

Contents

Preface *xi*

Abbreviations *xiii*

- 1 Property Tailoring of Gold Clusters via Surface Engineering and Supramolecular Assembly** *1*
 - 1.1 Introduction *1*
 - 1.2 Surface Modification of Gold NCs *2*
 - 1.2.1 Ligand Exchange *2*
 - 1.2.1.1 Thiolate/Selenolate as Incoming Ligands *2*
 - 1.2.1.2 Alkynyl as Incoming Ligands *3*
 - 1.2.1.3 N-Heterocyclic Carbenes (NHCs) as Incoming Ligands *5*
 - 1.2.2 Surface Locking Through Coordination *6*
 - 1.2.3 Post-Assembly Surface Modification *7*
 - 1.3 Gold Cluster-Assembled Materials (GCAMs) *8*
 - 1.3.1 1D Cluster Arrays Bridged by Metal–Metal Bonds *9*
 - 1.3.2 Covalently Bridged Oligomers and Networks *10*
 - 1.4 Applications *13*
 - 1.4.1 Biomedical Application *14*
 - 1.4.2 Semiconductivity *16*
 - 1.4.3 Magnetism *17*
 - 1.5 Conclusion *18*
 - References *18*

- 2 Modification and Assembly of Atomically Precise Silver Clusters** *23*
 - 2.1 Introduction *23*
 - 2.2 Precise Modification of Discrete Silver Clusters *23*
 - 2.2.1 Modification by Supramolecular Interactions *24*
 - 2.2.2 Modification by Functionalizing and Protecting Ligand *26*
 - 2.2.2.1 Substitution of Labile Solvent Molecules *26*
 - 2.2.2.2 Modulating Weakly Coordinated Non-S Auxiliary Ligands *27*
 - 2.2.2.3 Replacing Coordinated S-containing Ligand by Other Functional S-containing Ligands *32*
 - 2.3 Assembly of Silver Clusters into Atomically Precise Extended Structures *39*

2.3.1	Supramolecular Assembly of Silver Clusters	39
2.3.2	Coordination Assembly of Silver Clusters	42
2.3.2.1	Inorganic Ion Linkers	42
2.3.2.2	POMs Linkers	44
2.3.2.3	Organic Bi/Multidentate Linkers	45
2.4	Applications	54
2.4.1	Luminescent Switching and Sensing Oxygen and VOCs	54
2.4.2	Ratiometric Luminescent Temperature Sensing	56
2.4.3	Catalytic Properties	57
2.5	Conclusion and Perspectives	58
	References	59
3	Modification and Assembly of Copper Clusters	65
3.1	Introduction	65
3.2	Synthesis and Properties of Cu Clusters	66
3.3	Modification and Assembly of Copper Clusters	68
3.3.1	Thiolates Ligands Modified Copper Clusters	68
3.3.2	Phosphine Ligands Modified Cu Clusters	74
3.3.3	Alkynyl Ligands Modified Copper Clusters	77
3.3.4	Other Ligands Modified Copper Cluster	82
3.3.5	Assembly of Copper Clusters	84
3.4	Conclusion and Perspectives	85
	References	85
4	Recent Advances in Post-Modification of Polyoxometalates: Structures and Properties	93
4.1	Introduction	93
4.2	Synthetic Strategies and Structural Overviews	94
4.2.1	Surfactant-Encapsulated POM Clusters	95
4.2.2	Assembly of Janus POM-POSS Co-clusters	101
4.2.3	Porous POM-Based Metal–Organic Framework (MOF) Materials	102
4.3	Applications	107
4.3.1	POM-Based Nanostructures for Asymmetric Catalysis	107
4.3.2	POM-Based Nanostructures for Electrochemistry and Electrocatalysis	110
4.3.3	POM-Based Nanostructures for Photocatalytic	117
4.3.4	POM-Based Nanostructures for Biological Applications	119
4.4	Conclusion and Perspectives	122
	References	123
5	Small Transition Metal Chalcogenide Superatom Clusters	131
5.1	Introduction	131
5.2	Synthesis and Properties of $M_6E_8L_6$ Superatoms	132
5.2.1	Synthesis of $M_6E_8L_6$ Superatoms	132

- 5.2.1.1 Gas-Phase Synthesis 132
- 5.2.1.2 Solution-Phase Synthesis 133
- 5.2.1.3 Solid-Phase Synthesis 133
- 5.2.2 Properties of $M_6E_8L_6$ Superatoms 133
- 5.3 Modification and Assembly of $M_6E_8L_6$ Superatoms 134
- 5.3.1 Modification of Superatoms 134
- 5.3.1.1 Functionalized Superatoms 134
- 5.3.1.2 Site-Differentiated Superatoms 135
- 5.3.2 Assembly of Superatoms 137
- 5.3.2.1 Discrete Bridged and Fused Oligomers of Superatoms 137
- 5.3.2.2 Supermolecule Assembly 138
- 5.3.2.3 Covalent Superatomic Crystals 142
- 5.4 Collective Properties of Superatomic Crystals 145
- 5.4.1 Electrochemical Properties, Single-Electron Currents, and Electronic Transport 145
- 5.4.2 Thermal Transport 148
- 5.5 Conclusion and Perspectives 151
- References 151

6 Synthesis and Assembly of Cadmium Chalcogenide Supertetrahedral Clusters 157

- 6.1 Introduction 157
- 6.2 Synthesis and Structure of Cadmium Chalcogenide Supertetrahedral Clusters 158
- 6.2.1 Tn -Type Clusters 158
- 6.2.2 Pn -Type Clusters 160
- 6.2.3 Cn -Type Clusters 161
- 6.3 Assembly of Cadmium Chalcogenide Supertetrahedral Clusters 163
- 6.3.1 Inorganic Open Frameworks 163
- 6.3.2 Organic Open Frameworks 169
- 6.3.2.1 N-Donor Ligands 169
- 6.3.2.2 Other Organic Ligands 175
- 6.4 Properties 176
- 6.4.1 Photoluminescent Properties 176
- 6.4.2 Photodegradation of Organic Dyes 178
- 6.5 Conclusion and Perspectives 179
- References 180

7 The Modification and Assembly of Fe–S Clusters 185

- 7.1 Introduction 185
- 7.2 The Modification of the First and Second Coordination Sphere on Fe–S Clusters 187
- 7.2.1 The Modification of the First Coordination Sphere by Phosphine Ligands 187

- 7.2.2 The Modification of the First Coordination Sphere by NHC and Chelated N-Based Ligands 189
- 7.2.3 The Modification of the Second Coordination Sphere by Aliphatic Dithiolate Bridged Ligands 190
- 7.2.4 The Modification of the Second Coordination Sphere by Aromatic Dithiolate Bridged Ligands 191
- 7.2.5 The Modification of the First and Second Coordination Sphere by Photosensitive Ligands 193
- 7.3 The Assembly of Fe–S Clusters 195
 - 7.3.1 The Assembly of Fe–S Clusters to Form Polynuclear Fe–S Complexes 195
 - 7.3.2 The Assembly of Fe–S Clusters to Form CPs 195
 - 7.3.3 The Assembly of Fe–S Clusters Anchored Onto Heterogeneous Supports 198
- 7.4 The Application of [2Fe2S] Clusters in Photocatalytic H₂ Production 202
- 7.5 Conclusion and Perspective 206
- References 206

- 8 Indium Phosphide Magic-Sized Clusters 217**
 - 8.1 Introduction 217
 - 8.2 Synthesis of InP MSCs 218
 - 8.2.1 The Low Temperature Method 219
 - 8.2.2 The Ligands Method 220
 - 8.2.3 The Doping Method 223
 - 8.3 Growth of InP QDs from InP MSCs 228
 - 8.3.1 The Synthesis Methods from InP MSCs to InP QDs 228
 - 8.3.2 The Influence on the Synthesis of InP MSCs to InP QDs 230
 - 8.3.3 The Synthesis Mechanism from InP MSCs to InP QDs 233
 - 8.4 Other Applications of InP MSCs 235
 - 8.4.1 The Synthesis of Diverse Morphology in InP Nanostructures 235
 - 8.4.2 Developing the Luminescent Property of InP MSCs 236
 - 8.5 Conclusion and Perspectives 237
 - References 238

- 9 Ligand-Tailoring Platinum and Palladium Clusters 241**
 - 9.1 Introduction 241
 - 9.2 Synthesis of Platinum and Palladium Clusters 242
 - 9.2.1 Synthesis of Pt/Pd Carbonyl Clusters (PCCs) 242
 - 9.2.1.1 Direct Carbonylation Method 242
 - 9.2.1.2 Redox-Induced Methods 244
 - 9.2.1.3 Chemically/Physically Induced Methods 245
 - 9.2.2 Synthesis of Pt/Pd-Clusters Protected by Organic Ligands 247
 - 9.3 Ligand Regulation and Modification of Platinum and Palladium Clusters 255
 - 9.3.1 Ligand-Tailoring and Assembly of Platinum Clusters 255

- 9.3.2 Modification of Palladium Clusters 260
- 9.4 Conclusion and Perspectives 262
- References 263

10 Metal Oxo Clusters 271

- 10.1 Introduction 271
- 10.2 Structure and Properties of Zirconium Oxo Clusters (ZrOCs) 272
 - 10.2.1 Formation of Zr Oxo Cluster in Aqueous Medium 273
 - 10.2.2 Formation of Zr Oxo Clusters in Organic Medium 275
- 10.3 Structure and Properties of Titanium Oxo Clusters (TiOCs) 278
 - 10.3.1 Structural Diversity of Titanium Oxo Clusters 278
 - 10.3.1.1 Carboxylate Ligands-Stabilized Titanium Oxo Clusters 279
 - 10.3.1.2 Phosphonate-Stabilized Titanium Oxo Clusters 280
 - 10.3.1.3 N-Donor Ligands Participating in Titanium Oxo Clusters 281
 - 10.3.2 Bandgap Engineering of Titanium Oxo Clusters 283
 - 10.3.2.1 Ligand Modification 283
 - 10.3.2.2 Metallic Doping 283
- 10.4 Structure and Properties of Lanthanide Oxo Clusters (LnOCs) 287
 - 10.4.1 Synthetic Strategy for High-Nuclearity Lanthanide Clusters 287
 - 10.4.1.1 Ligand-Controlled Hydrolysis Approach 288
 - 10.4.1.2 Anion Template Method 289
 - 10.4.1.3 Slow Release of Anion Templates 289
 - 10.4.1.4 Multiple Anion Templates, Including Mixed Templating Anions 290
 - 10.4.2 Building Blocks for the Assembly of High-Nuclearity Lanthanide Clusters 292
- 10.5 Conclusion and Perspective 294
- References 294

Index 301

