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Silica-Based Nanomaterials in Chemistry Education

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Abstract

Silica-based materials play an important role in various aspects of everyday life such as coatings, filters or anti-caking agents in foodstuff like baking powder or salt. Especially nanoporous silica materials have been considered for many technological applications such as HPLC, catalysis or storage. In our contribution, we address the meaning and versatility of silica materials in school chemistry education by presenting some basic and easy-to-implement model experiments, including areas like sorption. Additionally, we present the fabrication of artificial opals using self-manufactured monodisperse spherical silica nanoparticles, which are ideally suited to give pupils an impression of the size of the 'nano' dimension. Finally, on the example of (nano) porous silicones we will demonstrate possibilities to link current research in materials science to basic concepts in school chemistry education such as polar and nonpolar interactions, hydrolysis and condensation.

1. Introduction

Nanotechnology is one of the key technologies of the 21st century connecting basic and applied research and development from various scientific disciplines such as chemistry, physics and biology. The considerable progress in nanotechnology innovations over the last years can particularly be attributed to its interdisciplinary character, resulting in new research perspectives in basic sciences and more importantly in the development of new materials present in almost all areas of everyday life. The latter concerns for example nano additives for foods, drugs and cosmetics, self-cleaning surfaces, scratch resistant coatings and new materials for energy conversion and storage. Although nanotechnology is highly relevant for scientific research and everyday life, the topic has not been successfully integrated into (German) school curricula or teacher training at the university level. This is also confirmed by the fact, that the term 'nano' is missing in nearly all German science school books (chemistry, physics, biology) and module descriptions of teacher training institutions like universities and 'Studienseminaren' (= second phase of teacher education in Germany). In contrast a recent explorative study (n = 100) about the knowledge of and the interest in nanotechnology of pupils from grades 5 to 12, revealed a great interest in this topic. More than 87 % of the interviewed pupils would like to learn more about nanotechnology in school. This interest can be attributed to several reasons, *e.g.* to the frequent utilization of the term 'nano' in advertising (iPod nano, 45 nm technology, nano coating, etc.), news reports about sustainable energy conversion and storage using nanomaterials as well as risks using nanoparticles in food, cosmetics etc.

In order to demonstrate pupils the interesting properties of nanomaterials, silica-based materials are particularly suited for school chemistry education due to their ubiquity in everyday life as well as their simple, cheap and comprehensible fabrication. In this contribution two kinds of silica-materials will be presented in detail:

a) Stöber particles: These are monodispersed nanoscaled spherical silica particles, which are applied for the fabrication of scratch resistant surfaces as well as artificial opals, for improving the flow properties of creams, food (ketchup), and as calibration substance in particle measuring technology.

b) Nanoscaled porous silica materials (*e.g.* SBA-15, MCM-41): These materials consist of ordered nanopores (range between 2 and 15 nm), with large surface areas up to 1000 m^2g^{-1}, small pore size distribution and high temperature stability. These materials are employed in medicine for controlled

drug release and in environmental technology for adsorption of liquids and gases, size selective separation in chromatography, or carrier for metal (-oxide) catalysts.
Besides the already mentioned reference to everyday life, these silica-based nanomaterials possess a high didactical potential with respect to teaching chemistry because a great variety of chemical fundamentals can be linked to their characteristics. These include for example reaction mechanisms like hydrolysis/condensation, principles of self-assembly, chemistry of surfactants, adsorption and catalysis. Additionally, by means of Stöber particles, the size of the nano dimension can be made accessible to pupils.

2. Synthesis of Silica-Based Nanomaterials: Stöber Particles and Nanoporous Silica

2.1 Stöber Particles

The synthesis of monodisperse silica particles is accomplished according to a bottom up process by precipitation of SiO_2 particles in a solution of ethanol, water, ammonia, and tetraethyl orthosilicate (TEOS) as the SiO_2 precursor. The mechanism of particle formation is complex and not fully understood yet. However, the main processes can be simplified and described in the following way: under alkaline conditions TEOS hydrolyses to silicic acid (1) followed by condensation of the silicic molecules which involves the formation of small primary particles. In a second step these particles grow to their final size which depends on the concentrations of TEOS, ammonia, ethanol and water.

$$Si(OEt)_4 + 4\ H_2O \leftrightarrows Si(OH)_4 + 4\ EtOH \qquad (1)$$
$$n[Si(OH)_4] \rightarrow n[SiO_2] + 2n\ H_2O \qquad (2)$$

Bogush et al. empirically found a formula (3) to describe the relation between the concentration of the involved chemical species and the final size *d* of the particles which is afflicted with an error of approx. 20 %.

$$d = A[H_2O]^2 \exp(-B[H_2O]^{1/2}) \qquad (3)$$

with

$$A = [TEOS]^{1/2} (82 - 151[NH_3] + 1200[NH_3]^2 - 366[NH_3]^3)$$
$$B = 1.05 + 0.523[NH_3] - 0.128[NH_3]^2$$

2.2 Nanoporous Silica

For the synthesis of nanoporous silica like SBA-15, MCM-41, ordered supramolecular aggregates of amphiphilic molecules (*e.g.* block copolymers or surfactants) serve as so called ‘soft matter templates’ for the creation of nanopores in the final solid. At a sufficient concentration of these amphiphilic molecules in an aqueous solution, discrete micelles are initially created. In dependence of the concentration (lyotropic system) and/or temperature (thermotropic system) supramolecular aggregates with different geometries (*e.g.* hexagonal or cubic) are formed. When adding a SiO_2 precursor like TEOS to this solution, hydrolysis and condensation reactions occur analogue to the formation of Stöber particles. During these processes the organic template is incorporated in the forming solid, resulting in a composite material which is composed of the silica material and the supramolecular aggregates (template). Final removal of the template by calcination (thermal combustion) or solvent extraction yields the respective nanoporous solid. Figure 1 displays the main processes which are involved in the synthesis of nanoporous silica materials.

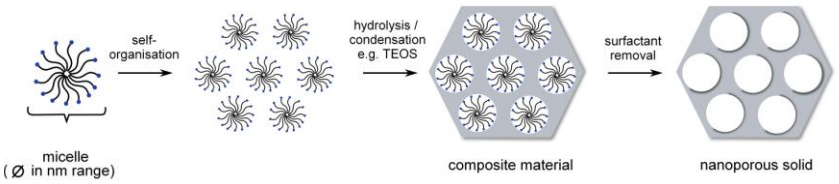

Fig. 1. Processes of soft matter templating during the fabrication of nanoporous silica materials

3. Example Experiments

The following selected experiments give a short insight of the great variety of school experiments using monodisperse Stöber particles and nanoporous silica. Both materials can be synthesized using cheap and easily handled chemicals.

3.1 Fabrication of a Synthetic Opal

12.5 g (13.8 mL) of an ammonia solution (25 %) are mixed with 100 g (127 mL) of ethanol before 1.4 mL tetraethyl orthosilicate (TEOS) are added while the reaction mixture is continuously stirred (see Figure 2, left). The turbidity which is observed after some minutes indicates the start of particle formation, which is shown in Figure 2 (centre). After the reaction mixture has been stirred for 24 hours the suspension (Figure 2, right) is centrifuged (U = 3000 min^{-1}) and the resulting sediment is washed with ethanol several times while the supernatant fluid is carefully removed during the washing steps.

Fig. 2. Stages of the formation of formation of Stöber nanoparticles in a school experiment directly after addition of TEOS (left), after 20 minutes (centre) and after 24 hours (right).

The thus-obtained sediment of SiO_2 particles is then redispersed in a few (!) drops of ethanol either by slightly shaking or stirring with a magnetic stirrer. A thoroughly cleaned object slide is attached with all four sides to a flat ground by means of glue strips. Afterwards 2-3 drops of the before-prepared SiO_2 suspension in ethanol are deposed on one of the glue strips (see Figure 3, left). A glass rod is slightly pressed on the object slide where the drops are deposed and is then rolled slightly pressing over the whole slide. During this procedure care has to be taken that the glass rod is not touched next to where the drops are deposed and the slide should be coated homogeneously by the suspension. The small amount of fluid evaporates after only a few seconds and the glue strips can be carefully removed if the optical result is satisfying. When the optical interference cannot be observed the deposed SiO_2 film can easily be removed and the experiment can be repeated.

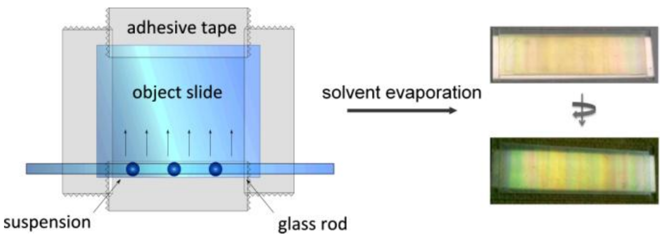

Fig. 3. Simple experiment for the fabrication of an opalescent layer on an object slide using self-manufactured Stöber silica particles.

Learning goals: hydrolysis/condensation (S_N2-mechanism), interference and diffraction phenomena on thin layers (photonic crystals), sol-gel chemistry.

3.1.1 Size Comparison of Stöber Particles with Macroscopic Objects

Since the size of Stöber particles can be varied by the modification of synthesis conditions (see section 1), particles are ideally suited to give students an impression of the size of the nano dimension by measuring the size of the particles with a scanning electron microscope (SEM) and relating this to the size of macroscopic observable objects, like a hair (see Figure 4). Using these SEM images, students can easily deduce the amount of particles which is required to obtain the length of the diameter of a hair by comparison of the different objects' images. For example: 800 particles with a diameter of 125 nm correspond to the thickness of one hair (100 µm).

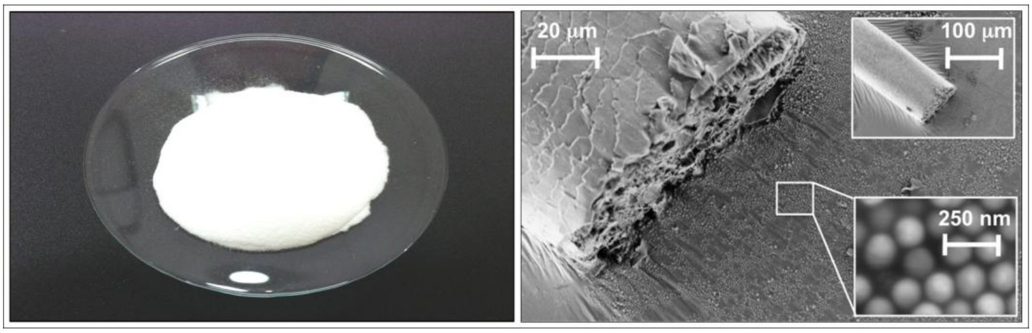

Fig. 4. Stöber particles macroscopic (left), SEM-images of an hair and Stöber particles with a diameter of ca. 125 nm.

Learning goals and contexts: Setup of a Scanning Electron Microscope, size of nano dimension, fundamental mathematical operations.

3.2 Fabrication of Nanoporous Silica Material

2.4 g cetyltrimethylammonium bromide (CTAB) are dissolved in 120 mL of water and are stirred until a clear solution is obtained (if necessary by slight heating). After addition of 8 mL ammonium solution (32 %) the reaction solution is stirred for another 5 minutes before 10 mL of tetraethyl orthosilicate (TEOS) are added. The mixture is then further stirred for 24 hours (see Figure 5 a,b). The resulting gel is transferred to a lab flask and heated to 80 °C for 24 h in an oven, (see Figure 5 b, c). Afterwards the mixture is filtered and the residue is washed with water and ethanol before it is dried at 60 °C. The surfactant can finally be removed by calcination using a gas burner or by repeated washing with acetone yielding the nanoporous silica material (see Figure 5, d-f).

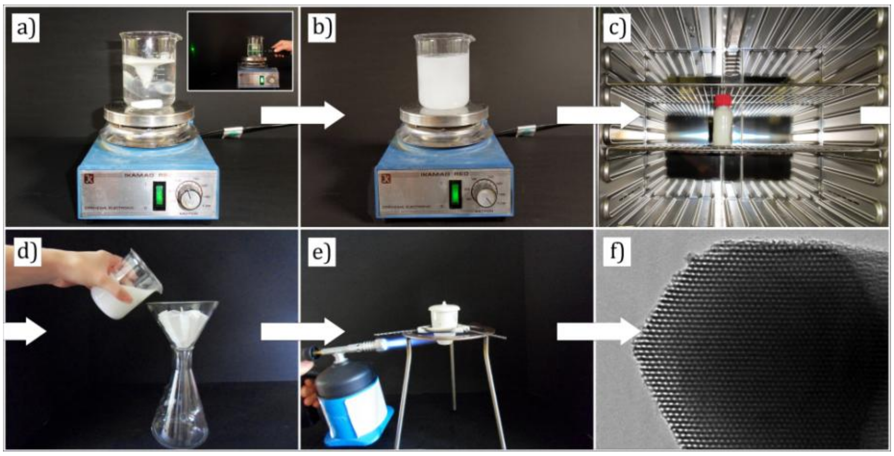

Fig. 5. Synthesis steps for the fabrication of nanoporous silica material.

Learning goals: surfactant chemistry, self-assembly, hydrolysis/condensation, sol-gel chemistry, properties of organic/inorganic matter.

3.2.1 Gas Adsorption Experiment Using Nanoporous Silica MCM-41

The high surface-to-volume ratio of nanoporous MCM-41 silica makes the material an ideal system to demonstrate gas-adsorption on porous materials to pupils, while a variety of learning contexts, like energy storage, can be linked to this topic. The gas-adsorption properties can be demonstratively developed by means of a simple experimental set-up (see Figure 6, left). In this experiment the resulting pressure is measured while the volume is reduced in a closed system where adsorbent porous and non porous silica materials are used. The analysis of the obtained *pV*-curves reveals a reduced pressure in the case of the porous material, which can be attributed to adsorption of gas molecules on the inner surface of the porous silica material. This is schematically depicted in a model (see Figure 6, right).

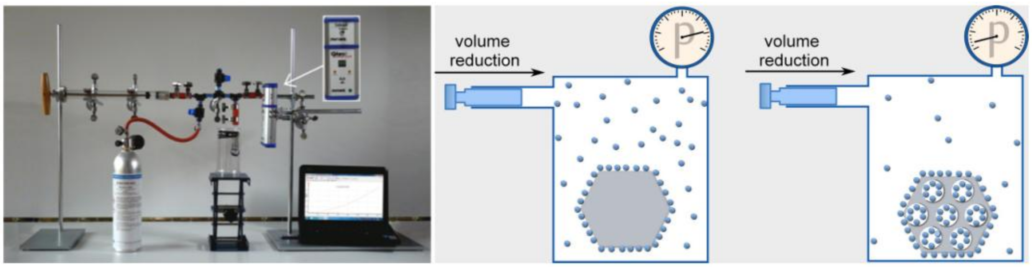

Fig. 6. Simple experimental setup for the demonstration of gas adsorption on nanoporous silica by measuring.

Learning goals and contexts: adsorption, gas and energy storage

4. Experiences and Outlook

The topic of silica-based nanomaterials has already been taught in various workshops at the Georg-August-University Göttingen with pupils from grades 10 and 11. These workshops have additionally been evaluated in explorative studies by means of structured observations and interviews with respect to the pupils' interest in this topic as well as their difficulties in understanding. The teaching projects consisted of short presentations focusing on the characteristics of nanomaterials and concepts for their fabrication and properties. Subsequently, these concepts have been deepened, with silica-based materials as an example, by exercises carried out in group work and in a lab course. The analysis of the studies shows that the pupils barely know about the presence of nanomaterials in everyday life. However a motivating access to this topic can be achieved by means of silica-based materials. Understanding of relevant chemical aspects such as the size of the nano dimension or the role of the surface for adsorption and catalysis can ideally be developed. The described experiments have been rated as particularly demonstrative and motivating. Based on these results current work is focusing on further silica-based teaching materials with nanoporous silicones which address aspects such as storage, temperature stability and separation.

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