Recent advances in the synthesis of hierarchically mesoporous TiO$_2$ materials for energy and environmental applications

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ABSTRACT

Because of their low cost, natural abundance, environmental benignity, plentiful polymorphs, good chemical stability and excellent optical properties, TiO$_2$ materials are of great importance in the areas of physics, chemistry and material science. Much effort has been devoted to the synthesis of TiO$_2$ nanomaterials for various applications. Among them, mesoporous TiO$_2$ materials, especially with hierarchically porous structures, show great potential owing to their extraordinarily high surface areas, large pore volumes, tunable pore structures and morphologies, and nanoscale effects. This review aims to provide an overview of the synthesis and applications of hierarchically mesoporous TiO$_2$ materials. In the first section, the general synthetic strategies for hierarchically mesoporous TiO$_2$ materials are reviewed. After that, we summarize the architectures of hierarchically mesoporous TiO$_2$ materials, including nanofibers, nanosheets, microparticles, films, spheres, core-shell and multi-level structures. At the same time, the corresponding mechanisms and the key factors for the controllable synthesis are highlighted. Following this, the applications of hierarchically mesoporous TiO$_2$ materials in terms of energy storage and environmental protection, including photocatalytic degradation of pollutants, photocatalytic fuel generation, photoelectrochemical water splitting, catalyst support, lithium-ion batteries and sodium-ion batteries, are discussed. Finally, we outline the challenges and future directions of research and development in this area.

Keywords: hierarchically mesoporous, TiO$_2$, energy, environment

INTRODUCTION

Since the first discovery of photocatalytic water splitting on a TiO$_2$ electrode under ultraviolet (UV) light, TiO$_2$ materials have been widely investigated over the past few decades due to their unique properties such as non-toxicity, abundance, easy availability and stability [1,2]. For the moment, TiO$_2$ materials present great potential in applications from the conventional areas (e.g. pigment, cosmetic and toothpaste) to the latest developed areas including catalysis, energy storage and conversion, biomedicine, environmental remediation and so on [3,4]. Beyond all question, TiO$_2$ materials offer new candidates to overcome the energy, environmental and health challenges facing humanity today.

Not only the intrinsic electronic structures but also the micro-/nano-structures of TiO$_2$ materials affect their physical and chemical properties [5–7]. Various TiO$_2$ nanomaterials with different structures have been fabricated and applied in different areas and reveal excellent performances. Among them, mesoporous TiO$_2$ materials, especially with hierarchically mesoporous structures, have received increasing interest due to their attractive features, such as high surface areas, large pore volumes, tunable pore structures and nano-confined effects [8–11]. Those features enable the high performances of hierarchically mesoporous TiO$_2$ materials in many areas. The high surface area can provide abundant active sites for surface- or interface-related processes such as adsorption and catalysis. The large pore volume has shown great potential in the loading of guest species and the accommodation of structural change, and the...
Table 1. A comparison of synthetic methods for hierarchically mesoporous TiO$_2$ materials.

| Methods               | Advantages                                                                 | Disadvantages                       | Applied architectures       |
|-----------------------|-----------------------------------------------------------------------------|-------------------------------------|-----------------------------|
| Template-free method  | Simple; Easily processable; Highly crystalline products                     | Products with disordered structures | Nanofibers; Microparticles; Films; Spheres |
| Soft-template method  | Controllable mesostructures and pore sizes; Potential for large-scale synthesis | Highly sensitive to the reaction conditions; Relatively low crystallinity | Nanofibers; Nanosheets; Microparticles; Films; Spheres; Core–shell structures |
| Hard-template method  | Low sensitivity to the reaction conditions; Highly crystalline products     | Time consuming; High cost           | Nanofibers; Nanosheets; Microparticles; Films; Nanospheres; Core–shell structures; Multi-level architectures |
| Multiple-template method | Hierarchically and fully connected porous structures                      | Time consuming; High cost; Requires multiple templates | Nanofibers; Nanosheets; Microparticles; Films; Spheres; Core–shell structures; Multi-level architectures |

A porous structure can facilitate the diffusion of reactants and products, which is of benefit for reaction kinetics [12–14]. In the past, many comprehensive reviews have summarized the synthesis, properties and applications of TiO$_2$-based nanomaterials, but an overview of the architectural diversity of hierarchically mesoporous TiO$_2$ materials and the structure–performance relationship is lacking. Here, we try to focus on those points overlooked by previous reviews. First, the generally synthetic routes for hierarchically mesoporous TiO$_2$ materials are reviewed briefly. After that, the critical issues for the controllable synthesis of hierarchically mesoporous TiO$_2$ materials with different geometries, including nanofibers, nanosheets, spheres, microparticles, films, core–shell and multi-level structures, are summarized. In the third section, applications of hierarchically mesoporous TiO$_2$ materials in energy- and environment-related areas, and the structure–performance relationship, are discussed. Finally, we present a brief conclusion and some perspectives on the future development of this area.

SYNTHETIC STRATEGIES

Generally, the synthetic methods for hierarchically mesoporous TiO$_2$ materials can be classified into four categories: template-free, soft-template, hard-template and multiple-template routes [15,16]. The template-free route is facile and the mesopore voids stem from the aggregation of nanoscale building blocks, but it usually produces products with randomly distributed mesopores. The soft-template method is based on the self-assembly between amphiphilic surfactant molecules and TiO$_2$ precursors. In this approach, the interaction between TiO$_2$ precursors and surfactant molecules is crucial to the formation of mesostructures. To create a hierarchically porous structure, dual templates or post-treatment, such as calcination or ultrasonication, is necessary. The advantage of the soft-template strategy is that the resultant materials possess some attractive features, including controllable mesostructures and pore sizes, tunable morphologies, and easy processing. However, this method is highly sensitive to the reaction condition and the products suffer from the low crystallinity. The hard-template approach, also known as nanocasting, uses preformed nanostructures as templates, such as mesoporous materials, photonic crystals and biotemplates. The most significant merit of this route is that the resultant materials are highly crystalline. Nevertheless, this approach is tedious and time-consuming. The multiple-template is a general and facile method to produce hierarchically (macro/meso, meso/meso, meso/micro) porous materials. Different synthetic approaches can produce hierarchically mesoporous TiO$_2$ materials with different geometries (Table 1), resulting in architectural diversity.

DIVERSE ARCHITECTURES

Nanofibers

Nanofibers, which show many exceptional characteristics, such as large surface-to-volume ratios, quantum confinement effects, etc., have received considerable attention in recent years [17]. The large
Surface-to-volume ratio can significantly increase the number of surface reaction sites and modulate the catalytic activity of the surface atoms. The quantum confinement effect can change the electron and hole transport behavior [18,19]. Hierarchically mesoporous TiO2 nanofibers possess both merits of the porous structure and 1D morphology, which show significant potential in catalysis and energy storage.

One representative method to produce the hierarchically mesoporous TiO2 nanofibers is using the porous materials with 1D channels as hard templates to confine the assembly process of TiO2 precursors and surfactants [20]. In this case, the diameter of the 1D channel should be big enough, usually >50 nm, to accommodate the assembly process, otherwise this process may happen on the outer surface. Besides, the surface property of the 1D channel is critical because the TiO2 precursor infiltrate the 1D channel driven by the capillary force.

Alternatively, by using fibrous frameworks as the shape-directing agents, hierarchically mesoporous TiO2 nanofibers with hollow structures can be produced [21–24]. One critical issue for this process is the surface property of the fibrous framework. For fibrous templates with abundant surface hydroxyl, the TiO2 precursor can uniformly form a deposit on their surface. However, for the fibrous templates with a low concentration of surface hydroxyl, the interaction between the TiO2 precursor and the fibrous template is weak, resulting in homogeneous nucleation of the TiO2 precursor, instead of heterogeneous nucleation on the surface of fibrous frameworks. Therefore, in this case, surface modification of the fibrous frameworks is critical. For example, Liu et al. have produced hierarchically mesoporous TiO2 nanofibers by using nitric acid-treated multi-wall carbon nanotubes (CNTs) as the shape-directing agent [21]. After nitric acid treatment, abundant carboxyl and hydroxyl groups are formed on the surface of CNTs, enabling the uniform deposition of the surfactant/titania-oligomer composite micelles by a layer-by-layer growth route. Another effective modification method is the introduction of a buffer layer on the surface of fibrous frameworks. For instance, after introducing a SiO2 buffer layer on the surface of CNTs, hierarchically mesoporous TiO2 nanofibers can be formed by using tetraethyl titanate (TBOT) and cetyltrimethylammonium bromide as the precursor and pore-forming template, respectively. The SiO2 interlayer can not only enable the uniform deposition of titania species, but also prevent the aggregation of the TiO2 particles and protect the fragile fibrous structure [22].

Another efficient technique to produce nanofibers is electrostatic spinning. In this process, polymers are mixed with TiO2 precursors first, which can help to achieve the desired viscosity and the formation of fibers. In addition, the polymers can act as the in situ templates to produce porous structures [25–30]. To further synthesize TiO2 nanofibers with hierarchically mesoporous structures, introducing the secondary template is necessary. Wu and coworkers have developed a foaming-assisted electrospinning method for the synthesis of hierarchically mesoporous TiO2 nanofibers with increased specific surface areas. In this case, a foaming agent, diisopropyl azodicarboxylate, is used as the secondary template to produce pores in the primary porous frameworks [31,32], leading to the formation of the hierarchically porous structure. However, the resultant nanofibers by this route show random distributed mesopores. On account of this, by using amphiphilic triblock copolymers [33–35] to replace the foaming agent, ordered hierarchically mesoporous TiO2 nanofibers can be synthesized. The advantage of the electrostatic spinning is that the obtained nanofibers possess uniform and controllable sizes. Nevertheless, the necessity of special equipment limits their wide applications.

Nanosheets

Producing mesopores in nanosheets is an appealing endeavor in materials science, which can combine the advantages of porous structures and 2D nanostructures.

Early attempts to construct hierarchically mesoporous TiO2 nanosheets used flat substrates or freestanding surfaces as the structure-directing template, which is similar to the synthesis of TiO2 nanofibers [36–40]. Li et al. produced hierarchically mesoporous TiO2 nanosheets by using graphene oxide (GO) as the template [39]. The plentiful functional groups on the surface of GO and the slow hydrolysis and condensation rate of TBOT enable GO sheets to be conformably coated by amorphous TiO2 shells first. After annealing, the amorphous TiO2 shells would be locally crystallized; at the same time, hierarchical mesopores are generated due to the aggregation of TiO2 nanocrystals. This method circumvents the lattice mismatch that would inevitably arise if crystallized TiO2 shells with the hierarchically porous structure are directly grown on the GO sheets. To increase the regularity of the porous structure, a surfactant–template strategy was developed by using Pluronic P123 as the template [37]. The P123 template can self-assemble with the TiO2 precursor into
the ordered mesostructure by rationally controlling the hydrolysis and condensation of titanium isopropoxide (TIPO).

Although the assembly of micelles on 2D substrates is widely used for the preparation of nanosheets, the removal of substrates can be troublesome. On account of this, Lan et al. have developed a solvent-confined assembly approach (Fig. 1) to synthesize free-standing TiO₂ nanosheets with the hierarchically porous structure [41]. In this case, the stable Pluronic F127/TiO₂ spherical monomicelles are generated first, and can be used as the subunit. The obtained monomicelles are subsequently dispersed in the mixed solvent of ethanol and glycerol, and are tightly surrounded by glycerol due to the strong hydrogen bonding. During the hydrothermal process, the assembly process of F127/TiO₂ monomicelles occurred in a parallel direction only due to the confinement effect of glycerol networks with high viscosity. After removing the template, free-standing hierarchically mesoporous TiO₂ nanosheets can be produced. The resultant nanosheets possess only one layer of mesopores, a high surface area of 210 m² g⁻¹ and a uniform thickness of 5.5 nm. Additionally, the thickness of the nanosheets can be further manipulated from 5.5 to 27.6 nm by simply tuning the precursor concentration or solvent ratio. Notably, without the confinement effect of glycerol, the monomicelles can be randomly aggregated, resulting in the formation of spherical mesostructures with the lowest surface energy.

**Microparticles**

Mesoporous TiO₂ microparticles with irregular morphologies are one of the most widely studied architectures, and can be produced by template-free, soft-, hard- and multiple-template routes. As mentioned above, for the soft-template method, the critical issue is to rationally control the hydrolysis and condensation process of titanium precursors, thereby enabling the co-assembly with surfactant molecules. Therefore, early attempts to synthesize mesoporous microparticles were mainly carried out in acidic conditions, which could effectively mediate the hydrolysis and condensation rate of titanium precursors [42]. After that, a self-adjusted acid–base strategy was developed. In this case, titanium alkoxide and TiCl₄ acted as a source of base and acid, respectively. The self-regulation between the acidic and basic precursors allows the control of the hydrolysis and condensation process of the titanium precursor and the cooperative assembly between the precursor and template, yielding highly ordered mesoporous TiO₂ microparticles with tunable mesostructures [43].

However, the above-mentioned mesoporous TiO₂ microparticles usually present amorphous or partially crystallized frameworks due to the collapse of mesostructure during template removal and framework crystallization at high temperature. The main reason for this is that commercial amphiphilic copolymers, such as the Pluronic type, are too easily decomposed, which cannot support the mesostructure at high temperature. Therefore, to obtain high-crystalline TiO₂ microparticles, the rational design of surfactants is very important [44–46]. Wiesner and coworkers have demonstrated a cooperative assembly method that combines advantages of both soft structure-directing assemblies and hard-templating chemistries (CASH) [46]. In this method, the block copolymer (poly(isoprene-block-ethyleneoxide), PI-b-PEO) was prepared as a template. Under appropriate heating conditions, the hydrophobic PI block with sp²-hybridized carbon can convert to a sturdy amorphous carbon in the mesochannels. This in situ-formed carbon layer is sufficient to act as a rigid support keeping the mesostructures at temperature as high as 1000°C. The critical issue for this synthesis is that the block copolymers with a high content of sp²-hybridized carbon in the hydrophobic segments are relatively stable and could be in situ-converted into residual carbon at high temperature to support the mesostructure.
However, the lab-produced block copolymers show limited potential for the scalable synthesis. On account of this, in 2010, our group synthesized hierarchically mesoporous TiO$_2$ microparticles with a highly crystalline framework by using sulfuric acid to carbonize the surfactants (P123) inside the mesochannels, instead of decomposition during calcination, which could support the mesostructure during the high-temperature crystallization (up to 650°C) [47]. In addition, an ethylenediamine (EN) protection route has also been demonstrated to produce thermally stable and highly crystallized hierarchically mesoporous TiO$_2$ microparticles by using F127 as the template [48]. In this case, EN species with positive charges can effectively attack the surface of mesoporous TiO$_2$ primary particles with negative charges, which can inhibit undesirable grain growth and phase transformation of TiO$_2$ nanoparticles during the calcination process. As a result, the hierarchically mesoporous structure could be maintained even up to 700°C.

Using pre-formed and fully crystallized TiO$_2$ nanocrystals to replace molecular Ti precursors as the framework building blocks is an alternative way to synthesize hierarchically mesoporous TiO$_2$ microparticles with high crystallinity. The interaction between the crystallized TiO$_2$ nanocrystal and surfactant is the prerequisite for this process. Therefore, the surface chemistry of the crystallized nanocrystal is of great importance, and in some cases the surface modification by removing and/or exchanging the surface ligands is necessary. Besides, the driving forces for the coassembly between nanocrystals and surfactants are mainly weak interactions, such as hydrogen bonds. Therefore, nanocrystals with a large particle size cannot work in this system [49,50]. Based on the above-mentioned principles, Milliron and coworkers have produced hierarchically mesoporous TiO$_2$ microparticles by using the pre-synthesized TiO$_2$ nanorods or nanospheres as the building blocks [50]. Lab-made poly(N,N-dimethylacrylamide)-block-polystyrene, PDMA-b-PS was selected as the structure-directing agent because the PDMA can mimic the dynamic adsorption interaction of dimethylformamide at the surface of TiO$_2$ nanocrystals. Hence, the hierarchically mesoporous TiO$_2$ with a high surface area and fully crystalline framework can be produced.

Alternatively, the hard-template route is a facile and general way to synthesize hierarchically mesoporous TiO$_2$ microparticles crystalline frameworks [51–53]. For example, Crossland et al. have reported a general seeded nucleation and growth method to synthesize the mesoporous anatase single-crystal with a high surface area (70 m$^2$ g$^{-1}$) by using monodisperse silica spheres as the template (Fig. 2) [51]. The results suggest that ‘seeding’ the template with microscopic nucleation sites is vital for the
confining growth of single crystal TiO2, which directly overwhelms the homogeneous nucleation.

However, in the above cases, the secondary pores in the hierarchically mesoporous frameworks are generated by the accumulation of nanoparticles, which show uncontrollable sizes and distribution. To further increase the size and regularity of the secondary pores, the multiple-template route, i.e. a combination of soft- and hard-templating, was developed [54–56]. For example, hierarchically mesoporous TiO2 materials have been produced by removal of SiO2 in the mesoporous crystalline TiO2–SiO2 nanocomposites. In this case, highly ordered 2D hexagonal mesoporous TiO2–SiO2 nanocomposites with variable Ti/Si ratios were firstly obtained by co-assembly of TiPO, tetraethyl orthosilicate (TEOS) and Pluronic P123. Utilizing sodium hydroxide (NaOH) as an etchant to remove SiO2 can produce secondary pores. The final products, possessing hierarchical mesopores, are highly connected by uniform intrawall mesopores while retaining mesostructural integrity and regularity. Besides, the size of the secondary pore can be fine-tuned from 0.9 to 4.8 nm by changing the crystallization temperature and Ti/Si ratio [57,58]. To better control the hierarchically porous structures, colloidal crystals constructed by SiO2 or polymer nanospheres were introduced as the hard templates [59,60]. For example, Su and coworkers have synthesized ordered hierarchically mesoporous TiO2 microparticles by using P(St-MMA-SPMAP) spheres and P123 as the hard and soft templates, respectively (Fig. 3) [61]. By this route, the pore size, pore structure and wall thickness can be well controlled. Close-packing of the P(St-MMA-SPMAP) spheres with uniform size is crucial for the formation of ordered hierarchically porous structures.

Films

Mesoporous TiO2 films are very useful for the fabrication of devices such as dye-sensitized solar cells, electrochromic devices, antifogging, antibacterial, self-cleaning coatings and many others. The most widely used method to synthesize mesoporous TiO2 films is the evaporation-induced self-assembly (EISA) approach. To date, various kinds of mesoporous TiO2 films have been fabricated by employing different ionic and non-ionic surfactants, like commercially available non-ionic triblock copolymers of the Pluronic family with the general formula EOxPOyEOx [62–64]. However, those resultant mesoporous TiO2 films exhibit poor thermal stability, and mesostructures would collapse at high temperature. Moreover, the sizes of the mesopores are usually less than 10 nm. To circumvent the above problems, a series of lab-made copolymers [65–67], which contain a high content of sp2-hybridized carbon, were synthesized to produce highly crystalline mesoporous TiO2 films with tunable mesostructures and pore sizes. For instance, Feng et al. have reported a ligand-assisted EISA method to produce mesoporous TiO2 films on various substrates via using PEO-b-PS as the template [67]. Acetylacetone was utilized as the ligand to reduce the hydrolysis and condensation rate of the titanium precursor, enabling the cooperative assembly with the surfactant. Besides, the PS segment containing sp2-hybridized carbon can generate carbon residues as a protection layer to support the TiO2 framework during the pyrolysis, thereby sustaining the mesostructure. The obtained TiO2 films possess a monoclinic mesostructure distorted from a (110)-oriented primitive cubic structure, and the thickness can be well controlled from 150 nm to several micrometers by changing the parameters of dip-coating.

The orientation of mesopores is a crucial parameter of mesoporous films. In most reported cases, the alignment of mesopores is parallel to the substrate surface due to the principle of the lowest energy. Actually, mesopores with vertical alignment are highly desired because such structures can improve the transportation of electrons, ions and fluids in the films, which is especially important for solar cells, fuel cells and separation technologies [68]. To this end, Wu et al. have reported a unique structural transformation process to prepare mesoporous
Porous TiO$_2$ materials have stimulated intensive research for applications in energy storage, photocatalysis and environment recombination. In order to achieve spherical morphology, various hard templates, such as mesoporous nanospheres and reverse opals, have been initially adopted to confine the sol–gel self-assembly process [73,74].

Soft-template methods for the synthesis of mesoporous TiO$_2$ nanospheres have been successively proposed to simplify the hard-template route. It is vital to develop a facile and reproducible sol–gel method to prepare monodisperse and uniform mesoporous TiO$_2$ nanospheres. Chen et al. have creatively combined the sol–gel process with a solvothermal treatment in the presence of hexadecylamine (HDA) as the structure-directing agent [75]. The lipophilic interactions between the long-chain alkyl groups in alkylamine can drive the self-assembly process of the hydrolyzed Ti species/oligomers to produce monodisperse nanospheres. This strategy is facile to fabricate hierarchically mesoporous TiO$_2$ nanospheres [76].

To improve the universality and repeatability of this route, Zhu et al. have reported a double surfactant-directed assembly method to prepare monodisperse hierarchically mesoporous TiO$_2$ nanospheres by using n-dodecylamine (DDA) and Pluronic F127 as templates [77,78]. In this process, F127 and DDA can assemble into cooperative spherical micelles in the alcohol/water solution. After interacting with the hydrolyzed titanium species, a stronger lipophilic interaction can be formed between the resultant spherical micelles/oligomer composites, which could promote the self-assembly of those spherical micelles/oligomer composites, leading to a fast phase separation process to form small-sized TiO$_2$ nanospheres. Besides, by varying the concentration of surfactants, the diameter sizes of hierarchically mesoporous TiO$_2$ nanospheres can be simply changed from 50 to 250 nm.

The aerosol-assisted self-assembly (spray drying) process is another very promising strategy aimed at the low-cost, and scalable synthesis of mesoporous spheres [79–81]. Pal et al. have introduced a relatively low drying temperature (170°C) and an additional ultrasonication route to synthesize hierarchically mesoporous TiO$_2$ spheres by using Pluronic P123 as the soft template [80]. During post-sonication treatment, the low-polymerized TiO$_2$ frameworks undergo further hydrolysis and condensation, thereby transforming into an aggregate of small TiO$_2$ grains and resulting in the formation of the hierarchically porous structure [82]. The spray-drying technique is a feasible strategy for controlling the diverse surface morphology of hierarchically mesoporous TiO$_2$ spheres as well. For example, by controlling drying temperature, the droplet jet dispersed in the drying chamber can rapidly dry, resulting in the formation of hierarchically mesoporous TiO$_2$ spheres with a wrinkled surface [81].

The above-mentioned strategies suffer from a common problem that because of the spontaneously random assembly of micelles, these materials have polycrystalline pore walls that are generally irregularly oriented in space, which adversely...
Figure 4. (a) Schematic representation of the formation process of hierarchically mesoporous TiO$_2$ microspheres with a single-crystal-like pore wall through EDOA approach. (b) The SEM image of a single ultramicrotomed, radially oriented hierarchically mesoporous TiO$_2$ microspheres. Inset: structure models for the radially oriented channels with interchannel pores. (c) The TEM image of a single ultramicrotomed, hierarchically mesoporous TiO$_2$ microsphere. Inset: the selected-area electron diffraction (SAED) pattern taken from the cylindrical pore bundles region with [010] incidence. Adapted from [83] with permission from the American Association for the Advancement of Science. Copyright 2015.
process, resulting in the splits on the surface of spheres [87].

To produce hierarchically mesoporous TiO2 spheres with ordered porosity, Liu et al. have reported the synthesis of highly crystalline hierarchically ordered macro/mesoporous TiO2 hollow microspheres through using the multiple-template route (Fig. 5) [88]. In this case, 3D-ordered macroporous carbon scaffolds (3DOMC, inverse opal structures) with uniform cavities and Pluronic F127 were used as hard and soft templates, respectively, to produce ordered mesopores and hollow structures. The resultant hierarchically macro/mesoporous hollow microspheres possess controllable ordered mesostructure symmetry (hexagonal $p6mm$ or cubic $Im3m$) and highly crystalline anatase frameworks. Later, similar hierarchically ordered macro/mesoporous TiO2 spheres were synthesized by using 3DOMC and Pluronic P123 as templates by Luo and coworkers [89]. Interestingly, in Luo’s work, through tuning the relative amount of the precursor solution in the 3DOMC (partially or completely filling), hierarchically mesoporous TiO2 particles with unique morphologies, such as hemispheres, can be produced.

**Core–shell structures**

Core–shell structured nanomaterials provide a platform for integrating multiple building blocks into a single functional system, exhibiting enhanced or new physical and chemical properties that are not available in the isolated components [90,91].

In 2012, Li et al. for the first time, reported a versatile kinetics-controlled coating method for the preparation of core–hierarchically mesoporous TiO2 shell nanomaterials in a pure ethanol system with ammonia as the catalyst [92]. In this system, the concentration of ammonia that can mediate the reaction kinetics of TBOT is critical. Under the condition of a low concentration of ammonia, the reaction rate is slow, resulting in the heterogeneous nucleation on the core surface and then the formation of uniform shells. However, a high concentration of ammonia leads to a high reaction rate, leading to the simultaneous heterogeneous and homogeneous nucleation. As a result, large and aggregated nanoparticles are formed. Notably, this method is very straightforward, versatile and can be widely used for the synthesis of various core–mesoporous TiO2 shell nanomaterials with tunable shell thickness [93].

Later, Lou and coworkers developed a universal cooperative assembly method for coating TiO2 shells with the hierarchically porous structure on various cores with different compositions and morphologies [94]. In this work, HDA was used as the template. The amino groups of HDA molecules can participate in hydrogen-bonding interactions with TIPO hydrolysis products to form inorganic–organic composites, which can be coated on the nanoparticles. Besides, the long hydrophobic carbon chains of HDA self-organize into rodlike micelles that can produce pores in TiO2 domains. This method is simple and universal, and can rapidly produce hierarchically mesoporous TiO2 shells on various inorganic, organic and inorganic–organic composite materials, including silica, metals, metal oxides, organic polymers, carbon-based and metal–organic framework (MOF) nanomaterials.
Moreover, this strategy also provides a versatile platform toward the fabrication of various TiO$_2$-based novel and hierarchical nanostructures, including hollow and yolk–shell structures with tailored cavity sizes, shell thicknesses tailored cavity sizes and shell thicknesses.

To better control the sizes of mesopores, our group has demonstrated a general confined interfacial monomicelle assembly approach for coating mesoporous TiO$_2$ shells (Fig. 6) [95]. In this process, the F127/TiO$_2$ composite monomicelles are obtained first, which can act as the subunit. After redispersal into the solution containing ethanol and glycerol, the monomicelles tend to collide and attach on the surface of functional cores by a side by side packing manner due to the confinement effect of glycerol and the shear force generated by stirring, resulting in the formation of an ordered structure. After removing the template by calcination, mesoporous shells can be produced. This assembly process shows precise controllability and great versatility, endowing the coated TiO$_2$ layers with highly tunable thickness, mesopore sizes, and switchable coated surfaces. Furthermore, the accurate controllability of such a confined assembly process enables the formation of TiO$_2$ shells from mono- to multilayers (up to five layers) of mesopores, and the mesopore size can be manipulated from 4.7 to 18.4 nm by tuning the amount of swelling agent. This method is highly reproducible and reliable and provides a deep insight into rational design and precise synthesis.

After removing the interior core in the core-shell nanomaterials mentioned above, hollow hierarchically mesoporous structures can be produced [96–99]. However, in some cases, the pristine morphologies cannot be maintained because of the structural collapse during the removal of interior cores. To circumvent this problem, Yin and coworkers have developed a silica-protected calcination process, which relies on an additional silica coating to limit the structural rearrangement of TiO$_2$ [100], but the resultant material shows poor crystallinity. To better control the nanoscale crystallinity in the hierarchically mesoporous TiO$_2$ shells, the same group has developed a novel partial etching and re-calcination process. The partial etching step produces a small gap between SiO$_2$ and TiO$_2$ layers, which allows space for the further growth of TiO$_2$ into large crystal grains. The re-calcination process leads to highly crystallized TiO$_2$, which maintains the hierarchically porous structure due to the protection of the partially etched outer silica layer [101].

Multi-shelled mesoporous architectures manifest remarkable superiority toward some specific applications [102,103]. Ren et al. have developed a sequential templating approach to synthesize multishelled mesoporous hollow TiO$_2$ nanospheres with hierarchical pores by using carbonaceous nanospheres and TiCl$_4$ as sacrificial templates and precursors, respectively [104]. The adsorption of Ti species in carbonaceous nanospheres is a prerequisite for the successful synthesis. The concentration of Ti species in carbonaceous nanospheres plays an essential role in this route: too low or too high results in the formation of electronegative anions [Ti$_{n}$O$_{4n}$]$^{4n-}$ or [Ti(OH)$_{3n}$Cl$_{6-n}$]$^{2n-}$, respectively, which are the repulsion with negatively charged carbonaceous nanosphere templates. Moreover, by changing the calcination parameters, the shell numbers, shell thicknesses and the spacing between shells of the multi-shelled structure can be well controlled. After that, by regulation of the reaction conditions (precursors, post-hydrothermal treatment, calcination, etc.), a series of multi-shelled hierarchically mesoporous TiO$_2$-based heterostructures such as SrTiO$_3$–TiO$_2$ [105], anatase–TiO$_2$(B) [106] and TiO$_{2-x}$–TiO$_2$ [107], were synthesized by the same group.

**Multi-level architectures**

Bio-templating is an efficient and universal approach to synthesize hierarchically mesoporous materials with multi-level architectures. The main advantage of this method is that a variety of natural materials with low-cost and environment-friendly properties can act as templates. Generally, the
synthetic process for the bio-template method involves: (i) after absorbing the titanium precursors by the cell walls of bio-templates through capillary adsorption, an amorphous TiO$_2$ replicated from bio-templates can be formed, and (ii) the natural templates are removed by calcination; at the same time, hierarchically mesoporous TiO$_2$ materials with multi-level architectures with similar characteristics to the pristine natural templates can be obtained.

Butterfly wings, which display diverse colors and patterns due to their periodic surface scales, are representative bio-templates and can be used for the synthesis of hierarchically porous materials with unique properties [108,109]. By using butterfly wings of different breeds, a variety of hierarchically mesoporous TiO$_2$ materials with quasi-honeycomb-like shallow concavities and cross-ribbing structure can be produced [110]. Apart from butterfly wings, recently, a series of bio-templates such as bacteria [111], cellulose [112] and yeast [113] have been used for the synthesis of hierarchically mesoporous TiO$_2$ materials with multi-level architectures. However, it is difficult to precisely control the resultant structures at nanoscale due to the non-uniformity of bio-templates.

To address this issue, Liu et al. have reported a confined microemulsion self-assembly approach to synthesize an unprecedented type of 3D highly ordered hierarchically mesoporous TiO$_2$ with bouquet-posy-like architectures (Fig. 7) [114]. 3DOMC was used as the template, in which F127/TiO$_2$ oligomer micelles separate into uniform microemulsion droplets due to the surface tension. The Level-1 hierarchically mesoporous superstructures, which consist of one spherical core and 12 symmetric satellite hemispheres, resulted from an interface tension-induced shrinkage procedure. The THF evaporation can increase the interface tension force, which tends to pull the formed microemulsion droplets to complete filling of the center macropores of 3DOMCs, leading to the formation of a spherical core at the center of the microemulsion droplets. At the same time, the volume of the microemulsion droplets in macropores is dramatically decreased with the continuous evaporation, and the shrinkage of microemulsion droplets occurs, making one spherical core coupled with 12 satellite hemispheres via 12 connected macropore windows of the 3DOMC scaffolds. Notably, by increasing the size or content of impregnated TiO$_2$ precursor emulsion droplets, a more complex and asymmetric superstructure with 13 spherical cores and up to 44 symmetric satellite hemispheres can also be well manipulated.

APPLICATIONS
Owing to its unique physical, chemical and optical properties, hierarchically mesoporous TiO$_2$ materials have been widely utilized in various applications concerning the major three challenging themes in the 21st century, including energy, environment and health. In this section, we highlight the applications of hierarchically mesoporous TiO$_2$ materials in the energy and environment, including photocatalytic degradation pollutants, photocatalytic fuel production, photoelectrochemical cells, catalyst support, lithium-ion batteries and sodium-ion batteries.

Photocatalytic degradation of pollutants
Hierarchically mesoporous TiO$_2$ materials are of great interest in the area of photocatalytic degradation of pollutants due to their high surfaces and large pore volumes. High surface areas can provide a large number of active sites for adsorption and reaction of reactants. Besides, large pore volumes can facilitate the transport of chemicals in the bulk of TiO$_2$ materials, enabling the accessibility of active sites. When being used as photocatalysts for removal of acetaminophen in water, the decomposition rate of the mesoporous TiO$_2$ microspheres is significantly faster than that of nonporous commercial P25 due to their high surface areas [115]. Moreover, the photocatalytic performance can be further improved by the fabrication of hierarchically porous structures [74]. However, the activities of TiO$_2$ materials are greatly limited by the wide band gap and low quantum efficiency.

Heteroatoms doping is an effective modified way to introduce additional extrinsic electronic levels in the energy band gap, thereby promoting light absorption. Recently, a series of heteroatoms dopants, including metal and non-metal atoms, have been reported to enhance the performances of TiO$_2$ materials [116,117]. For example, compared with the undoped form, iodine-doped hierarchically mesoporous TiO$_2$ can remove toxic organic pollutants more effectively [117]. Co-doping with two heteroatoms can further improve the activity of hierarchically mesoporous TiO$_2$. The C,N-co-doped hierarchically mesoporous TiO$_2$ material shows a better visible-light photocatalytic activity on the degradation of ibuprofen than single heteroatom doped and undoped forms [118]. However, for doped TiO$_2$, the lattice defects resulted from the dopants can unavoidably introduce new charge carrier trapping and recombination centers, which have negative effects on the photocatalytic performance.
Figure 7. (a) Schematic representation of the formation process of hierarchically mesoporous TiO$_2$ bouquet-posy-like superstructures through confined-microemulsion self-assembly process. FESEM (b, c) and TEM (d) images of the Level-1 hierarchically mesoporous TiO$_2$ superstructure. FESEM (e, f) and TEM (g) images of the Level-2 hierarchically mesoporous TiO$_2$ superstructure. Adapted from [114] with permission from the American Chemical Society. Copyright 2016.
Hydrogenated TiO$_2$ materials, without the introduction of unwanted carrier recombination centers from dopants, were firstly reported by Mao and coworkers in 2011 [119] to decrease the band gap of TiO$_2$. Zhou et al. have reported the band gaps of hydrogenated hierarchically macro/mesoporous TiO$_2$ materials is significantly smaller than that of the pristine one [120]. Moreover, the resultant materials show excellent solar-driven photocatalytic activity and long-term stability for complete mineralization of floating insoluble hexadecane. In addition, the photocatalytic reaction apparent rate constant $k$ is 7 times higher than that of commercial P25 under AM 1.5 irradiation (Fig. 8). Later, by using urea as a nitrogen resource, the same group further synthesized hydrogenated hierarchically mesoporous TiO$_2$ doped by N, which can degrade 96% methyl orange under visible light in 180 min [121].

Construction of hierarchically mesoporous TiO$_2$ nanocomposites, such as metals–TiO$_2$ [122,123], metal sulphides–TiO$_2$ [124] and carbon–TiO$_2$ [125] is also a promising way of promoting the activities.
The intimate contact of TiO$_2$ and other materials leads to the formation of heterojunctions, which remarkably favors the separation of photogenerated electrons and holes. Jiang and coworkers have fabricated the hierarchically mesoporous TiO$_2$/graphene composites for degrading methyl blue [125]. The apparent rate constant for the hierarchically mesoporous TiO$_2$ films with graphene can up to be 0.071 min$^{-1}$, almost 1.6 times that for hierarchically mesoporous TiO$_2$ films without graphene.

**Photocatalytic fuel production**

Developing renewable energy epitomizes one of the major scientific challenges for the 21st century. One of the cleanest approaches is photocatalytic fuel production (H$_2$ generation, CO$_2$ reduction, etc.). Recently, various advanced TiO$_2$ nanostructures have been developed to achieve this goal. Here we summarize some key progress regarding hierarchically mesoporous TiO$_2$ materials for photocatalytic fuel production.

**Photocatalytic H$_2$ generation**

Photocatalytic water splitting has been proven to be an ideal, sustainable, eco-friendly and inexhaustible approach to producing H$_2$ without environmental pollution. Porous TiO$_2$ materials are some of the most investigated photocatalysts for H$_2$ generation due to their low cost, abundance and environmental benignity. Lasa and coworkers have demonstrated that hierarchically mesoporous TiO$_2$ shows excellent photocatalytic performance for H$_2$ production [126]. The quantum yield is estimated to be 22.6%, which is significantly higher than that of nonporous commercial P25. However, as mentioned above, for real applications, the performance of hierarchically mesoporous TiO$_2$ is greatly limited by its wide band gap and low efficiency of charge separation.

Surface hydrogenation of TiO$_2$ is an effective way because hydrogenation can lead to the formation of defects, which can increase the solar-light adsorption and improve the charge separation and transportation [53]. Zhou et al. for the first time, have prepared hydrogenated mesoporous TiO$_2$ materials for catalytic H$_2$ generation [127]. The photosresponse of the resultant hydrogenated TiO$_2$ can extend from UV light to visible and infrared light regions. As a result, the obtained materials show excellent photocatalytic hydrogen generation performance with a rate of 136.2 $\mu$mol h$^{-1}$ by using Pt and methanol as the co-catalyst and sacrificial reagent, respectively, which is almost twice as high as that of the pristine one (76.6 $\mu$mol h$^{-1}$). By filtering out incident light with wavelengths shorter than $\sim$400 nm, the resultant materials still exhibit a good photocatalytic activity, while the pristine one shows no visible-light activity.

In addition, construction of TiO$_2$ phase junctions can promote the separation of charges and holes significantly, thereby improving performances of TiO$_2$ materials. For example, hierarchically mesoporous microspheres with an anatase/rutile ratio of 77:23 have shown excellent photocatalytic performance with an H$_2$ generation rate up to 12.6 $\mu$mol h$^{-1}$ g$^{-1}$—significantly higher than that of hierarchically mesoporous single-phase microspheres and commercial P25 [85]. Notably, the hierarchically mesoporous microspheres possess excellent visible-light activity, too. The H$_2$ generation rate can be up to 293 $\mu$mol g$^{-1}$ h$^{-1}$ after cutting off the UV light shorter than 400 nm (Fig. 9). After introducing the defects with controllable distribution to the hierarchically mesoporous TiO$_2$ microspheres with anatase-rutile phase junctions, the H$_2$ generation rate can be further improved, reaching 21.3 $\mu$mol h$^{-1}$ g$^{-1}$ and 852 $\mu$mol g$^{-1}$ h$^{-1}$ under AM 1.5 G and visible light, respectively [128]. Single-crystals also present great potential for photocatalytic H$_2$ generation. Hierarchically mesoporous rutile TiO$_2$ microspheres with the single-crystal-like wall and dehiscent architecture can produce hydrogen gas steadily at $\sim$12.2 $\mu$mol h$^{-1}$ g$^{-1}$, almost three times higher than that of commercial P25 [87].

**Photocatalytic CO$_2$ reduction**

The photocatalytic CO$_2$ reduction into hydrocarbon fuels is a promising approach for the direct conversion of CO$_2$ to value-added chemicals (CO, methane, methanol, etc.) by sunlight. This process is much more complicated than water splitting for the following reasons: (i) reduction of CO$_2$ requires a higher energy input for breaking the O=C=O double bond; (ii) the side reaction happens simultaneously during CO$_2$ reduction, resulting in low selectivity for target products [129]. It has been reported that hierarchically mesoporous TiO$_2$(B) shows excellent performance in catalyzing CO$_2$ to methanol and methane [130]. However, when using TiO$_2$ materials as CO$_2$ reduction photocatalysts, some issues, like wide band gap, low quantum efficiency and weak interaction between the TiO$_2$ surface and CO$_2$, should be addressed.

One common and effective way is doping. Ye and coworkers have prepared cobalt (Co)-doped hierarchically mesoporous TiO$_2$ for catalytic CO$_2$ reduction [131]. The introduction of Co ions can change the location of the conduction band and valence band of TiO$_2$, leading to visible-light absorption. Thus, such designed material exhibits a high activity for the reduction of CO$_2$. By varying the molar ratio
of Co/Ti, the optimal generation rate of CH$_4$ can be increased to 0.258 μmol g$^{-1}$ h$^{-1}$.

Additionally, fabrication of heterostructures is optional. Cu$_2$O-modified hierarchically mesoporous TiO$_2$ hollow spheres have been demonstrated to catalyze the conversion of CO$_2$ to CH$_4$ under visible-light [132]. Cu$_2$O is a typical p-type semiconductor with a narrow optical band gap of ~2.1 eV. When combined with TiO$_2$, the high separation efficiency of photo-induced charges and holes can be achieved due to the formation of p–n junctions between Cu$_2$O and TiO$_2$. Thus, the overall CH$_4$ generation rate can be up to 0.16 μmol g$^{-1}$ h$^{-1}$. In addition to metal oxides–TiO$_2$ heterostructures, construction of noble metals–TiO$_2$ heterostructures can improve the photocatalytic performance of CO$_2$ reduction, too [133,134]. In this system, the formation of Schottky junctions between noble metals and TiO$_2$ can improve the separation and transportation of charge carriers, and the local surface plasmon resonance (LSPR) effect of noble metals can extend the photoresponse of TiO$_2$ from the UV to the visible-light region. For example, Tu et al. have prepared the Au@mesoporous TiO$_2$ yolk–shell spheres for plasmon-induced photocatalytic reduction of CO$_2$ [135]. The resultant materials show high generation rates of CH$_4$ and C$_2$H$_6$ of 2.52 and 1.67 μmol g$^{-1}$ h$^{-1}$, respectively, indicating that the introduction of Au can accelerate multiple electron/hole reactions, and thus generate more valuable high-grade carbon species via an enhanced C–C coupling reaction. Jiao et al. have designed 3D hierarchically porous TiO$_2$-supported Au nanoparticles with enhanced visible-light-responsive properties for CO$_2$ photoreduction (Fig. 10) [136]. The resultant materials possess well-defined hierarchically porous structures, which are highly interconnected with one another by small pore windows, and the Au nanoparticles are uniformly dispersed and supported on the inner walls. As a result, the obtained materials exhibit high catalytic activity for the photocatalytic reduction of CO$_2$ to CH$_4$ under visible illumination with a high production rate of 1.48 μmol g$^{-1}$ h$^{-1}$.

**Photoelectrochemical water splitting**

Photoelectrochemical (PEC) water splitting, which integrates solar energy collection and water electrolysis into a single photoelectrode, provides a more effective way of H$_2$ production than photocatalysis and electrolysis. Mesoporous TiO$_2$ films are among the best candidates as a host matrix for PEC water splitting because of their large surface areas, uniform pore sizes, and structural homogeneity and integrity. Construction of macropores in the mesoporous films to produce the hierarchically porous structure can increase the availability of the internal surface and the accessibility of active sites, thus improving the photon to current conversion efficiency. Hierarchically porous anatase films with high crystallinity, a high surface area (240 m$^2$ g$^{-1}$) and large pore volume (1.2 cm$^3$ g$^{-1}$) have been synthesized for PEC cells, which possess a high photocurrent of 1.07 mA cm$^{-2}$ and photocurrent efficiency of 0.67% [71]. After N-doping, the PEC performance of the N-doped hierarchically porous film is further improved because of the extension of the light response, the photocurrent and photoconversion efficiency can increase to 8.54 mA cm$^{-2}$ and 5.23%, respectively (Fig. 11).

Incorporation of quantum dots (QDs) with hierarchically mesoporous TiO$_2$ frameworks can improve the PEC performance, too, because of the high separation efficiency of photoinduced charges and holes at the heterointerfaces. Feng et al. have used CdS QDs-sensitized hierarchically
Visible light (SPR effect) CO$_2$ + 2H$^+$ \rightarrow CO$_4$ + H$_2$O
2H$_2$O \rightarrow O$_2$ + 4H$^+$ + 4e$^-$
\[ e^- + h^+ \rightarrow e^- + e^- \]
CB
VB
Empty state
Filled state

Figure 10. (a) The mechanism for photocatalytic reduction of CO$_2$ with H$_2$O to methane over hierarchically porous Au/TiO$_2$ catalysts. SEM (b) and TEM (c) images of hierarchically porous TiO$_2$. (d) CH$_4$ production amounts over P25, hierarchically mesoporous TiO$_2$ and Au/TiO$_2$ catalysts: a, P25; b, TiO$_2$; c, TiO$_2$ with 0.5 wt% Au; d, TiO$_2$ with 1 wt% Au; e, TiO$_2$ with 2 wt% Au; f, TiO$_2$ with 4 wt% Au; g, TiO$_2$ with 8 wt% Au. Adapted from [136] with permission from Elsevier. Copyright 2015.

mesoporous TiO$_2$ films as photoanodes for water splitting [67]. An excellent photocurrent density of 6.03 mA cm$^{-2}$ and a photoconversion efficiency of 3.9% can be obtained. A novel photoanode based on N-doped sub-5 nm graphitic pencil nanodots (N-PNDs)-inserted hierarchically mesoporous TiO$_2$ films with a high surface area of 97 m$^2$ g$^{-1}$, and large pore size of 13.5 nm, have been demonstrated recently [68]. The resultant material exhibits a high photocurrent density of 1.73 mA cm$^{-2}$, a 183% and 108% increase of the values for the pristine and undoped PND-TiO$_2$, respectively. Moreover, the incident photo-to-current conversion efficiency (IPCE) measurements show that the N-PND-inserted hierarchically mesoporous TiO$_2$ films have an IPCE value of $\sim$50% over the wavelength range of 325–425 nm, which is more than twice that of the pristine hierarchically mesoporous TiO$_2$ films.

**Catalyst support**

TiO$_2$ is not only the most studied photocatalyst but also a good catalyst support for active metal nanoparticles in many reactions. The thermal stability, high surface areas, and large pore sizes and volumes of hierarchically mesoporous TiO$_2$ materials make them ideal catalytic supports. The high surface area can provide more surface active sites, thus improving the activities of catalysts because the chemical reactions take place only when active sites are available on the surface. Besides, the large pore size and volume can facilitate the diffusion of chemicals, promoting the reaction kinetics [137,138].

Hao et al. have reported that the hierarchically mesoporous Au/TiO$_2$ hybrid nanofibers can efficiently catalyze the reduction of 4-nitrophenol to 4-aminophenol by sodium borohydride [139]. The results show that, with the increase in Au loading, the apparent reaction rate constant is raised but the turnover frequency (TOF) value of the catalyst decreases. This can be attributed to the smaller sizes of Au nanoparticles, which possess higher catalytic activity. By regulation of the architecture and porous structures of mesoporous TiO$_2$ materials, the catalytic performance can be improved significantly. For instance, Zhao and coworkers have demonstrated the 3D hierarchically mesoporous bouquet-posy-like TiO$_2$/Au as a catalyst for the semihydrogenation of alkynes by using biorenewable formic acid as the hydrogen source [114]. The produced catalyst (0.2 mol% Au) displays 100% diphenylacetylene conversion within 40 min, and the selectivity to cis-stilbene is measured to be $\geq$99%. Moreover, the superstructure catalyst can catalyze a wide range of aromatic and aliphatic terminal alkynes to convert to the corresponding alkenes with a high conversion ($\geq$99.7%) and selectivity ($\geq$96%). Furthermore, the superstructure catalyst can be reused 25 times without performance degradation. The high performance of the hierarchically mesoporous TiO$_2$ superstructure can be attributed to the unique structure with more nanoreactor units.

By fabrication of active-nanoparticles@hierarchically mesoporous TiO$_2$ materials the leaching and aggregation of nanoparticles can be prevented in harsh catalytic environments. Lee et al. have explored Au@TiO$_2$ yolk–shell structures as catalysts for promoting CO oxidation [140]. In this case, the hierarchically porous TiO$_2$ shells can act as a physical barrier to prevent the thermal migration
Figure 11. SEM (a) and TEM (b) images of ordered hierarchically macro/mesoporous TiO$_2$ films. (c) Photoelectrocatalytic water-splitting performance of the ordered hierarchically macro/mesoporous TiO$_2$ films (H-TiO$_2$) and the pristine ordered mesoporous TiO$_2$ films (M-TiO$_2$). Adapted from [71] with permission from Wiley-VCH. Copyright 2014.

and sintering of Au nanoparticles at high temperature. In fact, the Au@TiO$_2$ yolk–shell catalyst remains stable upon calcination at high temperatures up to 775 K, with no change in the size and shape of the Au nanoparticles and of the structural integrity of the TiO$_2$ shell. In contrast, under similar heat treatment, the reference Au/TiO$_2$-P25 catalyst (gold nanoparticles supported on commercial P25-TiO$_2$) results in significant sintering and formation of large Au nanoparticles with diameters up to 50 nm. The catalytic results showed that the Au@TiO$_2$ catalyst is indeed quite active in promoting the oxidation of carbon monoxide, displaying comparable reaction rates, relative to the exposed surface of the gold nanoparticles, to those obtained with the traditional Au/TiO$_2$-P25 catalyst.

Lithium-ion batteries

Lithium-ion batteries (LIBs) are currently the predominant power source for portable electronics and are expected to be applied in electric vehicles in the near future because of their advantages of high energy density, long lifespan, no memory effect and environmental benignity. TiO$_2$ has been considered as a potential alternative material to the traditional graphitic carbon anode because it exhibits excellent Li-ion insertion/extraction reversibility with a low volume change (~4%) and a high operating voltage ranging from 3 to 1 V (vs. Li/Li$^+$), avoiding the formation of solid electrolyte interphase (SEI) layers and the problem of lithium dendrites, thereby yielding better battery safety [141,142]. However, practical applications of TiO$_2$ materials for LIBs still present a great challenge due to their low ionic and electrical conductivity.

Employing various nanostructured mesoporous TiO$_2$ materials, especially for those with hierarchically porous structures as anodes for rechargeable LIBs, is popular [143]. For instance, hierarchically macro/mesoporous TiO$_2$ microparticles possess an excellent initial capacity of 235 and 202 mAh g$^{-1}$ at 0.2 and 1 C, respectively [61]. The reversibility study demonstrates that the hierarchically macro/mesoporous TiO$_2$ microparticles display excellent cycling capacity, superior rate behavior and higher coulombic efficiency because the higher surface area provides more active sites and the presence of the inner-particle mesopores serve as a bicontinuous transport path and affords a shorter path length for diffusion of Li ions. The reversible capacity of 106 mAh g$^{-1}$ for the hierarchically macro/mesoporous TiO$_2$ microparticles can be retained after 200 charge–discharge cycles at a relatively high current rate of 4 C.

To improve the ionic and electrical conductivity of TiO$_2$, highly conductive carbon materials, including mesoporous carbon, carbon nanotubes and graphene, are used to combine with TiO$_2$ anodes [144,145]. Li et al. have reported the preparation of uniform hierarchically mesoporous TiO$_2$/graphene/TiO$_2$ sandwich-like nanosheets and used them as the anode of LIBs [35]. Because of the small particle size of the primary TiO$_2$, the 3D interconnected mesoporosity, the relatively thin layer and the high surface area, the obtained nanosheets deliver an extra high capacity, an excellent high-rate capability and a long cycle life. More recently, hierarchically mesoporous TiO$_2$–graphitic carbon nanocomposites have been developed for anode materials [96]. In this case, all TiO$_2$ nanocrystals in the synthesized material are conformably encapsulated in ultrathin graphitic carbon layers. Due to the high specific surface area of 298 m$^2$ g$^{-1}$, a high pore volume of 0.31 cm$^3$ g$^{-1}$, a large pore size of 5 nm and a well-defined hollow structure, the resultant materials achieve excellent electrochemical reactivity and stability. A high specific capacity of 137 mAh g$^{-1}$ can be achieved up to 1000 cycles at a current density of 1 A g$^{-1}$ (5 C). To further improve the electrochemical stability of C–TiO$_2$ anodes, for the first time, we have prepared hierarchically mesoporous TiO$_2$/TiC@C
TiC nanodots with high conductivity and electrochemical inactivity at the TiO$_2$–C interface can significantly enhance the electrical conductivity and structural stability of the C–TiO$_2$ composites. Hence, the TiO$_2$/TiC@C membranes deliver a high capacity of 237 mAh g$^{-1}$ at a current density of 0.4 A g$^{-1}$ and an ultra-long cycling life (up to 5000 cycles with over 68.4% reversible capacity retention).

Conducting polymer–TiO$_2$ nanocomposites also show great potential for anode materials. Hierarchically mesoporous polyaniline/TiO$_2$ spheres with core–shell structure show excellent performance. The discharge capacity of 123.9 and 157.1 mAh g$^{-1}$ can be obtained at the high current density of 1500 and 2000 mA g$^{-1}$, respectively. In addition, some recent reports have shown that the introduction of Ti$^{4+}$ can efficiently improve the intrinsic conductivity of TiO$_2$ frameworks [99]. Hierarchically mesoporous Ti$^{4+}$ doped TiO$_2$ hollow spheres have demonstrated excellent lithium storage performance with stable capacity retention for over 300 cycles and enhanced rate capability even up to 10 C, which is better than that of the undoped form.

**Sodium-ion batteries**

Recently, sodium-ion batteries (SIBs) have drawn great attention and would become one of the low-cost alternatives to LIBs since sodium is earth-abundant and environmental friendly. Owing to their superior safety, stability and sodium storage capability, TiO$_2$-based materials have been extensively investigated as anodes [146–149]. For example, hierarchically mesoporous TiO$_2$ nanosheets have achieved an excellent reversible capacity of 220 mAh g$^{-1}$ at 100 mA g$^{-1}$. Moreover, the capacity is retained at 44 mAh g$^{-1}$ even at a high current density of 10 A g$^{-1}$ after 10 000 cycles [41].

To further enhance the performance of TiO$_2$ materials for SIBs, it is necessary to increase their conductivity. One effective way is combination with high-conductive carbon [150]. For example, the as-obtained rod-in-tube mesoporous TiO$_2$/C nanocomposites with a uniform carbon coating have demonstrated a high discharge capacity of 277.5 and 153.9 mAh g$^{-1}$ at 50 and 5000 mA g$^{-1}$, respectively, and almost 100% capacity retention over 14 000 cycles at 5000 mA g$^{-1}$. More recently, Zhao and coworkers have reported that the rate capability and cyclability of mesoporous TiO$_2$ for SIBs can be further improved by producing mesopores in the coated carbon layers to produce the hierarchically mesoporous C–TiO$_2$ heterostructure (Fig. 13) [151]. The hierarchically mesoporous vertical heterostructure, which consists of well-ordered monolayered mesoporous TiO$_2$ nanosheets surrounded by two mesoporous carbon monolayers, provides a highly accessible surface area for effective access of electrolyte and well-defined interstices for volume strain, enabling excellent rate capability and cyclability. Moreover, a pseudocapacitive contribution of 96.4% at a low sweep rate of 1 mV s$^{-1}$ can be achieved because of the efficient electrochemical faradaic redox resulting from the efficient interfacial electron transfer.

**CONCLUSION AND PERSPECTIVES**

Undoubtedly, hierarchically mesoporous TiO$_2$ materials with various pore structures and morphologies show great potential in many fields, which can get more attention in the future. In this review, we summarized the recent advances in the controllable synthesis and applications of hierarchically mesoporous TiO$_2$ materials. The synthetic routes and formation mechanisms of hierarchically mesoporous TiO$_2$ nanosheets in
energy and environmentally related areas, such as photocatalytic degradation of pollutants, photocatalytic fuel generation, photoelectrochemical water splitting, catalyst support, lithium-ion batteries and sodium-ion batteries, are discussed in detail based on the structure–performance relationship.

However, some key scientific problems still remain in the preparation of hierarchically mesoporous TiO\(_2\) materials. Firstly, the synthetic processes and mechanisms for hierarchically mesoporous TiO\(_2\) materials require further in-depth understanding at the atomic level, laying a solid foundation to achieve the precise synthesis of hierarchically mesoporous TiO\(_2\) materials with desired structures at nanoscale, even sub-nanoscale. Therefore, developing techniques to monitor the real-time and real-space growing process of hierarchically mesoporous TiO\(_2\) materials in solution is essential. Secondly, a facile and reliable approach for the synthesis of hierarchically mesoporous TiO\(_2\) materials with...
well-controlled mesostructures, pore sizes and architectures is still in demand. A promising breakthrough is based on the super-assembly of unconventional building blocks, such as monomericelles, nanoparticles and nanoclusters. Those building blocks can act as ‘artificial atoms’ and then hierarchically mesoporous materials with complex mesostructures, like Ia3d, or morphologies, like Janus, satellite-like core-shell can be fabricated. Thirdly, the crystal phase control of hierarchically mesoporous TiO2 materials should gain more attention. Based on the theoretical prediction, there are more than 20 crystal phases of TiO2. Tuning the cross-link manner of the [TiO6] octahedron during the cooperative assembly process can produce hierarchically mesoporous TiO2 materials with new crystal phases and then change their physical and chemical properties significantly.

Concerning applications, the central task is to develop a reliable structure–performance relationship that can guide the synthesis and rational design of hierarchically mesoporous TiO2 materials. In the photocatalytic conversion area, which is the most promising for the practical application of TiO2 materials, there is still a demand for further increasing the utilization of sunlight. To this end, it is necessary to the fabrication of highly efficient heterojunctions with more complex structures such as tandem junctions with perfect band alignment and/or full-spectrum absorption. In addition, the coupling of light and electricity/heat in an integrated system is a promising method. In terms of batteries, the low conductivity and capacity of the TiO2 materials severely limit their performances. Hybridization of TiO2 materials with other components that possess a high conductivity and capacity to achieve a long cycle life, excellent rate performance and high energy density are necessary. Besides, the high surface area and porous structure of the hierarchically mesoporous material can result in side reactions and low volume energy density. Therefore, the fabrication of advanced nanostructures of hierarchically mesoporous TiO2 materials to balance the porous structure and volume energy density is very important. Furthermore, the large pore volumes make the hierarchically mesoporous TiO2 materials as ideal hosts for active materials, using hierarchically mesoporous TiO2 materials to develop novel battery systems, such as lithium–sulfur, lithium metal and sodium metal batteries, is a potential field. For catalyst support, the essential issue is the fabrication of hierarchical porous TiO2 materials with ultrahigh surface areas (>300 m2 g−1), which can facilitate the diffusion of reactants and products, thus improving the catalytic efficiency.

Overall, the development of hierarchically mesoporous TiO2 materials provides new opportunities for overcoming the energy and environmental issues in our lives. We hope that, in the future, significant breakthroughs can be made in research areas from synthetic, fundamental and practical viewpoints.

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