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Experiments with Fluorescent Zinc Oxide Nanoparticles: A Teaching Course Design for Upper Secondary Chemistry Class

Timm Wilke[1], Nicolai ter Horst[2], Thomas Waitz[3]
Department for Chemistry Education, Georg-August-University Göttingen (Germany)
[1]twilke2@gwdg.de, [2]nicolai.terhorst@stud.uni-goettingen.de, [3]twaitz@gwdg.de

Abstract

Nanotechnology is considered one of the key technologies of the 21st century and a broad variety of high-performance functional materials are already part of our everyday life. Due to its versatile applications, zinc oxide nanoparticles are currently subject of intensive research in various scientific domains [1, 2], which is also reflected by the large number of publications on the subject which has increased by a factor of 2000 since 1990.

In this contribution, a chemistry class project on zinc oxide nanoparticles and nanotechnology in our day-to-day lives is presented. The developed teaching unit comprises (1) an introductory seminar during which the participants focus on the general characteristics of nanomaterials, (2) a laboratory course including several experiments with zinc oxide nanoparticles as well as (3) teaching materials on the use of nanotechnology and nanomaterials in various fields that aim at promoting a reflected assessment of existing applications and the students' critical capacity towards new technologies in general.

1. Introduction

Nanotechnology is one of the key technologies of the 21st century with a significant impact on our day-to-day lives[3]. As a platform technology, it possesses the potential to deliver answers and solutions to major technical and social challenges, such as energy production, drinking water supply and several serious diseases. While these solutions are yet to come, many applications based on or enhanced by nanotechnology have found their way into our lives already; shoe sprays, tooth paste and coatings are only some examples from the wide variety of products in the many different domains.

Due to its interesting physical properties, zinc oxide is regarded as one of the most important nanomaterials which is emphasized by the wide variety of applications such as sunscreens, cell markers, cosmetics, gas sensors, catalysts and displays which represent only a small, arbitrary selection from the numerous present and future products. In addition to these connections to students' everyday lives, this nanomaterial is non-poisonous, cheap, stable and many scientifically relevant contents can easily be linked to basic chemical knowledge. Therefore, zinc oxide especially offers itself for school chemistry education.

Due to its important role in the sciences, the economy and our everyday products, a detailed conceptualization of nanotechnology in general is gaining more and more importance which is why a couple of projects and initiatives have found their way into schools by now. This contribution presents selected contents of a nanotechnology teaching course for K-12 chemistry education and school laboratories which aims to provide the students with a theoretical and practical overview of this topic in order to further promote nanotechnology in schools.

2. Nano Zinc Oxide Project

The course structure is comprised of three parts. University teacher students have been trained and included in theoretical and practical phases of the whole project in order to dismantle potential barriers and fears of contact with this relatively new subject.

The first section is an introduction to the elementary and most relevant theoretical principles of nanoscience. Hereby, special emphasis is placed on the respective characteristic properties, (natural) occurrence and production as well as the spatial dimensions of nanomaterials. The second part of the course is experimental and students focus on the synthesis and properties of zinc oxide nanoparticles, such as fluorescence and photocatalysis, during six experiments. The final section addresses the responsible use of several nanomaterials as well as their management in various fields of application. Here, students are meant to develop their critical capacity towards new technologies and provide a reflected assessment of existing applications. The course was developed for six to eight 45-minute lessons, with the length and content depth remaining flexible depending on the students' and teachers' specific needs. Starting in grade 10 (ages 15 – 16), pupils can maximally benefit from this subject as they are familiar with the necessary basic knowledge in chemistry. Furthermore, this particular course structure is based on the results and insights of a previously developed class project on titanium dioxide nanoparticles[4].

2.1 Introductory Seminar

The theoretical basics of nanotechnology are introduced to the students during a 45-minute introductory seminar structured similarly to university courses. Special attention is paid to misconceptions and problems that have been identified in preceding studies[5], such as the recognition of the use of nanomaterials in everyday products and accurate representations of the spatial dimensions.

To give an example of the latter, the spatial size is often introduced via analogies, *e.g.* "*the relationship between a nanometer and a meter is the same as that between the diameter of a hazelnut and the diameter of the earth*" (Fig. 1a). But since the diameter of the earth is also intangible, we propose a different method. Figure 1b shows one of the thinnest "familiar" macroscopic objects, a human hair, and silicon dioxide nanoparticles on the same scanning electron microscope image. By means of the scale bars, students can now calculate the number of nanoparticles that fit into the diameter of one hair. The resulting number, 800, appears to be easier to visualize and is significantly more memorable for the students.

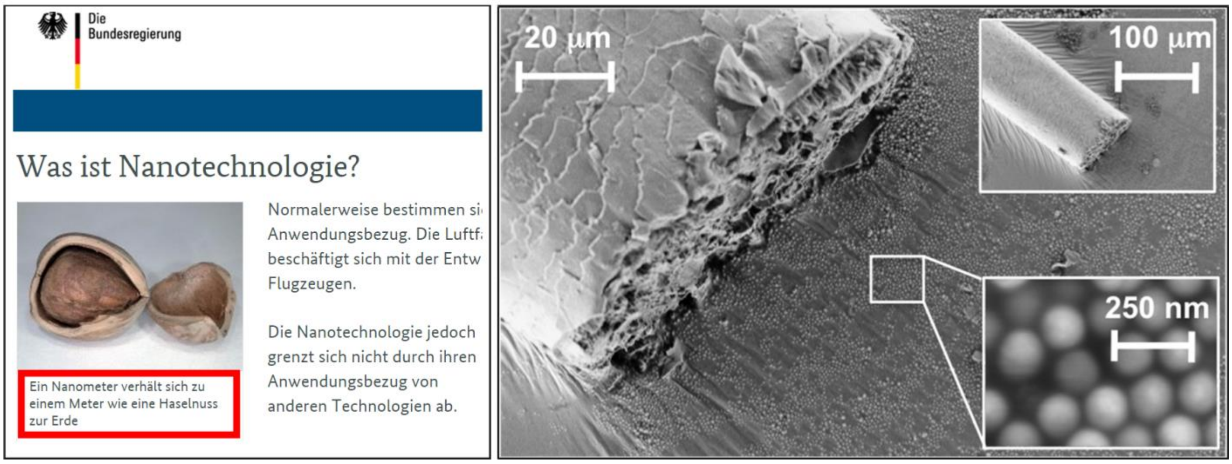

Figure 1: *a) Frequently used analogy introducing the size of a nanometer. The content of the marked textbox can be translated as: "The relationship between a nanometer and a meter is the same as that between the diameter of a hazelnut and the diameter of the earth."[6] b) Size comparison between a human hair and silica nanoparticles.*

Additionally, two important characteristics of nanomaterials are discussed during the introductory seminar; the surface-to-volume-ratio with its influence on material properties (reactivity, adsorption) as well as the surface atom properties. At all times, examples from everyday life (shark skin, lotus effect, sun screen) are included to highlight the already existing everyday connections.

2.2 Laboratory Course

In the subsequent laboratory course, the students conduct six easy and safe (model) experiments with zinc oxide nanoparticles using common affordable chemicals and equipment. Supported by a laboratory script, students synthesize fluorescent zinc oxide nanoparticles, investigate their properties and discover actual or potential applications of this nanomaterial. In this section, two example experiments will be presented.

2.2.1 Synthesis of Zinc Oxide Nanoparticles

The synthesis of zinc oxide nanoparticles can be accomplished with simple, cheap and safe chemicals in a short period of time. For chemistry class, the precipitation reaction with zinc salts appears to be convenient. The obtained products exhibit particle sizes between 5 – 7 nm that can be easily detected by fluorescence.

Equipment and chemicals: ethanol, sodium hydroxide pellets (NaOH), zinc acetate dihydrate (ZnAc), magnetic stirrer, 3 beakers (100 mL, 2 x 250 mL), UV light source (Hanau, Fluotest, 18 W) or UV bank note verifier.

Experimental: For the preparation of a 0,2 M ethanoic sodium hydroxide solution, 0,28 g NaOH are grinded in a mortar and subsequently dissolved in ethanol at 40 °C while stirring in a beaker (V = 100 mL). At the same time, 2,2 g ZnAc are stirred in 100 mL ethanol at 60 °C until the solid dissolves completely. Under UV light, the two clear and warm solutions are combined in the third beaker. Within seconds, an intensive yellow fluorescence can be observed, as shown in fig. 2.

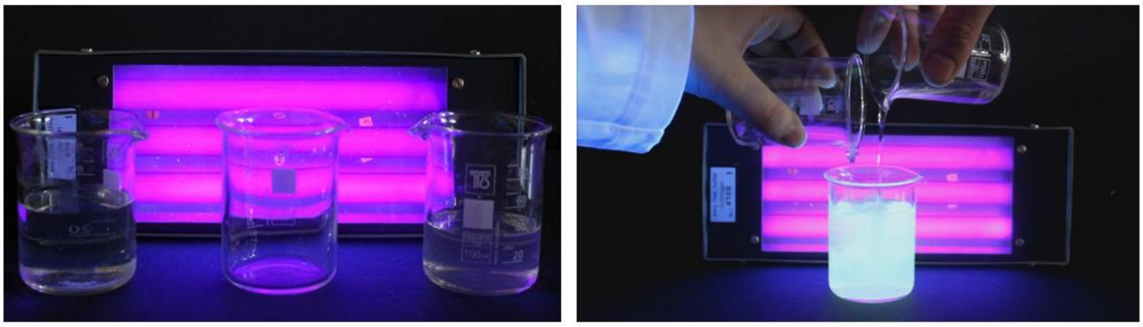

Figure 2 – *Experimental setup of the zinc oxide nanoparticles synthesis showing the initial zinc acetate dihydrate und sodium hydroxide solutions (left) as well as the fluorescing zinc oxide nanoparticles (right).*

Interpretation: When combining the two solutions, zinc oxide nanoparticles are obtained from a precipitation reaction:

$$Zn(CH_3COO)_2 \cdot 2\,H_2O \;+\; 2\,NaOH \;\rightarrow\; ZnO \;+ 2\,CH_3COO^- \;+\; 2\,Na^+ \;+ 3\,H_2O$$

These zinc oxide nanoparticles in the specific particle size range from 2 - 8 nm are responsible for the intensive fluorescence. While the scientific background has not yet been conclusively discussed, the nanoparticles' oxygen defects are considered the main cause for this phenomenon. Due to these lattice defects, additional energy levels (so-called acceptor states) are generated between valence and conducting band resulting in further possibilities for light-emitting electron transitions[7].
In chemistry class, it appears convenient to introduce fluorescence based on a simple, didactically reduced band model. Figure 3 illustrates how electron-hole-pairs are formed by means of UV radiation. Due to the supplementary energy levels, recombination does not take place directly but subsequently to several non-emitting transitions (lattice vibrations). As a consequence, the emitted photon exhibits a significantly reduced energy amount (red-shift) compared to the initial UV light and appears as yellow fluorescence.

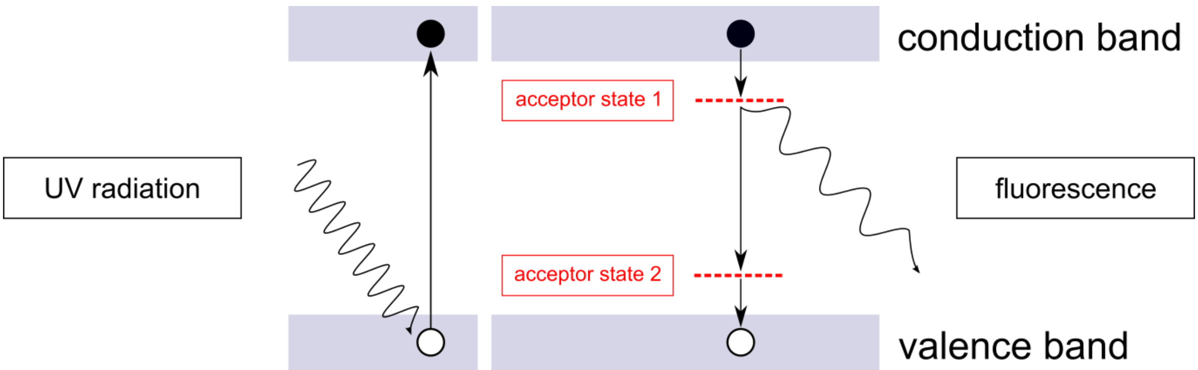

Figure 3 – *Left: band model of the zinc oxide nanoparticle fluorescence. Excitation of an electron by UV radiation from the valence band (VB) into the conduction band (CB) and generation of an electron-hole pair. Right: Recombination with red-shifted photon emission (fluorescence)[8].*

2.2.2 Photocatalytic Activity

In this experiment, students investigate the photocatalytic properties of zinc oxide nanoparticles with the example of the degradation of malachite green. With the help of a didactically reduced band model and a flow chart, the respective underlying processes can easily be conveyed.

Equipment and chemicals: magnetic stirrer, 3 beakers (25 mL), UV light source (*e.g.* Ultra Vitalux), malachite green, ethanol, zinc oxide nanoparticles solution (from the preceding experiment).

Experimental: One crystal of malachite green (Ø < 1 mm) is dissolved in 60 mL of ethanol. The obtained light green solution is then divided into three equal parts of 20 mL and filled into three breakers. 5 mL of the zinc oxide nanoparticles solution from the preceding experiment are each added to samples 2 and 3. Then ample 2 is covered with a porcelain lid. The solutions are stirred under direct UV light exposure from above. After a few minutes, sample 3 turns colorless whereas no change can be observed in the other samples.

Interpretation: The observed discoloration is a result of the photocatalytic activity of zinc oxide nanoparticles. Again, electron-hole pairs are created within valence and conduction bands through radiation with UV light. The resulting electron deficient areas in the valence band and the supplementary electrons in the conduction band are now able to react in redox reactions with surrounding molecules at the particle surface, generating several radical species, *e.g.* with ethanol or water. These radicals cause the degradation of malachite green (under ideal conditions and continued irradiation) to carbon dioxide and water.

These experiments offer many learning opportunities for school chemistry education. The experimental setup, for instance, can be designed by the students themselves, thus providing them with the possibility to determine the necessary conditions for photocatalysis – UV light and the presence of a photocatalyst. Many classical concepts of chemistry education such as (photo)catalysis, redox reactions, radicals and a band model can be introduced . Moreover, the application of zinc oxide nanoparticles as cell markers (bioimaging), in sunscreen, wastewater treatment and many other areas can be discussed and investigated in further experiments.

2.3 Teaching Material on the Use of Nanotechnology

As described in the previous sections, students have gained subject-related knowledge on nanotechnology and have performed several experiments related to existing and potential applications of zinc oxide nanoparticles. The final section widens this focus and aims at reflecting the potential risks or benefits of the use of nanomaterials. This offers an interesting context especially since current debates have credited nanomaterials as either *the solution to many major technical or social challenges of the 21st century* or as *a dangerous new technology bearing the same risks as asbestos.* Based on the acquired information during the previous sections and guided by teaching materials, students can analyze and discuss these points of view as well as the present and (desired) future role of this technology, thus promoting their critical capacity towards new technologies in general. Finally, here teachers and students can access the enormous pool of high quality online resources since this debate is not appropriately reflected in schoolbooks yet.

3. Experiences

In this contribution, a teaching course model on nanotechnology with several experiments on zinc oxide nanoparticles has been presented. The results of a qualitative evaluation after the course's implementation in a grade 11 class (ages 16-17) show that overall, a significant increase of the subject-related knowledge can be observed, particularly with respect to the two thematic priorities of the introductory seminar (spatial dimension and surface-to-volume ratio). Not only do the test results show a high interest in the experiments, described as "illustrative" and "exciting", but also in further educational projects on nanotechnology in general, since it "strongly concerns us all every day, today and especially in the future".

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