

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

Gustavo Larsen,^{*,†} Raffet Velarde-Ortiz,[†] Kevin Minchow,[†] Antonio Barrero,[‡] and Ignacio G. Loscertales^{*,§}

University of Nebraska-Lincoln, Department of Chemical Engineering, 207 “O” Othmer Hall, Lincoln, Nebraska 68588, University of Sevilla, Mecánica de Fluidos, Esc. Superior de Ing., Avda. de los Descubridores, s/n, 41092 Sevilla, Spain, and University of Málaga Ing. Mecánica y Mec. de Fluidos, E.T.S. Ing. Industriales, Pza. El Ejido, s/n, 29013 Málaga, Spain

Received October 16, 2002; E-mail: glarsen@unlserve.unl.edu

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 $\mu\text{L/h}$ – 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 nanofibers^{4a–d} are explained by theory.^{5,6} 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.

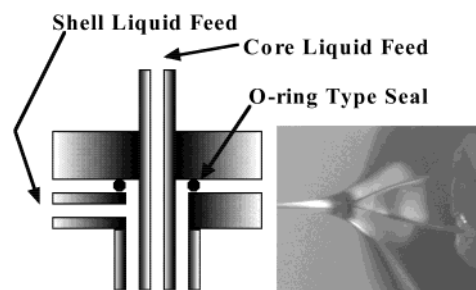


Figure 1. Olive oil/water compound Taylor cone (inset). Outer diameter of the coaxial double-capillary tip is approximately 230 μm .

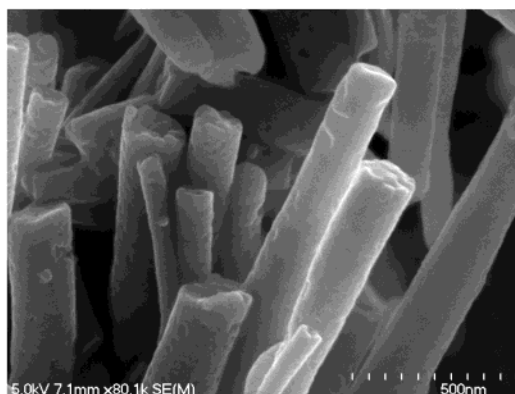


Figure 2. $\alpha\text{-Al}_2\text{O}_3$ nanofibers. SEM image is 1.4 μm wide.

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 $\alpha\text{-Al}_2\text{O}_3$ fibers with diameters below 200 nm made from aged sols of aluminum di-*sec*-butoxide ethylacetate in acidic $\text{H}_2\text{O}/\text{EtOH}$ 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

[†] University of Nebraska-Lincoln.

[‡] University of Sevilla.

[§] University of Málaga Ing. Mecánica y Mec. de Fluidos.

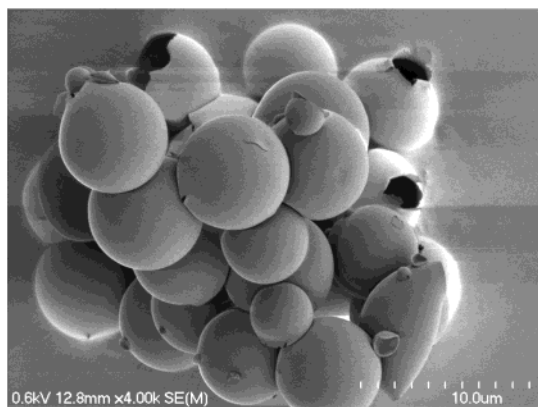


Figure 3. 3–7 μm silica/siloxane hybrid vesicles with nanometric shells. Full width of SEM image is 30 μm .

catalysis) and polymerization of the inorganic precursor sol close to its gel point. Subsequently, and thanks to a dramatic increase in the air–sol interface on electrified jet formation, a small amount of solvent evaporation between the delivery point (capillary) and the CP is all it takes to effect the sol–gel transition. Postsynthetic thermal and chemical treatment of the uncured gel nonwoven deposits may be used to effect crystallization and removal of organic mater, such as unreacted alkoxy groups and residual solvent. A key aspect of the SG/EHD technique is that, unlike nanofibers made from dissolved organic polymers and EHD,^{4a–d} aged gels that could ultimately lead to inorganic nanofibers are essentially insoluble in most solvents. Thus, dissolution of a preformed material is generally not possible prior to using EHD to make inorganic, submicrometer fibers, and gelation must occur during the “time-of-flight” of the electrified sol–gel between the capillary tip and the CP. Interestingly, another method to make alumina nanofibers (discontinuous) based on a physical phenomenon called “wire electroexplosion” has recently been reported.⁹ The SG/EHD method proposed in this communication is viewed as more general than that reported in ref 9. The reader interested in the synthesis of inorganic nanorods and nanotubes by purely chemical methods is referred to an excellent review article by Patzke et al.¹⁰

We then speculated that a combination of the methods described in refs 7 and 8 was to provide a new SG route for the rational design of vesicles in the nanometer and micrometer ranges. Figure 3 shows 3–7 μm vesicles made from a partially polymerized ethanolic solution of tetraethyl orthosilicate and a permethylated cyclic oligosiloxane (shell liquid), and olive oil (core liquid). Similar sol–gel chemistry was used by one of us to synthesize glassy hybrid catalysts and sorbents.¹¹ The vesicles, which have a porous, hybrid shell with a thickness below 100 nm, were solvent-extracted with Cl_2CH_2 to remove the olive oil core, dried at 110 $^\circ\text{C}$, and later mechanically broken to expose their “egg-shell” appearance. In this case, it was necessary to use a corona discharge to neutralize the core–shell assemblies at a short distance from the Taylor cone, to extend the “time-of-flight” for effective shell-hardening. What is particularly noteworthy is that we were also able to use water as

core liquid, thanks to shell–solvent evaporation time scales below those typical of 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 level. 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.

Acknowledgment. We thank the National Science Foundation for financial support under Grants DMI-0210850, CTS-0129190, and CTS-0 001524.

Supporting Information Available: Chemical and EHD methods for synthesis and characterization of the $\alpha\text{-Al}_2\text{O}_3$ 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

- (1) For example, Section 14f of the American Institute of Chemical Engineers Annual Meeting, Indianapolis, November 2002, <http://www.aiche.org/conferences/techprogram/paperdetail.asp?PaperID=640&DSN=annual02>.
- (2) (a) Wang, Z.-M.; Lin, Y. *J. Catal.* **1998**, *174*, 43–51. (b) Adeogun, M. J.; Hay, J. N. *Chem. Mater.* **2000**, *12*, 767–775. (c) Besson, S.; Gacoin, T.; Jacquiod, C.; Ricolleau, C.; Babonneau, D.; Boilot, J.-P. *J. Mater. Chem.* **2000**, *10*, 1331–1336. (d) Pang, J. B.; Qiu, K. Y.; Wei, Y. *J. Non-Cryst. Solids* **2001**, *283*, 101–108.
- (3) (a) Brinker, C. J.; Scherer, G. W. *Sol-gel Science: The Physics and Chemistry of Sol-gel Processing*; Academic Press: Boston, 1990. (b) Klein, L. C. *Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics, and Specialty Shapes*; Noyes Publications: Park Ridge, NJ, 1988.
- (4) (a) Fong, H.; Chun, I.; Reneker, D. H. *Polymer* **1999**, *40*, 4585. (b) Doshi, J.; Reneker, D. H. *J. Electrostat.* **1995**, *35*, 151. (c) Fang, X.; Reneker, D. H. *J. Macromol. Sci.* **1997**, *36*, 169. (d) Boland, E.; Wnek, G.; Simpson, D.; Pawlowski, K.; Bowlin, G. *J. Macromol. Sci. A* **2001**, *38*, 1231. (e) Bognitzki, M.; Frese, T.; Steinhart, M.; Greiner, A.; Wendorff, J. H.; Schaper, A.; Hellwig, M. *Pol. Eng. Sci.* **2001**, *41*, 982–989. (f) Wang, X.; Drew, C.; Lee, S.-H.; Senecal, K. J.; Kumar, J.; Samuelson, L. A. *J. Macromol. Sci. A* **2002**, *39*, 1251. (g) Deitzel, J. M.; Kosik, W.; McKnight, S. H.; Beck Tan, N. C.; DeSimone, J. M.; Crette, S. *Polymer* **2002**, *43*, 1025–1029. (h) Lenggoro, I. W.; Okuyama, K.; Fernandez de la Mora, J.; Tohge, N. *J. Aerosol Sci.* **2000**, *31*, 121. (i) Gomez, A.; Bingham, D.; De Juan, L.; Tang, K. *J. Aerosol Sci.* **1998**, *29*, 561.
- (5) Melcher, J. R.; Warren, E. P. *J. Fluid Mech.* **1971**, *47*, 127–143.
- (6) (a) Gañán-Calvo, A. M. *J. Fluid Mech.* **1997**, *335*, 165. (b) Gañán-Calvo, A. M.; Pantano-Rubino, C. *J. Aerosol Sci.* **1993**, *24*, S19. (c) Spivak, A. F.; Dzenis, Y. A. *Mech. Res. Commun.* **2000**, *27*, 37. (d) Hohman, M. M.; Shin, M.; Rutledge, G.; Brenner, M. P. *Phys. Fluids* **2001**, *13*, 2201–2220. (e) Reneker, D. H.; Yarin, A. L.; Fong, H.; Kumbhongse, S. *J. Appl. Phys.* **2000**, *87*, 4531–4547.
- (7) Loscertales, I. G.; Barrero, A.; Guerrero, I.; Cortijo, R.; Márquez, M.; Gañán-Calvo, A. M. *Science* **2002**, *295*, 5560.
- (8) Larsen, G.; Dzenis, Y. U.S. Patent pending (09/11/01).
- (9) Tepper, F.; Lerner, M.; Ginley, D. *Am. Ceram. Soc. Bull.* **2001**, *80*, 57.
- (10) Patzke, G. R.; Krumeich, F.; Nesper, R. *Angew. Chem.* **2002**, *41*, 2446–2461.
- (11) Larsen, G.; Wagner, J.; Vu, D.; Nguyen, C.; Lotero, E. *Chem. Mater.* **1998**, *10*, 3756.

JA028983I