

WILEY-VCH

Edited by
Qingfeng Yan and George Zhao

Functional Materials from Colloidal Self-assembly



Functional Materials from Colloidal Self-assembly

Functional Materials from Colloidal Self-assembly

Edited by Qingfeng Yan and George Zhao

WILEY-VCH

Editors

Prof. Qingfeng Yan

Tsinghua University
Department of Chemistry
Haidian District
100084 Beijing
China

Prof. George Zhao

The University of Queensland
School of Chemical Engineering
Don Nicklin Bldg
4072 Brisbane St. Lucia
Australia

Cover Image: © oxygen/Getty Images

■ All books published by **WILEY-VCH** are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <<http://dnb.d-nb.de>>.

© 2022 WILEY-VCH GmbH, Boschstr. 12, 69469 Weinheim, Germany

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Print ISBN: 978-3-527-82795-4

ePDF ISBN: 978-3-527-82871-5

ePub ISBN: 978-3-527-82873-9

oBook ISBN: 978-3-527-82872-2

Typesetting Straive, Chennai, India

Printed on acid-free paper

10 9 8 7 6 5 4 3 2 1

Contents

Preface xv

1	Colloidal Molecules and Colloidal Polymers	1
	<i>Etienne Duguet, Etienne Ducrot, and Serge Ravaine</i>	
1.1	Introduction	1
1.2	Colloidal Molecules: Mimicking Organic and Inorganic Molecules	3
1.2.1	Clustering of Isotropic Colloids	3
1.2.1.1	Clustering Assisted by External Fields	3
1.2.1.2	Clustering Assisted by Geometrical Confinement	4
1.2.1.3	Clustering Assisted by Physical or Chemical Interactions	6
1.2.2	Clustering of Patchy Particles	8
1.2.2.1	Self-aggregation of One-Patch Particles, i.e. Janus Particles	8
1.2.2.2	Stoichiometric Attachment of Colloidal Satellites Around Patchy Particles	10
1.3	Colloidal Polymers: Mimicking Organic Macromolecules	13
1.3.1	Dipole-Directed Formation of Colloidal Polymers	14
1.3.1.1	Electric Dipoles	14
1.3.1.2	Magnetic Dipoles	14
1.3.2	Formation of Colloidal Polymers by Nanowelding	15
1.3.3	Formation of Colloidal Polymers Under Physical or Chemical Confinement	15
1.3.4	Field-Directed Formation of Colloidal Polymers	17
1.3.4.1	Electric Fields	17
1.3.4.2	Magnetic Fields	19
1.3.5	Ligand-Directed Formation of Colloidal Polymers	22
1.3.5.1	Electrostatic Interactions	22
1.3.5.2	Covalent Bonding	23
1.3.5.3	Noncovalent Attachment	25
1.4	Conclusion and Outlook	30
	References	31

2	Self-assembly of Anisotropic Colloids in Solutions	37
	<i>Yiwu Zong, Huaqing Liu, and Kun Zhao</i>	
2.1	Introduction	37
2.2	Fabrication of Anisotropic Colloids	38
2.2.1	Bottom-Up Routes	38
2.2.1.1	Template(Seed)-Assisted Synthesis	38
2.2.1.2	Cluster-Based Methods	41
2.2.1.3	DNA-Based Assembly Methods	41
2.2.1.4	Surface Modification Methods	42
2.2.2	Top-Down Routes	42
2.2.2.1	Photolithographic Fabrication Methods	42
2.2.2.2	Physical Methods	43
2.2.3	Anisotropic Colloids from Natural Materials	44
2.3	Self-assembly Mechanisms of Anisotropic Colloids	44
2.3.1	Self-assembly Through Specific Interactions	44
2.3.1.1	Electrostatic Interactions	44
2.3.1.2	Hydrophobic Interactions	45
2.3.1.3	Entropic Depletion Interactions	47
2.3.1.4	DNA-Mediated Interactions	52
2.3.2	Assembly in External Fields	54
2.3.2.1	Electric Field Assisted	54
2.3.2.2	Magnetic Field Assisted	56
2.3.2.3	Self-propelled Colloidal Motors	58
2.4	Applications of Self-assembly of Anisotropic Colloids	60
2.4.1	Liquid Crystals	60
2.4.2	Photonic Crystals	61
2.4.3	Sensors	63
2.4.3.1	Metal Ions	63
2.4.3.2	Biomolecules	65
2.4.3.3	Gases	66
2.4.3.4	Other Environmental Cues	68
2.4.4	Electrode Materials	68
2.4.5	Other Applications in Making Functional Materials	71
2.5	Summary and Outlook	74
	Acknowledgment	74
	References	74
3	Self-assembly Enabling Materials Nanoarchitectonics	87
	<i>Katsuhiko Ariga</i>	
3.1	Introduction	87
3.2	Fullerene Nanoarchitectonics	91
3.3	Layer-by-Layer Nanoarchitectonics	97
3.4	Conclusions	104
	Acknowledgments	105
	References	105

4	Self-assembly of Colloidal Crystals: Strategies	109
	<i>Junchao Liu, Jingxia Wang, and Lei Jiang</i>	
4.1	Introduction	109
4.2	Assembly Mechanism of Latex Particles	110
4.2.1	General Assembly Process	110
4.2.2	Influence of Substrate Wettability on the Assembly Process	111
4.2.3	Influence of Magnetic/Electric Field on the Assembly Process	113
4.3	Assembly Strategies of Colloidal Crystal	115
4.3.1	Large-Area Colloidal PC	115
4.3.1.1	Vertical Deposition	115
4.3.1.2	LB Approach	116
4.3.1.3	Doctor Blade	118
4.3.1.4	Spin Coating	118
4.3.1.5	Spray Coating	120
4.3.1.6	Other	121
4.3.2	Patterned Colloidal PC	123
4.3.2.1	Physical Confinement: Geometric Defect	123
4.3.2.2	Wettability-Induced Template Assembly	124
4.3.2.3	Direct Dropping	125
4.3.2.4	Direct Writing	126
4.3.2.5	Inkjet Printing	127
4.3.3	Specific Structure Colloidal PC	128
4.3.3.1	Cylinder Assembly from Capillary Tube	128
4.3.3.2	Electrospun	130
4.3.3.3	Microfluidics	131
4.4	Conclusions	133
	References	133
5	2D and (2+1)D Colloidal Photonic Crystal	139
	<i>Lijing Zhang, Jiaqi Han, and Bofan Liu</i>	
5.1	Colloidal Photonic Crystals	139
5.2	2D Colloidal Photonic Crystal	140
5.2.1	Preparation Methods	140
5.2.1.1	Solvent Evaporation-Induced Self-assembly	141
5.2.1.2	Spin Coating	142
5.2.1.3	Electrophoretic Deposition	142
5.2.1.4	Air/Liquid Interface Self-assembly	142
5.2.1.5	Other Strategies	146
5.2.2	Optical Properties	150
5.2.2.1	Diffraction	150
5.2.2.2	Debye Diffraction Ring	151
5.2.3	Application	152
5.2.3.1	Templates	152
5.2.3.2	Detection and Sensing	157
5.3	(2+1)D Colloidal Photonic Crystal	160

5.3.1	Preparation Method	161
5.3.1.1	The Langmuir–Blodgett Method	162
5.3.1.2	PDMS Sheet-Assisted Layer-by-Layer Transfer Technique	164
5.3.1.3	Layer-by-Layer Scooping Transfer Technique	164
5.3.1.4	<i>In Situ</i> Annealing Combined Layer-by-Layer Transfer Technique	164
5.3.2	Optical Properties	167
5.3.2.1	Comparison Between (2+1)D and 3D	167
5.3.2.2	Bandgap Engineering	171
5.3.3	Application	173
5.3.3.1	Engineering of Complex Macroporous Materials	174
5.3.3.2	High-Performance Back Reflector	174
5.3.3.3	FL Enhancement Substrate	174
5.4	Outlook	179
	References	180
6	Structural Color due to Self-assembly	183
	<i>Yong Qi and Shufen Zhang</i>	
6.1	Structural Color in Nature	183
6.2	The Type of the Structural Color and Its Formation Mechanism	186
6.2.1	Structural Color due to Interference	186
6.2.2	Structural Color due to Scattering	187
6.2.3	Structural Color due to Diffraction	188
6.3	The Assembly Methods of the SCMs	191
6.3.1	Evaporation Self-assembly	191
6.3.2	Membrane Separation-assisted Assembly	194
6.3.3	Air–Liquid Interface Self-assembly	195
6.3.4	Oil–Oil Interface Self-assembly	200
6.3.5	Oil–Water Interface Self-assembly	200
6.3.6	Controlled Micellization Self-assembly	202
6.3.7	Layered Hydrogels Self-assembly	205
6.3.8	Spray Coating Self-assembly	207
6.3.9	Unidirectional Rubbing Self-assembly	210
6.3.10	Edge-Induced Rotational Shearing Self-assembly	210
6.3.11	Screen Printing Self-assembly	213
6.3.12	Magnetic-Induced Self-assembly	215
6.3.13	Photoinduced Self-assembly	218
6.3.14	Atomic Layer Deposition Self-assembly	220
6.3.15	Physical Vapor Deposition Self-assembly	220
6.3.16	Surface Wrinkling	223
6.4	Typical Applications of Structural Color	226
6.5	Conclusions	228
	Acknowledgments	230
	References	230

7	Colloidal Photonic Crystal Sensors	237
	<i>Zhongyu Cai, Xiaoying Xu, Zihui Meng, Bushra Rafique, and Ruixiang Liu</i>	
7.1	Introduction	237
7.2	Fundamentals of Colloidal Photonic Crystal Sensors	239
7.3	Responsive Materials and Novel Photonic Structures	242
7.4	Colloidal Photonic Crystal Sensors Responsive to Physical Stimuli	243
7.4.1	Colloidal Photonic Crystals Responsive to Humidity	243
7.4.2	Mechanically Responsive Colloidal Photonic Crystals	245
7.5	Colloidal Photonic Crystal Sensors Responsive to Chemicals	247
7.5.1	Colloidal Photonic Crystals Responsive to Solvents	247
7.5.2	Colloidal Photonic Crystals Responsive to Vapors (VOCs)	249
7.5.3	Colloidal Photonic Crystals Responsive to Ions	250
7.5.4	Colloidal Photonic Crystals Responsive to Organophosphates	253
7.5.5	Colloidal Photonic Crystals Responsive to Surfactants	256
7.6	Colloidal Photonic Crystal Sensors Responsive to Biological Species	256
7.6.1	Colloidal Photonic Crystals Responsive to Carbohydrates	257
7.6.2	Colloidal Photonic Crystals Responsive to Proteins (Enzyme, Antibodies)	260
7.6.3	Colloidal Photonic Crystals Responsive to Amino Acids	264
7.6.4	Colloidal Photonic Crystals Responsive to Biomarkers	265
7.6.5	Colloidal Photonic Crystal Sensors for Microorganisms Detection	267
7.7	Summary and Outlooks	269
	Acknowledgment	269
	References	270
8	Self-assembled Graphene Architectures for Electrochemical Energy Storage	277
	<i>Pei Li, Junwei Han, and Quan-Hong Yang</i>	
8.1	Introduction	277
8.2	Self-assembly Strategies	278
8.2.1	Langmuir–Blodgett (LB) Technique	281
8.2.2	Layer-by-Layer (LbL) Assembly Approach	281
8.2.3	Flow-Directed Self-assembly	282
8.2.4	Interface-Induced Self-assembly	283
8.2.5	Template-Directed Self-assembly and Hydrothermal Process	284
8.2.6	Spinning and Space Confinement Self-assembly	286
8.3	Methods for Tailoring the Assemblies	286
8.3.1	Structural Tuning and Surface Modification	287
8.3.1.1	Compact Assembly via Capillary and Mechanical Compression	287
8.3.1.2	Tunable Porous Structure and Surface Chemistry	289
8.3.1.3	Assembly in the Electrostatic and Magnetic Field	291
8.3.2	Composite Materials Prepared by Self-assembly	291
8.3.2.1	Graphene/Carbon Material Assembly	291

- 8.3.2.2 Graphene/Polymer Assembly 292
- 8.3.2.3 Graphene/Metal or Metal Oxide Assembly 292
- 8.4 Applications of Self-assembled Graphene Architecture 293
 - 8.4.1 SCs 293
 - 8.4.2 LIBs 296
 - 8.4.3 Li-S Batteries 297
 - 8.4.4 Challenges for Practical EES Applications 299
- 8.5 Conclusions 300
 - Acknowledgments 300
 - References 300

9 Patterning Assembly of Colloidal Particles 305

Minxuan Kuang and Yanlin Song

- 9.1 Introduction 305
- 9.2 Strategies of Patterning Assembly 306
 - 9.2.1 Inkjet Printing of Assembly Patterns 306
 - 9.2.1.1 Ink Formulations 306
 - 9.2.1.2 Surface Wettability 310
 - 9.2.2 Patterned Substrate-Induced Assembly 314
 - 9.2.3 External Stimuli-Induced Assembly 316
 - 9.3 Applications of PC Patterns 316
 - 9.3.1 Displays 316
 - 9.3.2 Sensors 319
 - 9.3.3 Anticounterfeiting 324
- 9.4 Summary 326
 - References 326

10 Light Extraction Efficiency Enhancement in GaN-Based LEDs by Colloidal Self-assembly 331

Tongbo Wei

- 10.1 Introduction 331
- 10.2 Nanostructure Fabrication by MCC 333
- 10.3 Applications of Nanostructures to LEDs 335
 - 10.3.1 Surface Texturing 335
 - 10.3.2 Submicron Lenses 339
 - 10.3.3 Photonic Crystals (PhCs) 341
 - 10.3.3.1 Surface PhCs 342
 - 10.3.3.2 Bottom PhCs 344
 - 10.3.4 Localized Surface Plasmon (LSP) 346
 - 10.3.5 Nano-patterned Sapphire Substrates (NPSS) 348
 - 10.3.6 Optical Reflector 352
- 10.4 New Applications for Optoelectronic Devices 354
 - 10.4.1 Nanorod LEDs 354
 - 10.4.1.1 Top-Down Nanorod LEDs 355
 - 10.4.1.2 Bottom-Up Nanorod LEDs 357

10.4.2	Microdisk Lasers	357
10.5	Conclusions and Perspectives	359
	References	361
11	Self-assembled Photonic Crystals for Solar Cells	365
	<i>Likui Wang</i>	
11.1	Introduction	365
11.2	The Application of Self-assembled PCs in DSSCs	368
11.2.1	Application of Dye-Sensitized IOs as Photoanodes of DSSC	369
11.2.2	Self-assembled Photonic Crystals for Light Harvesting Enhancement in DSSCs	375
11.3	Self-assembled Photonic Crystals for Perovskite Solar Cells	384
11.4	The Application of Self-assembled PCs in Silicon-Based Solar Cells	389
11.5	Summary and Outlook	390
	References	391
12	Mesoporous Zeolites: Synthesis and Catalytic Applications	397
	<i>Feng Yu and Feng-Shou Xiao</i>	
12.1	Introduction	397
12.2	Synthesis of Mesoporous Zeolite	398
12.2.1	Bottom-up Zeolite Synthetic Strategies	399
12.2.1.1	Hard Templating Methods	399
12.2.1.2	Soft Templating Methods	404
12.2.1.3	Non-templating Methods	411
12.2.2	Top-down Approaches via Demetallization	414
12.2.2.1	Dealumination	414
12.2.2.2	Desilication	415
12.2.3	Mixed Synthetic Approaches	417
12.3	Catalytic Application of Mesoporous Zeolites	419
12.3.1	Fuel Chemistry	419
12.3.1.1	Catalytic Cracking	419
12.3.1.2	Fischer–Tropsch Reaction	422
12.3.1.3	Methanol to Gasoline or Olefins	423
12.3.2	Selective Organic Reactions	425
12.3.2.1	Hydrogenation	427
12.3.2.2	Oxidation	428
12.3.2.3	Friedel–Crafts Alkylation	429
12.3.2.4	Isomerization	430
12.3.2.5	HDO Phenolics	432
12.3.3	Catalytic Combustion	432
12.3.4	Biomass Valorization via Catalytic Fast Pyrolysis	433
12.4	Conclusions and Perspectives	435
	References	436

13	Colloidal Self-assembly of Block Copolymers for Drug Loading and Controlled Release	455
	<i>Guangze Yang, Yun Liu, and Chun-Xia Zhao</i>	
13.1	Introduction	455
13.2	Block Copolymers	456
13.2.1	Diblock Copolymers	456
13.2.2	Triblock Copolymers	458
13.2.3	Self-assembly Mechanism	459
13.3	Nanoscale Structures	460
13.3.1	Micelles	460
13.3.2	Nanoparticles	461
13.3.3	Vesicles or Polymersomes	462
13.4	Drug Loading	463
13.4.1	Single Drug Encapsulation	463
13.4.2	Dual Drug Encapsulation	464
13.4.2.1	Similar Hydrophobicity	464
13.4.2.2	Opposite Hydrophobicity	465
13.4.3	Multiple Drugs	466
13.4.4	Drug and Imaging Reagent	468
13.5	Drug Release	470
13.5.1	Drug Release Mechanism	470
13.5.2	pH-Triggered Release	471
13.5.3	Thermo-Triggered Release	472
13.5.4	Redox-Triggered Release	472
13.5.5	Other Triggered Release	473
13.5.6	Multiple-Triggered Release	475
13.6	Conclusions	475
	References	477
14	Heat Management by Colloidal Self-assembly	493
	<i>Qimeng Song, Marius Schöttle, Pia Ruckdeschel, Fabian Nutz, and Markus Retsch</i>	
14.1	Introduction	493
14.2	Fabrication Methods	494
14.2.1	Categories of Colloidal Assemblies	494
14.2.2	Self-assembly Strategies	495
14.3	Fundamentals of Thermal Transport in Dielectric Materials	497
14.3.1	Thermal Transport in Crystalline Matter	497
14.3.2	Thermal Transport in Amorphous Matter	498
14.3.3	Thermal Transport in Composite and Porous Materials	499
14.4	Characterization Methods	501
14.4.1	Laser Flash Analysis (LFA)/Xenon Flash Analysis (XFA)	501
14.4.2	Transient Plane Source (TPS)/Modified Plane Source (MPS) Technique	503

14.4.3	Time-Domain Thermoreflectance (TDTR) and Frequency-Domain Thermoreflectance (FDTR) Methods	504
14.4.4	Guarded Hot Plate (GHP) and Heat Flow Meter (HFM)	506
14.4.5	Photoacoustic (PA) Method	509
14.4.6	Lock-In Infrared Thermography (LIT)	509
14.5	Heat Transport in Colloidal Structures	512
14.5.1	Porous Structures	512
14.5.2	Dense Structures	520
14.6	Heat Management Applications	527
14.6.1	Thermal Recorders	527
14.6.2	Thermal Switches	527
14.6.3	Thermal Rectification	530
14.6.4	Thermoelectrics	531
14.6.5	Passive Cooling	532
14.7	Conclusion and Summary	532
	References	533
	Index	539

Preface

Functional materials represent a fast-growing research field in materials science. Functional materials generally refer to those that possess particularly intrinsic properties and functions of their own. For example, ferroelectric materials, piezoelectric materials, thermoelectric materials, magnetic materials, semiconductor materials, optoelectronic materials, and many others. However, there is a special type of functional materials, i.e. metamaterials, the function of which comes from their designed structures. The metamaterial is usually an artificial material that exhibits unique properties not found in nature, such as a negative index of refraction, in its interaction with electromagnetic radiation, sound, or other wave phenomena. Such properties are a consequence of the metamaterial's structure at the microscopic or macroscopic level rather than of the intrinsic properties of its components.

As a representative optical metamaterial, photonic crystals have some extraordinary physical properties, such as effective negative parameters, bandgaps, negative refraction, etc., and have attracted extensive attention due to their promising application potentials. Photonic crystals exist in nature and can be artificially created by controlling structural periodicity of dielectric materials. When their feature size goes to micro- or nanometer and their periodicity extends to three dimensions, the fabrication of photonic crystals with a full bandgap has been a grand challenge.

In this regard, nature has been a great mentor, teaching humans how to construct a substance having a complex structure. The beauty of gemstone opal originates from a densely packed, highly ordered arrangement of silica spheres with a diameter of several hundred nanometers. Silica spheres themselves have no intrinsic color, while a periodic arrangement endows their entirety an amazing color. Such ordered nanostructure is a typical example of natural photonic crystals, which can be formed by spontaneous sedimentation of silica spheres in nature or by a colloidal self-assembly process.

Colloidal particles normally have a diameter in the range from a few nanometers to a few microns – large enough to be visualized under optical microscope, yet small enough to sustain Brownian motion when dispersed in a fluid medium. Self-assembly of colloidal particles provides an efficient approach for the biomimetic construction of functional materials for manipulation of the flow of light, energy storage and conservation, anticounterfeiting, green printing, dynamic color display, environmental sensing, fabric coloring, heat management, and so on.

The past several decades have witnessed a number of encouraging advancements in colloidal self-assembly for functional materials. This book intends to provide an overview of the state-of-the-art colloidal self-assembly for functional materials ranging from emerging colloidal building blocks and self-assembly mechanisms and strategies to applications in structural color, light emitting diodes (LEDs), solar cells, catalysts, drug load and release, and heat management. In addition to providing accounts of recent developments in the respective topics, the authors also note the challenges and present their perspectives on the individual directions in the future.

Traditional colloidal particles have been spherical in shape, being viewed as “big atoms” suitable for studying various physical phenomena in atomic crystals, such as crystallization, glass transition, and defect evolution. Advances in the areas of functional materials demand for the development of complex colloidal particles, which are rich in component, shape, and surface chemistry. Benefiting from recent remarkable research breakthroughs, in advanced synthesis methods, and fabrication techniques, new colloidal building blocks have emerged and expanded the boundaries of conventional colloidal self-assembly.

In Chapter 1, Ravaine and coworkers discuss recent advances in the synthesis of clusters of isotropic colloids and patchy particles, as well as the self-assembly of these complex colloidal particles toward the so-called colloidal molecules and colloidal polymers. Compared with their isotropic spherical counterparts, anisotropic colloids show unique physiochemical properties and much richer phase behavior. In Chapter 2, Zhao and coworkers summarize the latest advances in both fabrication techniques and self-assembly mechanisms of anisotropic colloids, as well as the progress in the applications of assembled structures. Due to the extraordinary characteristics either from their unique shapes or well-designed particle interactions, they show a much broader range of assembled structures than isotropic colloids. With such a variety of accessible structures that could possess special properties, self-assembly of anisotropic colloids show great potential for applications in various fields. In Chapter 3, Ariga introduces the concept of nanoarchitectonics through self-assembly of different colloidal particles, focusing on fullerene assemblies at gas/liquid interfaces and assemblies based on layer-by-layer (LbL) technique. Due to the abundant surface and interface properties of graphene-based colloids, especially chemically modified graphene, various self-assembly strategies are developed to construct hierarchical structures and composite materials. In Chapter 8, Yang and coworkers review the recent advances in the self-assembly and tailoring methods of graphene-based colloids, highlighting important applications and perspectives on self-assembled graphene structures. In Chapter 12, Xiao and Yu present an overview of diverse synthesis approaches to the fabrication of mesoporous zeolites and their catalytic applications. In Chapter 13, Zhao and coworkers provide an overview of the colloidal self-assembly of diblock and triblock copolymers for drug loading and controlled release. The advantages and disadvantages of block copolymers as well as future directions for various drug delivery applications are also discussed.

In Chapter 4, Wang and coworkers discuss research progress on self-assembling strategies of colloidal photonic crystals, including assembly mechanisms and

approaches. Researches on 3D colloidal photonic crystals have been very extensive and in-depth, but less attention was paid to 2D colloidal photonic crystals and (2 + 1)D photonic crystals. In Chapter 5, Zhang and coworkers discuss the preparation, optical properties, and applications of 2D and (2 + 1)D colloidal photonic crystals. Furthermore, the current limitations and perspectives for their future developments are also discussed.

Structural colors are all kinds of colors produced by the microscopic structures corresponding to the light wavelength through interference, diffraction, scattering, and other ways to reflect the incident light at a specific wavelength and in a specific direction. Self-assembly of nanoparticles provides effective approaches for the fabrication of functional structural color materials. In Chapter 6 by Zhang and Qi, assembly mechanism and coloring mechanism during constructing functional structural color materials are discussed in detail.

A colloidal photonic crystal sensor is usually implemented with responsive materials or functionalized with recognition elements or created with defects within the colloidal photonic crystal for the detection of target analytes. In Chapter 7, Cai and coworkers highlight the significant progress achieved in the development of a variety of colloidal photonic crystal sensors, such as physical sensors, chemical sensors, and biosensors.

Device applications typically involve patterning. In Chapter 9, Song and Kuang present an overview of the strategies for fabricating patterned colloidal photonic crystals. The applications of patterned colloidal photonic crystal devices are also discussed, showing great potential in the area of display, sensor, and anticounterfeiting.

One of the important properties of photonic crystals is their photonic bandgap, with which photonic crystals can control the flow of light in a manner similar to what semiconductors do in controlling the flow of electrons. Such a property has found wide applications in photon management. In Chapter 10, Wei illustrates how to enhance the light extraction efficiency in GaN-based LEDs by using colloidal photonic crystals and colloidal monolayer-derived nanostructures. While in Chapter 11, Wang demonstrates the latest advancement on the enhancement of power conversion efficiency in dye-sensitized solar cells, perovskite solar cells, and silicon solar cells by integration of colloidal photonic crystals.

In the field of heat management, colloidal ensembles provide a versatile pathway to study thermal transport on a small length scale and reveal the governing structure–property relationships. In Chapter 14, Retsch and coworkers review the recent progress of advanced heat management by using colloidal self-assembly strategies.

Colloidal self-assembly holds a great promise for the creation of functional materials. The past decades have witnessed a number of encouraging advancements in this burgeoning area. A vast toolbox of appropriate colloidal building blocks has been established while more and more new building blocks are emerging and enriching the toolbox. Consequently, abundant functional materials can be accessed once these colloidal building blocks are able to self-assemble via a proper strategy. While the present book cannot provide a comprehensive collection of the current state-of-the-art colloidal self-assembly for functional materials, we do expect that

the chapters included in this book cover the most exciting developments in this prosperous field.

We would like to express our deep appreciations to all the contributing authors. Without their contributions and strong supports to this endeavor, it would not be possible to reach to the moment of having this book published, especially during this unprecedented challenging time due to the COVID-19.

October, 2021

Qingfeng Yan
George Zhao

1

Colloidal Molecules and Colloidal Polymers

Etienne Duguet¹, Etienne Ducrot², and Serge Ravaine²

¹Université de Bordeaux, Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB, UMR 5026), CNRS, Bordeaux INP, 87 avenue du Dr Albert Schweitzer, Pessac, 33600, France

²Université de Bordeaux, Centre de Recherche Paul Pascal (CRPP, UMR 5031), CNRS, 115 avenue du Dr Albert Schweitzer, Pessac, 33600, France

1.1 Introduction

The self-assembly of colloidal objects, inspired by self-organization phenomena observed in nature, is a relevant alternative to chemical synthesis route and top-down fabrication techniques for building increasingly complex structures and materials. It is also an effective tool to understand physicochemical processes that drive self-assembly phenomena as colloidal units are typically three orders of magnitude larger than atoms and molecules and thus can be tracked by optical microscopy techniques [1, 2]. For instance, isotropic spherical particles, often called colloidal atoms (CAs), helped to clarify crystallization and phase transition mechanisms and were observed as they assembled in different phases such as gels, glasses, and several crystal phases [3, 4]. It was shown that interactions between CAs can be tuned by varying the composition of the solvent, by applying external fields and/or concentration gradients, and by modulating the surface chemistry of the particles [5]. Driven by the desire to elaborate colloidal materials possessing new, interesting properties, the field of colloidal self-assembly has made a leap over in the last decades by synthesizing monodisperse particles of various shapes and sizes and by focusing on their assembly through a wide range of interactions [6–8]. In particular, nonspherical colloids stemming from the aggregation of a small number of particles, named “colloidal molecules” (CMs) by van Blaaderen [9], have attracted a lot of attentions these recent years because they are expected to show complex behavior (like low-molecular-weight compounds) dictated not only by the shape of the clusters but also by the variety of the interactions they could generate [10–13]. We have recently proposed a classification of CMs using and extending the well-known formalism of Gillespie derived from the valence shell electron pair repulsion (VSEPR) model (Figure 1.1) [14], which facilitates the reading of this chapter.

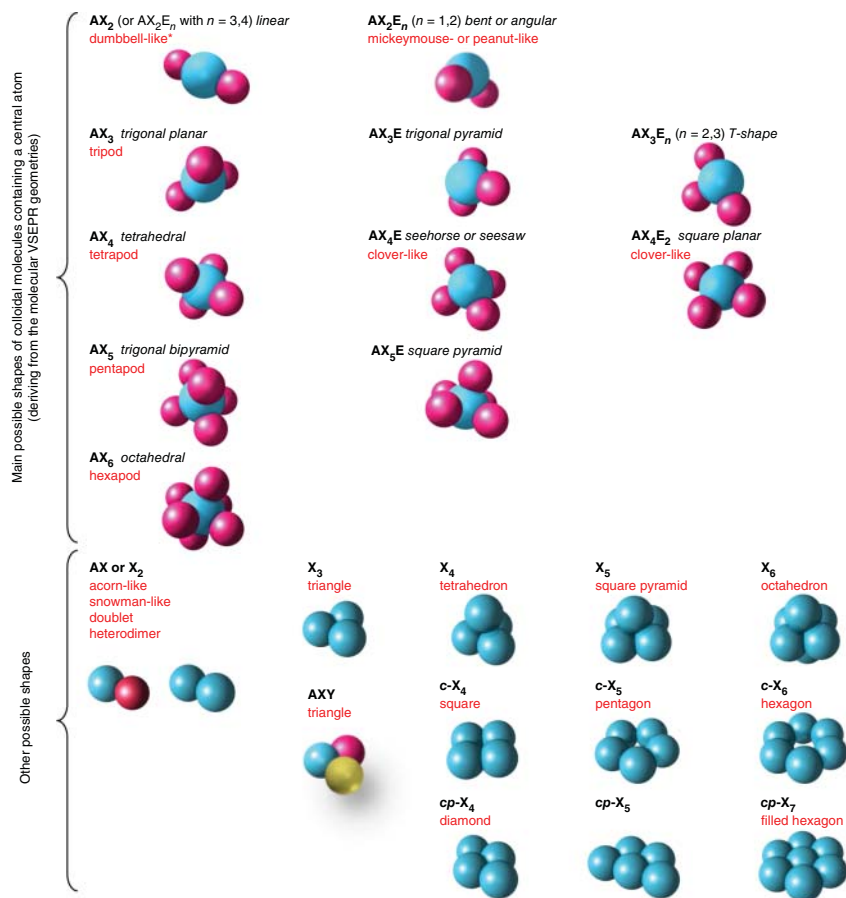


Figure 1.1 Proposition of classification for colloidal molecules based on spheres and mimicking space-filling models of simple molecules. Source: Duguet et al. [14] / with permission from the Royal Society of Chemistry.

The concept of using preformed particles as colloidal monomers has also received recent attention for the formation of one-dimensional (1D) structures, also called “colloidal polymers” (CPs) [15, 16]. A big challenge in the formation of CPs is that it requires strong anisotropic interparticle interactions to minimize side reactions, which is possible to achieve through the development of synthetic methods that allow one to embed anisotropic character to colloidal monomers.

We aim here to highlight and classify the major strategies hitherto reported to fabricate CMs and CPs by self-assembly of preformed particles. We first describe the synthesis pathways to CMs, emphasizing in particular the use of patchy particles as building units. We finally present the different inventive routes that have been developed to create CPs. We restrict the discussion to the synthesis routes and the morphology control, whatever the physical, biological, or chemical properties and potential applications of the CMs and CPs may be.

1.2 Colloidal Molecules: Mimicking Organic and Inorganic Molecules

From the point of view of the synthetic strategy, there exist two main ways to access CMs [14, 17]. The first one concerns essentially AX_nE_m -type CMs and starts from soft or hard preformed CAs decorated by satellite colloids directly generated at their surface, thanks to controlled phase separation or nucleation/growth phenomena, respectively. The second pathway consists in the controlled clustering of preformed CAs through physical routes, chemical routes, or 2D/3D geometrical confinement. The readers who want to embrace the full story have to refer to our previous reviews [14, 17] and/or to read excellent recent reviews written by others and addressing the field from other angles [10–12, 18–25]. In the present chapter, we propose to focus our description of the work in the literature on this second strategy, which relates to the general assembly process.

1.2.1 Clustering of Isotropic Colloids

The following pathways use isotropic spherical CAs, i.e. particles, which surface chemistry and topology are not patterned, meaning they are not spontaneously able to establish interactions in specific directions with other particles.

1.2.1.1 Clustering Assisted by External Fields

These strategies are usually implemented with microparticles on solid surfaces under optical microscope and generate essentially quasi-planar CMs. The strength of the used fields shall also be tuned to overcome the gravity and surface adhesion forces. In this context, Wu and coworkers have reported that applying external alternating current (AC) electric fields is an efficient and simple way to generate anisotropic dipolar and dielectrophoretic interactions between negatively charged polystyrene (PS) microparticles [26]. The morphology of the as-obtained CMs may be quite complex and varied by changing the field frequency via different assembly pathways that resemble chemical reactions of real molecules. Grzybowski and colleagues have shown that magnetic field microgradients established in a paramagnetic fluid can be used as virtual molds to serve as templates for the production of a variety of CMs, including A_4 , A_5 , A_6 , AX_2 , AX_3 , and AX_4 types (Figure 1.2) [27]. The assembly of CAs into CMs has also been driven by a magneto-acoustic method by Yellen and coworkers. The CM morphology can be tuned by varying the magnetic and acoustic fields that allow to control the interparticle interactions and the local density of particles by attracting them to the pressure nodes of the standing wave, respectively [28]. Although attractive for their ease of use and high morphology yield, these synthesis routes assisted by external fields suffer from very low production yield and sometimes from lacking fixation strategy for making the CM structure permanent (after suppression of the fields). However Grzybowski and colleagues have shown that this last issue may be solved by attaching the CMs to the substrate with carbamide bonds, making them permanent by silica deposition before their release into a liquid by sonication [27].

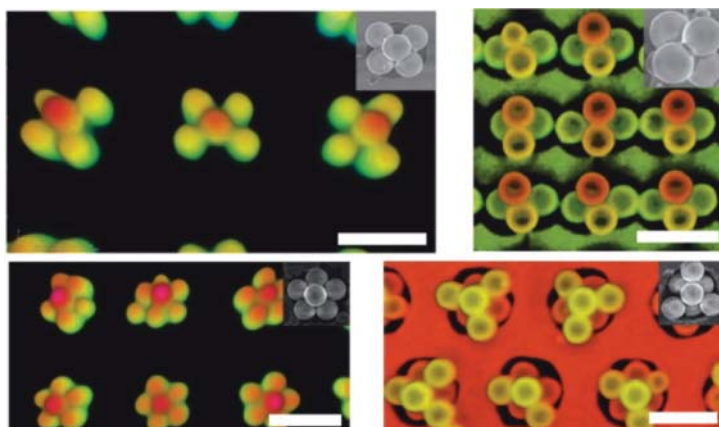


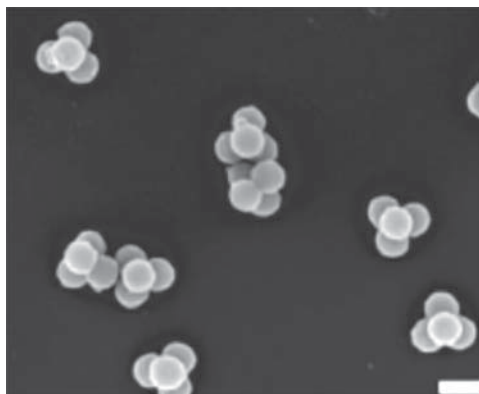
Figure 1.2 CMs of diamagnetic particles with X_4 , X_5 , X_6 , and X_7 geometries obtained under magnetic field microgradients established in a paramagnetic fluid. Scale bars: 2 μm . Source: Demirörs et al. [27] / with permission of Springer Nature.

1.2.1.2 Clustering Assisted by Geometrical Confinement

The patterning of 2D substrates with hydrophilic patches [29] or traps [30] allows the controlled sequential deposition of microparticles, resulting in the creation of a wide library of CMs, including 3D chiral objects. Nevertheless, the production yields remain low. Another strategy consists in the adsorption of particles onto emulsion droplets used as 3D templates, i.e. taking advantage of the Pickering effect, followed by their aggregation through the droplet phase evaporation. This is the pioneering pathway opened by Manoharan and colleagues [31] which has inspired van Blaaderen to develop the concept of CMs [9]. When during evaporation the CAs touch another on the surface of the droplets, removing more liquid causes the droplet to deform and generates capillary forces that collapse the CAs into a CM [31]. The structures of these CMs include familiar polyhedra, e.g. X_4 and X_6 , and ones that are more unusual. The selection of a unique packing arises almost entirely from geometrical constraints [32]. Nevertheless, the size polydispersity of the initial emulsion droplet leads to complex mixtures of different CMs that can be finally sorted by density gradient centrifugation. Using narrow droplet size distribution through ultrasonication, Witteman and coworkers have obtained similar CMs from 150-nm particles (Figure 1.3) [33]. Later, Monte Carlo simulations have allowed a full description of the dynamics correlated to experiments [34]. Crassous and colleagues have recently investigated again this route with thermosensitive particles, e.g. poly(*N*-isopropylacrylamide) (PNIPAM) microgels, and achieved CMs with externally tunable interaction sites by playing with temperature or ionic strength [35].

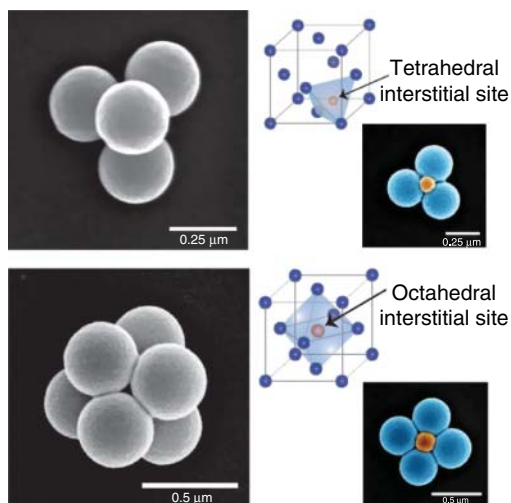
Another method of interest for the preparation of CMs is the crystal templating strategy, which relies on the use of binary colloidal crystals (CCs) as templates and leads exclusively to AX_{12} CMs. Zhang and coworkers have applied this strategy to soft PNIPAM microgel submicron CAs [36]. In *fcc*- or *hcp*-like CCs prepared by sedimentation from a 40 : 1 mixture of PNIPAM microspheres with surface thiol groups and surface vinyl groups, the latter are statistically in close contact with 12 CAs bearing

Figure 1.3 FESEM micrograph of tetrahedral CMs. Scale bar: 200 nm. Source: Wagner et al. [33] / with permission of American Chemical Society.



thiol groups. Under UV light irradiation, the thiol–ene reaction allows the covalent binding of the 13 microspheres, which are recovered as independent CMs after the destruction of the CCs. By-products with a higher number of microspheres have been found in the same batch but easily removed by density gradient centrifugation. The same strategy has been extended to AX_4 , AX_5 , and AX_6 CMs using vinyl-PNIPAM microspheres smaller than the thiol-PNIPAM ones in order to accommodate them in the interstitial sites of different close-packed lattices [37]. An enhanced crystal templating method has been investigated by Crocker and colleagues using PS microspheres coated with DNA strands (Figure 1.4) [38, 39]. They have demonstrated that interactions between these colloids can be reprogrammed using enzymes or reinforcing DNA strands to prepare CMs (AX_n with $n = 4, 6, 8, 10, \text{ or } 12$). In the enzymatic approach, two populations of DNA-coated CAs are mixed, with a large excess of the larger ones, and forced into close-packed crystal structures via centrifugation at low ionic strength [38]. At higher ionic strength, sequence-specific enzymatic ligation selectively creates a covalent bond between colloids of different natures. A final

Figure 1.4 SEM images of tetrahedral and octahedral CMs produced using a colloidal crystal as a template (scale bars: 250 nm (top) and 500 nm (bottom)). Source: McGinley et al. [38] / with permission of American Chemical Society.



washing step at low ionic strength destroys the crystals, thereby releasing the covalently bound CMs, which type depends on the size ratio between the two populations of colloids, i.e. the valence of the interstitial site occupied by the minority colloid.

According to a similar clustering strategy in 3D confinement, Tabelaing and coworkers have reported a strategy to obtain CMs (X_n with $n = 3-6$) in microfluidic channels, thanks to the coupling of hydrodynamic dipolar interactions and depletion forces [40].

1.2.1.3 Clustering Assisted by Physical or Chemical Interactions

Clustering into AX_n CMs can also be quite simply achieved, thanks to the single sticky protrusion emerging from the surface of cross-linked polymer CAs when they are swollen with monomer and temperature is raised. In these conditions, the central CA is generated *in situ* and made of the merged protrusions. In this way, Kraft et al. have obtained CMs with AX_2 – AX_9 morphologies from PS nanoparticles previously coated with vinyl acetate by delaying the polymerization of the protrusions for promoting coalescence upon collision before solidification upon polymerization [41, 42]. Interestingly, the swelling liquid can also be an apolar solvent allowing to reconfigure any CM into regular ones through minimization of the interfacial energy, thanks to a diffusion-limited aggregation process. The final morphology can be tuned by varying the surfactant concentration and swelling conditions, i.e. time, solvent nature, and ratio.

Close-packed planar CMs obtained under depletion conditions in a 2D cell have been achieved by Manoharan and coworkers [43]. Using this strategy it was possible to form CMs with AX_2 , AX_3 , AX_4 , and AX_6 morphologies with high yield, simply by choosing the appropriate size ratio between the spherical building units [44]. They have shown that a yield as high as 90% is achievable for the fabrication of AX_4 morphologies in the absence of confinement just by adjusting the size ratio between two size-monodisperse populations of colloids to 2.41. This strategy seems efficient whatever the driving force used for assembly, e.g. DNA hybridization or electrostatic interactions.

Thanks to the pioneering works of Alivisatos', Mirkin's, and Sleiman's groups, DNA hybridization anchored at the surface of CAs provides a flexible tool to control in solution the formation of CMs and in particular from CAs of different sizes or chemical compositions [45–48]. DNA origamis provide a new opportunity for CM design. Gang and coworkers have shown that they can guide directional and specific interactions between isotropic gold nanoparticles to achieve X_6 , planar $c-X_4$, and planar AX_4E_2 CMs in solution [49, 50]. Recently, Fan and coworkers developed a strategy to assemble gold nanoparticles into a large variety of CMs relying on a long single-stranded DNA chain containing polyadenine domains and encoding segments [51]. Once adsorbed at the surface of gold nanoparticles, thanks to the polyadenine domains, the DNA strands guide the assembly of satellite particles by hybridization of the encoding domains. They show fine control of the valence of the CMs as well as the size of each bound particles. Furthermore, chiral CMs have been realized by the introduction of three different DNA strands at chosen vertices of the origami frame combined with the use of three pairs of gold nanoparticles with

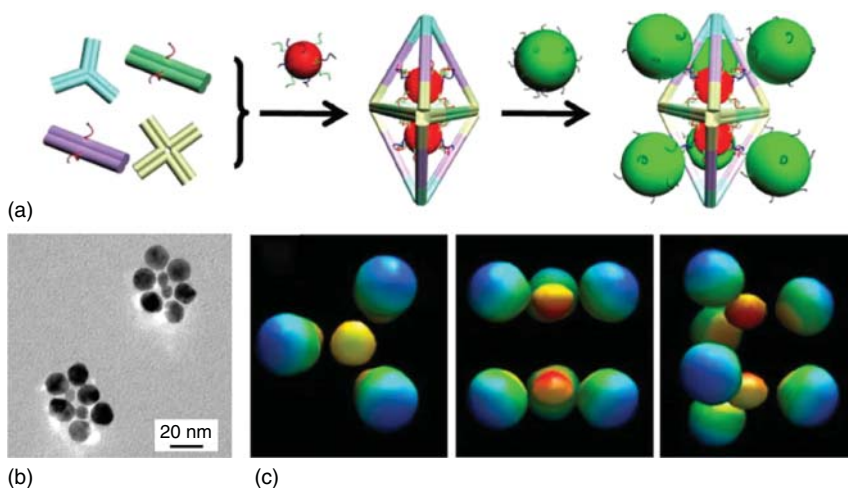


Figure 1.5 DNA frame guided-assembly of ethane-like CMs: (a) schematic representation of the assembly guided by a DNA cage, (b) corresponding TEM image, and (c) different views of the 3D reconstruction obtained by cryo-electron microscopy. Source: Li et al. [52] / with permission of American Chemical Society.

different sizes and complementary DNA shells [49]. Mao and coworkers have used DNA cages, i.e. smaller DNA constructs than origami that consist only of synthetic strands for trapping gold nanoparticles and guiding their assembly into AX_4 CMs with yields as high as 67%. This grants control over the geometry of AX_6 CM between octahedral and trigonal prismatic, as in SF_6 and $W(CH_3)_6$, respectively. Even more complex CMs such as dual-core ethane-like CMs frozen in an eclipsed conformation have been also achieved (Figure 1.5) [52].

To overcome the recurring problem of the too flexible DNA architectures that fail to maintain in the desired geometry the CMs made of bulky and heavy CAs, Chaikin and coworkers have designed a DNA origami belt that binds to the surface of 700-nm CAs and serves as guide for the later assembly of other DNA-coated CAs. This strategy not only yields X_4 -derived chiral CMs but also allows controlling the dihedral angle between the particles (Figure 1.6) [53].

In an opposite approach, it may be relevant to fabricate CMs flexible at a will to mimic, to a certain extent, scissoring, rocking, twisting, or wagging vibrations of conventional molecules. The recent emergence of surface mobile DNA linkers provides new types of AX_n CMs ($n = 2, 3,$ and 4) with flexible joints, where the satellite CAs remain free to move around the central one [54]. These central CAs forming these structures can be silica particles surrounded by a lipid-bilayer membrane into which DNA strands functionalized at their ends by cholesterol or stearyl moieties are anchored. As long as the lipid bilayers remain fluid, the DNA strands are free to move around the particles and so are the joints formed between CAs functionalized with complementary strands. These flexible CMs are physically stable but reorganize in permanence at high speed.

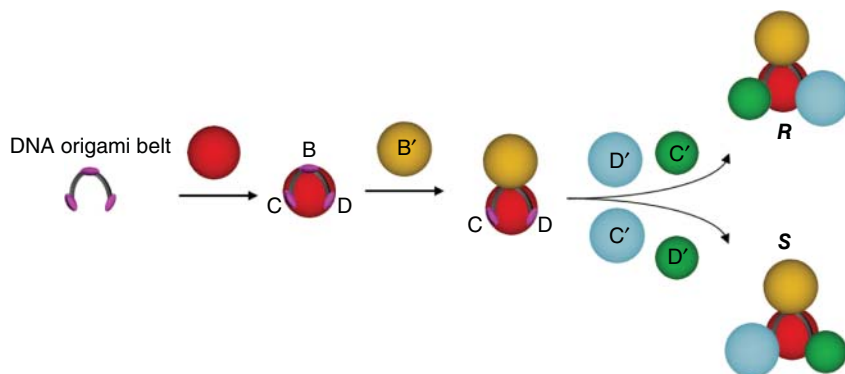


Figure 1.6 Schematic representation of the wrapping of a DNA origami belt around a first CA that guides the assembly of three other CAs into a chiral CM. Source: Modified from Ben Zion et al. [53].

1.2.2 Clustering of Patchy Particles

To mimic molecular geometry as best as possible, it is important to control not only the valence of the CAs but also the bond angles between them. We have shown in the previous section that this control can be exercised in an intrinsic way with more or less success by steric hindrance, electrostatic repulsions, or even the functionality of a DNA belt or origami. An increasingly explored alternative consists in programming this valence and directionality of interactions within CAs just as they are in conventional atoms, thanks to valence electrons. This is the concept of valence-endowed CAs, or patchy particles, where a patch is a surface discontinuity from the viewpoint of the chemistry or topography. They are promising colloidal building blocks not only for engineering CMs but also for open frameworks, if the number, relative location, size, and geometry of the patches can be precisely controlled [55]. The readers interested in a comprehensive description of the variety and synthesis pathways of patchy colloids is invited to refer to several recent reviews [17, 55, 56]. We focus here on their assembly capability to provide CMs. The patch-to-particle size ratio is one of the critical parameters to control the valence; roughly, the larger the patch, the higher the number of establishable bonds, especially as the patch number is low. Thus for getting CMs from patchy particles, there is mainly two routes: some X_n CMs may be more readily achieved from the clustering of one-patch particles, while AX_n ones can be generated from a central CA with the desired valence and the attachment of a single conventional CA to each of its patch.

1.2.2.1 Self-aggregation of One-Patch Particles, i.e. Janus Particles

As a subclass of patchy particles, Janus particles, named after the ancient roman god Janus [57], have extensively served as building blocks for CMs in the last few years, and the field has been recently reviewed [58–60]. Published examples concern Janus particles in the size range of 50-nm to 200- μ m clustering into complex mixtures of CMs with aggregation numbers varying in the 2–20 range (Table 1.1).

Table 1.1 Representative examples of X_n CMs obtained from one-patch particles.

One-patch particles	Assembly driving force	Aggregation number	References
1- μm carboxylate-coated PS spheres then half-coated with gold treated with (11-mercaptoundecyl) ammonium chloride	Electrostatic attraction	2–12	[61]
1- μm carboxylate-modified PS spheres half-coated with gold treated with alkanethiol	Solvophobic effect helped with electrostatic screening	2–9	[62]
1- μm sulfate PS spheres half-coated with gold treated with alkanethiol	Hydrophobic attraction and electrostatic repulsion	2–7	[63]
4- μm snowman-like PS particles with smooth body and rough head	Roughness-controlled depletion attraction	2–12	[64]
2- μm organosilica particles with a partially embedded 1- μm hematite cube	Magnetostatic binding forces	2–3	[65]
3- μm gold half-coated silica spheres	At tipping points of thermally switched wetting	4–~20	[66]
4- μm iron oxide half-coated latex spheres	Lipid-induced capillary bridging	2–5	[67]
120-nm organosilica sphere with one 44-nm gold head	van der Waals force and electrostatic force	2–3	[68]
50-nm silica sphere with one 45-nm gold head coated with alkanethiols	Solvophobic effect	4–7	[69]
1- μm organosilica sphere with a PS patch (patch ratio of 0.13) that is functionalized with DNA having self-complementary sticky ends	DNA-mediated attraction varied by varying the temperature	2–4	[70]

The nature of the driving forces is generally physical, e.g. electrostatic, hydrophobic, or solvophobic interactions, roughness-controlled depletion, capillary bridging, or temperature-mediated DNA hybridization, meaning that bonding is quite weak or easily reversed. Therefore, the as-obtained CMs are fragile, making their purification difficult to impossible to succeed [71]. As far as we know, their strengthening by a chemical or physicochemical process has not yet been reported.

Nevertheless, three studies have been reported about the preparation of robust AX_n CMs. Bon and coworkers have synthesized asymmetric dumbbells made of a PS microsphere and a poly(*n*-butylacrylate) lobe and showed their ability to self-aggregate in aqueous media [72]. The desorption of the poly(vinylpyrrolidone)

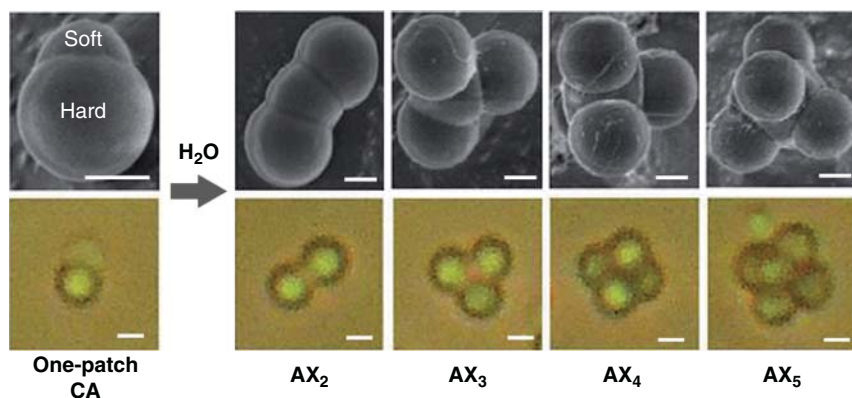


Figure 1.7 High resolution cryo-SEM (top row) and optical (bottom row) images of AX_n CMs in suspension obtained from polystyrene hard microspheres with a soft poly(*n*-butylacrylate) lobe (first column). Scale bars: 1 μm . Source: Skelhon et al. [72] / with permission of Royal Society of Chemistry.

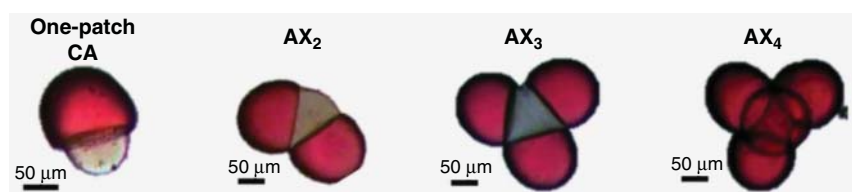


Figure 1.8 Optical microscopy images of CMs obtained from hydrophilic poly(ethylene glycol) diacrylate sphere with ethoxylated trimethylolpropane tri-acrylate lobe. Source: Ge et al. [73] / with permission of Wiley-VCH GmbH.

stabilizer from the particles trigger the assembly process through collision and merging of the soft poly(*n*-butylacrylate) lobes upon contact (Figure 1.7). Xu and colleagues have exploited the drying of aqueous Pickering emulsions made from 200- μm hydrophilic poly(ethylene glycol) diacrylate sphere with 160- μm ethoxylated trimethylolpropane tri-acrylate lobe prepared by microfluidics [73]. They have obtained quite regular CMs with aggregation numbers up to 8 (Figure 1.8). Lastly, we have recently reported the fabrication of CMs from silica/PS asymmetric dumbbell-like nanoparticles (Figure 1.9) [74]. In ethanol/DMF mixtures, the one-patch particles stick together by their PS lobe after swelling/plasticization by DMF. The as-obtained CMs present aggregation numbers from 2 to more than 6.

1.2.2.2 Stoichiometric Attachment of Colloidal Satellites Around Patchy Particles

Surface dimples or cavities on patchy particles are also named entropic patches because they can be exploited to attract and bind spheres with similar curvature radii through depletion forces [75]. Already exploited for the formation of CCs [76], the depletion technique has been extended to fabricate CMs from microparticles