

Photoreforming of Biomass - Producing Hydrogen from Sugar

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Abstract The future hunger for hydrogen in industry or for private cars will demand a growing production rate and will have to meet the requirements of sustainability. Photoreforming biomass to produce green hydrogen seems to be a promising way for fulfilling sustainable industrial processes. In this article the photoreforming of sugars is used as an example to implement this subject in science classes. For educational purposes an experiment is presented that demonstrates the photoreforming of a glucose solution with a TiO_2/Pt -photocatalyst. The developed gas can be examined by gas chromatography or a detonating gas test. The aim of implementing this subject in school is to pick out an innovative way of producing (green) hydrogen. Photoreforming of biomass is also a suitable context to discuss and evaluate social, environmental and economical perspectives for sustainable energy resources and industrial processes in the chemistry classroom. Students can discuss different ways of how to reach the sustainable development goals presented by the United Nations in 2015 and learn to deal with contradictions by reaching these goals. This subject is therefore ideal for integrating education for sustainable development (ESD) in school education.

Keywords: photoreforming, hydrogen, sugar, sustainability, ESD

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1. Introduction

The production of hydrogen with the help of a photocatalyst has been studied for half a decade so far. Fujishima and Honda were the first to report on the photocatalytic splitting of water in 1972 [1], using titanium dioxide. Another approach is the photocatalytic generation from organic compounds with TiO_2 such as methanol, glucose, starch and even cellulose, as reported in the works of Kawai and Sakata in 1980 [2]. By now this subject has gotten increasingly attractive for today's development of sustainable energy resources. The intended aim was to use the processes of photosynthesis in which high energy carbohydrates are formed from water and carbon dioxide and to reform the carbohydrates to clean fuels in the hydrogen energy system [2]. Even though an industrial production of hydrogen by means of photocatalysis is not that far in reach, the potential of developing and using photoreforming is high to satisfy the needs of hydrogen in the future. Especially the fuel cell-technology with the growing market of cars with alternative drives and the steel production will require a constantly high supply of (green) hydrogen.

2. Photoreforming Processes

The photoreforming of hydrogen from biomass feedstocks needs a suitable photocatalyst. The process of photoreforming

is not yet fully identified in detail for every bio substrate. But there are several proposed mechanisms for alcohols, sugars and natural polymers, which show the fundamental processes during photocatalysis [3].

They all have in common, that a photocatalyst is needed to absorb light energy, whose working principle is shown in Figure 1. In [2] a $\text{RuO}_2/\text{TiO}_2/\text{Pt}$ photocatalyst powder was used with higher efficiencies compared to the use of TiO_2 only. After the absorption of photons by the semiconductor, electrons are transferred to the conduction band, forming electron-hole-pairs which then cause redox reactions to take place. The hole (electron deficit) in the valence band can be filled by an electron via the oxidation of a substrate molecule ($\text{D} \rightarrow \text{D}^+ + \text{e}^-$). The electron in the conduction band is transferred to an acceptor molecule, which is thus reduced ($\text{A} + \text{e}^- \rightarrow \text{A}^-$). The semiconductor TiO_2 (e.g. P25, which contains a mixture of anatase and rutile TiO_2) absorbs light in the near UV-spectrum at wavelengths below $\lambda = 388 \text{ nm}$, and is used as a common photocatalyst. An animation for this process is also shown on the website of the department of chemical education of the University of Wuppertal (https://chemiedidaktik.uni-wuppertal.de/fileadmin/Chemie/chemiedidaktik/files/html_5_animations/cbl_group/photocatalysis/photocatalysis.html).

Photocatalysts that absorb visible light are sought after in order to optimize the process of photoreforming. There are several photocatalysts with cocatalysts that can be used in this process like TiO_2/Pt -, TiO_2/Au -, TiO_2/Pd -photocatalysts [4] or $\text{Co}/\text{CdS}/\text{CdO}_x$ -photocatalyst [5]. When a cocatalyst like platinum is added to the surface of

TiO₂-particles, after the formation of electron-hole-pairs the electron in the conduction band is transferred to the platinum deposit on whose surface reduction processes then take place. The role of the platinum or

other noble metal deposits is the easy charge migration and separation of electrons from the conduction band of TiO₂ into the metal's conduction band, where protons are reduced [4].

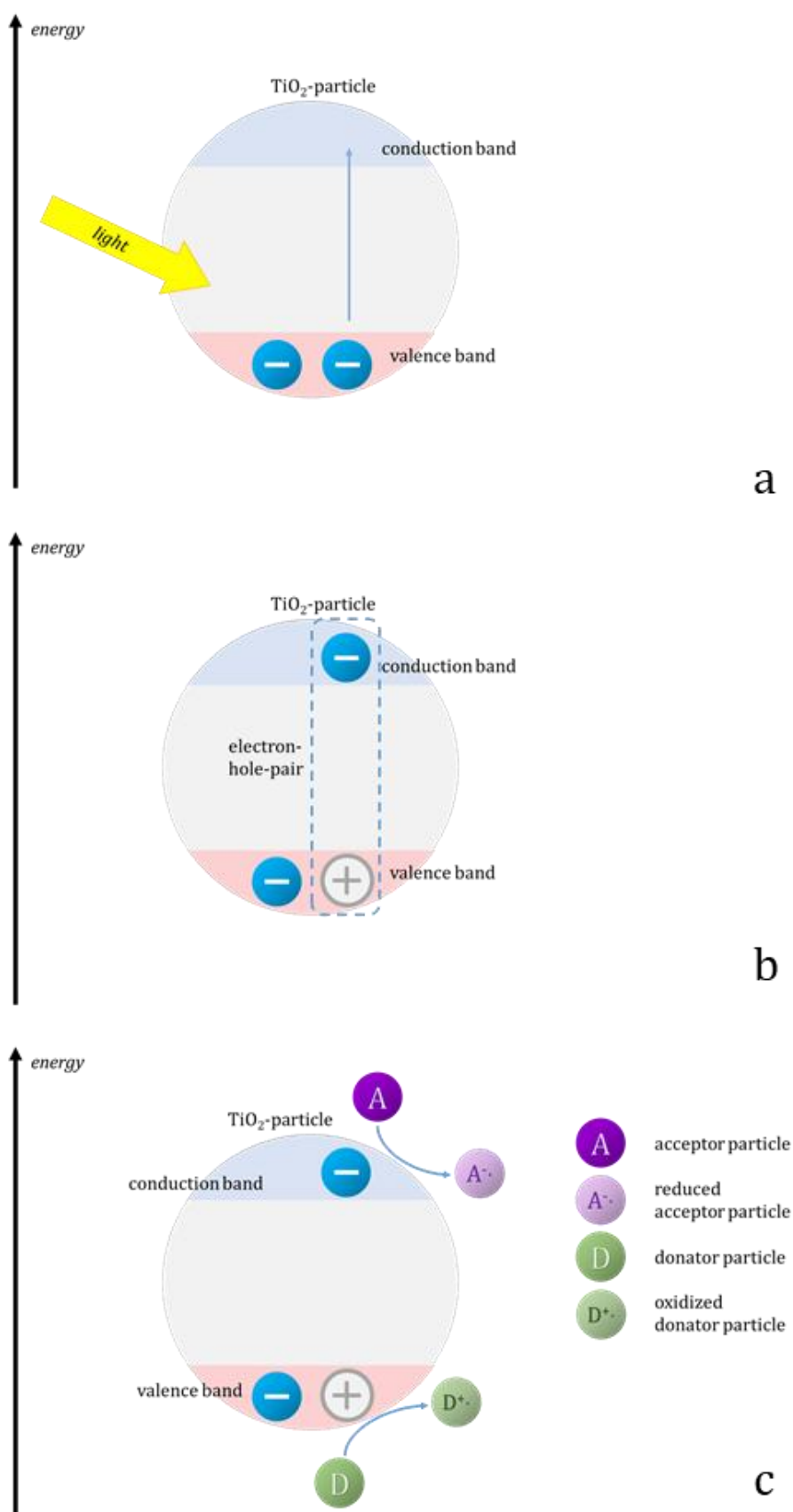


Figure 1. Schematic representation of the processes in a photocatalyst. a. light excitation, b. electron-hole-pair, c. redox reactions at the activated semiconductor

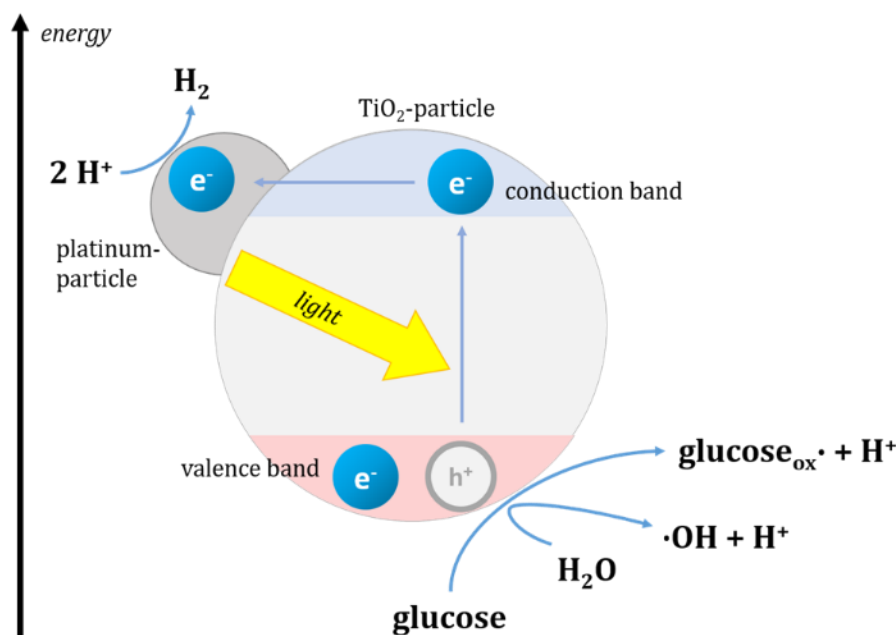
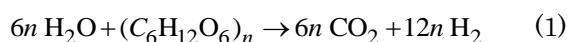


Figure 2. Simplified schematic representation of the photoreforming process of glucose

There are two crucial reactions for the generation of hydrogen via photoreforming, just like in artificial photosynthesis. The first one is the oxidation of water molecules, the second one is the reduction of protons. These protons are also delivered by organic substrates during the oxidation of substrates [3,4]. Glucose as a substrate is oxidized to smaller sugars like arabinose and erythrose, as well as formic acid [5,6] and other degradation products during the photoreforming process. A schematic illustration is shown in Figure 2. The ideal reaction (1) of the photoreforming of glucose that was first proposed by Kawai and Sakata was the reaction of glucose to hydrogen and carbon dioxide [2].



The different reaction products and steps that lead to various degradation products during photoreforming is not easy to be completely identified. One of several advantages of the photoreforming of glucose or biomass are the relative mild conditions like room-temperature or a slightly elevated temperature (30 °C – 60 °C) for this process [5].

3. Experiment

In this paper we present an experiment on the generation of hydrogen from glucose using a TiO₂/Pt-photocatalyst, which can be carried out in undergraduate courses of higher secondary education at schools.

3.1. Preparation of the Photocatalyst

The first step to set up this experiment into practice is the generation of the TiO₂/Pt-photocatalyst. A suspension of 1000 mg TiO₂ powder (P25) and 60 mL water are stirred while a lamp with a high amount of UV-radiation (Osram Ultravitalux, 300W) is turned on already. UV-protection goggles should be worn respectively.

150 μL of a H₂PtCl₆-solution (c = 1,54 mol/L) and 150 μL of the reducing agent triethanolamine solution (c = 1,5 mol/L) are added and irradiation continues for 5 minutes. The residue is filtered, washed with distilled water and dried in air. This light grey solid is now ground in a mortar and ready for use.

3.2. Main Set-up

The set-up of the photoreforming apparatus is shown in Figure 3. A glucose solution (c = 0,55 mol/L or 100 g/L) is heated to approximately 60 °C to drive out dissolved gas. The solution is added to a glass vessel with thread already containing 70 mg of the Pt/TiO₂-photocatalyst. The vessel should be filled up to the neck of the glass. The glass is closed with a pierced plug and the lid of the vessel. The developing gas during the photoreforming process is collected by a pneumatic setting as shown in Figure 3e. The water is also heated to reduce the amount of dissolved gas. The glass vessel with the suspension is set into a pneumatic bath that should have a temperature of 60 °C. A syringe without piston is placed above the aperture of the glass vessel and a two-way stopcock is put on top. With another syringe water is filled into the first syringe and the two-way stopcock is closed. For the irradiation of the substrate/photocatalyst suspension a lamp with a high quantity of UV-radiation (Osram Ultravitalux) is positioned at a distance of 5 cm from the setting. The gas that is developed in the first 10 minutes is discarded, because it consists mainly of gas from the dead volume of the apparatus. After 45 minutes of irradiation 10 mL of gas can be collected.

3.3. Examination of the Obtained Gas

About 6 mL of the colourless gas is mixed with 3 mL oxygen in a syringe. This mixture is then used in a detonating gas test (Figure 4).

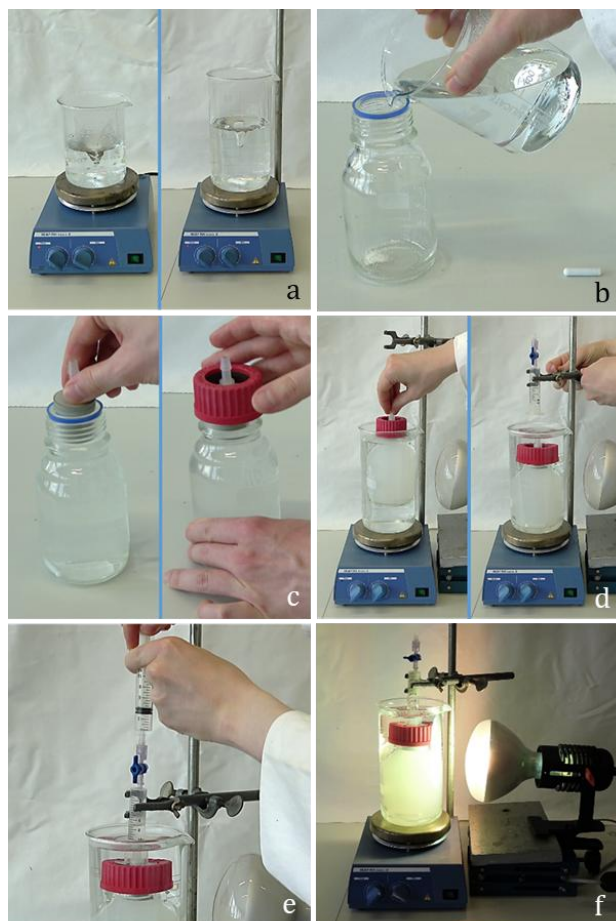


Figure 3. a. driving out dissolved gas from the glucose solution by heating, b. adding glucose solution in the glass vessel with the Pt/TiO₂-photocatalyst, c. closing the vessel with a pierced plug and cover, d. placing the glass vessel with the suspension into the pneumatic bath and a syringe without piston and a two-way stopcock on its top, e. filling the first syringe with water with the aid of a second syringe, f. irradiation of the substrate/photocatalyst suspension

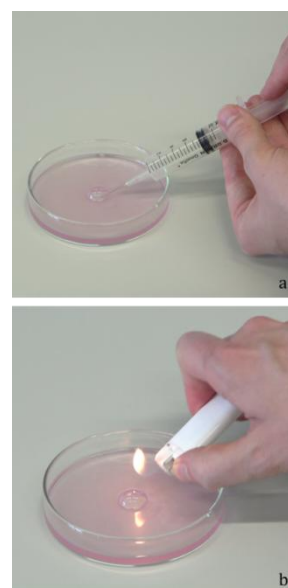


Figure 4. Set-up of the detonating gas test. a. inserting 1 mL of the gas mixture in a soap solution, b. igniting the gas mixture

The gas portion also can be examined by gas chromatography (Figure 5) to identify the gas as hydrogen and to find out about the amount of hydrogen gas in the collected gas portion in comparison to pure hydrogen gas as a reference. Long term irradiation of suspensions showed that after five hours almost 40 mL of hydrogen were produced (Figure 6). The gas volume after one hour suffices to easily perform a detonating gas test or to carry out three to five runs of gas chromatography. During an irradiation of 5 hours gas portions of about 10 mL were taken in intervals from the apparatus and analyzed by gas chromatography. The gas chromatography showed that with increasing time the amount of hydrogen in the gas portion rose from approximately 70 % to 85 %. The detonating gas test after 5 hours gave a characteristic sound for hydrogen.

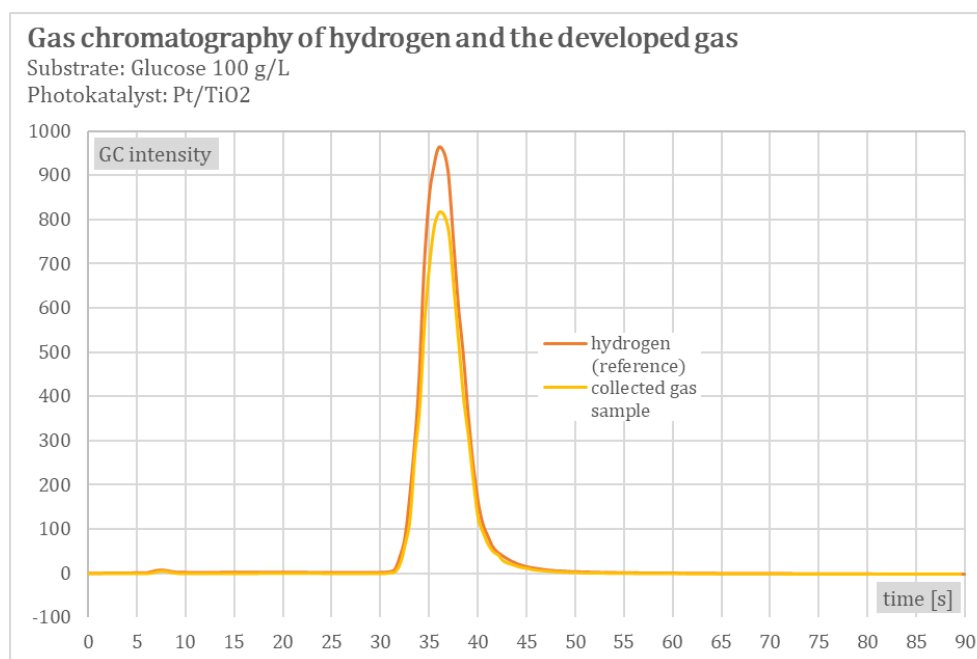


Figure 5. The peak caused by the collected gas appears after the same retention time as that of a control portion of hydrogen from a gas bottle

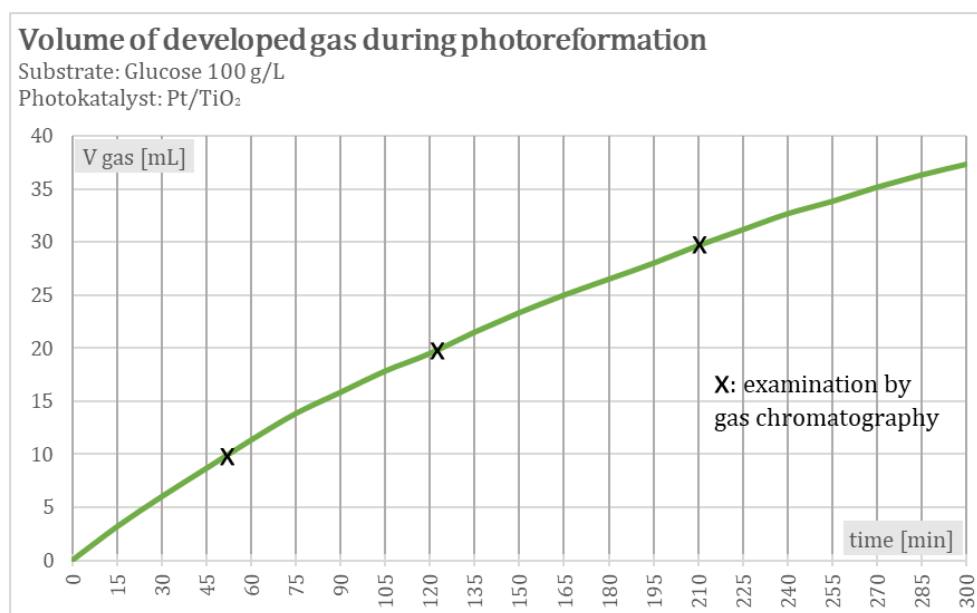


Figure 6. Volume of the collected gas during the photoreforming of glucose

4. Photoreforming and Education

The transformation from crude oil-based energy systems to a technology that promotes alternative drives is based on the use of regenerative energy resources like wind, water and solar power to produce chemical energy storages like hydrogen. It is one of several approaches to face today's global energy problems. The sustainability development of ecologic, economic and social processes is the heart of the Agenda 2030 [7] which was declaimed by the UN in 2015. The 17 sustainable development goals with their 169 targets intend to give perspectives for fulfilling these aims until 2030 on a global scale. In this transformation process the implementation of education for sustainable development (ESD) plays a major role. ESD is set by the UNESCO as a key enabler for all SDGs and a key element for quality education on sustainability [8].

4.1. Photoreforming in Science Class

The photoreforming of sugars or biomass in general is therefore an innovative and relevant example for one of several ways of (green) hydrogen production. It is a topic to be discussed with students regarding the use and limits of new production methods to satisfy the growing global demands of energy provision. The inclusion of experiments of photoreforming processes in education, especially in chemical education, provides the possibility to discuss and evaluate social, environmental and economical perspectives on sustainable energy resources. For a broad understanding of different production methods of hydrogen for industrial purposes or the transport sector it is important that students get to know different ways of production processes to reach goals like an affordable and clean energy system. The use of hydrogen in the transport system and the industrial production of steel can be profitably used in class to raise the students' awareness of the fact that social welfare today and in the future depends on both, a functionable industry as well as acting sustainably for climate protection. It's one of the main aims of ESD that

young adults have to evaluate different methods to reach these goals, but also to deal with contradictions [9]. Those contradictions can be discussed when dealing with photoreforming. Through the discussion of different ways of hydrogen production and different aims of various involved parties, the students get the opportunity to make their own decisions based on facts and reflect their own behavior [10]. Possible contradictions to be dealt with in class may be the tendency of governments to focus just on one of several forms of alternative drives. The expansion of sustainable energy sources is often accompanied by a further utilization of natural resources or the expanded exploitation and land use for the energy sector. But this use often conflicts with food production and measures to protect the environment.

This subject can be included in science classes and it is well suitable to show the different perspectives of integrating sustainable development in class. When dealing with photoreforming of sugars one should discuss also the choice of substrates. In the food industry tons of waste are produced every year. They contain marc of fruits and corn with high amounts of sugar, which can be potentially used in the energy sector. It is object of current scientific research to profit from several benefits of photoreforming food wastes in comparison with biogas like the possibility of using wet and mixed wastes, applying small and independent systems and the production of pure hydrogen [11]. For didactic purposes the experiment described here is carried out with glucose as a model substrate. This way it is easy to reproduce and glucose is inexpensive and easily available for schools. Nevertheless, the generation of energy from waste should be discussed in this context.

4.2. Costs of the Experiment

Several advantages make this experiment easy to carry out in science or chemistry classes. The simple set-up can be easily put to practice and the substances used are non-hazardous. A critical point for the implementation of new experiments are the costs. All materials are commonly

available in school chemistry labs. The lamp (Osram Ultravitalux) is available for about 40 €. Chemicals like glucose are cheap. The bottleneck is the preparation of the photocatalyst: Although the costs of the needed 70 mg photocatalyst amount to only 0,11 €, a H_2PtCl_6 -solution (8 wt % in H_2O) for the production of the photocatalyst has an average price of 20 € per mL, the smallest size of a package being 10 mL. This amount of H_2PtCl_6 -solution could be used to produce more than 60 g photocatalyst, which may be sufficient for more than 900 experiments. It seems to be the highest barrier for the implementation in school yet. Teacher visiting our teacher workshops will be provided with readily prepared photocatalyst.

5. Outlook

Besides the photoreforming of sugars for an educational purpose the next step for the wider implementation of photocatalytic processes is the photoreforming of natural polymers such as starch or cellulose. Both substances need a breaking down into their monomers before the actual photoreforming process. Further investigations need to explore the influence of different light sources like UV-LEDs with a smaller range of light radiation in the near UV-field. The benefit of LEDs is a higher efficiency and the use of a perfectly fitting spectral range in the absorption maximum of TiO_2 . The mentioned Ultravitalux lamp emits a wide spectrum of visible and invisible radiation not only in the UV-field, but also in the IR-field. Therefore, this lamp is also a light source that heats up the setting, which in this experiment has shown to be a favorable effect. Thermal processes in addition to photocatalytically-driven ones have to be observed in further studies to identify their influence on photoreforming processes, as thermal as well as photochemical processes take simultaneously place in other photoreforming processes, too. So, an optimal temperature range between 30 °C and 60 °C is proposed. The interplay of light and temperature will be investigated by variation of temperatures and wavelengths.

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