Silicon-based Functional Materials - A Practical Course Design connecting School and School Laboratories

Elena von Hoff[1], Timm Wilke[2]

Abstract

In our day to day lives we encounter several silicon-based materials, ranging from silica nanoparticles as drying agents in salt to silicone oils as lubricants as well as silicone baking forms. These functional materials display interesting properties and offer various learning opportunities within the frame of an educational context. Many of these properties, such as the temperature resistance or hydrophobia of silicones, can as easily be linked to students' everyday lives as to the basic concepts of school chemistry education [1-3].

However, for the successful implementation of suitable experiments into school chemistry education, a number of challenges need to be overcome, e.g. lacking chemicals, teaching materials and teacher expertise [4]. Taking these barriers into account, school laboratories may represent a more suitable environment for experiments on silicon-based functional materials.

A promising way to implement silicon-based functional materials into school chemistry education is the cooperation between school and school laboratories. While the experiments are performed at the school lab, both preparation and follow-up processes take place at school to promote long-term learning successes [5]. In this contribution, we present a proposal for a corresponding course design on silicon-based functional materials, which can be used to either introduce or deepen several aspects of the high school curricula.

1. Introduction

Nanotechnology is considered one of the 21st century's key technologies and is said to play a pivotal role in solving some of the greatest challenges of our time. Because of this technology's distinct influence on our future, it is predestined to be a part of today's school education. Yet, despite its economical and scientific relevance, this technology is not yet reflected appropriately in present school curricula.

Nanoscale materials, however, are not the only substances of great scientific and economical interest, since nanostructured materials possess at least equally as interesting characteristics as nanoparticles. Some prominent examples are already permanent fixtures in most chemical laboratories (*e.g.* activated carbon, molecular sieves), household items (*e.g.* zeolites in detergents) or food items (*e.g.* activated carbon as food coloring E153). At the same time, extensive research is being carried out especially in the field of catalytic applications as well as substance storage and separation [6]. In addition to a connection to a current nanoscience topic, such substances offer various learning opportunities, introducing or deepening contents such as templating, catalysis, hydrolysis, condensation and surfactants. Moreover, corresponding basic nanotechnological principles (*e.g.* nanostructured materials, bottom-up as well as top-down synthesis principles, surface-to-volume ratios, …) can be covered as well.

2. Didactic-Methodological Preliminary Considerations

Within this contribution it will be illustrated that (nano-) porosity is accompanied by significant function enhancements. Silica materials, allowing several links to students' everyday lives as well classical topics in chemistry class, offer particularly interesting perspectives for the use in educational settings.

For the content-related design of the teaching unit, known student perspectives regarding the topic "nano" [7] were being considered. However, in order to support the implementation of the offered contents into class, teacher perspectives were being considered as well. Corresponding surveys [4, 8] show that teachers perceive (1) missing curricular references, (2) the complexity of the material, (3)

---

[1] Department of Chemistry Education, Georg-August-University Göttingen, Germany

[2] Institute of Environmental and Sustainable Chemistry, Brunswick University of Technology, Germany

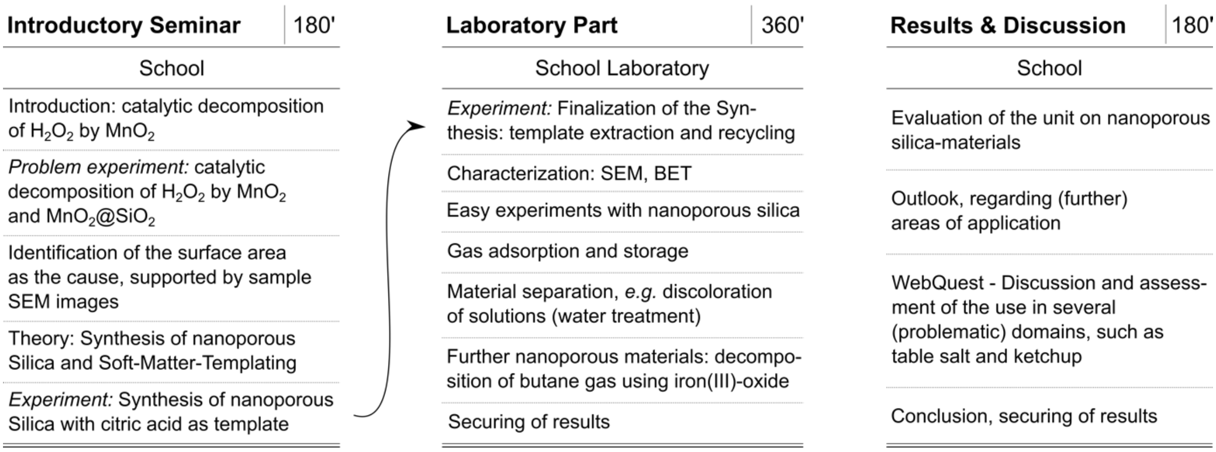
the lack of suitable teaching materials and (4) the insufficient experimental equipment in schools as major barriers for the implementation of “nano” into schools.

These barriers will be addressed within a concept combining both formal and non-formal learning environments. School laboratories oftentimes have the needed chemicals and experimental equipment at their disposal and therefore offer unique opportunities for the experimental exploration of certain topic areas. Hence, school laboratories offer ideal conditions for one-day visits, allowing extensive experimental activities within the scope of certain school units. The necessary theoretical background as well as the subsequent follow-up processing and securing of results takes place in schools before and after the visit, which has been proven as being very effective in terms of long-term learning successes [5].

In order to simplify and expediently organize the preparations for the participating teachers, prepared teaching materials and required chemicals are being provided by the school lab. Thus, the mentioned barriers are being met and the limited stay at the school lab is being efficiently utilized. Such a format offers the possibilities of deepened insights into this modern chemical topic, starting at the synthesis and the characterization, up to the exploration of possible properties and applications in various student experiments.

3. Course Design and Selected Materials

Following, the contents of the course on nanostructured silica materials will be presented. The course is divided into the three above mentioned sections, which contextually build up on each other. Figure 1 shows the outline of the overall concept, including the corresponding contents.



Introductory Seminar 180'

School

- Introduction: catalytic decomposition of H_2O_2 by MnO_2
- *Problem experiment:* catalytic decomposition of H_2O_2 by MnO_2 and $MnO_2@SiO_2$
- Identification of the surface area as the cause, supported by sample SEM images
- Theory: Synthesis of nanoporous Silica and Soft-Matter-Templating
- *Experiment:* Synthesis of nanoporous Silica with citric acid as template

Laboratory Part 360'

School Laboratory

- *Experiment:* Finalization of the Synthesis: template extraction and recycling
- Characterization: SEM, BET
- Easy experiments with nanoporous silica
- Gas adsorption and storage
- Material separation, *e.g.* discoloration of solutions (water treatment)
- Further nanoporous materials: decomposition of butane gas using iron(III)-oxide
- Securing of results

Results & Discussion 180'

School

- Evaluation of the unit on nanoporous silica-materials
- Outlook, regarding (further) areas of application
- WebQuest - Discussion and assessment of the use in several (problematic) domains, such as table salt and ketchup
- Conclusion, securing of results

Figure 1: Structure and selected contents of the presented teaching unit.

In the beginning of the teaching unit, the students’ prior knowledge can be activated in numerous ways. However, with regard to the later on presented possible applications the thematic field of catalysis is especially suited. Classically, this topic is illustrated in chemistry class by the decomposition of hydrogen peroxide using manganese dioxide. Based on this prior knowledge, an experiment in which nanostructured silica with a large surface area is being used as a carrier material for the manganese dioxide is being conducted in the sense of a problem experiment. The necessary chemicals and teaching materials are being provided by the school lab.

Experiment 1: Catalytic Decomposition of Hydrogen Peroxide Using Manganese Dioxide@Silica

2 mL of a saturated manganese nitrate solution are added to 2 g of the nanoporous silica-material (see experiment 2) and homogenized using mortar and pistil, consequently filling the pores of the silica-material with the manganese nitrate solution. The obtained composite material is transferred to a crucible, which is being heated with a gas burner until no more brown gas is being released (NO_2, fume hood!) and the material has taken on a brown coloration. During this process, the manganese nitrate thermally decomposes into manganese dioxide and nitrogen peroxide as per:

$$Mn(NO_3)_2 \rightarrow MnO_2 + 2\ NO_2$$

As a reference material for the catalytic activity, non-porous “bulk” manganese dioxide is being used. For its synthesis, another 2 mL of the saturated manganese nitrate solution is being thermally converted into the corresponding oxide. Afterwards, both powders are being suspended in 20 mL of water, using round-bottom flasks. After setting up an apparatus as shown in Figure 2, hydrogen peroxide solutions (c = 5 %) are being added into the flasks at the same time to start the reactions.

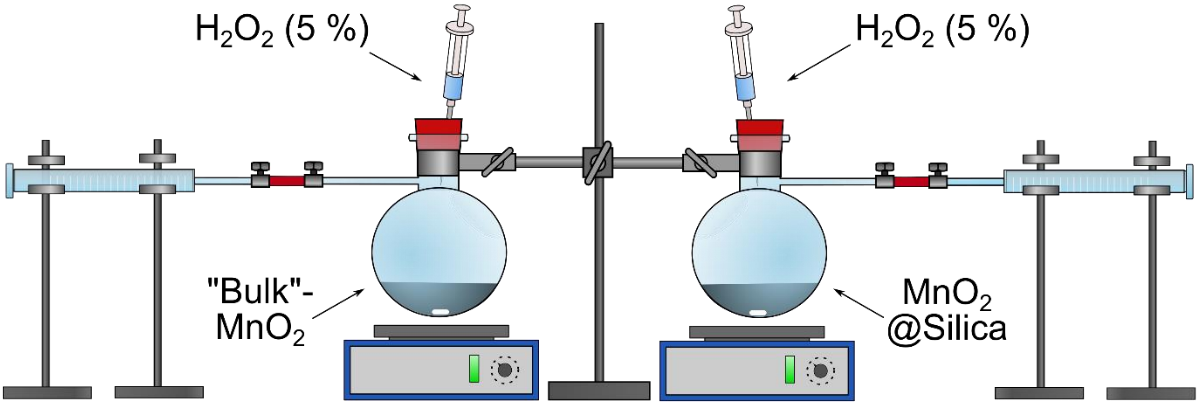


Figure 2: Experimental setup for the comparison of the catalytic efficiency of manganese dioxide vs. manganese dioxide@silica.

Within 5 seconds, 80 mL oxygen is being released into the gas syringe with the manganese oxide@silica composite material. For the bulk material, however, it takes 30 seconds to release the same amount of gas.

The diverging reaction periods clearly show that the manganese dioxide within the porous material is more proficiently catalyzing the decomposition of the hydrogen peroxide then its bulk analog. It should be made sure, however, that the amount of catalyst is the same in both cases. With the help of SEM images of the porous silica showing the existence of small and finely dispersed manganese oxide particles within the pores, the students conclude the higher catalytic activity. Compared to the bulk particles, they possess a significantly higher surface-to-volume ratio. Since the decomposition takes place at the surface of the particles, the (many) smaller particles show a particularly high catalytic activity.

Following the interpretation, the synthesis of the nanostructured silica material should be retraced by the students, which in general happens via structural molding using templates. The therefore necessary theoretical background on soft-matter templating can be explained using easy models with analogies to the students’ everyday lives (*e.g*. casting processes). While classically surfactants (*e.g.* CTAB, CTAC, Pluronic123$^{\copyright}$) are being used as templates [9], the following experiment is based on instructions by Wang et al. [10], using citric acid instead. Thus, not only the expenses are being lowered immensely, but also the template can easily be recovered and recycled in the sense of Green Chemistry.

Experiment 2: Green Chemistry Synthesis of Nanoporous Silica with a Citric Acid Template

In a typical synthesis, 21,01 g (0,1 mol) citric acid is being dissolved in 50 mL of distilled water; the solution is being stirred for 3 minutes, until the citric acid is completely dissolved. Vigorously stirring, 4,5 mL (0,02 mol) tetraethyl orthosilicate (TEOS, Alfa Aesar, 14 € / 100 mL) are slowly being added. Within the aqueous solution, a hydrolysis and a subsequent polycondensation of the TEOS are taking place. After 30 minutes of reaction time a gel is being obtained (Figure 3, left) which is being placed in a drying furnace at 60 °C overnight. The resulting opaque solid (Figure 3, center) is being washed several times in order to extract the citric acid from the pores. As soon as the fluid used in the washing process is pH-neutral (approx. 5x 75 mL demin. water), the remaining nanoporous silica is being dried at 100 °C. The obtained product is a fine white powder.

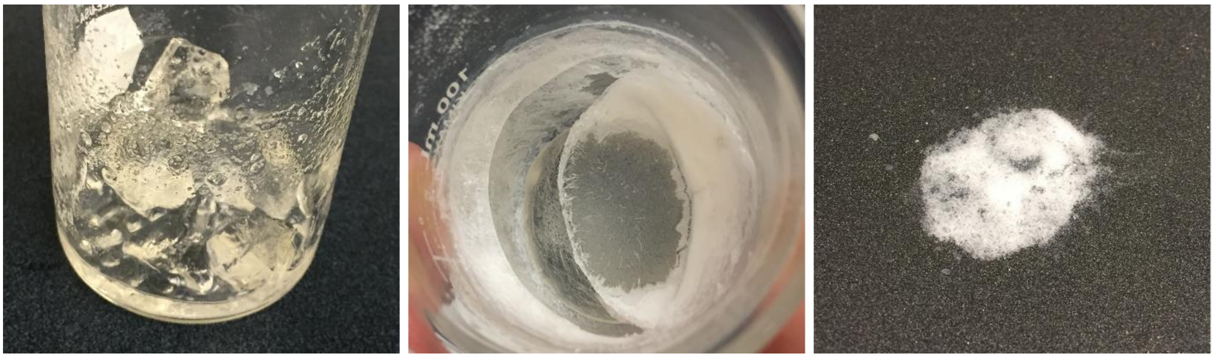


Figure 3: Silica gel after adding TEOS (left), dried silica with crystallized citric acid (center) and nanoporous silica (right).

Following, the silica materials can be characterized in school labs or neighboring research centers. Depending on the teacher’s intention, SEM can be used to determine the average pore size. Alternatively, the surface of the material can be illustrated using BET readings. Afterwards, additional experiments regarding material separation, catalysis or (gas-) adsorption may follow.

Subsequent to the stay at the school lab, the students’ observations and measurement values are being collected and compared in class. Exceeding the experiments, possibilities presented by the nanoporous silica for the application in our day-to-day lives, engineering and research are being discussed. Potential examples which may be considered during a WebQuest are the use of porous silica

- as release agents in seasonings or salt,
- for the adsorption of odor-forming substances in cat litter,
- as fillers in plastics or rubber, *e.g.* for lowering the rolling resistance in tires,
- as drying agents, *e.g.* for natural- and biogases.

4. Conclusion

Porous functional materials in general and nanoporous silica in particular, offer diverse opportunities for teaching a modern and interesting thematic field with high relevance for students’ everyday lives. Within a connective course concept, the strengths and resources of schools and school labs are being combined, as well as barriers of the educational implementation minimized. With the aid of the presented school unit, conceptual basics of the synthesis can be visualized in a simple manner, contributing to the comprehension of the templating process often used in the material sciences. Based on the experiments, the students ascribe the distinct properties of highly porous materials to their high surface-to-volume ratio, offering various links to thematic fields such as catalysis, material separation as well as energy storing.

References

[1] Venzmer, J., Chem. Unserer Zeit 42 (2), 2008, p. 72.
[2] Krees, S., PdN-ChidS 61 (8), 2012, p. 44.
[3] Wilke, T., Haffer, S., Weinberger, C., Tiemann, M., Wagner, T., Waitz, T., J. Nano Educ. 6 (2), 2014, p 117.
[4] Nonninger, R., Dege, J., Wilke, T., Waitz, T., in: Global Perspectives of Nanoscience and Engineering Education, edited by K. Winkelmann und B. Bhushan, Springer International Publishing, Cham, 2016, p 237.
[5] Streller, M., The educational effects of pre and post-work in out-of-school laboratories, Dresden, 2015.
[6] Dündar-Tekkaya, E., Yürüm, Y., Int. J. Hydrogen Energy 41 (23), 2016, p. 9789.
[7] Wilke, T., Waitz, T. in: Pixel (Eds.): New Perspectives in Science Education 2012, Libreriauniversitaria.it, 2012, pp. 105-109.
[8] Kähkönen, A.-L., Laherto, A., Lindell, A., J. Nano Educ. 3 (1), 2011, p. 1.
[9] Waitz, T., Wagner, T., Sauerwald, T., Kohl, C.-D., Tiemann, M., Adv. Funct. Mater 19 (4), 2009, p. 653.
[10] Wang, Y., Huang, S., Kang, S., Zhang, C., Li, X., Mater. Chem. Phys 132 (2-3), 2012, p. 1053.