

# Hierarchically Structured Porous Materials

From Nanoscience to Catalysis, Separation, Optics, Energy, and Life Science

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## Part I

### Introduction



# 1

## Insights into Hierarchically Structured Porous Materials: From Nanoscience to Catalysis, Separation, Optics, Energy, and Life Science

Bao-Lian Su, Clément Sanchez, and Xiao-Yu Yang

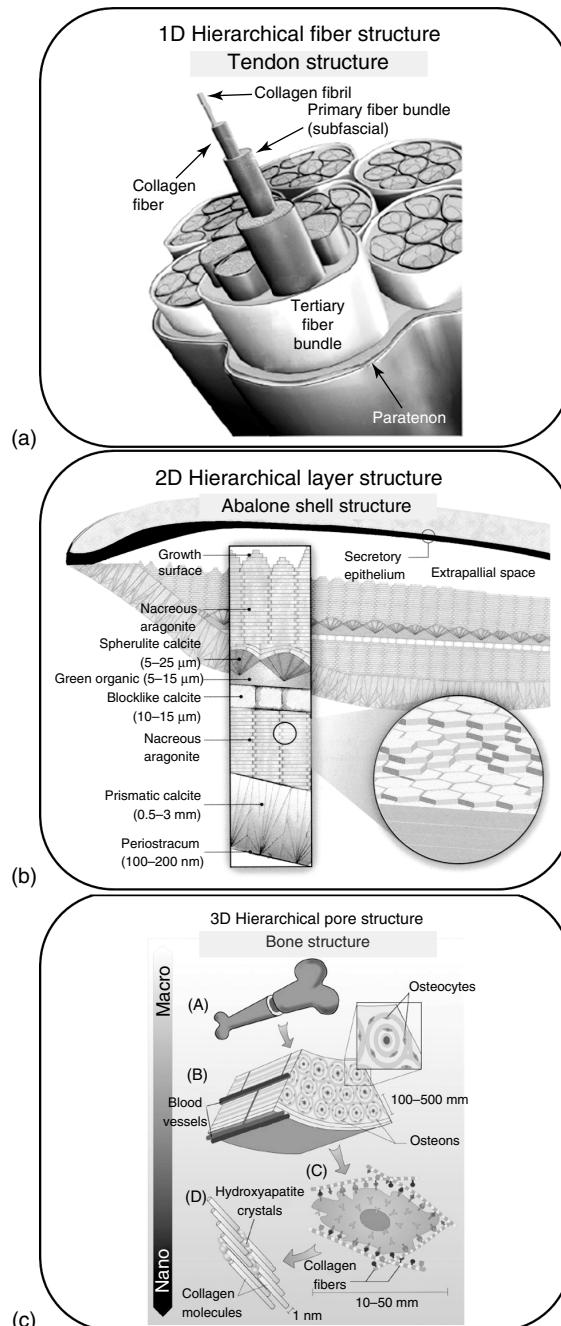
### 1.1 Introduction

Hierarchies are present everywhere in our environment such as in biological systems, from simple unicellular organisms to the more complex human body [1]. Natural hierarchical structures are self-organizations of molecular units or their aggregates that are assembled with other phases, which in turn are self-organized at increasing size levels. Such multilevel architectures, which have been generally divided into three categories (hierarchical 1D fibers, 2D layers, and 3D pores, see Figure 1.1) [2], are capable of conferring unique properties to all levels of the biological structural hierarchy [1].

Natural materials that are regarded as perfect hierarchically structured materials have been found to have growth mechanisms which use only weak interactions and ambient conditions, and thus are increasingly considered as a source of inspiration by a rapidly growing community of materials scientists [3].

“Learning from nature” has therefore been an important guiding principle to creating a new generation of synthetic hierarchical materials. This is a great challenge that can only be met through an understanding of the relationships between the architecture of natural materials and their specific functionalities, spanning not simply their microstructures but also encompassing the influence of structural parameters acting over multiple length scales, from the atomic to the macrolevel, and their interactions. Furthermore, it is essential to develop new fabrication techniques that are able to synthesize such hierarchical structured materials to exploit their intelligent design.

Conversely, although rules learnt from nature about assemblies, architecture, and composite parts can be applied to the design of synthetic hierarchical materials, the natural constituents themselves often have performance deficiencies such as thermal and chemical stability, resistance to environment changes, and very simple chemical compositions limiting their applications (Table 1.1) [1, 3]. These drawbacks are subject to remediation and should be taken into account when designing synthetic materials.



**Figure 1.1** The classification of natural hierarchical structured materials: hierarchical 1D fiber (tendon structure [2a]), 2D layer (abalone shell structure [2b]), and 3D pore (bone structure [2c]) structure.

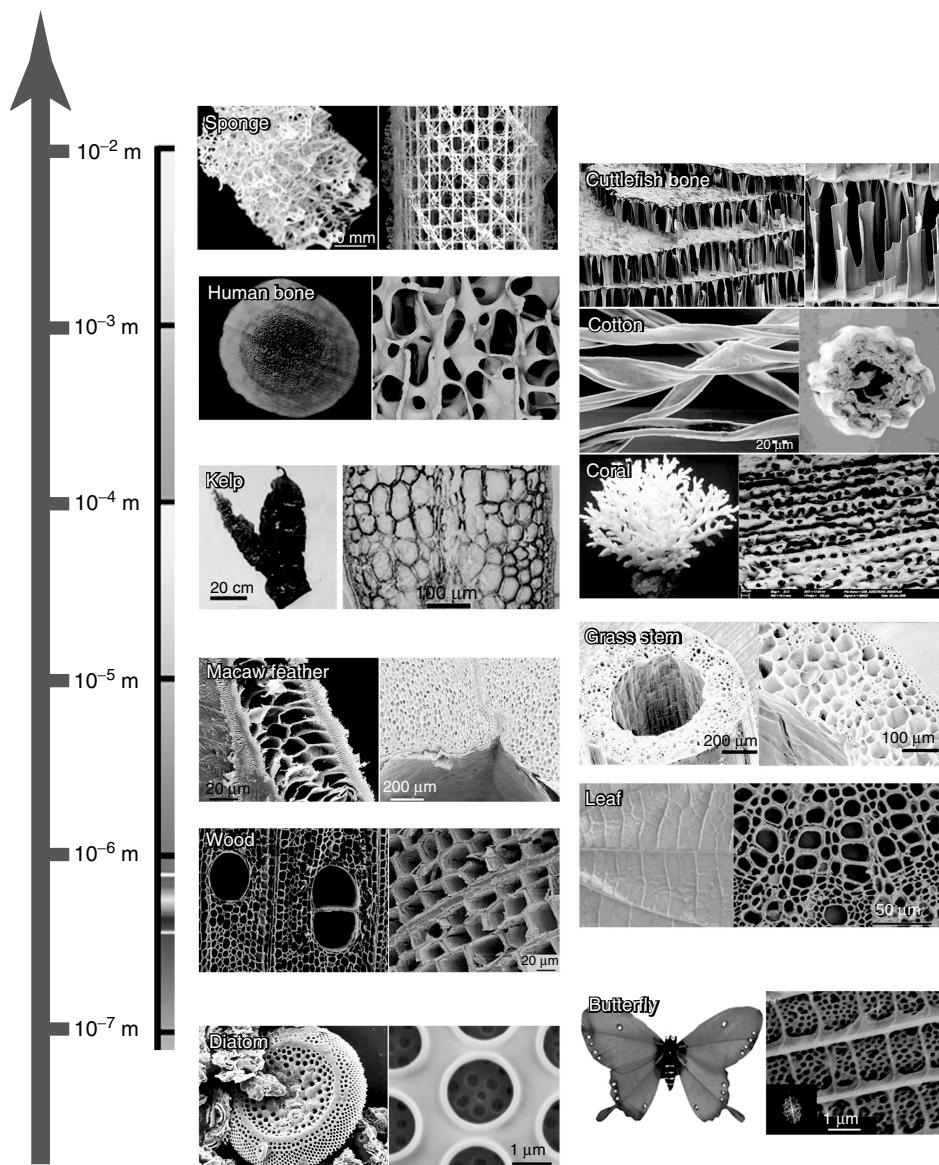
**Table 1.1** The contrasts of properties between natural hierarchical materials and synthetic hierarchical materials in composition, process, structure, length, morphology, function, lifetime, stability, and environment.

	<b>Natural hierarchical materials</b>	<b>Synthetic hierarchical materials</b>
<i>Textural property</i>		
Composition	Light elements dominate: C, H, O, N, S, P, Ca, Si, and so on.	Large variety of elements: C, H, O, N, S, P, Ca, Si, Ti, Zr, Al, Fe, Co, Ni, Cu, Zn, Y, Nb, and so on.
Process	Controlled self-assembly.	Templating synthesis or spontaneous synthesis.
Structure	Very precise and complex.	Relatively simple.
Length	Molecule, nano-, microlevels.	Molecule, nano-, microlevels.
Morphology	Some examples of self-changing according to the change of the environment.	Controlled size and shape.
<i>Functional property</i>		
Function	Specific functionality.	Multiple functionalities design.
Lifetime	Self-healing or self-repairing.	Few examples to self-repairing.
Stability	Very narrow temperature range and pH values range	Thermal and chemical stability.
Influence of environment	Natural condition (suited temperature, moisture, pressure, etc.)	Wide condition range.

Over the last decade, significant interest has been devoted to the synthesis and applications of hierarchically structured porous materials [4–205], which are defined as materials that contain a porous structure consisting of interconnected pores on different length scales from micro- (<2 nm), meso- (2–50 nm) to macropores (>50 nm). Whereas micro- and mesopores provide the size and shape selectivity for guest molecules, enhancing the host–guest interactions, the presence of macropores can considerably favor the diffusion to and the accessibility of the active sites by guest molecules. This is particularly important for the diffusion of large molecules or in viscous systems. These motivations spark the proliferation of hierarchically structured porous materials.

As a step toward a better understanding of the relation between functions and structures in the design of man-made technological materials which not only mimic functions of natural materials but also have new properties, a series of natural hierarchically structured porous materials, for instance, diatoms, butterflies, wood, leaves, macaw feathers, grass stems, kelp, coral, cotton, human bone, cuttlefish bone, and sponge (Figure 1.2), were studied and utilized as biotemplates in the design of new morph-genetic functional materials.

The imperative to develop new approaches in the fabrication of bi-, or even tri-modal porous structures has pushed this research field to the forefront. Many



**Figure 1.2** Overview of natural hierarchical structured porous materials, placed alongside the length scale according to their critical dimensions. The SEM or OM images of original biological hierarchically structured porous

structures are shown from bottom to up: diatom, butterfly, wood, leaf, macaw feather, grass stem, kelp, coral, cotton, human bone, cuttlefish bone, and sponge.

successful dual exotemplating methods have been developed to prepare these kinds of materials. Using a colloidal crystal as a template offers an efficient way to construct an ordered and interconnected meso-macroporous structure [4, 5]. An emulsion-templating strategy, with uniformly dispersed oil droplets and surfactants, has been used to realize hierarchically porous transition metal oxide materials [6–12]. Additional templates such as salts [13], ice crystals [14], gas bubbles [15–18], supramolecular aggregates [19–24], and biomaterials [25–40] as well as alterations to the chemical and physical parameters of a method, for example, the control of procedural (synthesis and aging) conditions [41–47], phase separation [48–58], templating replication [59–68] and posttreatment [69–104] have also successfully been employed. All these methods can be classified into two main approaches: (i) The introduction of macrotemplates into the reaction media, together with traditional small-scale templates or (ii) The modification of the chemical and physical parameters of a method. Subsequently, an innovative self-formation procedure has been developed and used to synthesize hierarchically porous materials [105–138]. These structures are made of parallel macropores with micro/mesoporous structured walls. There is a high degree of control over the structural and textural properties of such materials. A summary of the preparation strategies with the corresponding porous structures and material compositions is given in Table 1.2.

The applications of hierarchically structured porous materials emerge, owing to the presence of macro/meso structured porous system. All these emerging application are summarized in Table 1.3 [149–189]. Hierarchically structured porous materials are quite desirable for catalysis and separation processes [149–162]. The importance of macrochannels in macro/mesoporous  $\text{TiO}_2$  photocatalyst to act as light harvester has been well evidenced [172]. Their application in optics has shown the power to incorporate the hierarchy concept into known smart materials to achieve better functionalities such as lasing, waveguides, sensors, and other devices [158–162]. Hierarchically structured porous materials have been largely used for Li ion batteries [177] and supercapacitors [178] to improve the rate performance and charge-transfer rate in energy storage.

Owing to the light harvester properties of macrochannels in meso/macroporous materials, they are often used as electrodes in Dye Sensitized Solar Cells (DSSCs) [173, 174] and photochemical  $\text{H}_2$  production [171]. The photochemical bioreactor “Leaf like materials” inspired from plant leaves and designed on the basis of immobilization of biological species into hierarchically structured porous and transparent  $\text{SiO}_2$  hold bright future for sunlight conversion to chemical energy via photosynthesis [175]. The applications in drug delivery, biomedicine, and life science allow to open a new area to health care and implantable orgasms [186–196].

This chapter introduces this book with contributions from a series of internationally renowned experts in the field. This book contains 22 chapters divided into four parts: introduction; synthesis strategies; and applications in various emerging fields such as catalysis, separation processes, optics, energy, biomedicine and life science, and concluding remarks. Our attempt is to make each contribution complete in itself.

**Table 1.2** Methods employed for the synthesis of different hierarchically structured porous materials.

Method	Porous structure	Composition
Dually micellar [19–24]	Micro-meso; small meso-large meso	Aluminosilicate; oxides
Colloidal crystals [4, 5, 174]	Micro-macro; Meso-macro; small meso-large meso-macro	Polymer; aluminosilicate; oxides
Small nanoparticles (salt and ice, etc.) [13, 14]	Meso-macro	Aluminosilicate; oxides
Macroporous polymers [190–204]	Meso-macro	Oxides
Bio-inspired materials [25–40]	Meso-macro	Oxides
Small liquid drops (emulsion) [6–12] and gas bubbles [15–18]	Meso-macro	Oxides
Control of sol–gel processes [41–47]	Micro-meso; Meso-macro	Aluminosilicate; oxides
Phase separation [48–58]	Meso-macro	Oxides
Template replication [59–68]	Meso-macro	Carbon
Posttreatment and core–shell methodology [69–104]	Micro-meso; meso-macro; small meso-large meso micro@meso; meso@micro; micro@hollow; meso@hollow; micro@amorphous; meso@amorphous	Polymer; aluminosilicate; carbon; oxides, metal
Selective leaching [205]	Meso-macro	Oxides; metal
Template-free or spontaneous process [105–138]	Micro-macro; meso-macro; micro-meso-macro; meso@micro	Aluminosilicate; carbon; oxides

In Chapter 2, as part of the introduction, Fratzl and Giraud Guille nicely introduce the concept of “Hierarchy in Natural Materials.” They showed how natural materials achieve a large variety of functions by self-hierarchical structuring of their systems, highlighting the importance of studying each structural level of natural materials. This chapter shows that natural materials are increasingly considered as a source of inspiration [139–148].

## 1.2

### Synthesis Strategies to Hierarchically Structured Porous Materials

The synthesis of hierarchically structured porous materials has been described in Chapters 3–15 by different leading experts and the key factors have now been identified. Different strategies have been established such as soft templates, hard templates (including biotemplates) (Chapters 3–7), control of sol–gel processes,

**Table 1.3** Applications of hierarchically structured porous materials in catalysis, separation, optics, energy, and life science.

Applications	Types	Features
Catalysis	Acid catalyst [149–154] Oxidation catalyst [155–157]	(i) High accessibility of bulky molecules; (ii) high diffusion rate of reactant and product; and (iii) usually heteroatoms of zeolites or supported nanometal particles as active sites.
Separation	Preconcentration device [158, 159] Bioreactors and DNA purifier [160] Therapeutic apheresis device [161, 162]	(i) High permeability; (ii) homogeneous flow-through pore structure; (iii) controlled pore structures and surface properties; and (iv) usually particle-packed and monolithic column used.
Optics	Lasing [163] Sensor [164] Waveguide [165] Structural color and display device [166–169]	(i) Highly ordered and 3D structure; (ii) enhancement of spontaneous emission; (iii) no light energy loss in some examples; and (iv) controlled artificial defects.
Energy	Sunlight conversion [170–175] (including dye-sensitized solar cell [171, 173, 174] and photochemical bioreactors [175]) Fuel cell [176] Li battery [177] Supercapacitor [178]	(i) Efficient light-harvesting, especially in biomaterials replica or biocomposites examples; (ii) fast charge separation and high current density; (iii) high gas permeability; (iv) high storage density; (v) fast electron and ion transport; and (vi) small resistance.
Life science	Bioceramics [179, 180] Life engineering [181–185] Drug delivery [186–189]	(i) Biocompatibility and promoting cell adhesion and activity; (ii) good mechanical properties; (iii) controlled shape; and (iv) clinical use.

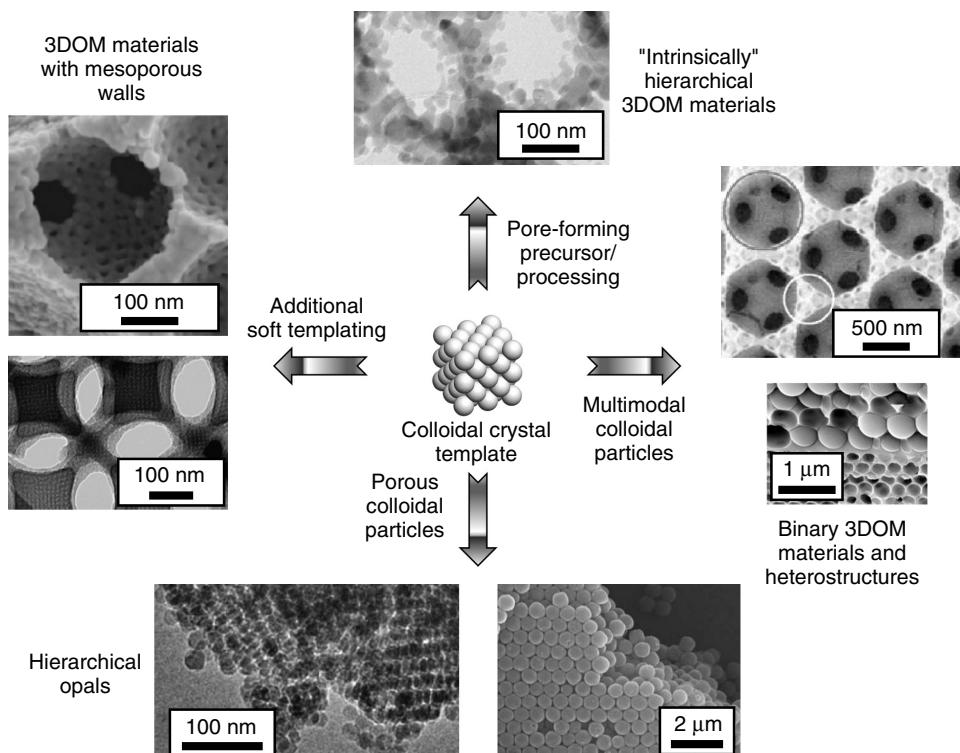
phase separation, and chemical leaching or etching (Chapters 8 and 9). This synopsis reveals that an ingenious combination of simple factors can offer great opportunities to create new families of hierarchically porous materials.

In Chapter 3, Sel and Smarsly describe a co-micellar templating approach. Two levels of porosity have been created by using two length-scaled templates. The self-assembled molecular aggregates or supramolecular assemblies can be used as the structure-directing agents in the elaboration of mesostructures. Meanwhile, larger templates, such as polystyrene spheres, are added during synthesis to create macroporosity within the forming material.

Chapter 4 presents nicely by Petkovich and Stein the colloidal crystal templating strategy that provides unique opportunities for generating well-ordered, periodic

pore structures at the macropore range ( $>50$  nm), the larger mesopore range ( $>$  circa 10 nm), or even on both ranges simultaneously. This method can also be readily combined with other templating methods, both hard and soft, to generate additional levels of porosity (Figure 1.3). Because both colloidal crystals and their inverse structures can be synthesized with additional porosity, these materials offer a pathway to hierarchical materials with a myriad of morphologies and compositions.

Chee Kimling and Caruso (Chapter 5) produced a range of morphologies of hierarchically porous materials with natural and synthetic polymers that contain macropores ( $>50$  nm). The macroporous polymer plays the role of a scaffold around which, or within which, chemical reactions can take place or nanoparticles can infiltrate, thereby guiding the morphology of the materials so that on removal of the polymer the material bears some structural properties reminiscent of the original template. The benefits of using macroporous polymers as templates include the stability, removability, and structural variability of the polymer. The mechanical and chemical stability of the polymer during the templating process are crucial to maintain structural integrity, while the ease of removal of the polymer, either via



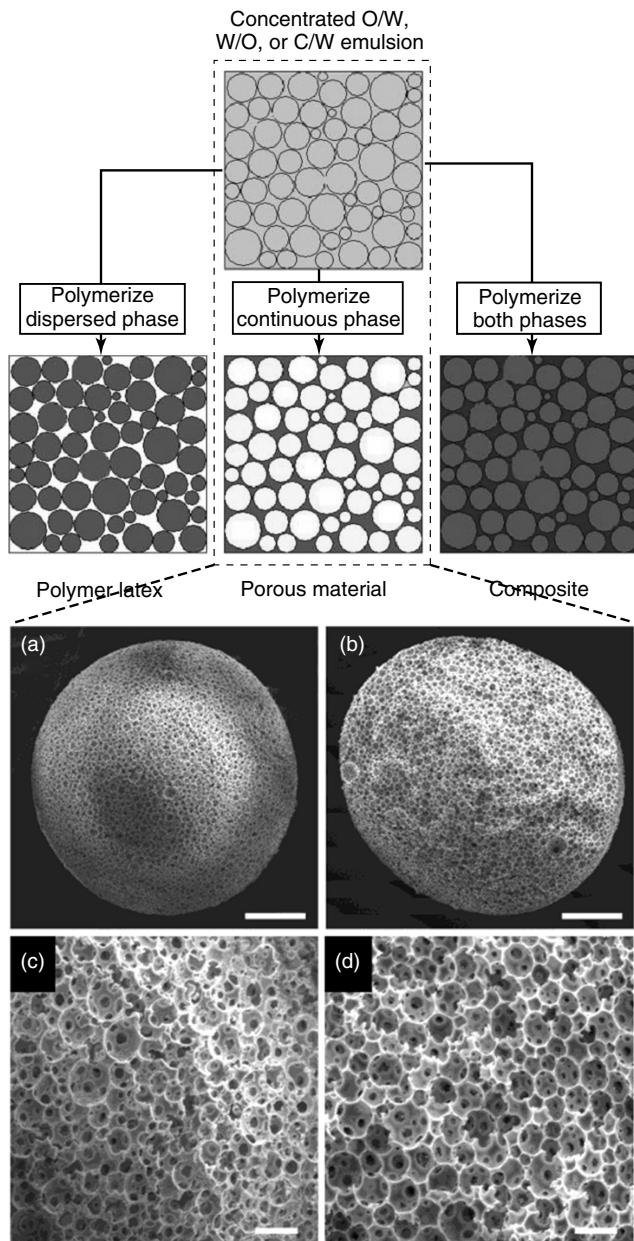
**Figure 1.3** Scheme that shows the four major routes to hierarchical porous structures through colloidal crystal systems.

pyrolysis or solvation, allows the final material to be produced. Significantly, the wide range of shapes, sizes, and porous structures in the macroporous polymers give the ability to tailor the morphological characteristics of the final material, for example, monolithic foam, fiber, and sphere structures.

Biological materials have evolved their intriguing structures over the course of a very long evolutionary process. The biotemplating approach presented by Ma and Yuan in Chapter 6 to prepare advanced materials is therefore one of the most promising scientific and technological challenges of the coming years. A great number of natural products such as plant leaves, butterfly wings, wood, and diatoms could be utilized as direct biotemplates and plenty of formation processes of the biological architectures could be simulated under experimental conditions to obtain hierarchical porous materials. The obtained materials are thermally stable, and have good mechanical and hydrothermal stability, which would meet the practical applications imposed in catalysis, adsorption, and separation. The advantages of low cost, a wide range of sources, and environmental friendliness make these strategies potentially applicable to many areas, and most practical for industrial production. The applications of biotemplated materials in energy conversion and storage are very hot field which will be commented in Chapter 19.

Emulsions are heterogeneous mixtures of one phase, in the form of droplets, suspended in another immiscible continuous phase, such as the dispersion of water droplets in an oil phase (so-called water-in-oil (W/O) emulsions) or dispersion of oil droplets in water (so-called oil-in-water (O/W) emulsions). Following above templating strategies, Zhang in Chapter 7 presents how to use emulsions, with small liquid droplets suspended in a continuous phase, to form hierarchically structured porous materials by solidifying the continuous phase around the liquid droplets followed by their subsequent removal. While microemulsions can be used to produce mesoporous porous materials, emulsion-templating methods are generally utilized to obtain macroporous materials with high internal phase emulsions (HIPEs) for highly interconnected porous materials (Figure 1.4). The advantages associated with using liquid droplets as templates have been commented.

Hierarchically structured porous monoliths prepared by phase separation are reviewed by Nakanishi in Chapter 8. The method of phase separation has been developed to enable the fabrication of hierarchically structured, high silica content, porous glasses. The incorporation of a water-soluble polymer into the alkoxysilane-based sol–gel process made it possible to fabricate pure silica gels having well-defined interconnected macropores in the micrometer range. The final morphology of the spinodally decomposed phase domains is strongly governed by the reaction dynamics, which, in turn, is driven by the interfacial energy. This method has been gradually extended, using various kinds of water-soluble polymers, surfactants, or other additives, to siloxane-based organic–inorganic hybrids and metal oxides such as titania, zirconia, and alumina. Even fully organic networks such as cross-linked polystyrenes and polyacrylates could be fabricated into well-defined macroporous monoliths based on the same phase separation method.



**Figure 1.4** Schematic representation of polymerization of an emulsion in the dispersed phase, continuous phase, and both phases for the preparation of colloids, porous materials, and composites, respectively [10a]. SEM images showing the emulsion-templated bead. (a) Bead surface. (b) Sectioned "half-bead" showing internal pore structure. (c) Porous surface at a higher magnification. (d) Internal porous structure at a higher magnification. Scale bars: 500  $\mu\text{m}$  for (a) and (b) and 100  $\mu\text{m}$  for (c) and (d) [10b].

In Chapter 9, Tian *et al.* established a leaching concept to design hierarchically structured porous materials. In fact, in the synthesis of macroporous structures, a template that is easily leached after material formation (so-called organic template-free) offers great opportunities for the design of advanced materials with a green process. Examples include gas expulsion, salt templating, ice templating, and selective leaching. These methods not only produced high-quality hierarchically porous materials with uniform structuration but also resulted in the extension of the hierarchically porous structure (long-range order). As the first example, Tian presented ice-templating method. This simple technique has been used to produce porous, complex-shaped polymeric, or ceramic materials. The desired porous microstructure is generated during freezing. There are other easy-leaching concepts than can be employed to target hierarchical materials using inorganic salts, dilute electrolytes, gas templating, chemical etching and sublimation, and so on.

The “Integrative Chemistry” concept, which crosses the boundaries of physical chemistry, colloid chemistry, polymer science, sol–gel technology, biology, and beyond demonstrated its influence in the development of new synthesis strategies. For the majority of these man-made synthesis methods, both the macroporosity and the mesoporosity can be easily and independently adjusted. Deleuze and Backov in Chapter 10 illustrate how to use the “Integrative Chemistry” to design emulsion-based porous materials though W/O HIPEs, O/W HIPEs, and Pickering-based macrocellular foams. In each of the above-mentioned foam families, they proposed a declination between the organic, inorganic, or hybrid organic foams’ chemical nature.

The Chapter 11 of Boissiere *et al.* deals with how to control hybrid organic–inorganic interfaces for the construction of materials with complex hierarchical structures such as coatings and membranes. Different strategies are presented. First, the multiple templating strategy including hierarchical inorganic nanopatterning, ionic liquid (IL)/block copolymer soft–soft templating, polymer/block copolymer soft–soft templating, block copolymer/latex beads soft–hard templating have been addressed. Second, dynamic templating including controlled phase separation and breath figures as smart templates has been reviewed.

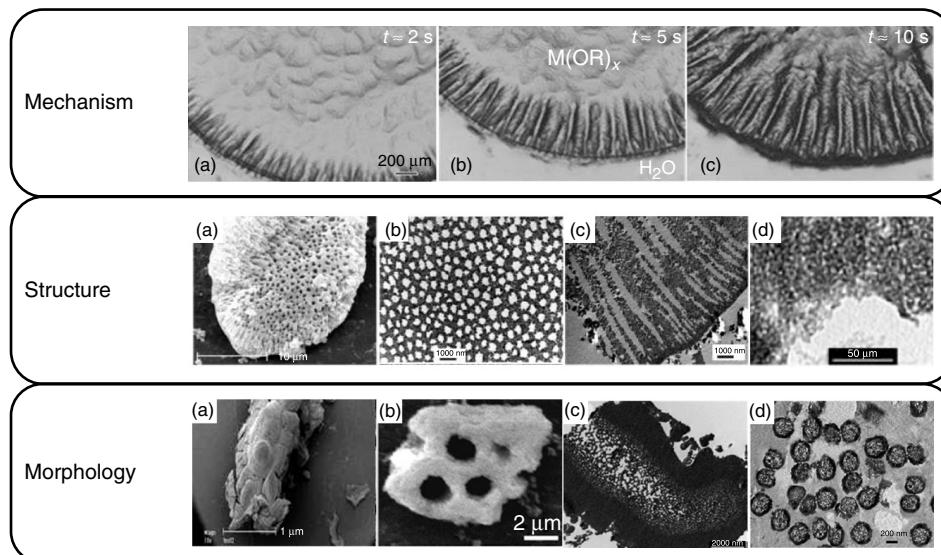
Hierarchical TiO<sub>2</sub> nanopatterns using a block copolymer template with a dip-coating process and soft inorganic chemistry have been prepared. The bimodal characteristic of the obtained perforated titania layer prepared by chemical liquid deposition is associated to the preparation of solutions that contain titania inorganic precursors and two distinct populations of micelles PB-*b*-PEO (with the same chemical nature but different sizes) and do not mix or aggregate. IL/block copolymer soft–soft templates have been used to prepare hierarchical thin films by evaporation-induced self-assembly of a solution-containing inorganic precursors, some PEO-(hydrogenated-PB) block copolymers with a high hydrophobic–hydrophilic contrast (called *KLE*), and a second, noninterfering structuring agent.

The removal of templates is a labor intensive and environmentally unfriendly step, rendering scaling-up very difficult. The synthesis of nanomaterials without any external template is a great challenge since man-made materials are usually

fabricated using processes not available in the natural world. An innovative synthesis strategy: the self-formation phenomenon of generating a porous hierarchy without the use of external templates, based solely on the chemistry of metal alkoxides and metalalkyls, has been presented in Chapters 12 and 13.

In Chapter 12, Yang *et al.* established an innovative self-formation procedure to synthesize hierarchically porous materials. These hierarchically structured meso-macroporous materials with single ( $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Nb}_2\text{O}_5$ , etc.) and multiple (mixed oxides, phosphates, and aluminosilicates) chemical compositions, possessing different morphologies such as monolithic particles, microtubular particles, core–shell structural particles, and smooth surfaces, and with unique hierarchically porous structures (well-ordered tubular or funnel-like macrochannels with mesoporous walls) have been targeted via a “one-pot” self-formation process, which is a technique based on the chemistry of metal alkoxides and alkylmetals (see Figure 1.5).

The key features in the synthesis of these materials are as follows: (i) unique porous structure (unique morphologies in which parallel macropores with micro/mesoporous networks established in the macropore walls are found throughout



**Figure 1.5** (Mechanism column) Optical microscopy images showing the growth of porosity and formation of a macrochannel pattern [135a]. (Structure column) (a) SEM image of meso-macroporous  $\text{ZrO}_2$ , and (b–d) TEM images of meso-macroporous  $\text{ZrO}_2$  [105]. (Morphology column) (a) SEM image of the meso-macroporous products controlled polymerization of a  $\text{Zr}(\text{OC}_3\text{H}_7)_4$  drop

[130], (b) typical SEM image viewed along the direction of the resultant microtubular zirconias [120], (c) low-magnification TEM image of an ultrathin section of CMI-Ti-80 [109], and (d) TEM images of as-synthesized bimodal nanoporous aluminosilicates with a hierarchically macroporous core inside an ordered mesoporous shell [137].

the particle); (ii) very simple molecular precursors (metal alkoxides and alkylmetals with or without co-reactant depending on the desired chemical compositions); (iii) pure composition; (iv) a wide range of very mild synthesis conditions (an aqueous acidic solution using different inorganic acids or in an alkaline solution using different bases, or in pure water as well as in the presence or absence of a surfactant or a cosolvent. The reaction is generally carried out at room temperature in an open system); (v) high reaction rate (the key to the formation of macropores); and (vi) up scalable process (a great benefit of this preparation method is its simplicity).

Following the precedent chapter, Lemaire and Su in Chapter 13 present new development in the field of self-formation procedure: Single-molecular alkoxy-precursor (SMAP) strategy. Hierarchically structured meso-macroporous aluminosilicates containing a higher level of tetrahedral aluminum were successfully developed via the controlled aqueous template-free polymerization of a SMAP  $(sec\text{-OBu})_2\text{-Al-O-Si-(OEt)}_3$ . This single-source possesses an intrinsic Al–O–Si linkage, which permits the formation of unrivaled chemically homogeneous aluminosilicate materials. To avoid rupturing this Al–O–Si linkage, which can occur in aqueous media, additional strategies such as high alkaline solutions, carboxylate chelating agents, and silica co-reactants were employed. The concept of the single-source precursor, in combination with additional strategies, is a promising synthetic route, which is able to facilely provide new and varied macroporous morphologies in functional materials in comparison with sophisticated templated methods.

Hierarchically porous zeolites have recently attracted much attention owing to the great potential of these kinds of materials to improve the sustainability of chemical processes. Two chapters will outline a series of innovative synthesis strategies in the preparation of mesoporous zeolites (Chapter 14) and micro-macroporous zeolites (Chapter 15).

Xiao presents in his Chapter 14 the successful synthesis of a series of disordered mesoporous zeolites with very thick walls by using solid templates such as nanostructured carbons and soft templates such as cationic polymers and organosilane surfactants. He then turns to comment the use of soft-templating method. Compared with solid templates, the use of soft templates for synthesizing mesoporous zeolites is simple because the soft templates are easy to self-assemble with silica-based species in the synthesis of zeolites; the pretreatment of mesoscale templates is not necessary. The key factor for the formation of mesoporous zeolites is an interaction between the mesoscale organic templates with silica-based species during the crystallization of zeolites. A successful example is lamellar single-unit-cell nanosheets of MFI zeolite.

Hierarchical micro-macroporous zeolite material is another popular bimodal porous material and is the focus of the Chapter 15 written by a joint effort from Tang's and Su's groups. A microporous structure generally provides active reaction centers and increases selectivity owing to space constraints, while a macroporous structure provides a fast pathway for mass transportation and molecule diffusion, which is believed to greatly improve the catalytic performance by increasing the reaction activity, selectivity, lifetime, and coke resistance in comparison to

conventional microporous catalysts. Hollow zeolitic structure is one of the most typical micro/macro bimodal porous materials. Microspheres are first used as sacrificial templates for the formation of the micro/macroporous hollow structure. A secondary hydrothermal treatment in a suitable gel or clear solution could improve the mechanical stability of the Layer by Layer (LBL) hollow nanozeolite spheres obtained after the removal of the spherical hard template core.

Microporous materials prepared within macroporous monoliths have also been an area of research that has commanded much interest in recent years. Various macroporous supports were used to prepare self-supporting micro-macroporous hierarchical materials: (i) using only a robust support, (ii) partial zeolitization, and (iii) complete zeolitization during the formation of micro-macroporous structure.

### 1.3

#### **Emerging Applications of Hierarchically Structured Porous Materials**

Hierarchically structuring both the porosity and the architecture of a material over different length scales have provided the opportunity to render the material suitable for a variety of functions that are desirable for a large series of applications. In this part of the book, a myriad of potential applications of hierarchically structured porous materials, from catalysis, separation, optics, energy, and biomedicine to life science (Chapters 16–20), has been described. The mechanical aspect of hierarchical biomaterials has also been analyzed (Chapter 21).

Catalytic processes usually require a sequence of different reaction steps, that is, the sequential coupling of, for instance, pretreatment, chemical conversion into valuable products, and purification of resulting product mixtures. Hence, the desired product is normally obtained only after several different stages, where the production of intermediates requires a defined catalyst with one precise porosity and one specific functionality. Faced with increasing energy demands and to reduce environmental impact, new processes should ideally be realized in one single reactor without any intermediary separation processes. The integration of multimodal porosities that could be individually functionalized within one single body could potentially allow for the successive realization of a complete reaction from starting reagents to final desired products. Separation and purification processes would inherently take place owing to the sieving capacity of the multipore system, such that the product of one reaction can become the reagent for the next reaction [127, 133].

Yoko and Tatsumi in their Chapter 16 describe the recent developments in hierarchical micro- and mesoporous aluminosilicates and titanosilicates as acid and oxidation catalysts, respectively. The improved catalytic performance of hierarchically porous materials has been considered as being due to the enhancement of mass transport. They predicted that the field of hierarchical materials will continue to attract increasing attention during the years to come.

Hierarchically structured porous materials have been considered as potential adsorbents for separation of gas and liquids. The Chapter 17 of Nakanishi deals

with monolithic silica with hierarchically distributed macro- and mesopores and its prominent application as a novel separation medium for High-Performance Liquid Chromatography (HPLC). They found that owing to its high permeability, the “monolithic silica column” distinguished itself from the conventional particle-packed column in terms of separation performance in HPLC. Besides HPLC columns, he illustrates the high permeability and homogeneous flow-through pore structure of macroporous silica for various purposes related to separation science. Manufacturing monolithic columns requires robust and sophisticated engineering processes that make the solution-based synthesis of solid porous structures highly reproducible. Many other applications of hierarchically porous monoliths such as gas–solid and liquid–solid heterogeneous catalysis, integrated multistep in-column reactions and purifications, miniaturized (bio)reactors and therapeutic selective removal of harmful substances, and use in biomedicals are commented.

Yan *et al.* in Chapter 18 describe the use of hierarchically structured porous materials as a new class of optical materials known as photonic crystals (PhCs). One of the amazing properties of a PhC is that it features a photonic band gap (PBG), in which photons having energy within this band gap are prohibited to propagate through the PhC. Thus, these materials exhibit promising properties such as structural color, suppression, or enhancement of spontaneous emission, and in wave guiding light through a sharp band without energy loss. A variety of high-performance photonic devices, such as low-threshold microlasers, high-speed optical switches, compact waveguides, and planar lenses, can be realized based on the PBG materials. Authors presented bottom-up self-assembly combined with an LBL technique to prepare polymer opaline hetero PhCs that exhibit more elaborate optical properties than their one-component counterparts and can find potential applications in optical nanocavities, optical filters, reflectors, waveguides, lasers, and so on.

Energy is the primary preoccupation of twenty-first century. There is not only demand to make the efficient use of current energy and to search new, renewable, and green energy sources. Hierarchization of materials in porosities and structures can provide us with superior materials that will unlock tremendous potential of many energy technologies currently at the discovery phase.

The Chapter 19 written by Su, one of the editors, starts by the applications of hierarchically structured porous materials prepared by using different natural structures such as plant leaves, butterfly wings, diatoms, and wood as biotemplates for the design of energy materials to take beneficial effect of natural structures of energy or light-harvesting functions. The obtained materials showed enhanced light-harvesting and photocatalytic H<sub>2</sub> evolution activity, very promising properties as photoanodes for DSSCs and for Solar Cells (SCs) and in Li ion batteries, respectively. All these biotemplated hierarchically structured porous materials can serve as good models for the design of man-made advanced energy materials. This chapter also commented a recent important development, still inspired from hierarchical structures of plant leaves. By immobilization of

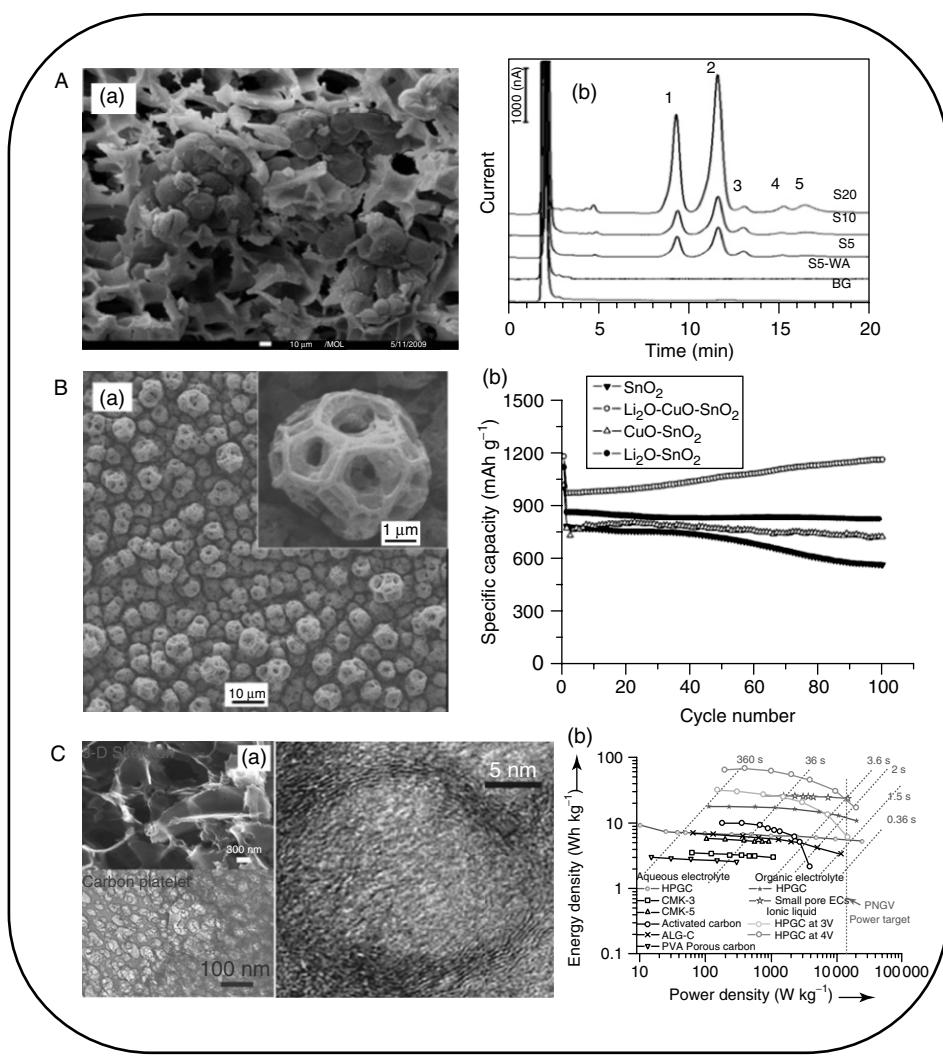
thylakoids, chloroplasts, whole cells extracted from plant leaves, and other photosynthetic cells into hierarchically porous  $\text{SiO}_2$  hydrogels (Figure 1.6A), the photosynthetic function of plant leaves can be prolonged and independent of season change.

The beneficial effect of hierarchically structured porous structures was found also in photocatalysis. In fact, due to the presence of macrochannels in the macro/mesoporous  $\text{TiO}_2$  materials, the reactivity and light harvesting can be highly enhanced since the macrochannels acted as a light-transfer path for introducing incident photon flux onto the inner surface of mesoporous  $\text{TiO}_2$ . This allowed light waves to penetrate deep inside the photocatalyst, making it a more efficient light harvester. This chapter also addresses different examples on the application of hierarchically structured porous materials in Li ion batteries (Figure 1.6B) and in supercapacitors (Figure 1.6C).

Vallet-Regí and Manzano in this Chapter 20 report the importance of the hierarchical structure of porous materials in relation to biology with special attention to those materials with possible applications in life science and drug delivery technologies. They indicated that during the design of porous materials for use in biomedical domains, it is very important to take into consideration the hierarchical porosity that can be found in nature. Upon mimicking such hierarchical porous structures, the replicated materials could perform a similar role to their natural counterparts.

In the first part of their Chapter, the bioceramics as implantable materials are discussed. Hierarchical porous calcium phosphates and porous glasses in bone tissue engineering are then reviewed. Finally, the hierarchically structured porous materials in drug delivery are commented. They indicate that the pore dimensions of the ordered mesopore materials are within the range of 2–50 nm, which are far from those of living cells, which are within 10–200  $\mu\text{m}$ . This makes impossible to cells to penetrate into the mesopores, and taking into consideration that bone cells rule the bone regeneration process, ordered mesoporous materials should be processed somehow to acquire macroporosity. 3D mesoporous bioglass-based scaffolds exhibiting hierarchical pore networks, with giant (30–1000  $\mu\text{m}$ ), macro-(10–30  $\mu\text{m}$ ), and meso-(5 nm) porosity can be adapted to the requirements of different tissues and organs.

In all applications, one important feature of hierarchically structured porous materials which should be taken very carefully into account is their mechanical strength due to large porosity. In this last Chapter 21, Zhu addresses this important point with a particular attention in biomedical application. By analysis of Young's modulus, tensile strength, flaw-tolerance, and toughness of biomaterials, he studies the mechanics of materials of the first and the higher level hierarchy. He concludes that compared to the stiff and strong nanosized mineral material, both the stiffness and the strength of a biomaterial decrease constantly with the hierarchical level number  $N$ . However, its toughness can increase and reach an optimal value. The achievement of these properties relies largely on the very weak and ductile matrix material. By modeling, it is possible to predict the mechanical strength



**Figure 1.6** (A) SEM picture of the immobilization of *A. thaliana* cells within a silica-based hierarchical porous matrix (a). Chromatograms showing the comparison between a blank gel (BG) and a hybrid gel after (S5) 5 days, (S10) 10 days, and (S20) 20 days. (S5-WA) corresponds to the supernatant of the hybrid gels after five days without acid treatment. The peaks correspond to 1, rhamnose; 2, galactose; 3, glucose; 4, xylose; and 5, mannose (b). Reproduced from Ref. [175]. (B) (a) SEM

image of the as-deposited thin film composed of a multideck-cage structured Li<sub>2</sub>O-CuO-SnO<sub>2</sub>. (b) Capacity retention of the thin film electrodes cycled between 0.01 and 3 V versus Li<sup>+</sup>/Li at 0.5 C. Reproduced from Ref. [177]. (C) (a) SEM and TEM images of the synthesized HPC. (b) Ragone plot of the HPC in aqueous solution, organic electrolyte, and ionic liquid in comparison with other typical porous materials reported. Reproduced from Ref. [178].

of the hierarchically structured porous materials, indispensable for their concrete applications.

## 1.4

### Conclusions

This introduction chapter starts from “Hierarchy in Nature” as an inspiration to develop synthesis strategies to target hierarchical structuring and multimodal porosities in one solid body. By learning from nature, a vast array of methods involving the use of supramolecular assemblies of amphiphilic polymers and surfactants, employed as macrotemplates, as well as other templates such as colloidal crystals, polymer foams, bio-celluloses, emulsions, inorganic salts, and ice crystals, coupled with the use of macroscopic phase separation techniques have been developed to realize hierarchically structured porous materials with various porous structures and pore scales. The “Integrative Chemistry” concept and the self-formation phenomenon of generating a porous hierarchy, based on metal alkoxide and metalalkyl chemistry, are akin to natural systems. Some practical applications of these attractive hierarchically structured porous materials have already emerged, including HPLC separation, catalysis, optics, energy storage and conversion, biomaterials engineering, controlled drug delivery devices, and membrane reactors. The widespread use of hierarchically structured porous materials in different processes can induce a new industrial revolution yet remains a great challenge. Multiple technological issues should be taken into account. We will not only undergo an industrial revolution but also a revolution of our society.

We hope that this very brief introduction to the content of this very rich and exciting book can give you appetite and can be a guide for the further lecture. We also sincerely hope that you can find inspiration from this book to take part in the development of this rapidly evolving field of current interest.

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