

Contents

List of Contributors XIII

- 1 Self-Organization of Inorganic Nanocrystals 1**
Laurence Motte, Alexa Courty, Anh-Tu Ngo, Isabelle Lisiecki, and Marie-Paule Pileni
- 1.1 Introduction 1
- 1.2 Surface Modification of Nanocrystals and Interparticle Forces in Solution 2
- 1.2.1 Van der Waals Forces 4
- 1.2.2 Magnetic Dipolar Forces 4
- 1.2.3 Electrostatic Forces 5
- 1.2.4 Steric Forces 5
- 1.2.5 Solvation Forces 5
- 1.3 What is Required to Provide Highly Ordered Self-Assemblies? 6
- 1.3.1 Nanocrystal Size Distribution Effect 6
- 1.3.2 Substrate Effect 6
- 1.3.3 Capillary Forces 8
- 1.3.3.1 Solvent Evaporation Process 8
- 1.3.3.2 Application of a Magnetic or Electric Field During the Evaporation Process 9
- 1.4 Self-Assemblies in the Absence of External Forces 9
- 1.4.1 Control of the Interparticle Gap Via the Coating Agent 16
- 1.4.1.1 Silver Sulfide Nanocrystals 16
- 1.4.1.2 Silver Nanocrystals 17
- 1.4.2 Influence of the Substrate 19
- 1.4.3 Thermal and Time Stabilities 24
- 1.4.3.1 Crystallinity Improvement Related to the Atomic and Nanocrystal Ordering 24
- 1.4.3.2 A New Approach to Crystal Growth 27
- 1.4.3.3 Stability with Time 29
- 1.5 Self-Assemblies in the Presence of External Forces and Constraints 31
- 1.5.1 Fluid Flow 31

1.5.2	Application of a Magnetic Field	34
1.5.2.1	Applied Field Parallel to the Substrate	34
1.5.2.2	Applied Field Perpendicular to the Substrate	40
1.6	Conclusion	45
	<i>References</i>	45
2	Structures of Magnetic Nanoparticles and Their Self-Assembly	49
	<i>Zhong L. Wang, Yong Ding, and Jing Li</i>	
2.1	Introduction	49
2.2	Phase Identification of Nanoparticles	49
2.2.1	Core–Shell Nanoparticles	49
2.2.2	FePt/Fe ₃ Pt Nanocomposites	55
2.3	Determining the Nanoparticle Shapes and Surfaces	58
2.3.1	The Shape of Fe ₃ O ₄ Nanoparticles	59
2.3.2	The Shapes of FePt Nanoparticles	60
2.4	Multiply Twinned FePt Nanoparticles	61
2.5	Phase Transformation and Coalescence of Nanoparticles	65
2.6	Self-Assembled Nanoarchitectures of Fe ₃ O ₄ Nanoparticles	69
2.7	Summary	72
	<i>References</i>	73
3	Self-Organization of Magnetic Nanocrystals at the Mesoscopic Scale: Example of Liquid–Gas Transitions	75
	<i>Johannes Richardi and Marie-Paule Pileni</i>	
3.1	Introduction	75
3.2	Simulation Studies of Liquid–Gas Transitions (LGT) in Colloids and Dipolar Systems	76
3.2.1	Liquid–Gas Transitions in Colloids	76
3.2.2	Liquid–Gas Transition in Dipolar Systems	77
3.3	Orientational and Structural Correlations in Dipolar Fluids	79
3.4	Mesoscopic Organization of Magnetic Nanocrystals in a Parallel Field	80
3.5	Mesoscopic Organization of Magnetic Nanocrystals in a Perpendicular Field	82
3.6	Conclusion	87
	<i>References</i>	87
4	<i>In Situ</i> Fabrication of Metal Nanoparticles in Solid Matrices	91
	<i>Junhui He and Toyoki Kunitake</i>	
4.1	Introduction	91
4.2	<i>In Situ</i> Fabrication of Metal Nanoparticles in Films	92
4.2.1	<i>In Situ</i> Fabrication of Metal Nanoparticles in Inorganic Films	92
4.2.1.1	<i>In Situ</i> Fabrication of Metal Nanoparticles in Mesoporous Inorganic Films	92

4.2.1.2	<i>In Situ</i> Fabrication of Metal Nanoparticles in Metal Oxide Ultrathin Films: the Surface Sol–Gel Process	95
4.2.1.3	<i>In Situ</i> Fabrication of Metal Nanoparticles in TiO ₂ Films Prepared from Anatase Sol by Spin-Coating	99
4.2.2	<i>In Situ</i> Fabrication of Metal Nanoparticles in Polymeric Films	101
4.2.3	<i>In Situ</i> Fabrication of Metal Nanoparticles in Layer-by-Layer Assembled Polyelectrolyte Thin Films	104
4.3	<i>In Situ</i> Fabrication of Metal Nanoparticles in Nonfilm Solid Matrices	106
4.3.1	<i>In Situ</i> Fabrication of Metal Nanoparticles in Inorganic Matrices	107
4.3.2	<i>In Situ</i> Fabrication of Metal Nanoparticles in Polymeric Matrices	110
4.4	Physicochemical Properties	112
4.4.1	Catalytic Properties	113
4.4.2	Optical Properties	113
4.4.3	Magnetic Properties	114
4.5	Summary and Outlook	115
	<i>References</i>	115
5	Three-Dimensional Self-Assemblies of Nanoparticles	119
	<i>Sachiko Matsushita and Shin-ya Onoue</i>	
5.1	Introduction	119
5.2	Mesoscopic Assembly of Inorganic Nanoparticles in Molecular Matrixes	120
5.2.1	Introduction	120
5.2.2	Random Assemblies of Inorganic Nanoparticles by Various Triggers	120
5.2.2.1	pH and Ions	121
5.2.2.2	Small Molecules and Polymers	121
5.2.2.3	Biological Components (Programmed Assemblies and Sensors)	121
5.2.3	Versatile Assemblies of Inorganic Nanoparticles Guided by Designable Templates: Superstructures and 1D and 3D Assemblies	123
5.2.3.1	Langmuir–Blodgett Films	123
5.2.3.2	Amphiphiles and Surfactants	124
5.2.3.3	Gels (Networks)	124
5.2.3.4	Polymer and DNA as a Template	124
5.2.3.5	Inorganic Templates	125
5.2.3.6	Others	126
5.2.4	Layer-by-Layer Assemblies Embedded with Inorganic Nanoparticles	126
5.2.4.1	Multifunctional Molecules and Polymers	127
5.2.4.2	Inorganic Molecules	127
5.2.5	“Key and Vision” for Future Development	128
5.3	Three-Dimensional Self-Assemblies via Nanoparticle Interactions	129
5.3.1	Liquid Colloidal Crystals	129

- 5.3.1.1 Control of the Lattice Structure 130
- 5.3.1.2 Control of the Orientation 131
- 5.3.1.3 Overcoming the Mechanical Fragility 133
- 5.3.1.4 Self-Assembly Preparations for Complicated Structures 133
- 5.3.2 Solid Colloidal Crystals 135
- 5.3.2.1 Control of the Orientation 136
- 5.3.2.2 Control of the Lattice Structure 137
- 5.3.2.3 Overcoming the Slow Growth Rate 137
- 5.3.2.4 Self-Assembly Preparations for Complicated Structures 137
- 5.3.3 Two-Dimensional Colloidal Crystals 137
- 5.3.3.1 Various Preparation Methods 140
- 5.3.3.2 Control of the Lattice Structure 142
- 5.3.4 Processing of Self-Assembled Structures 143
- 5.3.4.1 Submicrostructures Formed by Reactive Ion Etching in 3D Self-Assembled Structures 143
- 5.3.4.2 Flexible Self-Assembled Structures 144
- 5.3.4.3 Freestanding Colloidal Crystals 144
- 5.3.5 Dissipative Process for Fabrication of 3D Self-Assembly 145
- 5.4 Applications of Three-Dimensional Self-Assemblies of Nanoparticles 145
- 5.4.1 Photonic Crystals 148
- 5.4.2 Sensing Materials 150
- 5.4.3 Optical Switches 150
- 5.4.4 Optical Memory Media 150
- References 151

6 Dissipative Structures and Dynamic Processes for Mesoscopic Polymer Patterning 157

Masatsugu Shimomura

- 6.1 Introduction 157
- 6.2 Formation of Dissipative Structures in Drying Polymer Solutions 159
- 6.3 Regular Pattern Formation of Deposited Polymers After Solvent Evaporation 160
- 6.4 Preparation of Honeycomb-Patterned Polymer Films 164
- 6.5 Processing of Honeycomb Patterns 166
- 6.6 Application of Regularly Patterned Polymer Films 167
- 6.7 Conclusion 169
- References 169

7	Self-Assemblies of Anisotropic Nanoparticles: Mineral Liquid Crystals	173
	<i>Patrick Davidson and Jean-Christophe P. Gabriel</i>	
7.1	Introduction	173
7.2	Basic Principles and Investigation Techniques	174
7.2.1	Basic Principles	174
7.2.2	Investigation Techniques	177
7.3	Nematic Phases	178
7.3.1	The Onsager Model	179
7.3.2	Rigid Rodlike Nanoparticles	180
7.3.3	Semiflexible Wires, Ribbons, and Tubules	181
7.3.3.1	$\text{Li}_2\text{Mo}_6\text{Se}_6$ Wires	181
7.3.3.2	V_2O_5 Ribbons	182
7.3.3.3	Imogolite Nanotubules	189
7.3.4	Nanorods, Nanowires, and Nanotubes: A Wealth of Potential New MLCs	189
7.3.5	Disklike Nanoparticles	190
7.3.5.1	Clays	190
7.3.5.2	Gibbsite Nanodisks	193
7.4	Lamellar Phases	195
7.4.1	Numerical Simulations	195
7.4.2	“Schiller Layers”	196
7.4.3	Suspensions of $\text{H}_3\text{Sb}_3\text{P}_2\text{O}_{14}$ and HSbP_2O_8 Nanosheets	196
7.5	Columnar Phases	199
7.5.1	Numerical Simulations	199
7.5.2	Two-Dimensional Phases of Rodlike Particles	200
7.5.3	Hexagonal Phase of Disklike Particles	201
7.6	Physical Properties and Applications	202
7.6.1	Rheological Properties	202
7.6.2	Composite Materials	204
7.6.3	The Outstanding Magnetic Properties of Goethite Nanorods	205
7.6.4	Electric Field Effects	207
7.6.5	The Use of Mineral Liquid-Crystalline Suspensions for the Structural Determination of Biomolecules	207
7.7	Conclusion	209
	<i>References</i>	210
8	Collective Properties Due to Self-Organization of Silver Nanocrystals	213
	<i>Arnaud Brioude, Alexa Courty, and Marie-Paule Pileni</i>	
8.1	Introduction	213
8.2	Results and Discussion	214
8.2.1	Intrinsic Properties Due to “Supra” Crystal Formation	216
8.2.2	Dipolar Interactions	218
8.2.2.1	Absorption Spectroscopy	218

8.2.2.2	Reflectivity Measurements	220
8.2.2.3	Polarized Electron Spectroscopy	225
8.2.2.4	STM-Induced Photon Emission	226
8.3	Conclusion	228
	References	228
9	Scanning Tunneling Luminescence from Metal Nanoparticles	231
	<i>Fabrice Charra</i>	
9.1	Introduction	231
9.2	Mechanisms of Scanning Tunneling Luminescence	232
9.2.1	Electromagnetic-Field-Assisted Inelastic Tunneling	233
9.2.2	Local Plasmon Modes	234
9.3	Experimental Details	235
9.4	Tip-Formed Protrusions	236
9.5	Colloidal Silver Nanoparticles	238
9.5.1	Single-Particle Contact by STM	239
9.5.2	Collective Plasmon Modes	240
9.5.3	Individual-Site Dependence of Luminescence	243
9.5.4	Tip-Modified Luminescence	246
9.6	Conclusion	248
	References	249
10	Collective Magnetic Properties of Organizations of Magnetic Nanocrystals	251
	<i>Christophe Petit, Laurence Motte, Anh-Tu Ngo, Isabelle Lisiecki, and Marie Paule Pileni</i>	
10.1	Introduction	251
10.2	General Principles of the Magnetism of Nanoparticles: Theory and Investigation	252
10.2.1	Magnetocrystalline Anisotropy Energy and Blocking Temperature	253
10.2.2	Magnetic Characterization from the Hysteresis Curves	254
10.2.3	Demagnetizing Fields	254
10.3	Origin of the Collective Properties in Mesoscopic Structures of Magnetic Nanocrystals	255
10.3.1	Orientation of the Easy Magnetic Axes	255
10.3.2	Dipolar Interactions	256
10.4	Collective Magnetic Properties of Mesostuctures Made of Magnetic Nanocrystals	256
10.4.1	Materials and Mesoscopic Structures	257
10.4.2	Bidimensional (2D) Organization of Cobalt Nanocrystals	257
10.4.3	Three-Dimensional (3D) Organizations of Cobalt Nanocrystals	259
10.4.4	Does the Internal Order Play a Role?	260
10.4.5	Does the Structure Play a Role?	263
10.4.5.1	Linear Chains of Cobalt Nanocrystals	263
10.4.5.2	Patterned 3D Film of Magnetic Nanoparticles	266

- 10.4.5.2.1 Surface-Structured 3D Film 267
- 10.4.5.2.2 Tubelike-Structured 3D Film: Effect of a Volumic Texturation 269
- 10.5 Towards Collective Magnetic Properties at Room Temperature 270
- 10.5.1 Cigar-Shaped Maghemite Nanocrystals Organized in 3D Films 270
- 10.5.2 Organization of Cobalt Nanocrystals with High Magnetic Anisotropy Energy 272
- 10.6 Conclusion 276
- References 277

11 Exploitation of Self-Assembled Nanostructures in Optical Biosensors 279

Janos H. Fendler

- 11.1 Introduction 279
- 11.2 Substrate Preparation 280
- 11.3 Preparation of Self-Assembled Monolayers 282
- 11.4 Monolayer-Protected Metallic Particles 284
- 11.5 Layer-by-Layer Self-Assembled Ultrathin Films 284
- 11.6 Surface Plasmon Resonance Spectroscopy and Transmission Resonance Surface Plasmon Resonance Spectroscopy 286
- 11.7 Gold-Nanoparticle-Enhanced Surface Plasmon Resonance Spectroscopy 289
- References 292

12 Nano Lithography 295

Dorothee Ingerit and Marie-Paule Pileni

- 12.1 Introduction 295
- 12.2 Colloidal Lithography: Spheres Lithography 296
 - 12.2.1 Ordered-Particle Arrays: Nanosphere Lithography (NSL) 296
 - 12.2.2 Nonorganized particle patterns 297
 - 12.2.3 Applications 297
- 12.3 Colloidal Lithography: Copolymer Lithography 298
 - 12.3.1 Block Copolymer Used as a Lithographic Mask 298
 - 12.3.2 Hierarchical Pattern 299
- 12.4 Colloidal Lithography: Nanocrystals 300
 - 12.4.1 Process 301
 - 12.4.2 Mesoscale 301
 - 12.4.3 Nanoscale 302
- 12.5 Conclusion 304
- References 304

13 Shrinkage Cracks: a Universal Feature 307

Marie-Paule Pileni

References 316

Subject Index 317