Supercritical Fluid Facilitated Growth of Copper and Aluminum Oxide Nanoparticles

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Supercritical fluids (SCFs) possess properties that are intermediate between liquids and gases. As the pressure and temperature of a fluid exceeds the critical point, minute changes in pressure or temperature significantly alter the physicochemical properties of the SCF (e.g., density, diffusivity, or solubility characteristics). This is especially important for synthetic applications, where reaction conditions (e.g., selectivities, rates, pathways) may be sensitively manipulated. Such reaction control is impossible using traditional organic-based solvents. Further, owing to the deleterious effects that many organic solvents have on the environment or one's health, media such as halogenated hydrocarbons (e.g., chloroform, dichloromethane) are being phased out of use, and benign replacements are being developed. Supercritical carbon dioxide (sc-CO_2) is an attractive alternative since it is inexpensive and poses no threat to the environment or human health. Currently, supercritical fluid extraction (SFE) remains the most heavily used application for SCFs. Within the last five years, there has been an explosion of research devoted to performing organic, inorganic, and organometallic syntheses in supercritical fluids; more recent reports are now exploiting this medium for nanomaterials synthesis *(1 , 2).*

An important goal for undergraduate curricula should be the constant upgrading of content to include the most leading-edge techniques. Not only would this improve student interest and motivation, but would also better prepare the students for their future careers in industry or academia. To this end, this *Journal* has published a few articles related to SCF technology for undergraduates *(3).* Although a recent review focused on the use of SCFs for nanomaterial synthesis *(2),* there are no published laboratory experiments related to the application of this medium for materials synthesis. This article describes a module to introduce undergraduate inorganic chemistry students to an exciting area of nanotechnology that also incorporates SCFs, an environmentally-friendly alternative to organic solvents.

Experimental

A photograph and thorough description of the SCF system and reactants used in this module are available in the Supplemental Material.ᵂ The methodology used to synthesize aluminum oxide and copper nanoparticles is illustrated in Figure 1. To generate Al_2O_3 particles, aqueous sodium aluminate was combined with a surfactant, either sodium bis(2-ethylhexyl)sulfosuccinate (AOT) in heptane, or an ammonium carboxylate perfluoropolyether ($[NH_4][CF_3O(CF_2CF(CF_3)O)_3CF_2COO]$) in water. This solution was injected into the pressurized reaction chamber for reaction with CO_2. For copper nanoparticle growth, ethanolic copper ions were allowed to diffuse into an aqueous solution containing a reducing agent (phenylenediamine).

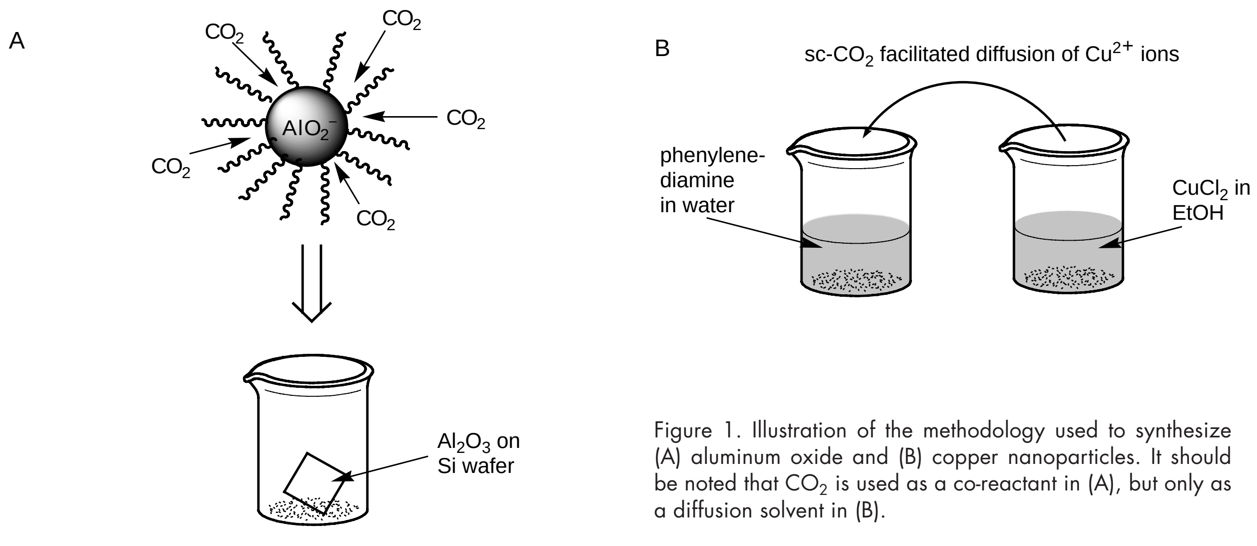

Figure 1. Illustration of the methodology used to synthesize (A) aluminum oxide and (B) copper nanoparticles. It should be noted that CO_2 is used as a co-reactant in (A), but only as a diffusion solvent in (B).

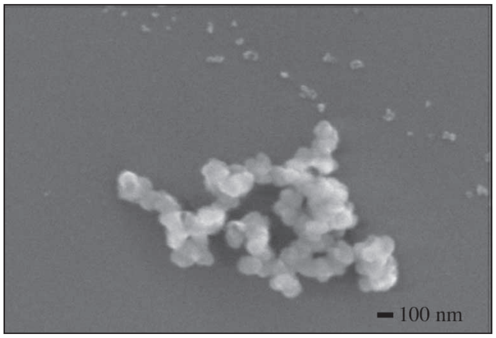

Figure 2. SEM for aluminum oxide nanoparticles deposited onto a silicon wafer.

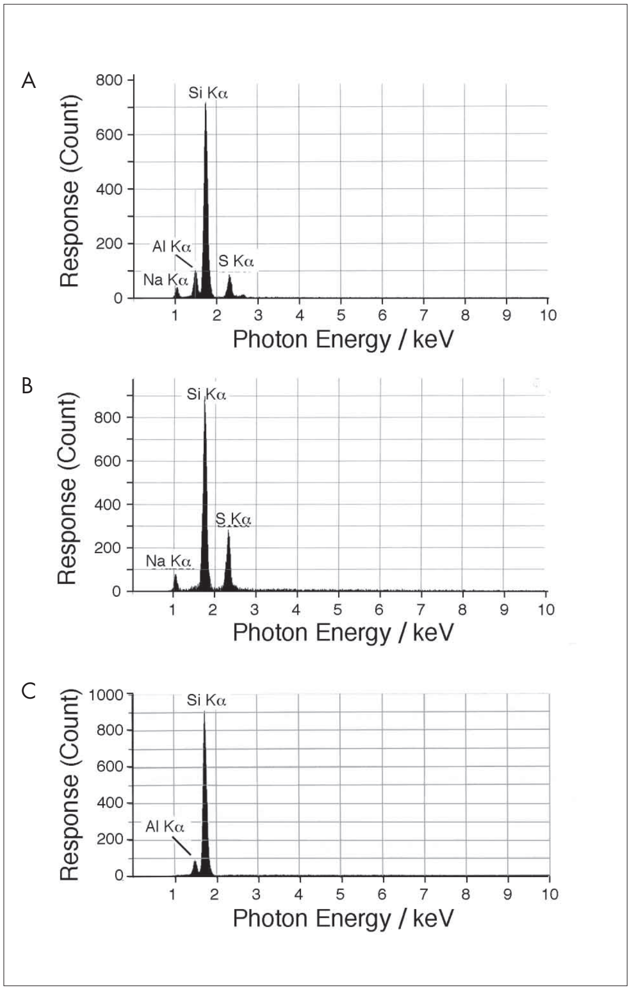

Figure 3. Energy-dispersive X-ray spectra for the analysis of aluminum oxide nanoparticles deposited onto a silicon wafer. Shown are representative spectra for:

(A) particles formed using AOT, followed by a heptane rinse

(B) particles formed using AOT, without a heptane rinse

(C) particles formed using the perfluorinated surfactant

Hazards

The SFT-150 supercritical fluid system utilized in the module was acquired from Supercritical Fluid Technologies, Inc. *(4)*. This equipment is designed with a variety of pressure-relief capabilities, is capable of safely withstanding 70 MPa/200 °C, and features hand-tightened connections, which are specifically important for undergraduate research and teaching. In addition, CO_2 used within this system is a nontoxic and nonflammable fluid. The reducing agent 1,4-phenylenediamine is stable, but oxidizes when exposed to air or light. This chemical is considered toxic if swallowed, inhaled, or absorbed through the skin, so appropriate safety protocols should be enforced.

Results

A representative student-generated scanning electron micrograph (SEM) image and energy-dispersive X-ray spectra (EDS) for aluminum oxide deposited onto a silicon wafer are shown in Figures 2 and 3, respectively. SEM showed significant particle agglomeration, with average particulate diameters on the order of 100 nm. However, discrete Al_xO_y nanoparticles on the order of 20–50 nm are also seen in Figure 2, which were verified for aluminum content using elemental dot-mapping, in association with EDS.

The particles formed on the silicon wafer were precipitated through simple venting of the supercritical chamber, providing an opportunity for co-deposition of the surfactant residue. The chemical analyses of the deposited particles with and without using a postrinse of heptane (for AOT) are shown in Figures 3A and B, respectively. In contrast to AOT, the fluorinated surfactant is completely soluble in CO_2 at all pressures and temperatures, allowing for a more efficient removal of surfactant using a dynamic CO_2 flow, resulting in the deposition of pure aluminum oxide particles (Figure 3C).

The redox reaction to generate copper nanoparticles utilized CO_2 as a traditional unreactive solvent. This method exploits the greater solubility of ethanol, relative to water, in nonpolar CO_2. Through simple diffusion involving dilute solutions (ca. 10^{-3} M), the solvated copper ions were brought into contact with the *p*-phenylenediamine (PPDA) reducing agent. Although mechanistic studies are currently underway, the route is most likely through single electron donation from both ends, resulting in a $PPDA^{\bullet +}$ Cl^- sideproduct. A representative student-generated transmission electron micrograph (TEM) image of the copper nanoparticles is illustrated in Figure 4. Although larger drops of solvent and byproduct salt are evident, high-contrast copper nanoparticles on the order of 10–15 nm are readily observed. There were no observable differences in particle diameters when deposited onto grids using aerosol delivery from suspended solvents, relative to RESS (rapid expansion of the supercritical solution) deposition. However, there is sufficient merit in introducing both techniques in the laboratory, as there are often large discrepancies in nanoparticulate diameters between these techniques.

Discussion

The combination of supercritical fluid technology with advanced characterization techniques such as electron micros-

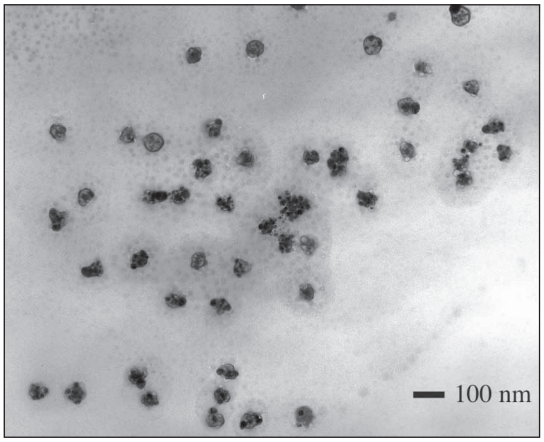

Figure 4. TEM image of metallic copper nanoparticles, sprayed onto a TEM grid from an aqueous suspension.

copy provided a practical and rewarding undergraduate laboratory experiment. A high level of student interest and motivation was observed during this laboratory, as students had the opportunity to synthesize and observe structures that hitherto have only been discussed in the literature. Comments from students were all positive in nature, with some students deciding to register in a biology course, related to SEM and TEM, in a future semester. It must be noted that the experiment was introduced into a class consisting of a broad range of student preparation, from sophomore to senior levels. However, even with such student disparity, every group was intrigued by the experiment and did not have any difficulties with the experimental procedure. As expected, the students that had not taken organic chemistry had a greater challenge with understanding the mechanisms for nanoparticle formation. However, consultations with the instructor and more advanced students quickly alleviated these problems.

A variety of pedagogical outcomes were realized by this module:

- **Hands-on experience with SEM–EDS and TEM:** In addition to learning the theoretical concepts related to SEM–TEM imaging and EDS measurements, students gained hands-on experience with proper sample-preparation techniques as well as careful operation of both instruments to obtain high-quality images. Students were particularly amazed at the size of individual quadrants contained on a single TEM grid and observed the problems associated with finding small-diameter nanoparticles on a grid (“finding a needle in a haystack!”).

- **Hands-on experience with supercritical fluid technology:** Prior to the semester, most students had heard of SCFs and some of the benefits that they provide. However, no student had the opportunity to work with such a system prior to this experiment. A questionnaire administered after the semester indicated that students had gained a valuable appreciation of the benefits and challenges of using SCFs; not only for nanoparticle growth, but for reaction chemistry, in general. All students commented on the simplicity of the system design, as students immediately became familiar with its key components and operation.

- **Considerations regarding nanoparticulate growth:** The SCF diffusion-based, nonsurfactant–micellar procedure used to grow copper nanoparticles has not been reported in the literature to date. This novel approach created instantaneous excitement and represented the most anticipated portion of the module. The larger agglomeration observed with aluminum oxide particles catalyzed useful discussion between the instructor and students, with many potentially useful alternatives being suggested to overcome the clustering. Some examples suggested by students were:

  Faster system venting to prevent nucleation

  Depositing nanoparticles of aluminum oxide onto TEM grids through direct venting (RESS)

  Changing the concentrations of reagents

  For copper particle formation: changing the nature or concentration of the reducing solution

- **Development of effective group participation:** The rotation of this module featured groups of two students that had to work together to prepare solutions, including calculating appropriate masses and selecting appropriate glassware. Further, each group was asked to independently schedule time with the SEM–TEM manager and hold a group meeting to compile results needed for their formal laboratory report.

As more chemistry departments are becoming interdisciplinary in nature, undergraduate experiments that feature current research interests in chemistry must also borrow resources from other departments. Hence, collaboration with engineering, materials science, or other departments with suitable instrumentation could be established to meet the instrumental needs of this experiment. For example, since the chemistry department at CMU does not have electron microscopy capabilities, suitable instrumentation was utilized through collaboration with the Department of Biology. Other options for smaller schools may be to collaborate with local industries possessing SEM–TEM instrumentation or send representative samples to laboratories that feature remote characterization facilities. This latter alternative has been demonstrated even at the high school level, where students are now able to analyze their own samples over the Web *(5)*. If suitable electron microscopy facilities are not available even through collaboration, techniques such as dynamic light scattering (DLS) may also be employed. DLS data for this experiment may also be found in the Supplemental Material.$^{\text{W}}$

Acknowledgments

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wSupplemental Material

Instructions for the students, including postlab questions, and notes for the instructor, including a photograph of the system and DLS spectra, are available in this issue of *JCE Online*.

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