Contents

1 Nanomaterials (NMs) in Analytical Sciences 1

۱v

- 1.1 Introduction 1
- 1.2 Types of NMs 2
- 1.2.1 Graphene 2
- 1.2.2 Carbon Nanotubes (CNTs) 3
- 1.2.3 Fullerenes (FULs) 4
- 1.2.4 Inorganic Nanoparticles 6
- 1.2.4.1 Gold and Silver Nanoparticles 6
- 1.2.4.2 Titanium Nanoparticles 7
- 1.2.4.3 Silica Nanoparticles 7
- 1.2.5 Magnetic Nanoparticles 7
- 1.3 Applications of NMs 8
- 1.3.1 NMs in Separation Processes 8
- 1.3.2 NMs in Biomedical Applications 8
- 1.3.3 NMs in Sensor Platforms 12
- 1.4 Conclusions 16 References 19
- 2 Special Properties of Nanomaterials (NMs) for Sample Preparation 27
- 2.1 Introduction 27
- 2.2 Mechanical Properties of NMs 28
- 2.2.1 Hardness and Strength 28
- 2.2.2 Ductility 30
- 2.2.3 Applications of Mechanical Properties 32
- 2.3 Thermal Properties of NMs 33
- 2.4 Electrical Properties of NMs 35
- 2.5 Optical Properties of NMs 36
- 2.6 Magnetic Properties of NMs 37
- 2.7 Adsorption Properties of NMs 38
- 2.8 Conclusions 39
 - References 40

vi Contents

3	Adsorption Mechanism on Nanomaterials (NMs) 47
3.1	Introduction 47
3.2	Adsorption Process 48
3.2.1	Adsorption Isotherms 48
3.2.1.1	Langmuir Isotherm 50
3.2.1.2	Freundlich Isotherm 50
3.2.1.2	Temkin Isotherm 50
3.2.1.3	Dubinin–Radushkevich Model 51
3.2.1.4	Harkins–Jura and Halsey Isotherms 51
3.2.1.6	Redlich–Peterson Isotherm 51
3.2.1.7	BET (Brunauer, Emmett, and Teller) Isotherm 52
3.2.1.7	Adsorption Kinetics and Thermodynamics 52
	Pseudo-first-order Kinetics 52
3.2.2.1	
3.2.2.2	
3.2.2.3	Intraparticle Diffusion Model 53
3.2.2.4	Thermodynamic Study 53
3.2.3	Adsorption Process on Nanoparticles 54
3.2.3.1	Silver Nanoparticles 54
3.2.3.2	Gold Nanoparticles 55
3.2.3.3	Zinc Oxide Nanoparticles 56
3.2.3.4	Magnetic Fe_3O_4 Nanoparticles 56
3.2.4	Adsorption Process on Carbon Nanomaterials 58
3.2.4.1	Activated Carbon 58
3.2.4.2	Carbon Nanotubes (CNTs) 59
3.2.4.3	Graphene Oxide (GO) 60
3.3	Conclusions and Future Perspective 63
	References 63
4	Carbon Nanomaterials (CNMs) as Adsorbents for Sample
•	Preparation 71
4.1	Introduction 71
4.2	Carbon Nanomaterials (CNMs) 72
4.2.1	Carbon Nanotubes (CNTs) 72
4.2.2	Graphene 73
4.2.3	Fullerenes (FULs) 75
4.3	Adsorption on CNMs 76
4.4	Applications of CNMs 77
4.4.1	Extraction and Separation Applications 77
4.4.2	Chromatographic Applications 80
4.4.2.1	Chromatographic Stationary Phases Having CNTs 81
4.4.2.2	Chromatographic Stationary Phases Having FULs 83
4.5	Conclusions 84
r.J	References 84
	NEICICIUCS 04

102

147

5	Membrane Applications of Nanomaterials (NMs) 93
5.1	Introduction 93
5.2	Traditional Membranes 93
5.3	Carbon Nanomaterial-based Membranes 94
5.3.1	Graphene-based Membranes 94
5.3.2	Carbon Nanotube-based Membranes 97
5.3.3	Fullerene-based Membranes 100
5.4	Nanoparticle-based Membranes 101
5.5	Molecularly Imprinted Polymer (MIP)-based Membranes
5.6	Conclusions 105
	References 108
6	Surface-Enhanced Raman Spectroscopy (SERS) with
0	Nanomaterials (NMs) 117
6.1	Introduction 117
6.2	Theory of SERS 118
6.3	SERS Mechanisms 118
6.3.1	Electromagnetic Enhancement 119
6.3.2	Chemical Enhancement 120
6.4	Determination of SERS Enhancement Factor 121
6.5	Selection Rules 121
6.5.1	Image Field Model 121
6.5.2	Electromagnetic Field Model 122
6.6	Fabrications of SERS Substrates 123
6.6.1	Template-assisted Fabrication 124
6.6.2	Hybrid Fabrication 124
6.6.3	Fabrication by Using Colloids 124
6.6.4	Direct Deposition 125
6.7	Applications of SERS 125
6.7.1	SERS-Based Separation Applications 125
6.7.2	SERS-Based Sensor Applications 126
6.7.2.1	Environmental Analysis 126
6.7.2.2	Forensic Analysis 129
6.7.2.3	Biological Applications 131
6.8	Conclusions 133
	References 133
7	Nanomaterials (NMs) for Biological Sample Preparations
7.1	Introduction 147
7.2	The Use of NMs in Diagnostic Platforms 148

- 7.2 The Use of NMs in Diagnostic Platforms *148*
- 7.2.1 The Optimization of NMs in Diagnostic Platforms *148*
- 7.2.2 Biofunctionalization of NMs in Diagnostic Platforms 149
- 7.3 NMs-based Lab-on-a-chip (LOC) Platforms 150

- 7.3.1 Paper-based LOC Platforms 152
- 7.3.2 Centrifugal LOC Platforms 152
- 7.3.3 Droplet-based LOC Platforms 152
- 7.3.4 Digital LOC Platforms 152
- 7.3.5 Surface Acoustic Wave-based LOC Platforms 152
- 7.3.6 LOC Platforms for Biological Applications 153
- 7.4 Biomedical Applications of NMs 155
- 7.5 Sensor Applications of NMs 157
- 7.6 Conclusions 162 References 162

8 Magnetic Nanomaterials for Sample Preparation 173

- 8.1 Introduction 173
- 8.2 Synthesis of Magnetic Nanoparticles 174
- 8.2.1 Thermal Decomposition Technique 174
- 8.2.2 Coprecipitation Technique 175
- 8.2.3 Sol-Gel Synthesis 175
- 8.2.4 Hydrothermal Synthesis 176
- 8.2.5 Microemulsion-Based Synthesis 176
- 8.2.6 Flow Injection Synthesis 176
- 8.2.7 Aerosol/Vapor-Phase-Based Synthesis 176
- 8.3 Solid-Phase Extraction (SPE) 177
- 8.4 Magnetic Solid-Phase Extraction (MSPE) 177
- 8.4.1 MSPE for Environmental Samples 178
- 8.4.2 MSPE for Food and Beverage Samples 183
- 8.4.3 MSPE for Biological Samples 185
- 8.5 Conclusions and Future Trends *186* References *187*

9 Lab-on-a-Chip with Nanomaterials (NMs) 195

- 9.1 Introduction 195
- 9.2 Lab-on-a-Chip (LOC) Concept 196
- 9.2.1 Paper-based LOC Systems 198
- 9.2.2 Centrifugal LOC Systems 198
- 9.2.3 Droplet-Based LOC Systems 198
- 9.2.4 Digital LOC Systems 199
- 9.2.5 Surface Acoustic Wave-Based LOC Systems 199
- 9.3 NM-Based LOC Platforms 199
- 9.3.1 NM-Based Transducers 199
- 9.3.1.1 Electrochemical Detection Systems 199
- 9.3.1.2 Optical Detection Systems 202
- 9.3.1.3 Other Detection Techniques 205
- 9.3.2 Nanoparticles as Labels in Microfluidics 206
- 9.3.3 NMs for Process Improvement 208
- 9.4 Conclusions and Future Perspectives 209 References 210

- **10** Toxicity and Risk Assessment of Nanomaterials 219
- 10.1 Introduction 219
- 10.2 Hazard Assessment of Nanomaterials 220
- 10.2.1 Dermal Toxicity of Nanomaterials 220
- 10.2.2 Inhalational Toxicity of Nanomaterials 221
- 10.2.3 Carcinogenicity and Genotoxicity of Nanomaterials 223
- 10.2.4 Neurotoxicity of Nanomaterials 226
- 10.3 Toxicity Mechanism of Nanomaterials 227
- 10.4 The Traditional Risk Assessment Paradigm 229
- 10.5 Strategies for Improving Specific Risk Assessment 230
- 10.5.1 Combining Life Cycle Methodology with the Risk Assessment Approach 230
- 10.5.2 The Support of Risk-Based Classification Systems 231
- 10.6 Conclusions 232 References 232
- 11 Economic Aspects of Nanomaterials (NMs) for Sample Preparation 241
- 11.1 Introduction 241
- 11.2 Toxicity Concerns of NMs 242
- 11.3 Global Market for NM-Based Products 243
- 11.4 Conclusions 245 References 246
- 12 Legal Aspects of Nanomaterials (NMs) for Sample Preparation 251
- 12.1 Introduction 251
- 12.2 Safety Issues of NMs 251
- 12.3 Regulatory Aspects of NMs 252
- 12.3.1 Ethical Concerns in the Environmental Effects of NMs 253
- 12.3.2 Ethical Concerns in Occupational Health and Safety of Workers 254
- 12.3.3 Ethical Concerns of NMs in Food 255
- 12.3.4 Ethical Concerns of NMs in Drugs, Cosmetics, and Human Health 255
- 12.4 Conclusions 256 References 257

13 Monitoring of Nanomaterials (NMs) in the Environment 261

- 13.1 Introduction 261
- 13.2 Toxicity and Safety Concerns of NMs 262
- 13.3 Main Sources and Transport Routes of Nanopollutants 264
- 13.4 Requirements of Analytical Approaches 266
- 13.5 Sampling of NMs in Environmental Samples 266
- 13.6 Separation of NMs in Environmental Samples 267
- 13.7 Detection Techniques for the Characterization of NMs 268
- 13.8 Conclusions 270
 - References 270

x Contents

14 Future Prospect of Sampling 275

- 14.1 Introduction 275
- 14.2 Sampling 276
- 14.3Sample Preparation276
- 14.4 Green Chemistry 278
- 14.5 Miniaturization of Analytical Systems 280
- 14.5.1 Miniaturization of Separation Techniques 281
- 14.5.2 Lab-on-a-Valve (LOV) as a Powerful Tool to Meet Green Chemical Principles 283
- 14.6 Conclusions 283 References 284

Index 289