

Contents

Preface *xiii*

1 Vapor Phase Growth of Metal-Oxide Thin Films and Nanostructures *1*

Lynette Keeney and Ian M. Povey

- 1.1 Introduction to Vapor Phase Deposition *1*
- 1.2 Vapor Phase Deposition Methodologies *1*
 - 1.2.1 Chemical Vapor Deposition *2*
 - 1.2.2 Atomic Layer Deposition *2*
- 1.3 Precursors and Chemistry *3*
- 1.4 Applications of Metal-Oxide Vapor Phase Deposition *4*
 - 1.4.1 Case Study 1: Ferroelectric Oxide Materials *4*
 - 1.4.1.1 Ferroic Thin Films *5*
 - 1.4.2 Case Study 2: Dielectric Oxide Materials *18*
- 1.5 Conclusions *27*
- References *28*

2 Addressing Complex Transition Metal Oxides at the Nanoscale: Bottom-Up Syntheses of Nano-objects and Properties *43*

David Portehault, Francisco Gonell, and Isabel Gómez-Recio

- 2.1 Introduction *43*
- 2.2 Multicationic Oxides *45*
 - 2.2.1 Layered Oxide-Based Materials *45*
 - 2.2.2 Oxidation States Stable in Organic Media: The Case of Perovskites *50*
 - 2.2.3 Oxidation States Poorly Stable in Organic Media: The Case of Perovskites *54*
- 2.3 Oxides with Uncommon Metal Oxidation States: The Case of Titanium(III) in Oxides and Extension to Tungsten Oxides *58*
 - 2.3.1 Crystal Structures and Requirements for the Synthesis of Oxides Bearing Titanium(III) Species *59*
 - 2.3.2 Ti_2O_3 Nanostructures *61*
 - 2.3.3 Mixed Valence Ti(III)/Ti(IV) Oxides: Magnéli Phases *63*

2.3.4	Comparison to Metal Oxidation States Stable in Organic Media: Mixed W(V)/W(VI) Oxides	68
2.4	Stabilization of New Crystal Structures at the Nanoscale	73
2.4.1	Hard Templating to Isolate Bulk Metastable Oxides at High Temperatures	74
2.4.2	Beyond Hard Templating for Isolating Nanostructures of Metastable Oxides	75
2.4.3	Colloidal Syntheses	75
2.5	Concluding Remarks	76
	References	77
3	Nanosized Oxides Supported on Arrays of Carbon Nanotubes: Synthesis Strategies and Performances of TiO₂/CNT Systems	89
	<i>Maria Letizia Terranova and Emanuela Tamburri</i>	
3.1	Introduction	89
3.2	Synthesis Strategies for Preparation of CNT Arrays	90
3.3	Selected Examples of Supported Nano-oxides	91
3.4	A Focus on the TiO ₂ /CNT Systems	93
3.4.1	Synthesis of TiO ₂ on CNT	99
3.4.1.1	Wet Chemistry	100
3.4.1.2	Vacuum Techniques	103
3.5	Concluding Remarks	107
	References	108
4	Computational Approaches to the Study of Oxide Nanomaterials and Nanoporous Oxides	111
	<i>Ettore Fois and Gloria Tabacchi</i>	
4.1	Introduction	111
4.2	Overview of Theoretical Approaches	113
4.3	Molecular Behavior at Nanomaterials Surfaces	114
4.3.1	Molecular Interactions on Manganese Oxide Nanomaterials	114
4.3.2	Insight on Molecule-to-Material Conversion in Chemical Vapor Deposition	116
4.4	Oxide Porous Materials	121
4.4.1	Structural Properties	121
4.4.2	Behavior Under High-Pressure Conditions	124
4.4.3	Hybrid Microporous Functional Materials	127
4.5	Outlook and Perspectives	131
	References	133
5	Functional Spinel Oxide Nanomaterials: Tailored Synthesis and Applications	137
	<i>Zheng Fu and Mark T. Swihart</i>	
5.1	Introduction and Topic Overview	137

5.2	Syntheses	138
5.2.1	Vapor Phase	138
5.2.1.1	Chemical Vapor Deposition	138
5.2.1.2	Atomic Layer Deposition	138
5.2.1.3	Spray Pyrolysis	140
5.2.1.4	Laser Pyrolysis	141
5.2.1.5	Plasma Methods	142
5.2.2	Solution Phase	143
5.2.2.1	Sol–Gel Methods	143
5.2.2.2	Hydrothermal Methods	143
5.2.2.3	Thermal Decomposition	143
5.2.2.4	Solvothermal Methods	145
5.2.3	Solid Phase	146
5.2.3.1	Solid-State Thermal Decomposition	146
5.2.3.2	Combustion	147
5.2.3.3	Ball Milling	148
5.2.3.4	High-Temperature Solid Solution Method	148
5.3	Structure–Effect Applications	150
5.3.1	One-Dimensional (1D) Structures	151
5.3.1.1	Nanorods	151
5.3.1.2	Nanowires	154
5.3.1.3	Nanotubes	154
5.3.2	Two-Dimensional (2D) Structures	159
5.3.2.1	Nanofilms	159
5.3.2.2	Nanosheets	159
5.3.2.3	Nanoplatelets	163
5.3.3	Three-Dimensional (3D) Structures	165
5.3.4	One- and Two-Dimensional (1&2D) Structure	170
5.3.5	One- and Three-Dimensional (1&3D) Structures	171
5.3.6	Two- and Three-Dimensional (2&3D) Structure	173
5.4	Self-Assembled Structures	175
5.5	Conclusions and Future Perspectives	180
	References	184
6	Photoinduced Processes in Metal Oxide Nanomaterials	193
	<i>Nikolai V. Tkachenko and Ramsha Khan</i>	
6.1	Introduction	193
6.2	Photophysics of Bulk MOs	195
6.2.1	Energy-Level Structure and Steady-State Spectra	195
6.2.2	Photoexcitation and Relaxation Dynamics	201
6.2.3	Emission Decay Kinetics, Time-Resolved PL	203
6.2.4	Transient Absorption (TA) Spectroscopy	205
6.3	Nanostructures	208
6.3.1	Quantum Confinement	208
6.3.2	Surfaces and Interfaces	211

6.4	Photophysical Aspects of MO Applications	218
6.4.1	Solar Cells	218
6.4.2	Light Emitting Devices	219
6.4.3	Photocatalysis	219
6.4.4	Photodegradation	219
6.4.5	Solar Driven Chemistry	220
6.5	Conclusions	220
	References	221
7	Metal Oxide Nanomaterials for Nitrogen Oxides Removal in Urban Environments	229
	<i>M. Cruz-Yusta, M. Sánchez, and L. Sánchez</i>	
7.1	Introduction: Photocatalytic Removal of Nitrogen Oxides Gases	229
7.2	TiO ₂ -Based Materials	230
7.2.1	Tailoring the Energy Band Gap and Edges' Potentials	231
7.2.2	Dopant Elements and Quantum Dots	234
7.2.3	Defects, Vacancies, and Crystal Facets in the TiO ₂ Nanostructure	235
7.2.4	Composites/Substrates	236
7.2.5	Titanium-Based Oxides	237
7.3	Alternative Advanced Photocatalysts	238
7.3.1	Bismuth Oxides	238
7.3.2	Tin- and Zinc-Based Oxides	242
7.3.3	Transition Metal Oxides	247
7.4	New Insights into the NO _x Gases Photochemical Oxidation Mechanism	251
7.5	Field Studies in Urban Areas	253
7.5.1	Photocatalytic Construction Materials	253
7.5.2	Field Studies of NO _x Abatement in Real Environments	254
7.6	Conclusions and Perspectives	256
	References	259
8	Synthesis and Characterization of Oxide Photocatalysts for CO₂ Reduction	277
	<i>Fernando Fresno and Patricia García-Muñoz</i>	
8.1	Introduction	277
8.2	Fundamentals of Heterogeneous Photocatalysis	279
8.3	Applications of Heterogeneous Photocatalysis	281
8.4	Photocatalytic CO ₂ Reduction: State of the Art and Main Current Issues	283
8.4.1	TiO ₂ -Based Photocatalysts for CO ₂ Reduction	286
8.4.2	Other Oxide Photocatalysts	291
8.5	Oxide-Based Heterojunctions and Z-Scheme Photocatalytic Systems	295
8.5.1	Cocatalysts for CO ₂ Reduction: Metal-Oxide Synergies	299
8.6	Conclusions and Future Perspectives	303
	References	303

9	Functionalized Titania Coatings for Photocatalytic Air and Water Cleaning	317
	<i>Ksenija Maver, Andraž Šuligoj, Urška Lavrenčič Štangar, and Nataša Novak Tušar</i>	
9.1	Introduction	317
9.1.1	Titania as a Photocatalyst for Air and Water Cleaning	317
9.1.2	Titania Functionalization	319
9.1.3	Fabrication of Titania-Based Coatings	320
9.1.4	Characterization of Titania-Based Materials	321
9.2	Case Studies	323
9.2.1	SiO ₂ -Supported TiO ₂ for Removal of Volatile Organic Pollutants from Indoor Air Under UV Light	323
9.2.2	Sn-Functionalized TiO ₂ as a Photocatalytic Thin Coating for Removal of Organic Pollutants from Water Under UV Light	325
9.2.3	SiO ₂ -Supported TiO ₂ Functionalized with Transition Metals for Removal of Organic Pollutants from Water Under Visible Light	329
9.3	Conclusion and Further Outlook	335
	References	335
10	Metal Oxides for Photoelectrochemical Fuel Production	339
	<i>Gian Andrea Rizzi and Leonardo Girardi</i>	
10.1	Introduction to Photoelectrochemical Cells	339
10.1.1	The Photoelectrochemistry Approach	344
10.2	Metal Oxides Photoelectrode Candidate Materials	347
10.2.1	Photoanodes	349
10.2.2	Photocathodes	349
10.3	Tailoring Surface Catalytic Sites and Catalyst Use	350
10.4	Metal Oxide Heterostructures	353
10.5	Metal Oxides as a Protective Anti-corrosion Layer in Photoelectrodes	354
10.6	Evaluation of Photoelectrode Efficiencies	359
10.7	Conclusions and Perspectives	365
	References	367
11	Tailoring Porous Electrode Structures by Materials Chemistry and 3D Printing for Electrochemical Energy Storage	379
	<i>Sally O'Hanlon and Colm O'Dwyer</i>	
11.1	Strategies for Functional Porosity in Electrochemical Systems	379
11.2	Benefits and Limitations of Structural Engineering for Electrochemical Performance	382
11.3	Tailoring the Pore Structure of Metal Oxides for Li-ion Battery Cathodes and Anodes	383
11.4	Developments in 3D Printing of Porous Electrodes for Electrochemical Energy Storage	389
11.5	Porous Current Collectors by 3D Printing	390

11.6	Battery and Supercapacitor Materials from 3D Printing	392
11.7	Conclusions and Outlook	394
	References	396

12 Ferroic Transition Metal Oxide Nano-heterostructures: From Fundamentals to Applications 405

G. Varvaro, A. Omelyanchik, and D. Peddis

12.1	Introduction	405
12.2	Ferroic Properties of Complex Transition Metal Oxides	408
12.2.1	Spinel Ferrites	408
12.2.2	Perovskites	411
12.2.3	Other Magnetic Oxides	412
12.3	Magnetic Oxide Heterostructures	413
12.3.1	Hard/Soft Exchange-Coupled Systems	413
12.3.2	Ferro(i)magnetic/Antiferromagnetic Systems	416
12.3.3	All-Oxide Synthetic Antiferromagnets	419
12.4	Artificial Multiferroic Oxide Heterostructures	421
12.4.1	Strain Transfer Mechanism	423
12.4.2	Charge Modulation Mechanism	426
12.4.3	Exchange Interaction Mechanism	427
12.5	All-Oxide Spintronic Heterostructures	427
12.6	Conclusion and Perspectives	430
	References	431

13 Metal-Oxide Nanomaterials for Gas-Sensing Applications 439

Pritamkumar V. Shinde, Nanasaheb M. Shinde, Shoyebmohamad F. Shaikh, and Rajaram S. Mane

13.1	Introduction	439
13.2	Types of Gas Sensors	442
13.3	Metal-Oxide Nanomaterial-Based Gas Sensors	443
13.4	Preparation of Metal-Oxide Gas Sensors	446
13.4.1	Operation Mechanism	446
13.4.2	Morphology-Related Structural Parameters	448
13.4.2.1	Grain Size	448
13.4.2.2	Pore Size	449
13.4.3	Crystallographic Defective and Heterointerface Structures	453
13.4.3.1	Defect Structure	453
13.4.3.2	Heterointerface Structure	455
13.4.4	Chemical Composition	458
13.4.5	Addition of Noble Metal Particles	458
13.4.6	Humidity and Temperature	461
13.5	Gas-Sensing Mechanisms	462
13.5.1	Adsorption/Desorption Model	462
13.5.1.1	Oxygen Adsorption Model	464

13.5.1.2	Chemical Adsorption/Desorption	467
13.5.1.3	Physical Adsorption/Desorption	470
13.5.2	Bulk Resistance Control Mechanism	471
13.5.3	Gas Diffusion Control Mechanism	472
13.6	Conclusions and Future Perspectives	474
	References	475
	Index	487