A Method for Making Inorganic and Hybrid (Organic/Inorganic) Fibers and Vesicles with Diameters in the Submicrometer and Micrometer Range via Sol–Gel Chemistry and Electrically Forced Liquid Jets

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There is growing interest in manipulating materials structures at the micro- and nanometer level with the aid of external fields.¹ Certain physical phenomena that are rather general might thus be able to add a new dimension to the issue of structure control and assist an already rich array of mature and emerging chemical methods (e.g., self-assembly) in the design of novel nano- and microstructures. For example, while reports on the use of sol–gel (SG) chemistry to produce template-mediated nanostructured materials are frequently encountered in the open literature,² this established synthetic approach is still typically associated with the template-free design of inorganic and hybrid (organic–inorganic) glassy monoliths, powders, and films.³ The SG process relies on controlled solvolysis and condensation of metal or metalloid centers with oxo ligands, such as alkoxides.

The use of electrohydrodynamics (EHD) to produce organic polymer fibers and electrospray-made nanoparticles is well documented.⁴ In brief, a liquid containing dissolved species is pumped through a capillary at μL/h-nL/h flow rates, and an electric field is created between this capillary and a “collection point” (CP, normally a flat metallic plate or foil) with the aid of a high-voltage source. A brief description of the EHD apparatus is provided as Supporting Information. The action of the electric field over a drop forming at the tip of the capillary is to change its shape into a charged conical meniscus known as the Taylor cone. In an effort to “close the circuit”, a very thin liquid jet is ejected off the tip of the Taylor cone. The reader interested in the physics of EHD is referred to a classic paper by Melcher and Warren,⁵ and to more recent theoretical work by others.⁶ The various forms of Taylor cone shapes and jet instabilities, from disruption of the electrified liquid jet into an electrospray to the bending instabilities that can ultimately lead to production of organic polymer nanofibers⁷⁻⁸ are explained by theory.⁶ Here, it suffices to say that viscosity, conductivity, density, surface tension, voltage, and flow rates play a key role in determining the ultimate shape of the Taylor cone and the jet instability type. Figure 1 (inset) shows the Taylor cone structure formed when two coaxial capillaries are used to feed two liquids, in this case olive oil and water.

A coaxial two-capillary tip similar to that shown in Figure 1 has recently been employed by some of us to demonstrate liquid-in-liquid assemblage in the micrometer and submicrometer range, and to produce vesicles with a fast-reacting photopolymer shell and a liquid core.⁷ Logically, limiting this technique to photopolymer shells is too confining from a materials design viewpoint.

Figure 1. Olive oil/water compound Taylor cone (inset). Outer diameter of the coaxial double-capillary tip is approximately 230 μm.

Figure 2. α-Al₂O₃ nanofibers. SEM image is 1.4 μm wide.

To the best of our knowledge, there are no reports available in the open literature on EHD/SG-mediated synthesis of submicrometer inorganic fibers and core–shell shapes. Shortly before ref 7 was published, we disclosed a procedure for making inorganic, nonoxide ceramic and hybrid nanofibers via single-capillary EHD and sol–gel chemistry.⁸ To illustrate the versatility of combining sol–gel chemistry with single-liquid EHD, Figure 2 shows a scanning electron micrograph of α-Al₂O₃ fibers with diameters below 200 nm made from aged sols of aluminum di-sec-butoxide ethylacetatoacetate in acidic H₂O/EtOH media.

Mechanical spinning of sols does not afford routine synthesis of continuous oxide fibers with such small diameters. Besides crystalline alumina, we were also able to make submicrometer fibers of other oxide and non-oxide ceramics via SG/EHD (see Supporting Information). Fibers in Figure 2 are discontinuous due to the grinding required for SEM specimen preparation. From a chemical synthesis viewpoint, this technique for making submicrometer fibers normally requires catalyzed hydrolysis (e.g., acid, base, or fluoride

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catalysts and sorbents. The vesicles, which have a porous, hybrid structure, are particularly noteworthy as we were also able to use water as a solvent (sol) and a core liquid, thanks to shell-evaporation time scales below that of typical liquid–liquid (core–shell) mixing (see Supporting Information). One of the advantages of the proposed technique is that the core-to-shell mass ratio can be precisely set by adjusting the two liquid flows, effectively providing a means (in conjunction with voltage) for shell- and core-size control.

In conclusion, we report for the first time on the use of SG and EHD to make inorganic and hybrid (organic/inorganic) materials with characteristic lengths controllable at the submicrometer and micrometer levels. Examples of fiber and vesicle structures are provided. The proposed approach is viewed as quite general and might find use, among other potential applications, in nanoreactor design, encapsulation, ultrafiltration, catalytic membranes, and reinforced materials.

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Supporting Information Available: Chemical and EHD methods for synthesis and characterization of the α-Al2O3 fibers and hybrid capsules, other examples, and description of the EHD unit (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References


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