

Encapsulation Nanotechnologies

Edited by Vikas Mittal

 Scrivener
Publishing

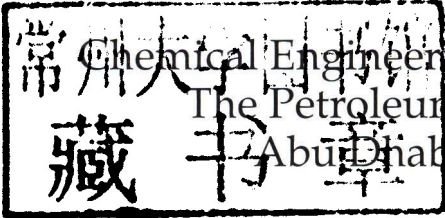
WILEY

Encapsulation Nanotechnologies

Edited by

Vikas Mittal

Chemical Engineering Department,
The Petroleum Institute,
Abu Dhabi, UAE



Scrivener
Publishing

WILEY

Copyright © 2013 by Scrivener Publishing LLC. All rights reserved.

Co-published by John Wiley & Sons, Inc. Hoboken, New Jersey, and Scrivener Publishing LLC, Salem, Massachusetts.

Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at <http://www.wiley.com/go/permission>.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at www.wiley.com.

For more information about Scrivener products please visit www.scrivenerpublishing.com.

Cover design by Russell Richardson

Library of Congress Cataloging-in-Publication Data:

ISBN 978-1-118-34455-2

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

Encapsulation Nanotechnologies

Scrivener Publishing
100 Cummings Center, Suite 541J
Beverly, MA 01915-6106

Publishers at Scrivener

Martin Scrivener (martin@scrivenerpublishing.com)
Phillip Carmical (pcarmical@scrivenerpublishing.com)

Preface

The encapsulation process is prevalent in the evolutionary processes of nature, where nature protects the materials from the environment by engulfing them in a suitable shell. These natural processes are well known and have been applied to numerous processes in the pharmaceutical, food, agricultural, and cosmetics industries. Thus, this allows one to combine the properties of the various components along with the time point of combination, if the release from such capsules can be controlled.

In recent years, owing to the increased understanding of the material properties and behaviors at nanoscale, research in the encapsulation field has also moved to the generation of nanocapsules, nanocontainers, etc. One such example is the generation of self-healing nanocontainers containing corrosion inhibitors which can be used in anti-corrosion coatings. The processes used to generate such capsules have also undergone significant developments. Various technologies based on chemical, physical and physic-chemical synthesis methods have been developed and applied successfully to generate encapsulated materials.

Owing to the high potential of the developed technologies and products in a large number of commercial processes, it is of significance to compile the recent technological advancements in a comprehensive volume. This volume not only introduces the subject of encapsulation to readers new to the field, but also serves as a reference for experts working in this area.

Chapter 1 details the copper encapsulation of carbon nanotubes. Since copper is a good electrical and thermal conductor and has a low binding energy to carbon, its encapsulation into CNTs would lead to many interesting practical applications. Chapter 2 describes the intercalation of ionically conductive polymers into the layers of molybdcic acid. The resulting intercalation compounds were characterized by powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), and ac

impedance spectroscopy. Chapter 3 discusses various aspects of the application of fluid-bed technology for the coating and encapsulation processes. Particular attention has been paid to the principles of the fluidization technique, the miscellaneous fluid-bed coating processes and various coaters configurations with special emphasis on fine powder coating, dry coating and encapsulation. Chapter 4 demonstrates the use of the electrospinning technique for encapsulation. The electrospinning technique, consisting of the application of an electrical voltage to a polymeric solution to generate fiber or capsule-like morphologies, has tremendous potential for the development of encapsulation structures of interest in a number of areas such as biomedicine, food technology, bioremediation, energy storage, etc. Chapter 5 details the concept of microencapsulation by interfacial polymerization. Interfacial polymerization, including polycondensation, polyaddition, *in situ* polymerization as well as other heterophase polymerization processes, is defined by the formation of the capsules shell at or on a droplet or particles by polymerization of reactive monomers. Chapter 6 summarizes the main contributions from the literature for the preparation of a specific example of such hybrid materials, core-shell particles composed of an inner silica core and a poly(methyl methacrylate) outer shell. Chapter 7 provides an overview of recent progress in encapsulation technologies for organic thin-film transistors (OTFTs). General mechanisms of environment-induced degradation to OTFTs is reviewed, along with a discussion on the general requirements of encapsulation. Chapter 8 demonstrates that the derivatives of a hyperbranched polymer (mainly hyperbranched polyethylenimine (PEI)) can encapsulate a variety of guest species, and the encapsulating system shows a rather high guest selectivity, in which a specific interaction is absent or very weak. Chapter 9 presents a description of the initiated chemical vapor deposition (iCVD) process, concentrating on aspects like molecular weight of the deposited polymer, which is important for stability, and deposition rate. Both aspects, molecular weight and deposition rate, are essential for large-scale application in hybrid gas barriers. Chapter 10 provides an overview of the current status of polymer capsule technology, with a specific focus on preparation methods and their areas of application. The preparation of polymer capsules and their general features for applications are addressed. Chapter 11 demonstrates the potentialities of encapsulated ionic liquids (IL) within porous moieties in the proton exchange membranes field.

One approach relies on the IL immobilization in large pore zeolites, which are further deployed as inorganic fillers to the polymer casting solution. Chapter 12 reviews the encapsulation and co-precipitation processes based on the use of supercritical fluids, i.e., carbon dioxide. These processes are classified according to the role of the carbon dioxide (solvent, antisolvent, solute or reaction medium). The focus is set on the process mechanisms description, as well as the evolution of different techniques for overcoming the challenges set according to the physical properties of the different processed materials.

Vikas MITTAL
Abu Dhabi

List of Contributors

Alvise Benedetti is a professor of physical chemistry at the Department of Molecular Sciences and Nanosystems, Università Ca'Foscari Venezia, Italy. He is the author of more than 120 papers published in international journals. His research has focused on physical-chemical studies, mostly from a structural point of view, of amorphous, partially crystalline and polycrystalline systems containing nanostructured phases both in surface and/or in bulk systems.

Rabin Bissessur received his PhD from Michigan State University in 1994, and is currently professor of chemistry at the University of Prince Edward Island. His research interests include the development of nanocomposites for lithium rechargeable batteries and carbon capture. He has co-authored 38 refereed articles, and 4 book chapters.

María José Cocero founded the High Pressure Process Group at the University of Valladolid (Spain) in 1998. Since then, she has published more than 200 papers on natural bioactive compounds extraction and formulation, supercritical water oxidation for the treatment of highly contaminated wastewater and biorefinary applications, among other topics.

Douglas C. Dahn received his PhD from the University of British Columbia in 1985, and is currently associate professor of physics at the University of Prince Edward Island. He has co-authored 22 refereed articles and two patents on topics including scanning probe microscopy and condensed matter and materials physics.

Adela Eguizábal received her diploma in chemical engineering in 2008 and the MSc degree in chemical engineering in 2010 from the University of Zaragoza, Spain. She is currently a research associate in the Department of Chemical and Environmental Engineering and also works in the Nanoscience Institute of Aragon (INA). Her research

interests are focused on composites based on microporous materials, high temperature PEMFCs and polymer based microsystems prepared by soft lithography for preconcentration and reaction applications.

Maria José Fabra is a post-doctoral researcher at the Novel Materials and Nanotechnology Group of IATA-CSIC. She has published thirty papers, one book and eight book chapters. The main research interests are the development of new biodegradable packaging materials and the encapsulation of functional and bioactive compounds.

Isidora Freris is a post-doctoral researcher at the Department of Molecular Sciences and Nanosystems, Università Ca' Foscari Venezia, Italy. She obtained her PhD in chemistry from Monash University, Australia in 2007. Her current research is focused on the development of nanostructured hybrid materials, particularly organic-inorganic core-shell hybrids and luminescent materials via sol-gel processing. She has co-authored 9 scientific publications.

Yu Fu received his doctorate degree in materials science and engineering from the National Taiwan University in 2011 and is now general manager of Yu Crystal Encapsulation Co.

Blakney Hopkins worked on an honours project under the supervision of Professor Rabin Bissessur. She graduated with a BSc (Honors) degree in chemistry in 2010 from the University of Prince Edward Island.

José M. Lagaron, PhD, is Founder and Group Leader of the Novel Materials and Nanotechnology Group of the IATA-CSIC (Valencia, Spain) and is part-time professor of materials science at the Universitat Jaume I. He has published more than one hundred peer-reviewed papers and has fourteen patent applications in nanotechnology applied to polymers.

Amparo López-Rubio PhD, is a research scientist and project leader in the encapsulation area within the Novel Materials and Nanotechnology Group of the Institute of Agrochemistry and Food Technology (IATA) of the Spanish Council for Scientific Research (CSIC). She has published more than forty five papers in peer-reviewed international journals on the subjects of food technology, nanotechnology, packaging and biopackaging.

Ángel **Martín** is a senior researcher at the University of Valladolid (Spain). During his PhD and postdoctoral visits to the universities of Delft (The Netherlands) and Bochum (Germany), he specialized in the development of new materials by supercritical fluids techniques for a wide portfolio of applications, from energy to pharmaceuticals.

Boateng Onwona-Agyeman received his PhD from Saga University in Japan. He is currently a senior lecturer at the Department of Materials Science and Engineering, University of Ghana. His current research includes the development of nanoporous structured materials and thin films for solar cell applications and has 30 publications in peer-reviewed journals.

Jong Myung Park is currently a professor in the fields of polymer materials and coatings in the Graduate Institute of Ferrous Technology at Pohang University of Science and Technology (POSTECH), Korea. He received his PhD in polymer science and engineering from Lehigh University, U.S.A. in 1990. He has more than 25 years of industrial R&D experience in the fields of organic coatings and corrosion protection/surface treatments and holds more than 90 patents and published more than 50 scientific papers. His research interests include (1) polymer synthesis and characterization, (2) morphology control for polymeric and hybrid particles, (3) functional coatings for corrosion control/self-healing and (4) functional nano-materials for bio- and energy-related areas.

Rocío Pérez-Masiá has an Msc in food science and engineering and is a PhD student in the Novel Materials and Nanotechnology group at IATA-CSIC. She is focused in the development of new materials through the electrospinning technology for active packaging applications and has coauthored 4 publications in the field of food packaging.

María Pilar Pina received her diploma in chemistry in 1994 and her PhD in chemistry in 1998 from the University of Zaragoza, Spain. She is currently associate professor with tenure at the Chemical Engineering and Environmental Department at the University of Zaragoza and active member of the Nanoscience Institute of Aragon (INA). Her research activities are mainly focused on microfabrication using zeolite membranes as structural layers for

reaction, separation and sensing applications; development of polymer based microsystems by soft lithography and modified with nanostructured materials; and chemical sensors for gas detection at trace level.

Jatindra Kumar Rath Manager Utrecht University lab at HTC, Eindhoven, Netherlands, has over 25 years of experience in thin films silicon solar cells and has published more than 250 papers. His main research interests are transient and dusty plasmas in PECVD, nanocrystalline silicon and quantum dots, multijunction and heterojunction solar cells and solar cells on nano-textured surfaces and plastics.

Soraya Rodríguez-Rojo is assistant lecturer at the University of Valladolid, Spain where she earned her doctorate in chemical engineering (2008) on the hydrodynamics of supercritical fluidized bed for microparticle coating. During her two post-doctoral research fellowships (ETH-Zurich, Switzerland, and ITQB-IBET, Portugal), she has specialized in the formulation of nutraceutical compounds.

Fabien Salaün is a professor assistant at ENSAIT/GEMTEX, France. His research interests focus on polymer synthesis, encapsulation, and functional coatings for textile applications. He obtained his PhD in 2004 from the University of Lille 1, France. He has published more than 20 articles in refereed journals and 3 book sections in these research fields.

Toshifumi Satoh received his PhD from Hokkaido University in 1996. He subsequently joined the faculty of this university and was promoted to a professor in 2013. He has 177 publications to his credit, including research papers, reviews, and book chapters. His current fields of interest are branched polymers and unimolecular micelles

Ruud Schropp received his PhD in science from the University of Groningen in 1987. After that he worked in R&D at Glasstech Solar, Inc. in Colorado, USA on solar cells. In 1989 he joined Utrecht University and in 2000, he was appointed Full Professor in "Physics of Devices". In 2012 he joined the Energy Research Center of the Netherlands (ECN), while continuing professorship in thin film photovoltaics at Eindhoven University of Technology.

Diederick Spee studied physics at Utrecht University where he completed his master thesis on back contacted HIT solar cells in 2009. Currently, he is completing his PhD research on the hot wire chemical vapor deposition of flexible thin film organic/inorganic multilayer moisture barriers.

Yong Sun received his PhD from Kyushu Institute of Technology in Japan. He is currently an associate professor at the Department of Applied Science for Integrated System Engineering, Kyushu Institute of Technology. His research area includes the electromagnetic and acoustic properties of nano-materials and semiconductors.

Roman Grzegorz Szafran is an assistant professor at the Wroclaw University of Technology, Faculty of Chemistry, Department of Chemical Engineering, Poland. He is a specialist in the field of chemical engineering, fluid-bed and spout-fluid bed systems, coating, CFD modeling and microengineering. He is the author of 44 publications and 9 patent applications.

Feng-Yu Tsai received his doctorate degree in materials science from the University of Rochester in 2002 and is an associate professor of materials science and engineering at the National Taiwan University. His research interests include atomic and molecular layer deposition, nanotechnologies, and organic and flexible electronics including light-emitting diodes, organic photovoltaics, and thin-film transistors. Dr. Tsai has more than 50 publications and patents in related fields.

Decheng Wan received his PhD from Fudan University in 1999. He joined the faculty of Tongji University in 2006 and was promoted to a professor in 2011. He has (co)authored 68 research papers, reviews, and book chapters. His research interest is macromolecular synthesis and supramolecular chemistry.

Contents

Preface	xiii
List of Contributors	xvii
1 Copper Encapsulation of Multi-Walled Carbon Nanotubes	1
<i>Yong Sun and Boateng Onwona-Agyeman</i>	
1.1 Introduction	2
1.2 Preparation of Copper Encapsulated CNTs	3
1.2.1 Arc Discharge	3
1.2.2 Chemical Vapor Deposition	15
1.2.3 Laser Ablation	30
References	37
2 Novel Nanocomposites: Intercalation of Ionically Conductive Polymers into Molybdic Acid	41
<i>Rabin Bissessur, Blakney Hopkins and Douglas C. Dahn</i>	
2.1 Introduction	41
2.1.1 Battery Technology	41
2.1.2 The Polymer Electrolyte	43
2.1.3 Intercalation Chemistry	45
2.1.4 MoO_3 and MoO_3 Derivatives	46
2.2 Experimental	47
2.2.1 Materials	47
2.2.2 Synthesis of POEGO	47
2.2.3 Synthesis of POMOE	48
2.3 Intercalation into Molybdic Acid	48
2.3.1 Intercalation of PEG into Molybdic Acid	48
2.3.2 Intercalation of POEGO into Molybdic Acid	48
2.3.3 Intercalation of POMOE into Molybdic Acid	48

2.4	Preparation of Polymer-Lithium Complexes	49
2.4.1	Preparation of POEGO/LiOTf Complexes	49
2.4.2	Preparation of POMOE/LiOTf Complexes	49
2.4.3	Preparation of PEG/LiOTf Complexes	49
2.4.4	Intercalation of Polymer/LiOTf into Molybdic Acid Compounds	50
2.5	Instrumentation	50
2.5.1	Powder X-ray Diffraction	50
2.5.2	Thermogravimetric Analysis	50
2.5.3	Fourier Transform Infrared Spectroscopy	50
2.5.4	Nuclear Magnetic Resonance Spectroscopy	50
2.5.5	AC Impedance Spectroscopy	50
2.6	Results and Discussion	51
2.6.1	Molybdic Acid	51
2.6.2	Polymers	54
2.6.3	Formation of Intercalated Nanocomposites	57
2.6.4	Ionic Conductivity	65
2.7	Conclusions	68
	Acknowledgements	68
	References	69
3	Fluid-Bed Technology for Encapsulation and Coating Purposes	71
	<i>Roman G. Szafran</i>	
3.1	Introduction	71
3.2	Principles of Fluidization	74
3.3	Classification of Powders	78
3.3.1	Goossen's Classification of Particles by Archimedes Number	79
3.3.2	Extended Geldart's Classification for Nanopowders	80
3.4	Fluidized Bed Coaters	80
3.4.1	Top-Spray Fluid Bed Coater	81
3.4.2	Conical Bottom-Spray Spouted Bed Coater	83
3.4.3	Spout-Fluid Bed Coater (Wurster Type)	84
3.4.4	Rotor (Tangential) Spray Coater	85
3.4.5	Fast Circulating Spout-Fluid Bed Coater	86
3.5	Fluid-Bed Coating and Encapsulation Processes	88
3.5.1	Fluidized Bed CVD, ALD, MLD	89
3.5.2	Dry Coating of Fine Particles	92

3.6	The Design, Optimization and Scale-Up of the Coating Process and the Apparatus	94
3.7	Numerical Modeling of Fluid-Bed Coating	97
	References	101
4	Use of Electrospinning for Encapsulation	107
	<i>Rocío Pérez-Masiá, Maria José Fabra, Jose Maria Lagarón and Amparo López-Rubio</i>	
4.1	Introduction	107
4.1.1	Generalities About the Electrospinning Technique	107
4.1.2	Advantages of Electrospinning for Encapsulation	109
4.2	Electrospun Structures for the Encapsulation of Bioactive Substances in the Food Area	112
4.2.1	Enzyme Encapsulation	113
4.2.2	Encapsulation of Probiotic Bacteria	114
4.2.3	Antioxidant Encapsulation	115
4.2.4	Encapsulation of Other Food Compounds	116
4.3	Electrospun Encapsulation Structures for Biomedical Applications	117
4.3.1	Post-Spinning Modification	118
4.3.2	Blending and Emulsion Electrospinning	121
4.3.3	“Core-Shell Electrospinning” or “Coaxial Electrospinning”	122
4.4	Other Uses of Electrospinning for Encapsulation	124
4.4.1	Energy Storage Devices	124
4.4.2	Optical and Electronic Devices	127
4.4.3	Biotechnical Plant Protection Systems	129
4.5	Outlook and Conclusions	129
	References	130
5	Microencapsulation by Interfacial Polymerization	137
	<i>Fabien Salaün</i>	
5.1	Introduction	137
5.2	Generalities	141
5.3	Encapsulation by Heterophase Polymerization	144
5.3.1	Emulsion Polymerization	144
5.3.2	Suspension Polymerization	145
5.3.3	Dispersion Polymerization	147
5.3.4	Miniemulsion Polymerization	148

5.4	Microencapsulation by Polyaddition & Polycondensation Interfacial	148
5.4.1	Location of the Film Formation	152
5.4.2	Reaction Rate	152
5.4.3	Shell Formation	153
5.4.4	Influence of the Synthesis Parameters on the Formation of the Shell	156
5.4.5	Influence of the Synthesis Parameters on the Particles Properties	157
5.4.6	Nanoencapsulation by Interfacial Polycondensation	158
5.5	Microencapsulation by <i>In Situ</i> Polymerization	158
5.5.1	Melamine-Formaldehyde Microcapsules	161
5.5.2	Urea-Formaldehyde Microcapsules	164
5.5.3	Silica Microcapsules	165
5.6	Conclusion	166
	References	167
6	Encapsulation of Silica Particles by a Thin Shell of Poly(Methyl) Methacrylate	175
	<i>Isidora Freris and Alvise Benedetti</i>	
6.1	Introduction	176
6.2	Synthesis of Silica (Nano)Particles and Their Surface Modification	178
6.2.1	Silica Synthesis	178
6.2.2	Surface Modification of Silica Particles	179
6.3	Encapsulation of Silica Particles in a Thin PMMA Shell	181
6.3.1	<i>In Situ</i> Conventional Heterophase Radical Polymerization	182
6.3.2	Controlled Living Radical Polymerization	195
6.4	Summary	198
	References	199
7	Organic Thin-Film Transistors with Solution-Processed Encapsulation	203
	<i>Feng-Yu Tsai and Yu Fu</i>	
7.1	Introduction	203
7.2	Environment-Induced Degradations of OTFTs	205
7.2.1	Pentacene-Based OTFTs	206
7.2.2	Polythiophenes-Based OTFTs	208
7.2.3	Requirements of Encapsulation	208