

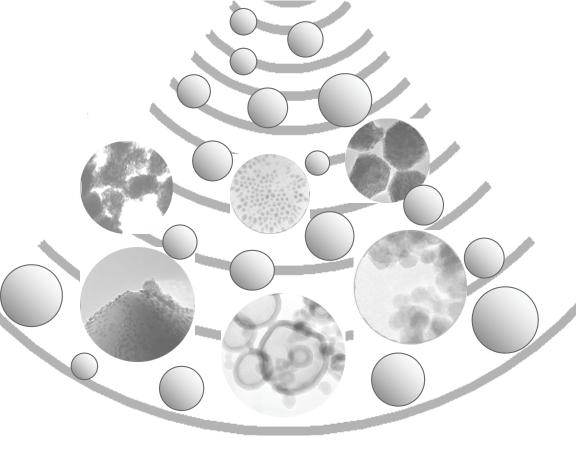
# Cavitation

A Novel Energy-Efficient Technique for the Generation of Nanomaterials

edited by Sivakumar Manickam Muthupandian Ashokkumar







# Cavitation

## Cavitation

## A Novel Energy-Efficient Technique for the Generation of Nanomaterials

edited by Sivakumar Manickam Muthupandian Ashokkumar



#### Published by

Pan Stanford Publishing Pte. Ltd. Penthouse Level, Suntec Tower 3 8 Temasek Boulevard Singapore 038988

Email: editorial@panstanford.com

Web: www.panstanford.com

#### **British Library Cataloguing-in-Publication Data**

A catalogue record for this book is available from the British Library.

### Cavitation: A Novel Energy-Efficient Technique for the Generation of Nanomaterials

Copyright © 2014 by Pan Stanford Publishing Pte. Ltd.

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the publisher:

For photocopying of material in this volume, please pay a copying fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. In this case permission to photocopy is not required from the publisher.

ISBN 978-981-4411-54-7 (Hardcover) ISBN 978-981-4411-55-4 (eBook)

Printed in the USA

### **Contents**

Fore	word			XV		
Prefa	асе			xvii		
1.	Devel	opment	of Multifunctional Nanomaterials			
	by Cavitation					
	Sivakumar Manickam, Tang Siah Ying, and					
	Muthi	Muthupandian Ashokkumar				
	1.1					
	1.2	Bimet	allic Nanoparticles	4		
		1.2.1	Copper-Silver Core-Shell Nanoparticles	4		
		1.2.2	Co-Sn-Graphite Nanoparticles	6		
	1.3	Metal	Oxide Nanoparticles	6		
		1.3.1	Zinc Oxide Nanoparticles	6		
		1.3.2	Manganese Oxide Nanoparticles	7		
		1.3.3	Tl <sub>2</sub> O <sub>3</sub> Nanoparticles	8		
		1.3.4		8		
		1.3.5	Synthesis of Pt-Graphene Oxide			
			(GO)-TiO <sub>2</sub>	10		
		1.3.6	Manganese Oxide Nanocrystals	10		
		1.3.7	Nanocrystalline NiO Powder	12		
	1.4	Magne	etic Nanoparticles	12		
		1.4.1	Magnetite Nanoparticles	12		
		1.4.2	Peroxidase-Like Fe <sub>3</sub> O <sub>4</sub> Magnetic			
			Nanoparticles	13		
	1.5		composites	14		
		1.5.1	CdS/TiO <sub>2</sub> Nanocomposites	14		
		1.5.2	CdS Nanoparticles and CdS/TiO <sub>2</sub>			
			Nanocomposites	14		
		1.5.3	Exfoliated Poly(styrene-co-methyl			
			methacrylate)/Montmorillonite			
			[P(MMA-co-St)/O-MMT]			
			Nanocomposites	16		
		1.5.4	Au-Polypyrrole (PPy)/Prussian			
			Blue (PB) Nanocomposites	16		

		1.5.5	Chitosan/Gold Nanocomposites	16
		1.5.6	Magnesium-Aluminum-Layered	
			Double Hydroxides Nanocomposite	17
	1.6	Chalco	genides	18
		1.6.1	Mercury Selenide Nanoparticles	18
	1.7	Metal	Bromide and Sulfate Nanoparticles	18
		1.7.1	AgBr Nanoparticles	18
		1.7.2	Barium Sulfate Nanoparticles	19
	1.8	Porous	s Materials	20
		1.8.1	N-Doped Nanocrystalline Anatase TiO <sub>2</sub>	20
	1.9	Other	Nanomaterials	21
		1.9.1	MoO <sub>3</sub> Nanospheres	21
		1.9.2	LiMn <sub>2</sub> O <sub>4</sub> Nanospheres	21
		1.9.3	Chromium Dioxide Nanowires	22
		1.9.4	Nanoclay Bentonite-FeCo	
			Nanocomposite Hybrid Hydrogel	22
		1.9.5	Silicoaluminophosphate Molecular	
			Sieve (SAPO)-34 Nanocrystals	24
	1.10	Conclu	isions	25
2.	Genera	ation of	Size, Structure, and Shape-Controlled	
			rticles Using Cavitation	29
	Kenji (	_	-	
	2.1	Introd	uction	30
	2.2		ontrol of Monometallic Nanoparticles	32
	2.3		ure Control of Bimetallic Nanoparticles	43
	2.4		Control of Metal Nanoparticles	48
	2.5	•	iding Remarks	50
3.			Synthesis of Noble Monometallic and	
	Bimeta	allic Nan	oparticles for Catalytic Applications	55
	Samba	andam A	nandan and Muthupandian Ashokkumar	
	3.1	Introd	uction	56
	3.2	Prepai	ration, Characterization, and Applications	
		_	nometallic Nanoparticles	57
	3.3		ration, Characterization, and Applications	
		of Bim	etallic Nanoparticles	70
	3.4	Conclu	-	79

1.		ound-As	=	thesis of Metal Oxide	89
	Chuanhao Li, Donald Ka Long Chan, and Jimmy C. Yu				
	4.1	Introd	luction		89
	4.2	Sonoc	hemical Sy	onthesis of Metal Oxide	
		Nanop	articles		90
		4.2.1	Methodo	ology	91
		4.2.2	Mechani	sm	92
			4.2.2.1	Reaction regions	92
			4.2.2.2	Reaction mechanism	92
		4.2.3	Advanta	ges	93
			4.2.3.1	High yield and fast reaction	93
				Small size and great	
				monodispersity	93
			4.2.3.3	Large surface area	93
			4.2.3.4	Pure phase	94
			4.2.3.5	Facile and green	94
		4.2.4	Synthesi	s of Metal Oxides with	
			Different	Functions	94
			4.2.4.1	Photocatalysts	94
			4.2.4.2	Electrode materials	97
			4.2.4.3	Gas sensors	99
			4.2.4.4	Magnetic materials	102
			4.2.4.5	Other functional materials	104
		4.2.5	Ultrason	ic Spray Pyrolysis Synthesis	
			of Metal	Oxide Nanoparticles	104
			4.2.5.1	Easy thin film fabrication	105
			4.2.5.2	Potential for mass	
				production	106
		4.2.6	Compari	son between Sonochemistry	
			and USP		106
		4.2.7	Synthesi	s of Metal Oxides with	
			Specific	Functions	106
			4.2.7.1	Electrode materials	106
			4.2.7.2	Gas sensors	108
			4.2.7.3	Luminescent films	109
	43	Concli	isions and	Perspectives	110

5.

Synth	esis of N	anomaterials Using Hydrodynami	С
Cavita			119
D. V. I	Pinjari, P.	R. Gogate, K. Prasad, and A. B. Pai	ndit
5.1	Introd	uction	120
5.2		al Methods	121
	5.2.1	Solid-State Synthesis	121
	5.2.2	Vapor Phase Synthesis	122
	5.2.3	Laser Ablation	124
5.3	Chemi	cal Methods	125
	5.3.1	Sol-Gel Processing	125
	5.3.2	Precipitation Method	125
	5.3.3	Water-in-Oil Micro-Emulsions (	Reverse
		Micelle) Method	126
5.4	Basic A	Aspects of Hydrodynamic Cavitat	ion 128
	5.4.1	Background of Generation of	
		Hydrodynamic Cavitation	128
	5.4.2	Mechanism for Nanomaterial	
		Synthesis	132
	5.4.3	Types of Hydrodynamic Cavitat	ion
		Reactors	134
		5.4.3.1 High-pressure homog	enizer 134
		5.4.3.2 High-speed homogeni	izer 134
		5.4.3.3 Low-pressure hydrod	
		cavitation reactor	135
5.5	Synthe	esis of Cellulose Nanofibrils	136
	5.5.1	Introduction	136
	5.5.2	Experimental Details	138
5.6	Result	s and Discussion	139
	5.6.1	Particle-Size Analysis	139
	5.6.2	X-Ray Diffraction Method	139
	5.6.3	Differential Scanning Calorimet	ry
		(Melting Temperature, $T_{\rm m}$ )	140
	5.6.4	Scanning Electron Microscopy	142
	5.6.5	Energy Balance Calculations	143
	5.6.6	Conclusions	143
5.7	Synthe	esis of Styrene–Butadiene Rubber	•
	Nanoe	mulsions	143
	5.7.1	Introduction	143
	5.7.2	Experimental Details	144

		5.7.3	Results and D	iscussion	145	
			5.7.3.1 Lim	iting/equilibrium		
			par	ticle size	147	
			5.7.3.2 Effi	cacy of energy utilization	148	
		5.7.4	Parameter ca	lculation	149	
		5.7.5	Conclusions		152	
	5.8	Synthe	sis of Nano Ca	lcium Carbonate	152	
		5.8.1	Introduction		152	
		5.8.2	Experimenta		153	
		5.8.3	Results and D		154	
				ct of orifice diameter and		
			_	metry of the orifice on the		
			rate	e of consumption of calcium		
			hyd	roxide	156	
				ct of calcium hydroxide		
				ry concentration on the		
				e of reaction	161	
		5.8.4	Conclusions		161	
	5.9	Overal	Conclusions		162	
6.	Sonoelectrochemical Synthesis of Nanomaterials					
	Jonath	an P. Me	tters, Craig E. I	Banks, and		
	Bruno	G. Polle	<u>.</u>			
	6.1	Introd	ıction		174	
	6.2	Experi	mental Configi	uration	175	
	6.3	Metall	c Systems		178	
		6.3.1	Copper and P	latinum	178	
		6.3.2	Magnesium		180	
		6.3.3	Tungsten		180	
		6.3.4	Aluminum		181	
		6.3.5	Lead and Cad	mium	181	
	6.4	Alloy a	nd Core-Shell	Nanoparticles	181	
	6.5	Polym	er Nanoparticl	es	182	
	6.6	Sonoe	ectrochemical	Nanoparticles		
		Incorp	orated into Ne	w Nanomaterials	183	
	6.7	Sonoe	actrochamical	Production of Noble		
	0.,					
	0.7	Metals		Electrocatalysts	185	
	0				185 186	

		6.7.3 6.7.4	Effect of Surfactants and Polymers Effect of Aqueous Solutions	191 193	
	6.8	Conclu	•	195	
7.	Prepar	ation of	Nanomaterials Under Combined		
	Ultrasc	ound/M	icrowave Irradiation	203	
	Gianca	rlo Crav	votto and Luisa Boffa		
	7.1	Introd	uction	204	
	7.2	Combi	ned Use of Ultrasound and Microwaves	205	
	7.3	Seque	ntial Use of Ultrasound and Microwaves	211	
		7.3.1	US and MW Sequential Irradiation in		
			the Same Reaction	211	
		7.3.2	Application of US and MW in Sequential		
			Reactions	219	
	7.4	Conclu	isions	222	
8.			sisted Preparation of Nanopolymeric and		
	-	-	ic Materials for the Encapsulation of	227	
	Bioactive Agents Francesca Cavalieri, Meifang Zhou, Mariarosaria Tortora,				
	and Mu	uthupan	ndian Ashokkumar		
	8.1	Introd	uction	228	
	8.2	Micro-	nanoencapsulation Techniques	230	
		8.2.1	Microemulsion and Nanoemulsion		
			Techniques	231	
		8.2.2	Layer-by-Layer Encapsulation Technique	234	
	8.3	Ultraso	onic Synthesis of Biopolymer-Based		
		Micro	capsules	237	
		8.3.1	Mechanism of Microcapsules Formation	237	
		8.3.2	Controlling the Yield and Size of		
			Proteinaceous Microspheres	240	
		8.3.3	One-Step Preparation of		
			Polysaccharides Microspheres		
			by a Sonochemical Method	243	
	8.4	The St	ructural and Functional Features		
		of the	Nanopolymeric Encapsulant	243	
		8.4.1	Polymeric Micro-Nanoparticles for		
			Encapsulation of Bioactive Agents	244	
		8.4.2	Polymersomes	246	

Polymerization

303

		10.1.2	Synergistic Effect of Ultrasound and	
			Initiator in Semibatch Polymerization:	
			A Case Study	306
	10.2	Ultrasc	ound-Assisted in situ Emulsion	
		Polyme	erization	311
	10.3	Specifi	c Examples of Nanocomposite Synthesis	
		via Ultı	rasound-Assisted Polymerization and	
		Their A	Applications	314
		10.3.1	Anticorrosive ZnO-Encapsulated	
			Functional Nanolatex	314
		10.3.2	Anticorrosive PANI-CaCO <sub>3</sub>	
			Nanocomposites Using Indirect	
			Ultrasound Technique	319
		10.3.3	Preparation of Semiconductor/Polymer	
			Photoanodes for Photoelectrochemical	
			Properties	326
		10.3.4	Synthesis of Polyaniline/Ag	
			Nanocomposite for Ethanol Vapor	
			Sensing Application	330
	10.4	Conclu		333
11.	Contro	lled Son	ochemical Fabrication of Mesoporous	
	Surface	es and M	1etal Sponges	343
	Ekater	ina V. Sk	orb and Dmitry G. Shchukin	
	11.1	Introdu	uction	344
	11.2		ound-Driven Development of Metal	
		Surface		348
	11.3		nemical Formation of Metal Sponges	353
	11.4		ound-Assisted Design of Metal	
			omposites	359
	11.5		ced Functional Materials	360
			Formation of Surface	
		11.0.1	Superhydrophobic "Lotus" Structures	360
		11.5.2	Self-healing Anticorrosion Coatings	000
			Based on pH-Sensitive Polyelectrolyte/	
			Inhibitor Sandwich-Like Nanostructures	361
		11.5.3	Sonochemically Designed Cerium-Rich	551
			Anticorrosion Nano-Network	364

		11.5.4	Applications of Metal Sponges with	
			Defined Porosity	367
			11.5.4.1 Preparation of catalysts	368
			11.5.4.2 Hybrid materials construction	369
			11.5.4.3 Implant development	370
			11.5.4.4 Containers with controllable	
			loading/release properties	372
	11.6	Conclu	sions	374
12.	Nume	rical Sim	ulations of Nucleation and Aggregation of	
	BaTiO <sub>3</sub>	3 Nanocr	ystals Under Ultrasound	381
	Kyuich	ii Yasui a	nd Kazumi Kato	
	12.1	Introdu	uction	382
		12.1.1	Acoustic Cavitation and	
			Sonochemistry	382
		12.1.2	Mesocrystal Formation Under	
			Ultrasound	387
	12.2	Particle	0.0100	390
			Theoretical Model	390
			Results and Discussions	393
	12.3		rystal Formation	397
			Theoretical Model	397
			Results and Discussions	401
	12.4	Conclu	sion	407
13.	Ultraso	onics and	d Sonochemistry: Some Issues and	
	Future	Perspec	tives	415
	Muthu	pandian	Ashokkumar and Sivakumar Manickam	
Index	r			423

#### **Foreword**

It was an honor to be asked to provide the foreword for this book, and it is with great pleasure that I do so. *Cavitation: A Novel Energy-Efficient Technique for the Generation of Nanomaterials* is a timely survey of a field that is mature in parts but with new, ever more complex applications emerging at a consistent rate. It is edited by two colleagues, Professors Manickam and Ashokkumar, who have made their own seminal contributions but also collaborated with a wide range of others in pushing forward the field of "sonochemical materials science".

There is a constant demand for developing novel technologies to synthesize multifunctional materials and, perhaps more importantly, control their properties. Having used ultrasound in the synthesis of functional polymers and materials for the past 25 years or so, I have always appreciated the extreme, but useful reaction conditions generated by acoustic cavitation but it has been interesting to watch the many clever and inventive ways that have surfaced for producing a huge range of materials. Over recent years, sonochemistry has shown significant growth in a variety of fields, but none more so than in the preparation of functional bio- and inorganic materials covering length scales from the nano- to the micro-. Many of these are described in this book along with emerging methods that combine with great effect cavitation with other methods such as electrochemistry, photochemistry, or microwaves. In parallel, cavitation generated by hydrodynamic forces has also been shown to be useful.

The book contains chapters from a number of leaders in the field of application of cavitation to nanomaterial synthesis. These chapters will serve as an excellent introduction for those new to the area and a welcome review of applications for those more familiar with sonochemistry. It has something for everyone and will not only be beneficial to sonochemists and materials scientists, but also to many interdisciplinary scientists. It represents an excellent addition to the literature.

Gareth J. Price Professor of Chemistry University of Bath, UK

#### **Preface**

Nanomaterials and their end products have started occupying the pinnacle position of consumer markets. At this juncture it becomes vital to consider the processing means through which naomaterials are generated. Especially, energy efficacy is the foremost concern while dealing with the processing of nanomaterials regardless of the scale of operation. Conventionally a gamut of top-down and bottom-up techniques are explored to obtain these nanomaterials. One of the green chemistry principles underlines the need for unusual energy sources to generate nanomaterials. Utilizing the energy from the collapse of cavitation bubbles, generated either by ultrasound or hydrodynamic forces, for the generation of nanomaterials is a merit to consider in this "green chemical processing era".

The past decade has witnessed the development of a wide range of nanomaterials using cavitation. A step forward is the coupling of cavitation with other techniques such as microwave, photochemistry, and electrochemistry, which have seen innumerous advantages in the generation of nanomaterials. In many instances, nanomaterials are attained with unique morphologies, a reduction in size, and narrow size distribution. While a few currently available books deal with the fundamental aspects of cavitation and sonochemistry, there is no book devoted specifically to the technologically important nanomaterials obtained by cavitation. This stimulus made us think about it, and we ended up editing this book. The chapters have been contributed by leading researchers working on utilizing cavitation for the generation of nanomaterials. This book will be most useful to those who explore cavitation for the facile synthesis of diverse nanomaterials. Some fundamental aspects of cavitation have been discussed only to a certain extent, as the core theme of this book is to understand the nanomaterials generated by cavitation.

In Chapter 1, Prof. Manickam, Dr. Tang, and Prof. Ashokkumar have discussed newly emerging multifunctional nanomaterials and the preparative strategies using ultrasound, where a clear evidence for the proper selection of ultrasonic parameters for the formation of nanomaterials has been revealed. Dr. Okitsu in Chapter 2 has

reviewed the role of sonochemical method in the synthesis of metal nanoparticles with precise control in size, shape, and structure. Dr. Anandan and Prof. Ashokkumar have focused in Chapter 3 on the ultrasonic synthesis of monometallic and bimetallic nanostructured materials with unique properties as well with their applications. Prof. Yu and coworkers have examined the recent advances in nanostructured metal oxides obtained using sonochemistry and ultrasonic spray pyrolysis methods in Chapter 4.

In Chapter 5, Prof. Pandit and coworkers have analyzed synthesizing nanomaterials using an alternative form of cavitation, that is, hydrodynamic cavitation. In this chapter, it is clearly shown that the control of the size of nanomaterials is possible using experimental parameters such as pump discharge pressure, liquid flow rate, and the design of the orifice plate employed. Moreover, they have shown the importance of this technique for obtaining hard, brittle, rubbery, and highly crystalline materials. Prof. Pollet and colleagues (Chapter 6) have discussed the concept of fabricating nanomaterials by combining power ultrasound and electrochemistry. More importantly, they have investigated the generation of intriguing nanostructures using this unique and combined methodology. Prof. Cravotto and Dr. Boffa (Chapter 7) have shed light on another hybrid technique, namely, a combination of ultrasound and microwaves and discussed the synergistic effects in the preparation of various nanomaterials.

Dr. Francesca's group (Chapter 8) has looked into the application of ultrasound technique in synthesizing and functionalizing micronanopolymeric materials for the microencapsulation of various bioactive agents. Prof. Gedanken and coworkers (Chapter 9) have discussed the principles behind the sonochemical process in embedding the nanoparticles onto textiles and discussed the advantages of this method compared with other coating techniques. Dr. Sonawane and coworkers (Chapter 10) discussed the generation of nanocomposites assisted by ultrasound via in situ emulsion polymerization. Dr. Ekaterina and Dr. Shchukin (Chapter 11) have provided the conceptual solutions for the controlled sonochemical fabrication of mesoporous surfaces and metal sponges. Following this, Dr. Yasui and Dr. Kato (Chapter 12) have provided a detailed discussion on the numerical simulations of nucleation and aggregation of BaTiO<sub>3</sub> crystals under ultrasound conditions. Finally, Prof. Ashokkumar and Prof. Manickam (Chapter 13) have discussed

the issues on the development of large-scale ultrasound reactors besides future perspectives.

We sincerely thank all the contributors of the chapters as well the reviewers for their excellent contributions towards the successful completion of this book. We trust that this book will be extremely beneficial to researchers involved in the exploitation of cavitation for the generation of nanomaterials for different technological applications.

> Sivakumar Manickam Muthupandian Ashokkumar Summer 2014