Development and Implementation of a Science Camp on Nanostructured Titanium Dioxide – From Colorful Surfaces to Sustainable Applications

Christoph Weidmann[1], Thomas Waitz[1]

University of Göttingen, Institute of Inorganic Chemistry, Department of Chemistry Education, Germany[1]

Abstract

Nanostructured materials are of great interest in industry and research. Their useful properties for a wide variety of applications are mainly caused by two phenomena: (a) Differences in the electronic structure related to particle size, resulting in changes in the band gap of semiconductors or the occurrence of surface plasmon resonance and (b) a vastly increased surface-to-volume ratio for particles and structures with dimensions in the order of < 100 nm.
In this contribution, we present a science camp on nanoscopic titanium dioxide structures. Nanostructured titanium dioxide is well known in literature to benefit from an increased specific surface area and makes a material which is otherwise most notably known as a white pigment useful for various functional application. Despite these advantages, TiO_2 nanoparticles are associated with health risks in several studies [1] and therefore not suited for use in schools and student laboratories. However, nanoporous titanium dioxide layers on metal surfaces which are not prone to dust formation and are therefore safe to handle can be easily prepared via anodic oxidation of titanium foil. This science camp was successfully conducted three times in the past years with more than 45 students from all over Germany and focused on the versatility of nanostructures, where the students prepared the titanium dioxide layers themselves from scratch and used them to build semiconductor gas sensors [2], dye-sensitized solar cells, sodium-ion batteries and composite electrodes for the electrochemical reduction of carbon dioxide [3]. Herein, we present a set of experiments with a schedule tested in an actual science camp with a duration of three to four days as well as teaching materials showing how the experiments are linked to recent research.

Keywords: *Nanostructures, Science Camp, Sodium-Ion Battery, Dye-sensitized Solar Cell*

1. Introduction

The characteristics of nanostructures (nanoparticles, nanoporous materials and thin films) are rarely taught in school. While some aspects are covered in German school curricula (for example an increased surface-to-volume-ratio in the curriculum of the federal state of Lower Saxony), these are limited to theoretical considerations in most cases. Therefore, we and other groups have developed experiments and experimental series suitable for chemistry class in the past years, for example covering various nanomaterials and their interesting properties like size-dependent fluorescence of zinc oxide nanoparticles [6] and the distinct color of gold nanoparticles [7].
Titanium dioxide (often referred to as titania) is a particularly interesting material for providing examples of real-world applications of nanotechnology for various reasons: First of all, titanium is of wide abundance in the earth's crust and therefore not facing any shortages and is widely used as a white pigment in wall paint, plastics and cosmetic products. However, for these applications, the pigment particles do not necessarily exhibit dimensions on the nanoscale and make use of the very high refractive index (< 2.5) as a macroscopic property. Nevertheless, titania films with a thickness on the order of several 100 nm can be easily obtained via a facile sol-gel process and are described as being suitable for experiments in the context of surface modification, i.e. to increase hydrophilicity and wettability [8]. Another approach for the synthesis of nanoscale titania is the process of anodic oxidation in which a sheet or foil of titanium is electrochemically oxidized to titanium dioxide. Depending on the composition of the electrolyte, either compact protective layers with a thickness of 10 to 100 nm or porous titania nanorods with a pore diameter of 50 to 100 nm and a large aspect ratio (layer thickness in the order of tens of micrometers) can be obtained. Due to the increased surface area compared to bulk titania, this material is particularly suited to serve as a versatile nanostructured semiconductor and as an intercalation host for experiments showing the properties and benefits of nanostructured materials.

Therefore, we developed a science camp combining an introduction to nanomaterials and surface modification with the hands-on synthesis and characterization of compact as well as porous titania layers with new and previously published experiments.

2. Contents and Schedule of the Science Camp

The science camp described herein takes place at the XLAB – Experimental Laboratory for Young People as a central facility of Göttingen University. It targets German high school students in grade 11 to 13 with a particular interest in STEM subjects and pursues the following objectives:

- Highlight the importance of (electrochemically) modified metal surfaces and the specific properties and benefits of nanomaterials
- Synthesis and characterization of nanoscale titania layers (i.e. increase of surface area)
- Conduct a variety of experiments emphasizing on sustainable chemistry, energy storage and photovoltaics to show the versatility of titanium dioxide
- Connect experimental procedures with authentic research publications
- Contribute to vocational orientation by local companies presenting career paths and opportunities

<table>
<tr><th></th><th>Day 1</th><th>Day 2</th><th>Day 3</th><th>Day 4</th></tr>
<tr><td>Morning program</td><td>Arrival</td><td>Characterization of porous layers by scanning electron microscopy</td><td>Dye-sensitized solar cells</td><td>Sodium-Ion Batteries</td></tr>
<tr><td rowspan="2">Afternoon program</td><td>Introduction to surface modification and nanotechnology</td><td rowspan="2">Photocatalysis and semiconductor gas sensing</td><td>Q&A with local companies</td><td rowspan="2">Departure</td></tr>
<tr><td>Synthesis of titanium dioxide layers</td><td>Electrochemical CO_2 reduction</td></tr>
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Table 1. Schedule of the Science Camp. Green indicates synthesis and characterization experiments, red and blue denote semiconductor and electrochemistry experiments, respectively.

The 16 students arrive at the XLAB at 1 pm on day 1 and after a short safety briefing, the scientific program starts with an introduction to the purpose and methods of surface modification and functionalization of different materials. This includes improved biocompatibility of metal implants, the control of wettability, increased corrosion resistance as well as decorative effects. While various other methods like sol-gel coating or plasma treatment exist for a wide variety of commercially valuable materials, the described science camp focuses on electrochemically generated titanium dioxide on titanium metal. Since compact titania layers obtained by anodic oxidation of titanium usually exhibit a thickness in the order of tens or hundreds of nanometers and will be covered in the first set of experiments, they provide the opportunity for an introduction to nanotechnology.
This theoretical part introduces the students to the nanoscale and the specific properties of nanomaterials like surface plasmon resonance occurring on gold nanoparticles, changes in the band gap of zinc oxide nanoparticles and most importantly the increased surface-to-volume ratio of nanostructures in general and the benefits for applications. This will become especially important later on in the science camp at days 2 to 4, because this ratio is accompanied with shortened diffusion pathways and more reactive surface sites due to enlarged phase boundaries.
The subsequent experiments familiarize the participants with the method of anodic oxidation of titanium and will conclude with proving the increased corrosion resistance and the creation of a colorful and decorative sample.
The second day starts with an introduction to electron microscopy, enabling the students to characterize their porous oxide layers from day 1 with regard to layer thickness and pore diameter. SEM images from top, bottom and side view help to make the growth mechanism plausible by showing the parallel pores/nanotubes with an open pore at the top and a cap at the bottom, i.e. the phase boundary between titanium and titanium dioxide. After a simplified calculation of the surface area increase compared to compact titania layers, the students will perform an experiment proving the

advantages of this enlarged surface area for the photocatalytic degradation of methylene blue by comparing the discoloration under UV irradiation in the presence of both compact and porous titania. After that, a second experiment makes use of titania's semiconductor properties as well, this time for the detection of reducing gases like ethanol vapor as indicated by a change in resistance.
The remaining days focus on the application of titania in upcoming new technologies for the sustainable generation, storage and use of electric energy by conducting experiments on dye sensitized solar cells, sodium-ion batteries and electrochemical carbon dioxide reduction.

2.1 Anodic Oxidation of Titanium

In order to highlight the versatility of titanium dioxide and the application possibilities of nanostructured titanium dioxide as a functional material and to convey that nanostructures can be synthesized easily with a simple lab setup, the students are tasked with preparing the samples and substrates for all experiments themselves by anodic oxidation of titanium.
Briefly, the anodic oxidation creates a thin layer of titania on the surface of a sheet of titanium where the growth of this layer is driven by the mobility of titanium and oxide ions through the oxide layer in an electric field. Since the ionic conductivity of titania is quite low, the growth of this layer will come to a halt after several seconds. However, its thickness is determined by the strength of the electric field, corresponding to the applied voltage. Therefore, the layer thickness can be controlled by choosing an appropriate anodization voltage where higher anodization voltages lead to thicker oxide layers.
In the presence of fluoride ions in non-aqueous electrolytes containing some percent of added water, partial dissolution of titania occurs by forming soluble $[TiF_6]^{2-}$, which causes the formation of a porous structure. Since the thickness of the oxide layer at the bottom of the pores remains very low under the appropriate conditions, a steady growth of the porous oxide layer can be maintained, leading to a layer thickness in the order of tens of nanometers. A more detailed discussion of the growth mechanism for both compact and porous layers can be found in [3].

3. Selected Experiments

Herein, we describe the process of anodic oxidation of titanium, yielding decorative and protective compact titania layers as well as porous nanostructures as a common method used in all subsequent experiment. Additionally, procedures for experiments developed exclusively for this science camp are given. Details to all other experiments listed in Table 1 not shown here can be found in references [2-4].

3.1 Anodic Oxidation

The anodic oxidation of titanium is carried out at voltages of 5 V to 60 V in a beaker using a titanium foil (thickness: 0.1 mm) for both anode and cathode.

Compact layers: In this case, the anodization is performed in an electrolyte consisting of 4 *wt-%* oxalic acid in water. At first, only the lower part of the titanium foil is immersed in the electrolyte and is anodized at 60 V for 10 seconds. Afterwards, the electrodes are lowered into the electrolyte some more, anodized at a lower voltage and this process is repeated until the voltage reaches 5 V. The anodized titanium sheet exhibits a color gradient due to interference effects with each color corresponding to a specific anodization voltage [3].
This correlation allows the students to choose a combination of two colors and their respective anodization voltages to perform an experiment creating decorative two-color layers. Therefore, the desired pattern, text or symbol is painted on the substrate with nail polish. After drying, the titanium sheet is anodized at the voltage corresponding to the background color (which must be chosen in a way that the voltage is higher than the one needed for the foreground color) while the foreground is protected from anodization by nail polish. Afterwards, the nail polish is removed with acetone and a second anodization is carried out with the "foreground voltage" (see Fig. 1).

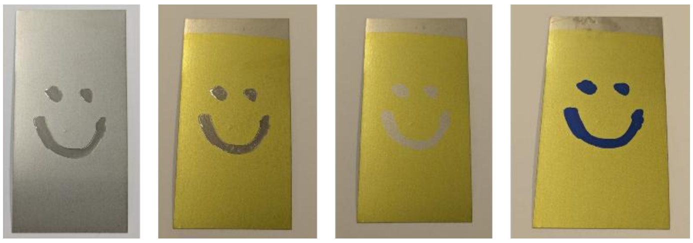

Fig. 1. From left to right: Titanium foil with nail polish before anodization; after anodization at 50 V; after removal of nail polish; after second anodization at 25 V.

In contrast to the anodic oxidation of aluminum, which leads to porous oxide layers and can be colored by incorporating dyes or pigments in the pores, the resulting titanium surfaces exhibit a color impression only by intereference and without using any chemical dye or pigment.

Porous layers: The electrolyte is prepared by dissolving 6.0 g ammonium fluoride in 3.0 mL water and filling up with ethylene glycol up to 200 mL. In contrast to the procedure described for compact layers, the anodization is carried out in a stirred electrolyte and in an additional water bath to control the electrolyte temperature at 50 V for 25 minutes.

3.2 Carbon Dioxide Reduction as an Example of Recent Research

Composite electrodes consisting of titanium dioxide and indium are considered as electrocatalysts for the selective electrochemical reduction of carbon dioxide to formic acid or formate, respectively. For this part, the students are provided with the actual research paper the experiment is based upon [5].
A porous titania layer prepared as described in 3.1 is electrolyzed in 20 mL 0.1 M potassium nitrate solution containing 30 mg indium nitrate for 100 s. According to the research paper, the voltage is manually controlled in a way that the potential versus an AgCl/Ag reference electrode is kept at -1.2 V. The resulting composite electrode is rinsed with water and dried in air. It can be observed that the electrode turns black, resulting from indium deposition and partial reduction of Ti(IV) to Ti(III) species.
The electrode is used in the actual carbon dioxide reduction experiment, where carbon dioxide is introduced as chunks of dry ice into the electrolyte solution (0.1 M potassium nitrate). The electrolyzation is carried out versus a platinum anode at a constant current of 50 mA.
Afterwards, a procedure described in [4] is used to detect the resulting formate ions as reduction product.

3.3 Dye-sensitized Solar Cell

A porous titania layer prepared according to experiment 3.1 was immersed in 0.01 M nitric acid for 10 seconds, rinsed with demineralised water and allowed to dry in air. It was then immersed in a solution of 5 mg ruthenium-based dye (N719) in 10 mL ethanol at 50 °C for 10 minutes and afterwards dried in air.
As the counter electrode, a glass slide with a transparent conducting fluoride-doped tin oxide (*FTO*) layer was thinly coated with graphite using a soft pencil and insulating tape was applied to separate both electrodes as shown in Fig. 2. After assembly together with Lugol’s iodine (1% iodine) using binder clips, a voltage of around 0.5 V and a short circuit current of 30 to 100 µA can be measured under irradiation with visible light. Although the resulting electrical power is not sufficient to drive a motor directly, the very pronounced current response to irradiation clearly proves the working principle of a dye-sensitized solar cell. In order to further demonstrate the generation of electric power, a capacitor (C = 1 F) can be charged over several minutes and subsequently used to power an electric motor with the energy generated from light energy using this simple device.

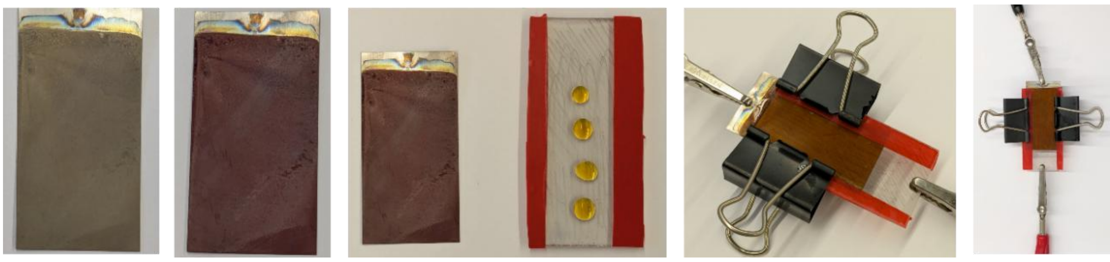

Fig. 2. From left to right: Porous titania electrode; electrode after immersion in N719 dye solution; preparation of FTO glass and application of Lugol's iodine; assembly of the final cell

4. Conclusion and Perspectives

The science camp developed for the XLAB offers great opportunities to experience how nanostructured surfaces can play a vital role in making society and industry more sustainable. As all the experiments make use of titanium dioxide layers synthesized by the students themselves, this demonstrates the versatility of this material and how it can be electrochemically synthesized in the first place. Despite of the relatively short time available in a four day sciece camp, it was possible to demonstrate this versatility, because the titania layer is intrinsically connected to the electrically conducting metal surface, allowing for very simple experimental setups as shown in Fig. 2 without the need to prepare electrodes based on nanoparticles or powder associated with health risks, too.
For the past three years, the science camp has been fully booked by motivated students from all over Germany. Although an empirical evaluation still has to be carried out, the responses to a feedback questionnaire were very positive and contained student's statements about what they learned and liked the most (translated from German)

"A lot of independently conducted experiments"

"The series of experiments from the preparation of a TiO_2 layer to the real application"

"How much the surface area can be increased by nanostructures"

"How versatile nanostructures are".

Future development is focused on extending the aspect of surface modification to other materials and techniques. The science camp will therefore be extended to five days and will include a set of experiments on plasma surface modification [9] in cooperation with the University of Applied Sciences and Arts (HAWK) in Göttingen. This provides students with insights into how small-scale laboratory techniques can be commercialized and implements an additional benefit in terms of vocational orientation. In this way, information about career paths originating from vocational training or studying STEM subjects at university are complemented by the possibilities and subjects a university of applied sciences has to offer.

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