Experimental Approach for Efficiency Determination of Photocatalytic Hydrogen Evolution

Philipp Lanfermann[1], Christoph Weidmann[1], Janina Dege[1], Steven Celik[2],
Alexander Tasch[1], Mona Christin Maaß[1], Thomas Waitz[1,*]

[1]Institute of Inorganic Chemistry, Department of Chemistry Education, Georg-August-Universität Göttingen, Germany
[2]Institute of Physical Chemistry, Georg-August-Universität Göttingen, Germany
*Corresponding author: twaitz@gwdg.de

Abstract This paper presents two related experiments aimed at determining the efficiency of photocatalytic hydrogen production on ZnS/CdS nanoparticles. In the first experiment, the method of chemical actinometry is applied to measure the number of light quanta emitted by the UV LEDs used. This utilizes the formation of an iron(II)-1,10-phenanthroline complex (ferroin), the concentration of which can be determined photometrically. In the second experiment, hydrogen is produced on prepared ZnS/CdS with the aid of these LEDs, the yield is determined by collecting the generated volume of hydrogen gas and the efficiency is calculated.

Keywords: actinometry, nanoparticles, hydrogen evolution, photocatalysis

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1. Introduction

Hydrogen is considered to be an important fuel for future energy supply, since its generation from renewable sources enables efficient storage and transportation of energy from sources like wind and solar energy [1]. The production of hydrogen from solar energy is often associated with electrolysis which makes use of electrical energy from photovoltaics to reduce water electrochemically. A one-step process without intermediate use of electricity involves the direct hydrogen evolution on semiconducting particles, the so called photocatalysts. Such processes are currently not commercially used but discussed in both scientific and educational publications with connection to an education for sustainable development [2,3].

Herein, we demonstrate a combination of an actinometry experiment with photocatalysis on ZnS/CdS to calculate photocatalytic efficiency. Therefore, we present a facile synthesis of a suitable photocatalyst and an experimental setup to measure the efficiency of the fabricated photocatalyst.

For this purpose, in a first step the number of emitted photons from the UV LEDs is determined by chemical actinometry (see 2.2.), which in a second step provides the energy for a photocatalysis to produce hydrogen. The gas is collected in order to calculate the efficiency of the reaction.

2. Photocatalysis and Efficiency Determination

2.1. Basics of Photocatalysis

Photocatalysis refers to the process of catalyzing a reaction in the presence of light and photocatalysts.
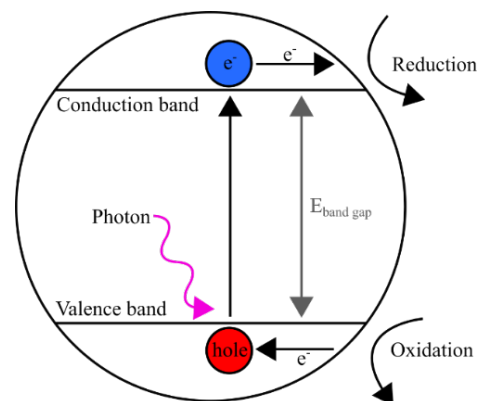
Figure 1. Schematic illustration of a semiconductor photocatalyst.

Semiconductor nanoparticles can act as such photocatalysts [4]. When particles are irradiated with light of sufficient energy, electrons can be excited from the valence band into the conduction band. This requires that

the band gap is smaller than the energy of the absorbed photons. The excited electron and the remaining hole – also called electron hole pair or exciton – are subsequently able to carry out redox reactions.

2.2. Actinometry and Efficiency Determination

The efficiency determination requires the number of irradiated photons and the amount of product. The former can be measured by chemical actinometry using potassium ferrioxalate in the presence of 1,10-phenanthroline. In this complex, the iron(III) ion can be reduced to iron(II) upon irradiation (see below) which causes the formation of a colored Fe(II)-1,10-phenanthroline complex.

$$2\left[Fe\left(C_2O_4\right)_3\right]^{3-} \rightarrow 2\left[Fe\left(C_2O_4\right)_2\right]^{2-} + C_2O_4{}^{2-} + 2\,CO_2$$
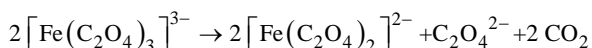
The phenantroline complex is intensely red and allows photometric determination of the Fe(II) concentration by UV/VIS spectroscopy using the Beer-Lambert law.

$$A = \varepsilon \cdot c \cdot d$$

According to literature, it can be assumed that approximately 1.2 Fe(III) ions are reduced per absorbed photon at the used wavelength (quantum yield) [5]. Since all emitted photons at 400 nm are of sufficient energy to drive the reaction, this correlation allows the calculation of the number of irradiated photons.

To calculate the subset of photons triggering a reaction in the actual photocatalytic process, the volume of generated hydrogen is measured, and the amount of substance is calculated using the ideal gas law. It must be noted here that two protons are reduced to produce one hydrogen molecule and thus two moles of photons are required for one mole of hydrogen gas. Twice the amount of hydrogen produced divided by the number of total photons irradiated onto the solution yields the efficiency ξ of the reaction.

$$\xi = \frac{2 \cdot \dfrac{n_{H_2}}{t}}{\dfrac{n_{h \cdot v}}{t}} \cdot 100\%.$$

3. Experimental Procedure

3.1. Actinometry

In this section, we describe the preparation of the required solutions for the actinometry experiments followed by the determination of a calibration curve. Subsequently, we describe the calculation of the molar decadic absorption coefficient of the solution in order to determine the number of emitted photons of the UV LEDs used by actinometry.

3.1.1. Determination of a Calibration Curve and Calculation of the Molar Decadic Absorption Coefficient

To obtain the calibration curve and thus determine the molar decadic absorption coefficient, the absorbance of a series of defined phenanthroline complex concentrations is measured.

Equipment: Standard cuvettes, UV-VIS spectrometer, precision balance, pipette, beakers, magnetic stirrer, stirring bar, büchner funnel, suction flask, filter paper.

Chemicals: Demineralized water, ammonium acetate, aqueous 1,10-phenanthroline solution (c = 0.007 mol/L), ammonium iron(II) sulfate · 6 H_2O, concentrated sulfuric acid, sulfuric acid solution (c = 0.05 mol/L).

Procedure: Preparation of buffer solution: 4.62 g (60 mmol) ammonium acetate are dissolved in 50 mL water and acidified with 1 mL concentrated sulfuric acid and then filled up to 100 mL.

Preparation of the ammonium iron(II) sulfate solution: 0.078 g (0.2 mmol) ammonium iron(II) sulfate is dissolved in 50 mL of water, acidified with 1.4 mL concentrated sulfuric acid and then filled up to 500 mL.

Seven cuvettes are prepared. Each contains 1.5 mL of demineralized water, 2.5 mL of the buffer solution and 1 mL of the 1,10-phenanthroline solution. In addition, sulfuric acid solution and ammonium iron(II) sulfate solution of different volumes are added to the solutions (see Table 1). The absorbance of each sample is then measured.

Observations:

Table 1. Measured absorbances.

Concentration of the phenanthroline complex / 10^{-5} mol/L	Absorbance at 400 nm
0	0.00
1.99	0.08
3.98	0.14
5.97	0.22
7.96	0.28
9.95	0.36
11.90	0.43

Calculations: The absorption coefficient is obtained from the absorbance by rearranging the Beer-Lambert law:
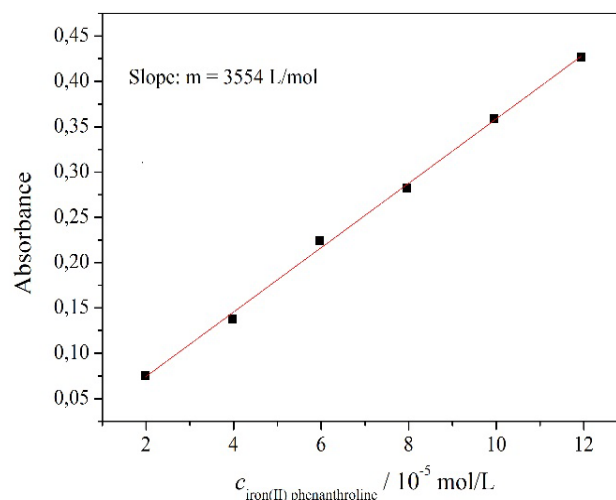
$$\varepsilon = \frac{A}{c \cdot d}$$

Figure 2. Plot of the iron(II) phenanthroline concentration against the absorbance measured in a standard cuvette with a thickness of 1 cm.

Thus, by plotting the concentration of iron(II) phenanthroline against the absorbance, the molar decadic absorption coefficient is obtained from the slope (see Figure 2):

$$\varepsilon = 3554 \ \frac{\text{L}}{\text{mol} \cdot \text{cm}}$$

3.1.2. Photon Number Determination

In this experiment, the number of photons emitted by the LEDs is determined via actinometry.

Equipment: experimental setup (see Figure 5), Standard cuvettes, UV-VIS spectrometer, pipette, LED lights (4 Avonec 3 W High Power LEDs in series connection operated at 14 V instead of 18 V which results in a total power of 8.5 W. Under these conditions the LEDs can be passively cooled using an aluminum heat sink. The emission spectrum can be found at https://avonec.de/images/390nm-400nm.jpg.).

Chemicals: sulfuric acid solution ($c = 0.05$ mol/L), potassium ferric oxalate, buffer solution, 1,10-phenanthroline solution ($c = 0.007$ mol/L).

Procedure: For the following steps, exposure to ambient light should be avoided since the ferric oxalate solution is sensitive to light (see 2.2.).

In a first step, 200 mL of a 0.05 mol/L sulfuric acid solution is mixed with 1.96 g of potassium ferric oxalate, which is filled into the round-bottom flask of the experimental apparatus. 1 mL of this actinometric solution is taken as a reference and mixed with 1 mL 1,10-phenanthroline solution, 2.5 mL buffer solution, 4 mL sulfuric acid solution and 1.5 mL demineralized water. The LEDs are turned on for 10 seconds and to monitor the evolution of iron(II) ions, 1 mL of the solution is removed and treated as above. This step is repeated ten times. The absorbance of all samples is then measured by UV/VIS spectroscopy.

Observations: The intensity of the red color correlates with the illumination time. The absorbances measured at 400 nm are shown in Table 2.

Table 1. Measured absorbances

Time / s	Absorbance
10	0.11
20	0.15
30	0.23
40	0.25
50	0.40
60	0.40
70	0.44
80	0.54
90	0.58
100	0.66

Calculations: In order to calculate the number of emitted photons of the LEDs, it is necessary to determine the amount of the formed phenanthroline complex at the different measurement times. Therefore, the following representation of the Beer-Lambert law is applied:

$$c_{\text{sample}} = \frac{A}{\varepsilon \cdot d}$$

The concentration of the complex in the measured sample and thus the concentration of iron(II) ions is used to calculate the amount of substance of iron(II) ions in the actinometric solution (as). Due to the dilution of the sample (1 mL + 9 mL), the concentration of the actinometric solution is given by:

$$c_{\text{as}} = c_{\text{sample}} \cdot 10$$

This allows the calculation of the amount of substance according to the following equation:

$$n_{\text{as}} = c_{\text{as}} \cdot V_{\text{as}}$$

The amount of substance is plotted against time (see Figure 3). The resulting slope of the linear fit describes the number of iron(II) ions produced per second.
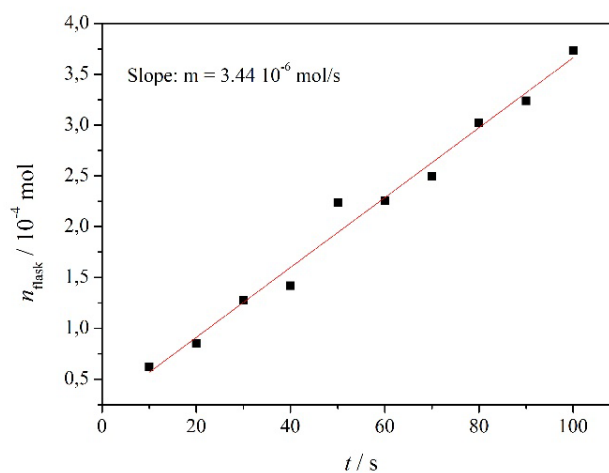

Figure 3. Plot of the amount of iron(II) ions against the time in seconds.

Combining this value and the quantum yield of the reaction (see 2.2.) results in the number of irradiated photons per second:

$$\frac{n_{h\cdot v}}{t} = \frac{1}{\phi} \cdot \frac{n_{\text{Fe}^{2+}}}{t} = \frac{3.44 \cdot 10^{-6} \ \frac{\text{mol}}{\text{s}}}{1.2} = 2.87 \cdot 10^{-6} \ \frac{\text{mol}}{\text{s}}$$

3.2. Hydrogen Evolution

After the number of incoming photons has been determined, the photocatalyst is synthesized in a precipitation reaction. This catalyst is used to carry out the photocatalytic process in order to calculate its efficiency by measuring the generated hydrogen volume.

3.2.1. Nanoparticle Synthesis

First, the photocatalyst is prepared, which consists of core-shell CdS/ZnS nanoparticles in a molar ratio of 2:1 [6].

Equipment: beakers, spatula, balance, heating stirrer, stirring bar, thermometer, büchner funnel, vacuum hose, suction flask, mortar and pestle, optional: drying oven.

Chemicals: water, acetic acid ($c = 0.1$ mol/L), cadmium carbonate, zinc carbonate, sodium sulfide.

Procedure: 1.72 g cadmium carbonate (0.01 mol) and 0.63 g zinc carbonate (0.005 mol) are dissolved in 250 mL 0.1 mol/L acetic acid solution, which was first heated to about 65 °C. Another solution at the same temperature is

prepared by adding 1.25 g sodium sulfide (0.016 mol) to 250 mL water. The first solution is then added dropwise to the sodium sulfide solution under stirring. The yellow precipitate is collected by filtration and dried either overnight at room temperature or for 3 hours at 70 °C in a drying oven.

Observations: Upon addition of the cadmium/zinc solution, a yellow precipitate is formed yielding a yellow powder after drying (see Figure 4).

Figure 4. CdS/ZnS photocatalyst after drying.

Interpretations: The dissolved zinc and cadmium ions combine with the sulfide ions to form sparingly soluble sulfide particles of nanoscale size, which precipitate.

$$Zn^{2+} + Cd^{2+} + 2\,S^{2-} \rightarrow \{ZnS:CdS\}$$
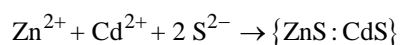
3.2.2. Photocatalytic Hydrogen Production

The previously synthesized nanoparticles are used to photocatalytically generate hydrogen. The gas is collected in order to be able to quantify the amount of substance and therefore enable the calculation of the efficiency.

Equipment: Experimental setup (round bottom flask, LEDs, gas syringe, housing, hose, hose clamps) (see Figure 5), beakers.

Chemicals: demineralized water, sodium sulfide, sodium sulfite, prepared photocatalyst (see 3.2.1).

Procedure: First, the electrolyte reaction medium is prepared. 4.68 g sodium sulfide (0.06 mol) and 11.35 g sodium sulfite (0.09 mol) are dissolved in 255 mL water. This solution is then mixed with the photocatalyst and transferred to the experimental setup. To obtain best results a thin layer of photocatalyst should cover the bottom of the flask so that almost all UV light is absorbed. The flask is then closed with a lid fitted with a tube to the gas syringe to collect the gas. Afterwards, the LEDs are switched on and the volume in the gas syringe is measured about 30 times over a two-hour period.


Figure 5. Experimental setup. Left: actinometry; right: hydrogen evolution.

Observations: As soon as the UV light illuminates the reaction mixture, gas evolution on the surface of the particles can be observed. After 30 minutes, measurable amounts of gas accumulate in the syringe. After 150 minutes, a total of 13.9 mL of gas has been accumulated (see Table 3).

Table 3. Measured volume per time in mL and calculated amount of substance.

t / s	V / mL	n / 10^{-5} mol
1800	0.7	3.10
2580	2.0	8.50
2820	2.8	11.69
3000	3.1	13.04
3120	3.5	14.38
3270	3.8	15.73
3420	4.0	16.63
3780	4.8	19.93
3960	5.1	21.13
4320	5.5	23.00
4500	6.2	25.62
4860	6.8	28.32
5280	7.6	31.47
5580	8.1	33.71
6180	9.1	37.76
6300	9.4	39.11
6720	9.9	41.35
7020	10.5	43.60
7200	11.0	45.85
7740	11.8	49.00
7980	12.3	51.24
8280	12.7	52.59
8640	13.4	55.74
8880	13.7	57.09
9000	13.9	57.99

Calculations and Discussion: The incoming UV light leads to the formation of electron (e^-) hole (h^+) pairs in the photocatalyst (see 2.1.) which is considered to initiate a complex reaction mechanism including the following most important reactions [7]:

$$\text{reduction: } 2\,e^- + 2\,H_2O \rightarrow H_2 + 2\,OH^-$$

$$\text{oxidation: } 2\,S^{2-} + 2\,h^+ \rightarrow S_2^{2-}$$
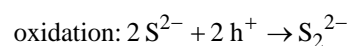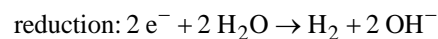
Disulfide reacts with sulfite to thiosulfate preventing the accumulation of yellow disulfide which would decrease the efficiency of the photocatalytic reaction by absorbing UV light [7]:

$$S_2^{2-} + SO_3^{2-} \rightarrow S_2O_3^{2-} + S^{2-}$$
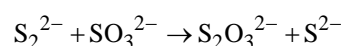
The amount of hydrogen gas is calculated using the ideal gas law:

$$n = \frac{p \cdot V}{R \cdot T}$$

Plotting these quantities against time results in a graph whose slope represents the hydrogen produced per second.
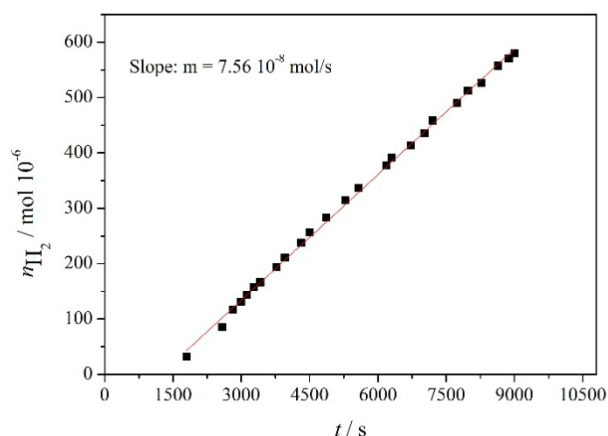
Figure 6. Plot of the amount of hydrogen in mole against time in seconds

This value and the number of photons per second derived in Chapter 3.1.2. allow the efficiency determination by:

$$\xi = \frac{2 \cdot \dfrac{n_{H_2}}{t}}{\dfrac{n_{h \cdot v}}{t}} \cdot 100\% = \frac{2 \cdot 7.56 \cdot 10^{-8}\, \dfrac{mol}{s}}{2.87 \cdot 10^{-6}\, \dfrac{mol}{s}} \cdot 100\% = 5.27\%$$

This is in good agreement with efficiency values presented in scientific literature [8].

4. Educational Perspectives

The presented experiments combine several aspects of chemistry and physics and are especially suited for advanced chemistry classes, extracurricular project courses or the education of student teachers. Embedded in the context of renewable energies and a possible future hydrogen economy, the experiments offer the opportunity to not only introduce basic chemical concepts of photocatalysis. It also emphasizes the role of efficiency in photocatalytic reactions on the example of an already described hydrogen evolution reaction. Furthermore, at least the basic mode of action of nanoscale photocatalysis can be illustrated on the basis of the experiments.

The efficiency determination using the actinometry method relies on basic principles of photometry like the Beer-Lambert law and can here be used as an application example of a scientific method in chemistry class. Even though the calculations required are manifold, they can be deduced by the students themselves with little support.

We consider this photocatalytic process to be highly valuable to stress that redox reactions are always consisting of electron transfers, i.e. coupled reduction and oxidation reactions. In this case, the excitons (electron hole pairs) in the photocatalyst mediate the reduction of water to hydrogen as well as the oxidation of sulfide, which acts as a sacrificial donor.

Implementing the complete process ranging from synthesizing the photocatalyst to determining the efficiency by relatively simple means and the agreement of this value with scientific data [8] can play an important role to motivate students in the STEM field.

5. Outlook

The experimental setup presented allows the efficiency of a wide variety of photocatalysts to be determined. This makes it possible to enable students to conduct their own comparative studies of different photocatalysts in line with the research-based learning method. The wavelength of the irradiated light can also be varied using different LEDs in order to gain insights into the efficiency of the reaction at different wavelengths.

Acknowledgements

References

[1] Preuster, P., Alekseev, A. and Wasserscheid, P., "Hydrogen Storage Technologies for Future Energy Systems," *Annu. Rev. Chem. Biomol. Eng.*, 8, 445-471, June 2017.

[2] Kosco, J. et al., "Enhanced photocatalytic hydrogen evolution from organic semiconductor heterojunction nanoparticles," *Nature Materials,* 19, 559-565, March 2020.

[3] Dege, J., *Nanotechnologie im Kontext einer Bildung für nachhaltige Entwicklung: Vom Konzept zur curricularen Innovation für den Chemieunterricht,* Georg-August-Universität Göttingen, 2019 [Dissertation].

[4] Serpone, N. and Emeline, A. V., "Semiconductor Photocatalysis – Past, Present, and Future Outlook," *J. Phys. Chem. Lett.*, 3(5), 673-677, March 2012.

[5] Demas, J. N., Bowman, W. D., Zalewski, E. F. and Velapoidl, R. A., "Determination of the Quantum Yield of the Ferrioxalate Actinometer with Electrically Calibrated Radiometers," *J. Phys. Chem.*, 85, 2766-2771, May 1981.

[6] Koca, A. and Sahin, M., "Photocatalytic Hydrogen Production by Direct Sunlight: A laboratory Experiment," *J. Chem. Educ.,* 80(11), 1314-1315, November 2003.

[7] Ka, H. C. et al., "Enhanced photocatalytic hydrogen production from aqueous sulfide/sulfite solution by $ZnO_{0.6}S_{0.4}$ with simultaneous dye degradation under visible-light irradiation," *Chemosphere,* 183, 219-228, September 2017.

[8] Lyubina, T. P. and Kozlova, E. A., "New Photocatalysts Based on Cadmium and Zinc Sulfides for Hydrogen Evolution from Aqueous Na_2S-Na_2SO_3 Solutions under Irradiation with Visible Light," *Kinetics and Catalysis,* 53(2), 188-196, April 2012.