

Using Sol-Gel Chemistry to Synthesize a Material with Properties Suited for Chemical Sensing

Development and Implementation of a Materials Science Experiment for the Undergraduate Curriculum

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Rationale

Materials chemistry is a field of high priority internationally, in terms of both fundamental and applied science. Research contributions to the advancement of this field come from a wide range of scientists who develop the synthetic processes, design the substances to produce the desired properties, perform the fundamental characterizations, and employ materials in a wide range of applications. However, materials chemistry continues to be a very minor segment of the undergraduate chemistry laboratory (1).

Sol-gel chemistry is an area of materials science that dates back to the mid-1800s. In recent years sol-gel chemistry has become a major topic of research. "Sol-gel" denotes a process by which largely inorganic polymers are synthesized. A "sol" is a dispersion of colloidal particles. A "gel" is an interconnected polymeric network formed by assembly of the sol. The gelation proceeds through stages by which the product's rigidity is increased. The final material produced in a room-temperature synthesis is a porous glasslike solid, which is termed a xerogel. Although "xerogel" implies a dry material, pore water is still present. Chemists continue to explore means of synthesizing xerogels with tailored properties. One property of interest is the internal pore structure. The pore structure can be controlled in a manner that traps species such as complexing reagents and biomolecules such as enzymes. Outcomes of new synthetic methods are formulations that are ideal for applications as diverse as chemical sensors, optical lenses, and electrodes for batteries and fuel cells.

Herein, we describe using sol-gel chemistry as a means of introducing first-year B.S. chemistry majors to a materials science experiment. Students synthesize silica xerogels in the laboratory using different preparation procedures. Metal salts, complexing reagents, and enzymes are "doped" within the xerogel's Si-O-Si network. Students investigate the influence of the synthesis and drying conditions on the porosity of the xerogels. Interpretations are made about how various aspects of the preparation procedure affect the outcome of their experiment. Conclusions are drawn based on measurements that reflect the pore diameters. Scientific literature is used in the development of hypotheses about the influence of variables on the properties of the product.

Cooperative learning is a major focus of this experiment. The strategy of cooperative learning has been shown to be successful in both the chemistry lecture and the laboratory through such intrinsic merits as development of higher-level thinking skills, increased student retention, and greater student satisfaction (2-6). We apply this approach to the laboratory by designing an experiment that is too broad for an indi-

vidual to complete but is feasible in a group setting. The class is divided into small groups to complete the assigned tasks of preparing and testing the xerogels. Students learn to construct spreadsheets and to employ linear regression analysis. Techniques such as thermogravimetric analysis (TGA) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) are used to obtain the data needed to characterize the pores of the xerogels. Xerogels that are doped with complexing reagents or enzymes as platforms for chemical and biochemical sensors are evaluated.

Experimental Background

One merit of sol-gel chemistry is that it offers a convenient method to synthesize a material for hosting chemical reactions. Many types of chemical species can be impregnated or "doped" within the pores of a xerogel by adding them to the sol. Organics (7, 8), organometallics (9), proteins (10), and enzymes (11) are just a few of the types of compounds that have been encapsulated in xerogels. An important example that has been emphasized in the recent literature is the doping of xerogels with biological compounds. It is found that biomolecules retain their activity when encapsulated in silica prepared by sol-gel chemistry. Monitoring the reactions is aided by the fact that the xerogel can be molded or cast into a variety of shapes (e.g., thin films, fibers, or monoliths).

The nature of xerogel synthesis allows students to investigate the control of pore size and to observe its influence on the properties of the material. The experimental variables of interest are drying and aging conditions (especially temperature) and the nature of the catalyst. As the drying time of xerogels is increased, more liquid is displaced from the pores, making the solid network more dense. Increasing the temperature at which xerogels are aged is, of course, a more direct means of drying. Acid or base catalysis increases the rate of hydrolysis and condensation reactions, which, in turn, increases the rate of water expulsion.

Experiments were developed to allow students to explore the interaction between the synthesis and drying conditions and the properties of the resulting xerogels, especially the pore diameters. The context was application of xerogels as sensor platforms, which is a topic widely reported in the literature. Avnir et al. summarized the use of sol-gel processes to obtain solids doped with organic reagents to serve as sensors for metal cations, anions, and hydronium ions (12). Here, the concept was adapted to an experiment in which complexing reagents for targeted metals were encapsulated in silica. The reaction was monitored by observing a color change. These colori-

metric sensors were evaluated on the basis of detectability, reproducibility, reusability, and response time.

Xerogels have been synthesized for application to biosensing. Biomolecules are known to denature outside of limited ranges of pH. The sol–gel process allows the xerogel matrix to form under conditions compatible with the biomolecules and, upon encapsulation, protects them from an otherwise hostile environment. The biomolecule can thus retain its normal stability and reactivity. Examples in the literature include using xerogels doped with hemoglobin, myoglobin, and glucose oxidase for the detection of oxygen, carbon monoxide, and glucose, respectively (13).

In the experiment run by the students, glucose oxidase is entrapped in a xerogel for the detection of glucose. Glucose oxidase is much larger than glucose, so the former is trapped in the xerogel whereas the latter can enter it via the porous structure. Hence, the enzyme-doped xerogel serves as a colorimetric sensor for glucose. It is important to note that a major purpose of this study is to have the students use the information from the sensor performance to draw conclusions about the pore structure of the xerogel.

In addition to possible sensor development, students examined parameters that affect xerogel porosity by performing leaching experiments. They were required to determine the amount of metal cation leached from a doped xerogel. Students doped xerogels with colored metal cation salts (e.g., salts of Ni(II) and Co(II)). Upon gelation, the xerogel is optically transparent but takes on the color of the doped cation. Xerogels were soaked in an aqueous solution, and the amount of leached cation was determined quantitatively. Varying amounts of cation were found to leach, depending on how the xerogel was prepared. The external solution (leachate) was analyzed using ICP–AES. The amount leached was interpreted in terms of pore diameter of the xerogel.

Thermogravimetry was another technique used to indirectly investigate xerogel structure. A thermogravimetric analyzer (TGA) was used to measure the amount of residual liquid, which is almost entirely water, present in the xerogel. In this case, the residual water was determined from the decrease in the mass of the xerogel at temperatures well above 100 °C. The amount of residual liquid was indicative of the pore volume.

A series of experiments involving these points was developed to give students the opportunity to collect both quantitative and qualitative data. Students obtained qualitative data regarding porosity by testing xerogels as colorimetric sensors. Quantitative data related to the porous nature of xerogels was provided by the residual liquid measurement and the amount of cation leached using TGA and ICP–AES, respectively.

Summary

This experiment was designed and written to serve as a collaborative laboratory project for first-year B.S. chemistry majors and to provide experience in materials chemistry. One portion of the experiment was discovery-based in that a detailed procedure was not given to students for testing xerogels as platforms for visual sensors (14, 15).

In contrast to a recently reported experiment on the combination of sol–gel chemistry with spectroscopy for an advanced undergraduate laboratory (16), the present experi-

ment is adaptable to a range of undergraduate student levels and to various instrumental methods. For example, the residual liquid can be determined by drying in a conventional oven, and the leaching can be quantified by colorimetry, atomic absorption spectroscopy, etc. In this regard, the leaching experiment is not restricted to the dopants used herein.

Cooperative learning and reporting results were also focuses of the experiment. Students were introduced to working in pairs and small groups to emulate what is common in the industrial workplace. Introduction to data handling, the requirement of a formal report in the style common in chemistry journals, and the introduction to use of scientific literature were considered important to prepare students for future work. Although many objectives are listed, however, the primary one was to introduce students to the synthesis and characterization of a material.

Equipment

The following equipment is needed for this experiment: polymethacrylate cuvettes, permanent markers, stir bars and stir plates, Oxford pipets, 1-mL pipets, volumetric flasks, and 50- or 100-mL beakers. Instrumentation needs include a thermogravimetric analyzer and an inductively coupled plasma–atomic emission spectrometer. A drying oven and either an atomic absorption or a UV–vis spectrophotometer are possible replacements.

Chemicals

The following chemicals are needed for this experiment: tetramethyl orthosilicate, methanol, water, hexadecyltrimethylammonium bromide, Triton X-114, and few-milliliter quantities of sodium hydroxide and hydrochloric acid. Also necessary are metal salts (e.g., nickel(II) nitrate, iron(III) nitrate, cobalt(II) nitrate etc.), colorimetric agents (e.g., dimethylglyoxime and sodium thiocyanate), glucose, glucose oxidase, and titanium(IV) chloride.

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^wSupplemental Material

Supplemental material for this article is available in this issue of *JCE Online*.

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