Bridging the Gap between School and University by a Laboratory Course on Functional Surfaces

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Abstract

The modification of surfaces for a specific change of material properties is a field of intense research, whereby the type of property change can be very diverse. Prominent examples are compact oxide layers that increase the corrosion resistance or generate colorful surfaces by interference effects. Additionally, porous surface layers enable the utilization of semiconductor or intercalation properties of the materials through major surface enlargement in order to make them applicable for solar cells or battery technologies. We developed a science camp held at the XLAB – Göttingen Experimental Laboratory for Young People providing school students with an experimental insight into this topic and the opportunity to explore the fascinating field of functional surfaces. The camp includes for example the functionalization of titanium through anodic oxidation, characterization by SEM at university facilities and experiments on novel battery technologies. Additionally, solar cells using titanium dioxide as semiconducting material are built and compared to silicon-based cells and novel perovskite solar cells developed by a collaborative research center at University of Göttingen (CRC 1073). We describe the concept of the camp and present an evaluation focusing on the learning progress of the participants on selected topics like semiconductor effects, mechanisms of oxide growth during anodic oxidation of titanium and the working principles of lithium or sodium-ion batteries.

Keywords: *surfaces, nano structures, functionalization, science camp*

1. Introduction

Various university research projects are concerned with the development of alternatives or successors to established technologies in the field of renewable energies. Examples include the development of new types of solar cells or battery technologies. Many of these technologies are also based on the modification of surfaces in order to either improve the desired effects or enable them in the first place. Students are surrounded by these technologies in their everyday lives, however the question arises as to what extent they are aware of their working principles. For this reason, an experimental camp was developed to introduce students to this subject area through a variety of experiments, which will be described in this article. In addition, an evaluation is presented to determine the prior knowledge of the participating students about selected aspects of these technologies and whether the camp leads to a measurable increase in knowledge.

2. Camp

The developed camp being held at the XLAB – Göttingen Experimental Laboratory for Young People is titled "Nanostructured Surfaces" and is set in the context of sustainable energy conversion and storage. In this camp, the participating students investigate various questions in this subject area, supported by scientific lectures and fascinating experiments. These issues include the development of new types of solar cells, the working principles of lithium-ion batteries and the sodium-ion battery as a more sustainable alternative as well as the electrocatalytic reduction of carbon dioxide. In this camp, titanium dioxide is used as a model substance that is both relevant in research and can be utilized in all of these subject areas. This substance can be generated by students themselves in the laboratory using a facile experimental setup through the anodic oxidation of titanium [1, 2]. Depending on the design of the experimental conditions, anodic oxidation can lead to the formation of compact or porous titanium dioxide layers. The former show interesting color effects depending on the thickness of the oxide layer (Fig. 1A), while the latter are suitable for the aforementioned applications due to their greatly increased surface area (Fig. 1B/C), e.g. as semiconductors for solar cell technology (Fig. 1D) or as electrode material.

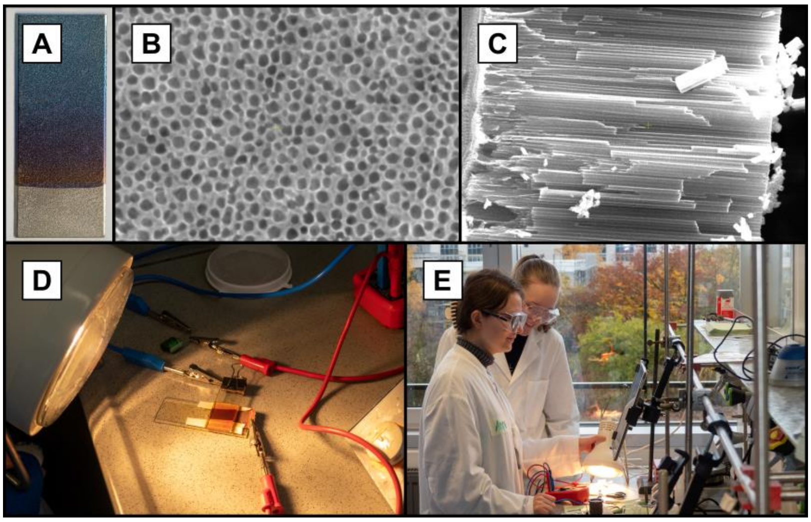

Fig. 1: A: Colored titanium sheet with titanium dioxide layer of varying thickness; B/C: Scanning electron microscope images of porous titanium dioxide layer; D: Constructed dye-sensitized solar cell using the porous titanium dioxide; E: Students testing their self-built solar cell.

The camp days are divided into thematic blocks, which always begin with an introductory lecture to provide the pupils with a subject-specific background to the respective topic. Experiments are then carried out independently by the students, who record their observations and initial interpretations before finally discussing them in a plenary session. An instructional script and supporting lab supervisors provide assistance while performing the experiments (Fig. 1 E). The days of the week are roughly divided into the various subject areas, with the first day focusing on the production and properties of compact and several porous titanium dioxide layers, while the following days are devoted to the application areas of these produced porous oxide layers (see Table 1). The camp concludes on the last day with a presentation prepared by the participants themselves, in which they give the group a rough overview of the insights they have obtained during the week.

Table 1: Schedule of the camp.

Monday	**Tuesday**	**Wednesday**	**Thursday**	**Friday**
Greeting and Orientation	Introductory lecture	Introductory lecture	Introductory lecture	Preparation of presentations
Introductory lecture	Examination of porous layers with the scanning electron microscope	Construction of a dye-sensitized solar cell with porous titanium dioxide and powdered titanium dioxide	Construction and comparison of lithium-ion batteries and sodium-ion batteries	Delivering the presentation and final discussion
Preparation of compact and porous titanium dioxide layers	Introductory lecture	Introductory lecture	Lecture about perovskite solar cell research in the CRC 1073	
Various experiments on the properties of the coatings created, such as hydrophilicity or corrosion resistance	Photocatalytic decomposition of methylene blue on porous titanium dioxide and construction of a gas sensor	Reduction of carbon dioxide using titanium dioxide composite electrodes		

3. Evaluation

An evaluation was carried out to assess the learning progress of the students participating in the camp. For this purpose, the 16 students were asked a total of 9 subject-specific comprehension questions that corresponded with the chemical and physical topics covered at the camp. The evaluation was conducted in a pre/post-test design, with the relevant questions for the respective day being tested before and after each camp day. The questions were multiple choice, each with three possible answers (A, B, C) and an “I don’t know” option (D). It was communicated to the students before the start of the evaluation that if they were unable to make an educated guess, they should choose the “I don’t know” option instead of guessing. The questions were formulated in such a way that they could be answered after listening to the daily presentation and completing the experiments.

3.1 Mechanisms of oxide growth during anodic oxidation of titanium

Three of the multiple-choice questions (see table 2 and figure 2) addressed the principles of the anodic oxidation of titanium, focusing on the mechanisms of the formation of compact titanium dioxide layers. Answering the first question requires a basic understanding of the terms anode/cathode and their relationship to the site of oxidation and reduction, as well as recognizing that titanium dioxide is oxidized titanium. Despite the advanced grade level of the students, only 33% were able to answer this question correctly in the pre-test. This initially seems low but is in line with studies on this topic by Marohn [3], which show a similar level of confusion regarding this subject matter. The response pattern for the second question is distributed similarly to the first question, although in this case the low number of correct answers in the pre-test is not surprising, as the concept in question is not directly found in the school curricula. Both questions were answered entirely correct after our intervention; this situation is different for the last question of the topic block. While the correct answer was barely selected in both the pre- and post-test, a strong increase was observed for the incorrect answer option A. We suspect that this is a consequence of frequently emphasizing in the lecture and laboratory course that the compact oxide layers formed are on a nanometer scale, furthermore the term “thin” was often used. At the same time, the phenomenon of ion migration though solids is typically not discussed at school and therefore might seem strange and unintuitive to the students.

Table 2: Questions and possible answers relating to the mechanism of anodic oxidation of titanium. The correct answers are highlighted in green.

Q1) The illustration depicts a cell for the electrolysis of an aqueous oxalate solution with titanium electrodes. The electrolysis produces titanium dioxide. Which statement is correct?		
A) The titanium dioxide layer is formed at the anode.	**B)** The titanium dioxide layer is formed at the cathode.	**C)** A titanium dioxide layer forms on both electrodes.
Q2) Which statement about the layer thickness of the titanium dioxide formed is correct?		
A) As long as electrical voltage is applied, the layer continues to grow.	**B)** The layer thickness depends on the level of applied voltage.	**C)** The layer thickness depends on the concentration of the electrolyte.
Q3) A current flows until the final layer thickness of the titanium dioxide is reached. However, titanium dioxide is an electrical insulator. Why does the electrolysis not stop immediately after the formation of a thin layer of titanium dioxide?		
A) The layer thickness of the titanium dioxide is very thin, so electrons can still pass through the layer.	**B)** Ions formed during electrolysis are able to migrate through the titanium dioxide layer.	**C)** As soon as the titanium dioxide has started to grow, it can continue to grow voluntarily for a short time without any further influence.

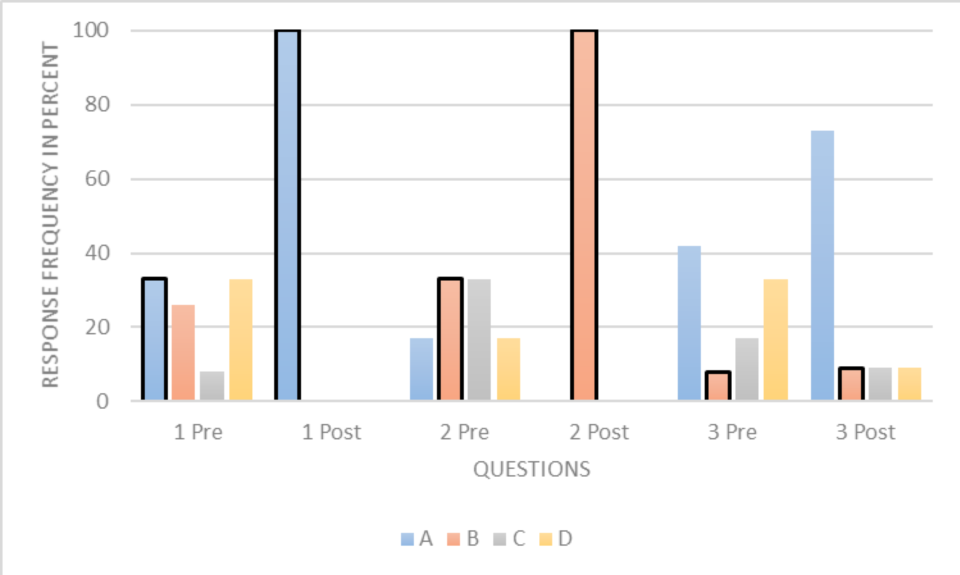

Fig. 2: Response frequency of questions 1 to 3 for both the pre- and post-test.

3.2 Areas of application for nanoporous titanium dioxide

Four of the multiple-choice questions (see table 3 and figure 3) covered different areas of application for nanoporous titanium dioxide. The fourth question concerned itself with the mechanism of photocatalytic decomposition of a model dye on the nanoporous titanium dioxide surface. Although this is a phenomenon that also plays a role in the students' everyday lives (e.g. in "self-cleaning" wall paints), only a quarter of the respondents were able to give a correct answer in the pre-test. Almost 40 % opted for answer A instead, which may be due to an association of the phenomenon with the lock-and-key principle known from biology class. After the intervention, this question was answered almost entirely correct.

Interestingly, for question 5, almost no change in response behavior was observed between pre- and post-test, although this phenomenon was not only discussed in the lecture but was also investigated directly in the laboratory during an experiment by the students themselves. We suspect that this is related to the multimeters used in the experiments. These had a resistance measuring range that started at 50 megohms. At room temperature, it was possible that the resistance of the samples was higher than this limit. Accordingly, the measuring device initially displayed an infinite resistance for some of the students, and it was only when the temperature was increased that a resistance could be measured, which then steadily decreased. Although this peculiarity of the measuring devices was already pointed out during the experiment, its effect still seems to have remained anchored in the minds of some students. To counter this misconception, this aspect was discussed again in the lecture the next day.

Question 6 was already answered correctly by 61% in the pre-test, which increased to 100% after the intervention. The remaining incorrect answers were mostly concentrated in the answer that silicon is indispensable for the construction of solar cells. This is not surprising, as the students (according to their own statements) were not familiar with other types of solar cells such as dye solar or perovskite solar cells but had only ever encountered silicon-based cells in their daily life. The classic misconception that thermal energy is also converted into electrical energy (answer A) could not be found in our test group [4].

The last question in this topic block again dealt with the location of oxidation and reduction during an electrolysis and its relationship to the terms anode and cathode. There was a similar response behavior in the pre- and post-test as in question 1, although this question had already been asked and clarified in the presentation and experiments a few days earlier. However, it must be considered that this question was formulated in a more complex way and several distractors were included. For example, it must be recognized that the nature of the electrodes does not change the potential site of oxidation and reduction and the conversion of carbon dioxide to formic acid must be understood as a reduction of the carbon atom.

Table 3: Questions and possible answers relating to areas of application for nanoporous titanium dioxide. The correct answers are highlighted in green.

Q4) Nanoporous titanium dioxide surfaces or titanium dioxide nanoparticles are able to decolorize a dye solution when exposed to UV light. What is the mechanism behind this phenomenon?		
A) The dye can adsorb on the nanosurface of the titanium dioxide. This spatial proximity enables the covalent bonds of the dye molecules to be cleaved after activation of the titanium dioxide with UV light.	**B)** When exposed to UV light, H_3O^+ ions form on the nano surface, which greatly reduce the pH value of the solution. The dye is not acid-stable and therefore decolorizes.	**C)** UV radiation creates radicals on the nanosurface, which are then able to attack the covalent bonds of the dye molecules.
Q5) Which statement regarding the electrical conductivity of a semiconductor is correct?		
A) The electrical conductivity increases continuously as the temperature rises.	**B)** The electrical conductivity decreases continuously as the temperature rises.	**C)** The electrical conductivity rises sharply when a material-specific temperature is exceeded.
Q6) Which of these statements about solar cells is correct?		
A) In addition to light energy, a solar cell also converts thermal energy into electrical energy.	**B)** Silicon as a semiconductor material is an indispensable component of every solar cell.	**C)** Solar cells cannot utilize the entire spectrum of incident sunlight.
Q7) The electrolysis of an aqueous solution with the introduction of carbon dioxide (CO_2) can produce formic acid (COOH). This can take place using tin electrodes as well as titanium dioxide composite electrodes as cathodes, whereby graphite or platinum can be used as anodes. Which of the following statements is correct?		
A) When using the titanium dioxide composite electrode, the formic acid is formed at the cathode, when using the tin electrode it is formed at the anode.	**B)** When using the titanium dioxide composite electrode, the formic acid is formed at the anode, when using the tin electrode it is formed at the cathode.	**C)** In both cases, formic acid is formed at the cathode.

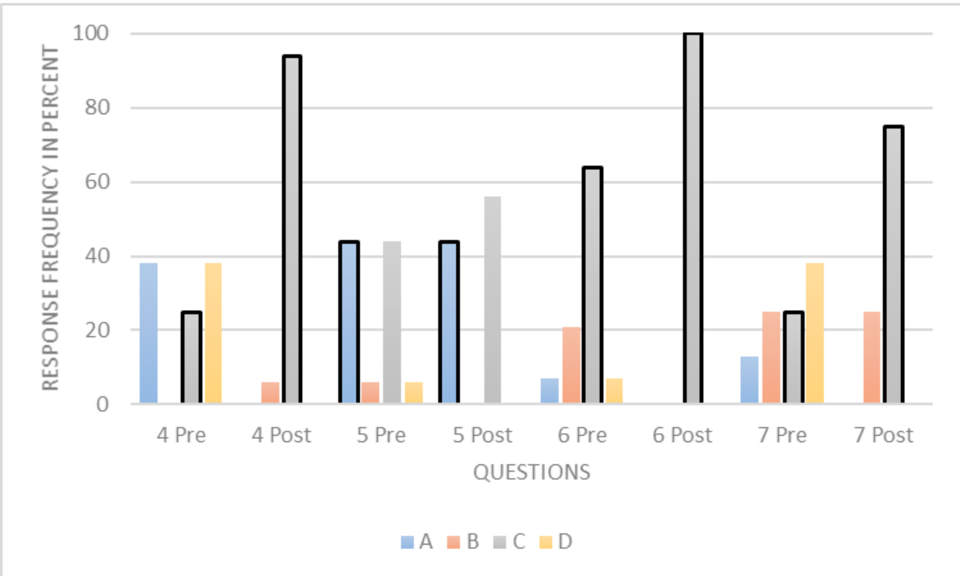

Fig. 3: Response frequency of questions 4 to 7 for both the pre- and post-test.

3.3 Working principles of lithium and sodium-ion batteries

The last two questions (see table 4 and figure 4) focussed on the working principles of lithium and sodium-ion batteries. Without having a deeper understanding of the reactions occurring in a lithium-ion battery, it is easy to assume that lithium in such batteries is oxidized and reduced during the charging and discharging process. The answer pattern for question 8 in the pre-test shows that this misconception is also present in our test group, representing 56 % of given answers. This is contrasted with only 25 % of students correctly answering that lithium is present as a cation in both the charged and discharged battery state. We are happy to report that our intervention was able to correct this almost entirely. The last question of our evaluation addressed potential differences between sodium-ion batteries and lithium-ion batteries. To answer correctly, one must recognize that the higher atomic mass of sodium compared to lithium results in a lower maximum gravimetric energy density of the battery type. As can be seen from the answer pattern, most students already seemd to be aware of this before the experimental day. Accordingly, no large increase was observed between the pre- and post-test.

Table 4: Questions and possible answers relating to the working principles of lithium or sodium-ion batteries. The correct answers are highlighted in green.

Q8) Which statement about the working principles of lithium-ion batteries is correct?		
A) Lithium is reduced and oxidized in a lithium-ion battery during the charging and discharging process.	**B)** Lithium is present as a cation in both charged and discharged batteries.	**C)** Lithium is present in both charged and discharged batteries in metallic form as an electrode.
Q9) Sodium-ion batteries are based on the same functional principle as lithium-ion batteries, but replace lithium with sodium. Which statement is false?		
A) In principle, sodium-ion batteries deliver a lower cell voltage than lithium-ion batteries.	**B)** Sodium-ion batteries are lighter than comparable lithium-ion batteries and therefore have high application potential in the mobile sector (smartphones, electromobility).	**C)** In principle, sodium-ion batteries can be produced in a more environmentally friendly way than lithium-ion batteries.

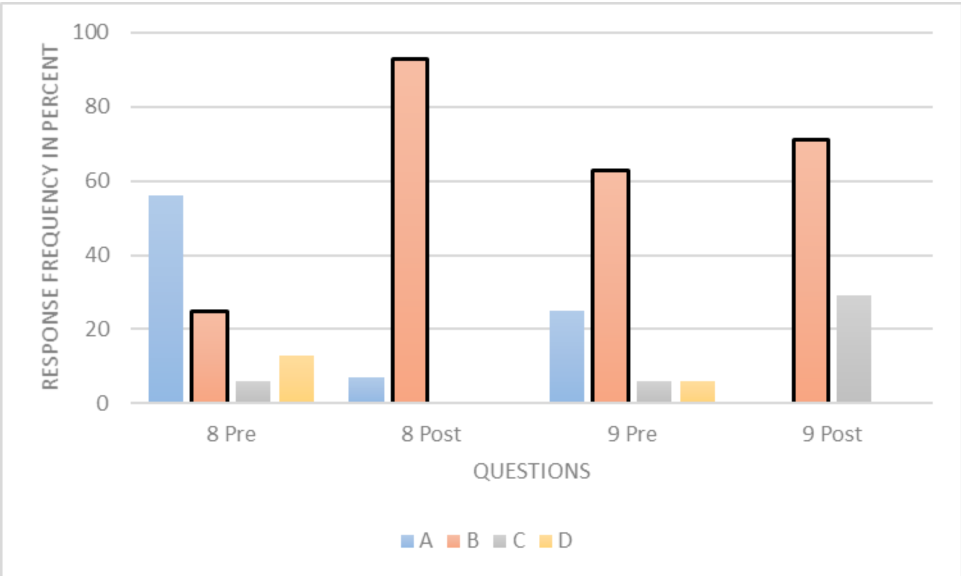

Fig. 4: Response frequency of questions 8 and 9 for both the pre- and post-test.

4. Summary

Overall, the evaluation showed that several typical misconceptions from the literature were also present in our test group, despite the advanced grade level of the pupils. The link between the terms anode and cathode and the location of oxidation and reduction can be highlighted here as a particularly widespread misconception among the test group. Our intervention through the lectures, guided experiments and answered questions was able to effectively remedy most of these misconceptions, as is demonstrated by the high frequency of correct answers in the post-test questionnaire.

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