Multilayer Thin Films

Sequential Assembly of Nanocomposite Materials

Edited by
Gero Decher, Joseph B. Schlenoff
Contents

Foreword V

Preface XV

List of Contributors XVII

1 Polyelectrolyte Multilayers, an Overview 1
G. Decher

1.1 Why is the Nanoscale so Interesting 1
1.2 From Self-Assembly to Directed Assembly 1
1.3 The Layer-by-Layer Deposition Technique 3
1.3.1 LbL Deposition is the Synthesis of Polydisperse Supramolecular Objects 4
1.3.2 Reproducibility and Deposition Conditions 6
1.3.3 Monitoring Multilayer Buildup 7
1.3.3.1 Ex-situ Characterisation 7
1.3.3.2 In-situ Characterisation 9
1.3.4 Multilayers by Solution Dipping, Spraying or Spin Coating 12
1.3.5 Post-preparation Treatment of Multilayer Films 12
1.3.5.1 Annealing 12
1.3.5.2 Photopatterning 15
1.4 Multilayer Structure 16
1.4.1 The Zone Model for Polyelectrolyte Films 17
1.4.2 Layered or Amorphous: What Makes Multilayers Unique Supramolecular Species? 20
1.4.3 Soft and Rigid Materials 23
1.4.4 Deviation from Linear Growth Behaviour 24
1.5 Multimaterial Films 24
1.6 Toward Compartmentalized Films: Barrier Layers and Nanoreactors 26
1.7 Commercial Applications 30
1.8 References 31
2 Fundamentals of Polyelectrolyte Complexes in Solution and the Bulk 47
V. Kabanov
2.1 Introduction 47
2.2 Interpolyelectrolyte Reactions and Solution Behavior of Interpolyelectrolyte Complexes 48
2.2.1 Kinetics and Mechanism of Polyelectrolyte Coupling and Interchange Reactions 52
2.2.2 Solution Properties of Equilibrated Nonstoichiometric Interpolyelectrolyte Complexes 61
2.2.3 Transformation of Interpolyelectrolyte Complexes in External Salt Solutions 66
2.3 Complexation of Polyelectrolytes with Oppositely Charged Hydrogels 74
2.4 Structural and Mechanical Properties of Interpolyelectrolyte Complexes in the Bulk 76
2.5 Conclusion 82
2.6 References 83

3 Polyelectrolyte Adsorption and Multilayer Formation 87
J.-F. Joanny and M. Castelnovo
3.1 Introduction 87
3.2 Polyelectrolytes in Solution 89
3.3 Polyelectrolytes at Interfaces 90
3.4 Polyelectrolyte Complexes 92
3.5 Multilayer Formation 94
3.6 Concluding Remarks 96
3.7 References 97

4 Charge Balance and Transport in Polyelectrolyte Multilayers 99
J. B. Schlenoff
4.1 Introduction 99
4.2 Interactions 101
4.2.1 Mechanism: Competitive Ion Pairing 101
4.2.2 Intrinsic vs. Extrinsic Charge Compensation 103
4.2.2.1 Key Equilibria 103
4.2.2.2 Swelling and Smoothing: Estimating Interaction Energies 105
4.2.2.3 Multilayer Decomposition 108
4.3 Excess Charge 109
4.3.1 Surface vs. Bulk Polymer Charge 109
4.3.2 Distribution of Surface Charge in Layer-by-Layer Buildup: Mechanism 113
4.3.3 Equilibrium vs. non-Equilibrium Conditions for Salt and Polymer Sorption 117
4.4 Equilibria and Transport 118
4.4.1 Ion Transport through Multilayers: the "Reluctant" Exchange Mechanism 118
4.4.2 Practical Consequences: Trapping and Self-Trapping 126
5 pH-Controlled Fabrication of Polyelectrolyte Multilayers: 
Assembly and Applications 133

M. F. Rubner

5.1 Introduction 133
5.2 Layer-by-Layer Assembly of Weak Polyelectrolyte Multilayers 134
5.3 Light Emitting Thin Film Devices 137
5.4 Microporous Thin Films 139
5.5 Nanoreactors, Electroless Plating and Ink-jet Printing 141
5.6 Surface Modification via Selective Adsorption of Block Copolymers 144
5.7 Patterning of Weak Polyelectrolyte Multilayers 145
5.7.1 Micro-Contact Printing 146
5.7.2 Ink-jet Printing of Hydrogen-Bonded Multilayers 148
5.8 Conclusions and Future Prospects 152
5.9 References 153

6 Recent Progress in the Surface Sol–Gel Process and Protein Multilayers 155

I. Ichinose, K. Kuroiwa, Y. Lvov, and T. Kunitake

6.1 Alternating Adsorption 155
6.1.1 Surface Sol–Gel Process 155
6.1.2 Adsorption of Cationic Compounds on Metal Oxide Gels 157
6.1.3 Multilayer Assembly of Metal Oxides and Proteins 162
6.1.4 Protein/Polyelectrolyte Multilayer Assembly 166
6.2 Recent Topics in Biological Applications 167
6.2.1 Biosensors 168
6.2.2 Nano-filtration 169
6.2.3 Bioreactors 171
6.2.4 Protein Capsule and Protein Shell 173
6.3 References 174

7 Internally Structured Polyelectrolyte Multilayers 177

K. Glinel, A. M. Jonas, A. Laschwesky, and P. Y. Vuillaume

7.1 Introduction 177
7.2 Experimental Considerations 179
7.3 Stratified Binary (A/B)_n Organic Multilayers 182
7.4 Stratified Binary (A/B)_n Hybrid Organic/Inorganic Multilayers 188
7.4.1 Initial Studies on Hybrid Assemblies 189
7.4.2 Layered Assemblies from Analogous Poly(diallyl ammonium) Salt Derivatives and Hectorite Platelets 190
7.4.2.1 General Structural Observations 190
7.4.2.2 Detailed Analysis of the Structure of Laponite-Based Hybrid LBL Films 192
7.4.3 Ordering in Hybrid Assemblies Employing Functional Polyions 194
7.4.3.1 Photocrosslinkable Polyelectrolytes 194
7.4.3.2 The Use of Mesomorphic Polions 195
7.5 Hybrid Superlattices of the \{(A/B)^m/(C/D)^p\}_n Type 196
7.5.1 Literature Survey 197
7.5.2 Hybrid Organic/Inorganic Compartmentalized Multilayers from Clay Platelets 198
7.6 Conclusions 201
7.7 References 202
8 Layer-by-Layer Assembly of Nanoparticles and Nanocolloids:
Intermolecular Interactions, Structure and Materials Perspectives 207
N.A. Kotov
8.1 Introduction 207
8.2 Layer-by-Layer Assembly of Nanoparticles and Nanocolloids 208
8.3 Structural Factors of Individual Adsorption Layers 217
8.3.1 Intermolecular Interactions in the LBL Process 217
8.3.2 Ionic Conditions 222
8.3.3 Effect of Particle Shape on the Density of the Adsorption Layer 224
8.4 Stratified LBL Assemblies of Nanoparticles and Nanocolloids 225
8.4.1 Self-standing LBL Films 227
8.4.2 Magnetic Properties of the Stratified LBL Assemblies of Nanoparticles 229
8.4.3 Nanorainbows: Graded Semiconductor Films from Nanoparticles 231
8.5 Conclusion 235
8.6 References 236
9 Layer-by-Layer Self-assembled Polyelectrolytes and Nanoplatelets 245
J.H. Fendler
9.1 Introduction 245
9.2 Self-assembled Polyelectrolytes and Clay Nanoplatelets 246
9.3 Self-assembled Polyelectrolytes and Graphite Oxide Nanoplatelets 250
9.4 Potential Applications 256
9.4.1 Pollutant Photodestruction 256
9.4.2 Electronic Applications 259
9.4.3 Charge Storage 263
9.5 References 268
10 Chemistry Directed Deposition via Electrostatic and Secondary Interactions:
A Nonlithographic Approach to Patterned Polyelectrolyte Multilayer Systems 271
P.T. Hammond
10.1 Introduction and Overview 272
10.2 Selective Deposition of Polyelectrolyte Multilayer Systems 273
10.2.1 Selective Deposition of Strong Polyelectrolytes 273
10.2.1.1 Basis of Selective Adsorption and Ionic Strength Effects 273
10.2.1.2 Formation of Complex Multilayer Structures 276
10.2.2 Understanding and Utilizing Secondary Interactions in Selective Deposition 277
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.2.2.1</td>
<td>Establishing the Rules for Weak Polyamine Deposition</td>
<td>277</td>
</tr>
<tr>
<td>10.2.2.2</td>
<td>Confirming the Rules of Selective Adsorption:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SFM Investigations</td>
<td>279</td>
</tr>
<tr>
<td>10.2.2.3</td>
<td>Using the Rules: Side-by-Side Structures</td>
<td>280</td>
</tr>
<tr>
<td>10.2.2.4</td>
<td>The Next Steps: Surface Sorting of Multilayers and Other Elements</td>
<td>281</td>
</tr>
<tr>
<td>10.3</td>
<td>Polymer-on-Polymer Stamping</td>
<td>282</td>
</tr>
<tr>
<td>10.3.1</td>
<td>Fundamental Studies of Polymer-on-Polymer Stamping</td>
<td>284</td>
</tr>
<tr>
<td>10.3.1.1</td>
<td>Stamping of Ionic Polymers</td>
<td>285</td>
</tr>
<tr>
<td>10.3.1.2</td>
<td>Stamping of Block Copolymers</td>
<td>285</td>
</tr>
<tr>
<td>10.3.2</td>
<td>POPS as a Template for Other Materials Deposition</td>
<td>287</td>
</tr>
<tr>
<td>10.4</td>
<td>Directed Assembly of Colloidal Particles</td>
<td>289</td>
</tr>
<tr>
<td>10.4.1</td>
<td>Selective Deposition and Controlled Cluster Size on Multilayer Templates</td>
<td>290</td>
</tr>
<tr>
<td>10.4.2</td>
<td>Surface Sorting with Particles on Multilayer Surfaces</td>
<td>292</td>
</tr>
<tr>
<td>10.4.3</td>
<td>Selective Electroless Plating of Colloidal Particle Arrays</td>
<td>293</td>
</tr>
<tr>
<td>10.5</td>
<td>Functional Polymer Thin Films for Electrochemical Device and Systems Applications</td>
<td>294</td>
</tr>
<tr>
<td>10.5.1</td>
<td>Electrochromic Polyelectrolyte Multilayer Device Construction</td>
<td>295</td>
</tr>
<tr>
<td>10.5.2</td>
<td>Ionically Conducting Multilayers for Electrochemical Device Applications</td>
<td>296</td>
</tr>
<tr>
<td>10.6</td>
<td>Summary</td>
<td>297</td>
</tr>
<tr>
<td>10.7</td>
<td>References</td>
<td>298</td>
</tr>
</tbody>
</table>

11 Layered Nanoarchitectures Based on Electro- and Photo-active Building Blocks

11.1 Introduction 301
11.2 Multilayer Assemblies of Electroactive Species of Chemically Modified Electrodes 304
11.2.1 Controlled Fabrication of Multilayers with a Single Active Component 305
11.2.2 Controlled "Cascade" Modification with Binary Active Components 309
11.2.2.1 Biocatalytic Assemblies of Glucose Oxidase and Glucoamylase 310
11.2.2.2 Alternating Assemblies of Glucose Oxidase and Polycationic Electron Transfer 313
11.2.3 The Incorporation of Conductive Species to Improve the Performance of the Modified Electrodes 314
11.3 Ionic Self-assembly of Photoactive Materials and the Fabrication of "Robust" Multilayer 318
11.3.1 Ways to Fabricate Covalently Attached Multilayer Assemblies 319
11.3.2 Stable Entrapment of Oligo-charged Molecules Bearing Sulfonate Groups in Multilayer Assemblies 323
11.3.3 Covalently Attached Multilayer Assemblies of Polycationic Diazo-resins and Polyanionic Poly(Acrylic Acid) 324
Contents

11.3.4 Robust Nanoassemblies with Complex and Hybrid Structures 326
11.4 Summary and Outlook 328
11.5 References 328

12 Coated Colloids: Preparation, Characterization, Assembly and Utilization 332
F. Caruso and G. Sukhorukov

12.1 Introduction 331
12.2 Preparation and Characterization of Coated Colloids 333
12.2.1 Layer-by-Layer Adsorption 334
12.2.1.1 Multilayered Coatings 337
12.2.1.2 Coating of Specific Cores 344
12.2.2 Colloid Precipitation 349
12.3 Assembly and Utilization of Coated Colloids 351
12.3.1 Mesoscopic Arrangement 351
12.3.1.1 Colloidal Crystals 351
12.3.1.2 Macro- and Mesoporous Materials 351
12.3.2 Enzymatic Catalysis 354
12.3.2.1 Dispersions 354
12.3.2.2 Thin Films 355
12.3.3 Optical Properties 356
12.3.4 Further Applications 357
12.4 Summary and Outlook 358
12.5 References 359

13 Smart Capsules 363
H. Möhwald, E. Donath, and G. Sukhorukov

13.1 Preparation and Structure 364
13.1.1 General Aspects 364
13.1.1.1 Core Materials 364
13.1.1.2 Wall Materials 365
13.1.1.3 Molecular Dynamics 368
13.1.2 Physics and Chemistry of Core Removal 369
13.1.2.1 Core Destruction 369
13.1.2.2 Core Material Release 372
13.1.2 Modification of Walls 375
13.2 Properties and Utilization 376
13.2.1 Permeability Control 376
13.2.1.1 Permeation Mechanisms 377
13.2.1.2 Controlled Release Profiles 378
13.2.1.3 Switchable Release 379
13.2.2 Stability and Mechanical Properties 380
13.2.2.1 Temperature Dependent Structures 381
13.2.2.2 Capsule Elasticity 382
13.2.2.3 Plasticity, Viscosity and Rupture Strength 385
13.2.3 Chemistry and Physics in Nanovolumes 385
13.2.3.1 Chemical Gradients from Inside to Outside 386
13.2.3.2 Precipitation and Dissolution 387
13.1.3.3 Chemistry in Capsules 389
13.3 Summary and Outlook 390
13.4 References 391

14 Multilayers on Solid Planar Substrates: From Structure to Function 393

D. G. Kurth, D. Volkmer, and R. v. Klitzing

14.1 Introduction 393
14.2 Formation and Structure of LbL Multilayers 395
14.2.1 Adsorption Kinetics of Polyelectrolytes 395
14.2.2 LbL Multilayer Formation 397
14.2.3 ζ-potential 398
14.2.4 Effect of Polymer Charge 398
14.2.5 Influence of Ionic Strength 400
14.2.6 Permeability of Polyelectrolyte Multilayer 401
14.2.7 Internal Structure 403
14.3 Implementing Metallsupramolecular Devices in Thin Layered Films 405
14.3.1 Introduction 405
14.3.2 Metallosupramolecular Coordination Polyelectrolytes 408
14.3.3 Polyoxometalate Clusters 415
14.4 Conclusions 421
14.5 References 423

15 Functional Layer-by-Layer Assemblies with Photo- and Electrochemical Response and Selective Transport of Small Molecules and Ions 427

B. Tieke, M. Pyrasch, and A. Toutianoush

15.1 Introduction 427
15.2 Photoreactive Assemblies 428
15.2.1 Diacetylene Derivatives 429
15.2.2 Azobenzene Derivatives 434
15.3 Diphenyldiketopyrrolopyrrole Derivatives 438
15.4 Electroactive Assemblies 441
15.4.1 Poly(metal tetrathiooxalates) 441
15.4.2 Prussian Blue and Analogues 442
15.5 Transport of Small Molecules and Ions Across Polyelectrolyte Multilayers 446
15.5.1 Transport of Small Molecules 446
15.5.1.1 Gas Permeation 446
15.5.1.2 Pervaporation Separation of Alcohol/Water Mixtures 447
15.5.2 Transport of Ions 451
15.5.2.1 Uptake of Ions 454
15.6 Summary and Conclusions 456
15.7 References 458