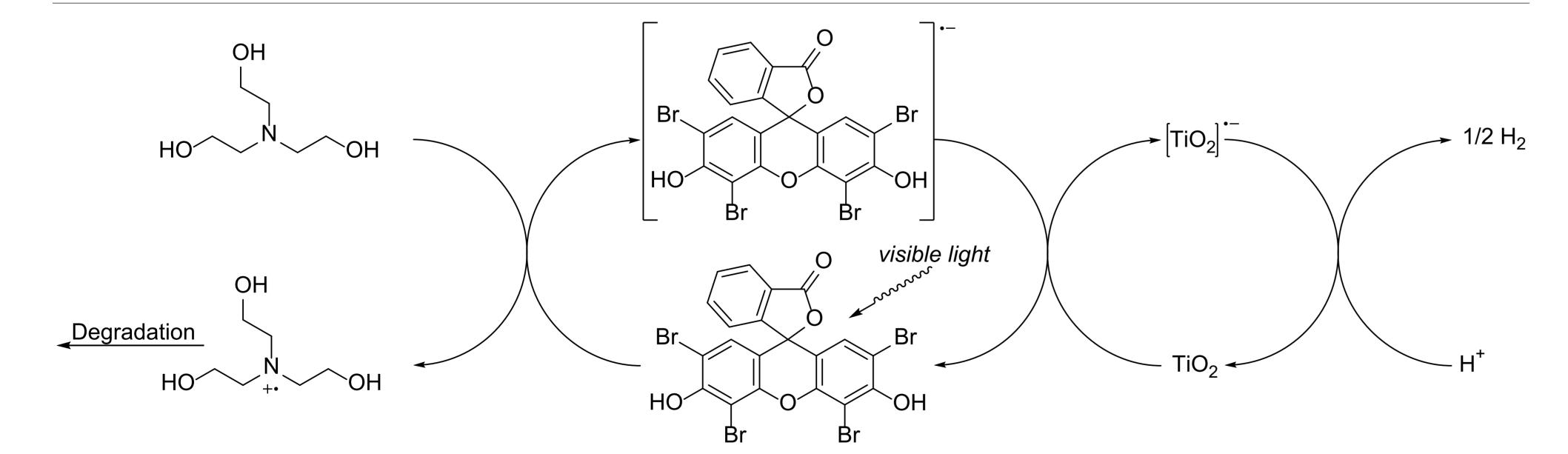


Fig. 2: Reaction scheme for visible light-induced hydrogen evolution catalysis using TEOA as sacrificial electron donor,

eosin Y as photosensitizer and TiO2 as catalyst.

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 literature. 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 [3]. With this polyelectrolyte combination we target a suitable soft matter matrix to perform photocatalytic investigations.

References

[1] Petersen, M. et al. (2021). Hydrogen Evolution Reaction with Sunlight for School Chemistry Education. WJCE 9/4, 190–196. [2] Bakbolat, B., et al. (2020). Recent Developments of TiO2-Based Photocatalysis in the Hydrogen Evolution and Photodegradation: A Review. Nanomaterials (Basel, Switzerland) 10/9. [3] Alonso, T., et al. (2013). Study of the multilayer assembly and complex formation of poly(diallyldimethylammonium chloride) (PDADMAC) and poly(acrylic acid) (PAA) as a function of pH. Soft Matter 9/6, 1920–1928. [4] Hofstein, A., Lunetta, V. N. (2004). The laboratory in science education: Foundations for the twenty-first century. Sci. Ed. 88/1, 28–54.

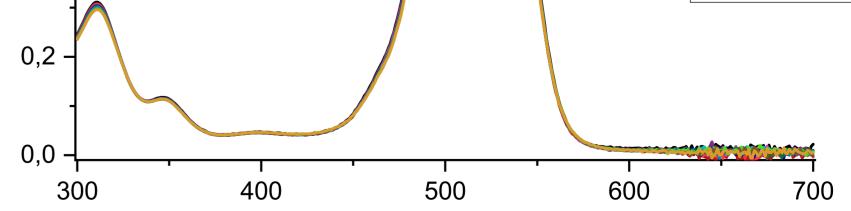
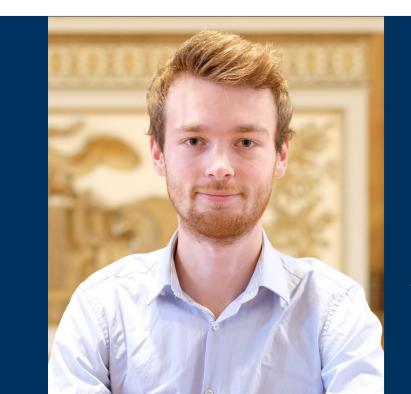


Fig. 4: UV/vis spectra of different kinetic investigations, c(eosin Y) = 22.2 μ M, c(TiO2) = 83.4 μ M, c(TEOA) = 83.3 mM. (A): Sample A (c(PAA) = 0.17 μ M, c(PDADMAC) = 0.23 μ M), (B): Sample B (c(PAA) = 0.34 μ M, c(PDADMAC) = 0.46 μ M), (C): Sample C (c(PAA) = c(PAA) = 0.51 μ M, c(PDADMAC) = 0.69 μ M), (D): Sample A without TEOA.



Malte Petersen Research Assistent Friedrich Schiller University Jena Chemistry Education Department

Chemistry Education Department August-Bebel-Str. 2, D-07743 Jena m.petersen@uni-jena.de All authors would like to thank the Deutsche Forschungsgemeinschaft (Transregio SFB TRR 234 CATALIGHT, projects B5 and Ö1).



FRIEDRICH-SCHILLER-UNIVERSITÄT JENA