ELECTROHYDRODYNAMIC FABRICATION OF INORGANIC AND HYBRID (ORGANIC-INORGANIC) FIBERS AND CORE-SHELL STRUCTURES WITH MICRO- AND NANOMETRIC DIMENSIONS

By

Raffet Velarde-Ortiz

A DISSERTATION

Presented to the Faculty of
The Graduate College at the University of Nebraska
In Partial Fulfillment of Requirements

For the Degree of Doctor of Philosophy

Major: Engineering (Chemical Engineering)

Under the Supervision of Professor Gustavo Larsen

Lincoln, Nebraska

September, 2004

UMI Number: 3143549

UMI

UMI Microform 3143549

ProQuest Information and Learning Company
300 North Zeeb Road
PO Box 1346
Ann Arbor, MI 48106-1346

ELECTROHYDRODYNAMIC FABRICATION OF INORGANIC AND HYBRID (ORGANIC-INORGANIC) FIBERS AND CORE-SHELL STRUCTURES WITH MICRO- AND NANOMETRIC DIMENSIONS

Raffet Velarde-Ortiz, Ph.D.
University of Nebraska, 2004

Advisor: Gustavo Larsen

This dissertation describes the fabrication of inorganic and hybrid (organic-inorganic) fibers and core-shell spheres and tubes with micro and submicrometric dimensions. These structures resulted from the application of electrohydrodynamic forces to carefully aged, viscous sol-gel precursors. The contribution of Dr. Larsen and Dr. Dzenis (Engineering Mechanics, UNL) to the field was to extend the electrospinning technique to the inorganic materials field. At a later stage, Dr. Larsen and collaborators made such structures with hollow geometries for the first time.

Using this technique, titania-silica, silica, alumina, mullite, zirconia and yttria-stabilized zirconia fibers of quasi-circular cross sections with diameters ranging from 0.15 to 1 μm, and fibers with non-circular cross sections (ribbons) with widths of 20-40 μm and thicknesses of just few microns were produced. The materials initially collected were amorphous, and after an appropriate thermal treatment they formed polycrystalline phases, and in all cases they displayed a remarkable structural stability retaining their individual fibrous identity.

Furthermore, using a coaxial nozzle that was previously used to carry out liquid-liquid encapsulations expanded the range of potential applications of this novel technique. The coaxial nozzle allows the generation of compound liquid jets. In this case the shell liquid was the aged sol and the core liquid was an inert, immiscible or slow-mixing liquid such

as olive oil, glycerin or water. The result was the formation of well-defined spherical hollow silica spheres and tubes with average diameters from 200 nm to 5 μm, and wall thicknesses of few nanometers to 2 μm. Since the injection of the shell and core liquids is done using independently controlled pumps, the flow rate ratio of both streams can be conveniently adjusted and different wall thicknesses can be obtained. On collection, certain liquid templates evaporate at room temperatures, thereby producing solid hollow structures without further processing. This approach is simple and very general and it is expected that other systems such as dissolved polymers can be used.

To Rita R. Stranik. Thank you so much for all your love, support, and understanding. It was a team work! You are my gin, I am your tonic.

A mis padres Sarita y Eduardo; y a mis hermanos Lalo y Hari. Ustedes sacrificaron tanto para que yo pudiera vivir esta experiencia. ¡Muchas gracias, les quiero a todos!

Acknowledgements

The work presented in this dissertation includes the projects that I carried out since I joined Dr. Larsen's lab in August of 1999. The success of my tenure would not have been possible without the collaboration of the current and former members of the group thank you for your teamwork. I am especially grateful for two people: Dr. Edgar Lotero, for his friendship and helpful discussions on all sorts of matters; and Dr. Rubén Spretz, not only for his invaluable editorial comments and suggestions during the writing process, but also for collaborating with me on many of the projects presented here. Special thanks are dedicated to Kevin Minchow (Mr. K) and James Randazzo (Mr. J) for their hard work and dedication to the Al_2O_3, SiC, and YSZ projects.

One of the most exciting aspects of my research came from the interdisciplinary nature of the projects that gave me the opportunity to interact with groups from different scientific backgrounds. I would like to thank Dr. Yuris Dzenis from the Laboratory of Nanostructured Materials Engineering Mechanics (UNL) and his team, Ms. Roshanak Nilchiani and Dr. Yongkui Wen, with whom I carried out the electrospinning of ZrO_2, TiO_2-SiO_2, $3Al_2O_3$-$2SiO_2$ fibers. The fabrication of hollow structures was possible thanks to the collaboration with Dr. Ignacio Gonzalez Loscertales from the *Laboratorio de Mecanica de Fluidos, Universidad de Malaga* (Spain), and his collaborators, Mr. Juan Francisco Navarro and Ms. Maria de los Angeles Jimenez Baena.

I would like to thank Mr. Brian Jones for his helpful suggestions and discussions regarding the XRD analysis of our samples. Special thanks go to Mr. Leonard Akert for his dexterous abilities in the fabrication of many, if not all, of the gadgets and equipment presented in this work. Thanks for introducing me into the world of photography. I will never forget the first time I hold a SLR on my hands. Also I would like to acknowledge

Ms. Nicole Church for her tireless dedication to the department. Her work contributed greatly to the realization of this work.

Gracias, Thank You, Merci Beaucoup, ありがとう, Terima Kasih, Dankie, спасибо, 감사합니다 , Tesekürler, to all of the wonderful friends from all over the world that I have met in Lincoln that have keep me sane during the time that I have been "dissertating".

Thanks you also to the extended Stranik family for welcoming me and making me feel at home in Nebraska. I have enjoyed all the holidays I have spent with your family.

Last but not least, I would like to thank my advisor, Dr. Gustavo Larsen, for giving me the opportunity to work under his wise guidance for the last five years. I have learned immeasurable lessons from him. I am grateful for his patience, sincerity, and for showing me the meaning of *rex non-verba*. I keep trying!

Contents

List of Figures

List of Tables

List of Equations

Chapter 1 Introduction

Fabrication of inorganic and hybrid (organic-inorganic) functional materials with micro- and nanometer scales is of vital importance because of their potential applications in catalysis, adsorption, electronics, drug-delivery, sensor technology, composite materials, and in many other scientific and technological fields. Sol-gel chemistry continues to be one of the most common synthetic methods used for the fabrication of these types of materials. For the most part, the control of the morphology, texture and characteristic dimensions of materials has been achieved by combining physical methods with chemical events (e.g., self-assembly). However, manipulation of structural features with micro- and nanometer dimensions is not a trivial task and current technologies present some limitations. For instance fabrication of inorganic fibers rely mostly on the use of rather conventional physical methods (e.g. fiber blowing, dry-spinning) and the minimum fiber diameter that can be achieved is 1-10 μm. Fibers and spherical structures with mesoporous textures and with diameters as small as 50 nm can be synthesized through chemical methods (e.g. self-assembly).

However, to rely on the occasional ability of certain molecules to self-assemble and act as structure directing agents is not a general strategy, i.e., its application to a system with different chemical composition than the one they were designed for is a difficult task. Other less-restrictive strategies involve the use of templates as building platforms. This is the case of the use of emulsions to fabricate core-shell and solid spherical particles, and the use of porous membranes and anodic alumina to produce fibrous structures. In either case the template must be selectively removed. The characteristic dimensions of the materials produced with such template-based methods are subject to the to dimensions of the template itself. Thus, the development of a simple, rather general technology for the

fabrication of inorganic and hybrid structures with micro and nanometer dimensions would be of great interest to scientist and engineers in a broad spectrum of fields.
Despite the fact that nature takes advantage of external fields rather routinely to create nano- and microstructures [1], engineers and material scientists have rarely taken advantage of gravitational, magnetic, or electrostatic fields to fabricate such structures. Recently, the use of external fields to manipulate nanostructured materials has received some attention [2]. For example, electromagnetic fields have been used to align silicate-surfactant liquid crystals. Polymerization of the silicate units using an acid catalyst formed a solid matrix that can be thermally treated to remove the surfactant. The result is a hierarchically structured silicon oxide material with macroscopic pore alignment and hexagonal mesoporosity [3].

Electrohydrodynamic forces have been successfully used in the atomization of liquids and solutions, in the fabrication of spherical particles from soluble biopolymers, polymers and sol-gel precursors. However, prior to the year 2001 there was no indication of the use of electrohydrodynamic forces for the fabrication of inorganic fibers in the open literature. For the most part, only soluble organic polymers, biopolymers, and molten polymers have been used as structural precursors. To close this gap Dzenis and Larsen proposed a simple method that combines electrohydrodynamics and sol-gel chemistry (SG-EHD) to fabricate inorganic and hybrid (organic-inorganic) submicrometer-size fibers [4].

The objectives of the work presented in this dissertation are: (a) to synthesize sol-gel precursors whose properties (e.g., viscosity, density, electrical conductivity, and surface tension) permit the use of electrohydrodynamic forces to fabricate inorganic and hybrid micro- and submicrometric fibers and hollow structures; (b) to find the experimental parameters (e.g., electrode separation, flow rate, and voltage gradient) necessary to fabricate such structures through the use of the proposed method. The accomplishment