Education for Sustainable Development and Experiments involving Titanium Dioxide

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Abstract The semiconductor titanium dioxide is used in a wide field of applications. The application as food additive has been under debate as it might be potentially carcinogenic. Therefore, experiments should be modified in order to prevent students from having direct contact with the substance. Three experiments relating to different fields of application are proposed in this paper. Accompanying teaching materials have the sustainable development goal 13 “climate action” as a leitmotif. The debate about titanium dioxide is a good didactic anchor to promote education for sustainable development (ESD) in school education in a multi-perspective approach.

Keywords: sustainability, ESD, SDG13 climate action, titanium dioxide, photoprocesses, photoreforming, photocatalysis


1. Introduction

For decades titanium dioxide has been used in everyday applications such as white pigment in paints with the colour index CI 77891, in cosmetics and for sun protection, in drugs, as food additive E171, as photoactive component in alternative solar cells and as photocatalyst for photochemical processes. Several experiments, digital media and teaching units with titanium dioxide have been proposed for school chemistry and for academic school labs [1,2,3,4,5,6]. Titanium dioxide has been considered attractive for school chemistry as it is available at low costs, connections to everyday life are possible and the experiments can be carried out in the context of properties and applications of nano materials which are a compulsory content in most German chemistry curricula for high schools. This last aspect has been the basis for a reevaluation of and discussions about titanium dioxide.

Since 2016 there have been doubts about the use as E171, as it was not clear if titanium dioxide was potentially genotoxic. Genotoxicity can possibly lead to carcinogenic effects, so it is essential to assess the potential genotoxic effect of a substance in the process of working out statements about possible hazards and recommended procedures. It is specifically nano-sized titanium dioxide which might be potentially hazardous as it is likely able to pass the intestinal barrier and maybe even the blood-brain barrier. In many discussions this assumption has been generalized and applied to the substance titanium dioxide regardless of the titanium dioxide particles’ size. In 2017 the EU chemicals agency ECHA’s Risk Assessment Committee classified titanium dioxide as "probably carcinogenic by inhalation" (H351). As a consequence, titanium dioxide was forbidden as food additive in some countries, e.g. in France. In January 2022 the use of titanium dioxide as food additive was finally forbidden for all European countries by the European Commission because of it being labeled as potentially carcinogenic by inhalation. The use of titanium dioxide in other applications was not included in the ban. In Europe the “Titanium Dioxide Manufacturers Association” (TDMA) represents the most important producers of titanium dioxide. They countered the court’s decision, stating, that the studies that had been considered were based on the effect of uncommonly high concentrations of titanium dioxide in the lungs of rats that were exposed to it by inhalation. As workers were not exposed to comparably high doses, the observed effect in the lungs could not be replicated in humans. In November 2022 the European Court (EuGH) withdrew its prior decision with the argument, that it had been based on wrong assumptions, neglecting that titanium dioxide agglomerates in most cases and is not intrinsically genotoxic as a substance [7]. Right now titanium dioxide is still forbidden as food additive but needn’t be labelled carcinogenic by inhalation unless it is a powder with at least 1 % TiO2 in particles with a diameter of less or equal 10 µm.

This case shows how difficult it is to come to correct statements about a substance and that a very differentiated view is necessary. It can be used to promote an understanding about different positions being results of differing interests from different groups such as health organisations, the chemical industry or politics.

With regard to school, the discussion about titanium dioxide is a good didactic anchor for promoting education...
for sustainable development (ESD). ESD addresses, among other aspects, the ability to cope with living with uncertainties and to learn to adopt a multidimensional perspective on various aspects of life. ESD contributes to fulfilling SDG 4 “Quality Education” and it is directly referred to by ESD 4.7. “By 2030, ensure that all learners acquire the knowledge and skills needed to promote sustainable development, including, among others, through education for sustainable development and sustainable lifestyles, human rights, gender equality, promotion of a culture of peace and non-violence, global citizenship and appreciation of cultural diversity and of culture’s contribution to sustainable development” [8]. In teaching units at school teachers should also address more SDGs to make their students aware of the necessity of climate action (SDG 13), of ways of contributing to clean water and sanitation (SDG6), to protect life on land (SDG 15) and life below water (SDG14), just to name a few. It is also vital that in university education, especially in teacher training programs, the students also experience learning opportunities in the field of ESD as they are the future multipliers.

This paper aims at proposing three experiments with titanium dioxide and teaching materials that can be linked to ESD. As a leitmotif for the teaching materials we chose the SDG 13 “climate action” and integrated tasks that address the three competence areas Recognising, Assessing and Acting, as referred to by the Curriculum Framework “Education for Sustainable Development” by the German Standing Conference of the German Ministers of Education and Culture (KMK) as well as the German Federal Ministry of Economic Cooperation and Development (BMZ) [9].

2. Experiments

In this section, three experiments are proposed in which titanium dioxide TiO₂ Aerioxide® P25 (CAS:13463-67-7) is either agglomerated and suspended or placed in a closed set up, e.g. the pure substance is locked in a box or fixed in an organic matrix. Thus the experiments can be carried out by the students, as the respective set-ups prevent students from direct exposure to the nano material. The topics that can be addressed are the conversion of UV into IR radiation as it takes place in physical sun screens to protect human tissue from UV-exposure, the cleaning of air via photocatalysis and the generation of green hydrogen via photo-reforming in order to reduce carbon dioxide emissions. They allow links to SDG13 “climate action” as can also be seen in the teaching materials.

2.1. Absorption and conversion of UV light by titanium dioxide

Semiconductors such as titanium dioxide or zinc oxide are used as UV blockers in suntan lotion. The use of nano-scale particles has become established, because these products leave a transparent film on the skin rather than a white one. Titanium dioxide absorbs the UV radiation reaching the skin and converts it into infrared radiation. The thermal energy is not perceptible on the skin, but it can be made visible with a thermal imaging camera. The energy conversion can be shown in a simple student experiment using a small heap of titanium dioxide powder [6]. This set-up had to be optimized from an open to a closed setting to prevent the students from potentially coming into contact with the powder, even though it is slightly agglomerated. So here we present the set-up in a new version transferred to a closed plastic box (Figure 1, left).

**Procedure:** The experiment uses a small-format thermal imaging camera (e.g. Seek Thermal) that can be controlled by a mobile device via a free app. The thermal imaging camera is directly pointed at the titanium dioxide powder through a hole in the lid of the plastic box. Through a second hole in the lid the beam of a UV flashlight (λ < 365 nm) is directed onto the powder in the camera’s field of vision. After calibrating the camera, the titanium dioxide powder is then irradiated for 1-2 minutes.

**Observation:** At the point where the UV light irradiates the titanium dioxide powder, the development of heat can be observed, cf. the reddish-white coloration in Figure 1. The experiment can be repeated with white and differently colored light using a multi-colour LED-based flashlight, but in these cases no changes in temperature can be observed.

**Figure 1.** Left: Set-up in a closed box with flashlight (left hole) and thermal imaging camera (right hole); Right: Thermal image of the heat light sources titanium dioxide can only absorb UV light. The absorption of UV-light by the semiconductor is followed by conversion into IR radiation, which can be made visible to the human eye via the thermal imaging camera. In this process, it is not the UV light source itself that emits heat. This interpretation has been offered to us in various teacher trainings and activities with students. To counter this frequently observed misconception, the experiment can be extended by irradiating the empty box without titanium dioxide and no evolving heat can be detected.

2.1.2. Immobilization of the nano titanium dioxide in an organic matrix

In order to prevent the inhalation of nanoscale titanium dioxide particles the photocatalyst can be immobilized in an organic matrix based on a starch/PVA film that can be obtained in a few steps.

**Procedure:** 5 g of polyvinyl alcohol (PVA) are dissolved in boiling water under constant stirring. In a kitchen mixer (or with a magnetic stirrer), 5 g starch, 4 g
glycerol and 1.5 g titanium dioxide nanoparticles are mixed with 100 mL water for 60 min. Both components are then mixed together for another 60 min under constant stirring. The mixture can then be spread in a big petri dish and left in a drying oven at 60°C for 24 h. The resulting films can then be carefully stripped from the Petri dish.

Discussion: The titanium dioxide film has a smooth, glossy, flexible structure and is moldable. In addition to its photocatalytic property, the film shows the same results as the heap of titanium dioxide in 2.1.1 when irradiated with UV light and observed via a thermal imaging camera, so it can also be used for this experiment (Figure 2). Additionally, a greyish-blue coloration of the film can be seen after irradiation, which is evidence of its photoactivity. On the surface of the titanium dioxide particles, irradiation with UV light causes a small amount of oxygen ions to be oxidized to oxygen molecules, with titanium(IV) atoms being reduced to titanium(III) atoms. This leads to a temporary coloration or graying of the pigment at the surface. However, this phototropy is reversible by exposure to atmospheric oxygen. This effect is particularly evident when, as in this case, the titanium dioxide particles are embedded in a thin film. But also in suspension, as in the photoreforming experiment in 2.3, a discoloration of the titanium dioxide particles becomes visible after an extended irradiation.

Due to its flexibility, the titanium dioxide film can be used in various set-ups for photocatalysis, even in an aqueous medium mentioned above, though it is subject to hydrolysis after some time.

2.2. Photocatalytic Degradation of Air Pollutants

The basics of photocatalysis have already been presented in many publications, e.g. [3,10] and therefore will be explained in this paper only very briefly. The first step is the absorption of UV radiation by the photocatalyst titanium dioxide, which leads to the generation of electron-hole pairs in the semiconductor. Electrons e' as well as holes h' can take part in redox reactions, which would not be possible elsewise. So even endergonic photoredox reactions are possible. These processes can be used for the degradation of pollutants. As already shown, pollutants dissolved in water can be degraded via heterogeneous photocatalysis [5,13]. The dye methylene blue is often used as a model substance in school experiments to illustrate the degradation of the dye by a visible fading of the blue color of the solution [13].

In everyday-applications the photocatalytic properties of titanium dioxide nanoparticles can also be used in wall paint to enable the degradation of atmospheric air pollutants, such as nitrous fumes NOx. This application has already been explored in numerous studies [14,15,16] and therefore photocatalysts have become a typical component of photocatalytic paints for exterior facades in inner cities. The possible redox reactions on the surface of the photocatalyst are shown in a simplified way in Figure 3.

![Figure 2](image)

Figure 2. Left: Films before and after irradiation with UV light, Right: Thermal image of the film irradiated with UV light: the conversion into IR radiation is clearly visible in the irradiated areas of the film (Pictures: Kaltrine Kosumi).

![Figure 3](image)

Figure 3 Simplified reaction equations of the photocatalytic degradation of nitrogen oxides according to Laufs et al. [17].

A series of school experiments has already been published on the degradation of atmospheric pollutants in the presence of the photocatalyst titanium dioxide, e.g. [4]. In order to minimize the risk of getting into contact with nitrous fumes and titanium dioxide powder, the experiments have been optimized and the set-ups simplified. Using medical technology, the nitrous fumes are directly collected in a syringe during their evolution (Figure 4 left). Then they are transferred into glass vials with a modified snap-on lid for the irradiation and the subsequent detection (Figure 4 middle). We recommend the teacher to carry out the production and the first transfer of the nitrous fumes.

Preparation: A total of 5 glass vials prepared with LUER-Lock connection (Figure 4 middle) are required. The degradation of nitrogen oxides can be detected qualitatively using commercial nitrite test strips or the Griess test for dissolved nitrates and nitrates. In the Griess test a pink-to red azo dye is formed when nitrites or nitrates are present.

![Figure 4](image)

Figure 4. Set-ups of the experimental steps: Step 1: Evolution of nitrous fumes, Step 2: Irradiation with UV-light in the presence of the photocatalyst (three UV-flashlights), Step 3: Transfer of a gas portion into a vial filled with Griess reagent via a syringe (Pictures: Lisa Schnödewind).

Procedure: The left part of Figure 4 shows the set-up in which nitrous fumes are formed and collected. The equipment should be set up under the fume hood because of the hazardous gas. A plastic syringe is filled with the produced nitrous fumes and connected with the LUER-
Lock connection of the prepared glass vial containing titanium dioxide powder (Figure 4, middle). The set-up with the nitrogen oxides is irradiated for 20 minutes. Three commercially available UV-LED-flashlights (e.g., Sidiou Group UV SDO-365) around the vial are sufficient to irradiate the content from all sides and to obtain a clear observation after 20 minutes. Additionally, a second glass vial is filled with titanium dioxide and nitrogen oxides and kept in the dark as a reference for the same amount of time.

For a detection using nitrite test strips, the strips should be moistened with distilled water and then the gases can be blown onto the test strips via a syringe. For the Griess test, two glass vials for the irradiated sample and the dark sample are filled with 2 mL of Griess reagent. Then the gases of the two samples are transferred with the syringe into one vial each. As another reference sample, the concentrated nitrous fumes of the gas evolution are transferred to a third vial with Griess reagent without having TiO₂ added or being irradiated.

Observations: After 20 minutes, the comparison between the irradiated and the dark sample clearly shows that the irradiation with UV light in the presence of titanium dioxide has led to an almost colourless solution, whereas the dark sample with titanium dioxide is still pink (Figure 5). The third vial filled with Griess reagent and the nitrous fumes without titanium dioxide contains a solution which is dark pink. The observation that the dark sample also exhibited a slight decolourization is due to the fact that a certain amount of nitrous gases can adsorb on the surface of the titanium dioxide particles [18].

![Figure 5](image)

Figure 5. Left: Detection of NO₂ concentration with the Griess test, Right: Detection with nitrite test strips (Pictures: Kaorine Kosumi).

![Figure 6](image)

Figure 6. Absorption spectra of the three samples.

Interpretation: As observed by comparing the dark sample with the reference sample, the concentration of NO₂ already decreases significantly without irradiation. Nevertheless, the results show that irradiation in the presence of the photocatalyst leads to a stronger decrease. In addition to the optically visible decolourisation of the Griess test, the photoactivity of the TiO₂ can be deduced from a comparison of the absorption spectra of the irradiated and the dark samples, see Figure 6.

2.3. Production of Hydrogen Via Photo-Reforming

Photoreforming is based on photocatalytic processes. With a photocatalyst, light energy is used to convert renewable resources into products via organic photoredox reactions as described in the literature, e.g. in [12] or [19]. The aim is to generate products that could be used as basic chemicals or in the energy sector. TiO₂-based photocatalysts, usually with a co-catalyst such as platinum, are suspended in solutions which also allows the use in school experiments. The substrates for photoreforming range from alcohols [19,20,21] and sugars (glucose [20], sucrose [22]) to biomass (starch [23] and cellulose [24]) and even plastics. The aim is to use either renewable resources or organic waste (e.g. food waste or plastics, [25]). One of the products is hydrogen gas, which unlike the hydrogen obtained in steam reforming, can be regarded as “carbon-neutral” or "green hydrogen". It is attractive e.g. for the production of steel and can help to reduce carbon dioxide emissions and to transform industrial processes in a more sustainable way. Attempts to make photoreforming applicable in school contexts have already been described, e.g. regarding the preparation of the photocatalyst and with a focus on using glucose as substrate [12]. In this paper we present a more compact set up (Figure 7) using ethanol as a substrate. For ethanol, the following reaction equation can be established for the first reaction step:

$$hν(λ = 365\text{ nm})$$

$$C_2H_5OH(\text{aq})[\text{Pt/TiO}_2]H_2(\text{g}) + C_2H_4O(\text{aq})$$

We also tested a variety of possible substrates including alcohols (methanol, ethanol), sugars (glucose and sucrose) or natural polymers (starch and cellulose) as well as artificial polymers (PVA). However, we found that smaller molecules such as ethanol molecules are easier and faster to convert than natural macromolecules, which is also described in the literature [26]. As the photocatalyst needs light in the region of UV light, a number of different light sources are suitable such as Sahlmann high-power LEDs (λ = 365 nm), flashlights such as the Darkbeam B40 - pro Max or alternatively Ultravitalux lamps (Osram). The last two mentioned light sources are much cheaper than the first one, but allow similar results.

Procedure: An ethanolic solution (10 Vol %) with the Pt/TiO₂-photocatalyst suspended in it is stirred and irradiated by UV-light. The resulting colourless gas is collected and subsequently tested for hydrogen using a school-grade gas chromatograph (AK Kappenberg) (Figure 8).

The exact experimental procedure can be taken from the material on photoreforming which is available at [27].

Observations: After 30 minutes up to 13 mL of a colourless gas can be collected at room temperature (22 °C). The gas can subsequently be identified as hydrogen via gas chromatography (Figure 8). Comparative measurements with pure hydrogen gas allow...
conclusions about the amount of hydrogen in the gas sample. Repeated experimental studies showed that the proportion of hydrogen in the gas samples during photoreforming is about 95% (Figure 8). Additionally, it is possible to identify the produced gas as hydrogen in an oxyhydrogen test (gas to oxygen gas ratio: 2:1) in a soap solution.

**Figure 7.** Compact set-up for photoreforming ethanol.

Ethanol, methanol, glucose, sucrose, starch as well as PVA can be used directly in this experimental set-up. In practice, more complex compounds yield smaller amounts of gas during the same irradiation time (methanol > ethanol > glucose > sucrose > starch > PVA).

It has been experimentally determined that slightly elevated temperatures at about 60 °C increase the yield of gas [28]. These relatively mild temperatures are in a range that is feasible in chemistry classes. The compact set-up from Figure 7 also allows for an investigation about the temperature dependence of photoreforming. For this purpose, the test tube is placed in a temperature-controlled water bath.

**Figure 8.** Gas chromatography of pure hydrogen (red) and the collected gas sample (blue); Carrier gas: nitrogen, column: silicon oil with chromosorb on silica gel, temperature: 22 °C, 0.5 mL gas injected.

**3. Teaching Materials**

Via the QR code from Figure 9 there are three worksheets available that can be used to carry out and understand the experiments. On the worksheets there are also integrated additional tasks that address the three competence areas Recognising, Assessing and Acting which are relevant for ESD. The tasks addressing these competence areas are colour-coded according to the colours of the German Curriculum Framework Education for Sustainable Development [9]. Worksheet 1 offers additional material on statements from different perspectives about titanium dioxide being hazardous. Working with these the students can deepen their literacy skills regarding a consideration of the authors’ intentions and evaluating information sources. They get an insight into the necessity to live with uncertainties connected with materials used for photocatalysis, which is understood to be a contribution to reduce exhaust emissions or to produce environmental-friendly energy carriers such as green hydrogen. Worksheet 2 also addresses the use of TiO$_2$-based wall paint as a contribution to a reduction of air pollutants and opens the perspectives towards a consideration of the effect of a release of dissolved nitric acid with regard to acidification and eutrophication, as well as ways to reduce the emission of nitrogen oxides in the first place. This helps to develop a larger picture considering effects and causes connected with the exhaust gases of combustion engines and furnaces. Worksheet 3 also focuses on the production of green hydrogen in comparison with grey hydrogen which is based on steam reforming. Students are asked to discuss statements given in interviews on green and grey hydrogen and to formulate proposals that they could address to political representatives regarding the conditions under which hydrogen can be used as an energy carrier in the future. Doing so they have to consider different positions from the economy, environment and society.

**Figure 9.** Exemplary mind map showing connections between the experiments and aspects related to SDG 13 and QR code leading to the worksheets.

Additionally, after having worked through the worksheets, students can try to relate the three experiments to SDG13 “Climate action” creating a mind map like in Figure 9.

According to the aim of addressing the individual, the regional and the global perspective when relating to ESD, in class the teacher can encourage the students to extend...
the mind map by adding items answering the following questions on the three mentioned perspectives: What can I contribute? What can stakeholders of my municipal or my national administration contribute? How can international stakeholders contribute to reach SDG13?

In order to offer EDS learning opportunities to cope with uncertainties and diverging interests of different groups, students can be encouraged to reflect on the function of titanium dioxide and the respective field of application based on their experiments, taking into consideration advantages and disadvantages of using titanium dioxide. They can research or be provided with additional information about further fields of applications and the history of the jurisdiction on the (restricted) use of titanium dioxide. This can finally serve as a basis for a panel discussion, in which the students have to adopt different roles.

4. Conclusion

Regardless of a classification of titanium dioxide as “potentially cancerogenic by inhaling” experiments with titanium dioxide are possible in suitable set-ups that prevent students from getting into direct contact with nanoscale particles by encasing, immobilizing or suspending the particles. In the first experiment students get to know titanium dioxide as a substance that can absorb UV-light, a precondition for being used as photocatalyst. This plays a role in the second experiment where titanium dioxide is irradiated by UV-light in order to degrade air pollutants via photocatalysis. In the third experiment titanium dioxide is used to photocatalytically produce green hydrogen via an environmental-friendly process.

The debate about titanium dioxide being classified as unsafe as food additive due to the fact that one cannot exclude genotoxicity, is valuable for teaching chemistry in the context of ESD. It is vital to have a closer look at the area of application and the particle size of a substance used in different applications, thus adopting a differentiated view. When decisions may be rejudged or even legally withdrawn, it can be interesting to see what party with which intention has caused a change in an evaluation. This promotes a multi-perspective consideration. As a critical view on information is to be promoted in the chemistry classroom, this can also contribute to a general scientific literacy and promotes the students’ communication and assessment competencies. More German materials for the promotion of ESD in the chemistry classroom and the promotion of a multi-dimensional approach to chemical topics can be found at [29].

References


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