Nano-/microstructure improved photocatalytic activities of semiconductors

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Photocatalysis has emerged as a promising technique owing to its valuable applications in environmental purification. With the demand of building effective photocatalyst materials, semiconductor investigation experienced a developing process from simple chemical modification to complicated morphology design. In this review, the general relationship between morphology structures and photocatalytic properties is mainly discussed. Various nano-/microsized structures from zero- to three-dimensional are discussed, and the photocatalytic efficiency corresponding to the structures is analysed. The results showed that simple structures can be easily obtained and can facilitate chemical modification, whereas one- or three-dimensional structures can provide structure-enhanced properties such as surface area increase, multiple reflections of UV light, etc. Those principles of structure-related photocatalytic properties will afford basic ideology in designing new photocatalytic materials with more effective catalytic properties.

1. Introduction

Since the pioneering research of the photocatalytic splitting of water on TiO₂ electrodes by Fujishima & Honda [1], semiconductor materials with photocatalytic properties have attracted much interest as the requirements relating to increased organic pollutants become more stringent [2–7]. So far, a number of investigations
have focused on the photocatalytic activities of various semiconductors, including ZnO, TiO₂, WO₃, Si, Fe₂O₃, CdS, ZnS, SrTiO₃, SnO₂, WS₂ and so on, due to their good characteristics of strong oxidizing power, able to use visible and/or near-UV light, inexpensive and non-toxic [8–10]. However, photocatalytic activities of semiconductors are limited by several aspects, such as light absorption range, recycling of materials and production cost, and the major limitation is the high recombination rate of photoinduced electron–hole pairs that causes the relatively low value of quantum efficiency [11–17]. Therefore, enhancing the photocatalytic activity of semiconductors especially for visible-light irradiation becomes an imperative task for both the conversion of solar energy and the purification of the environment [11,18,19]. Some successful methods have been achieved and can be generally classified into two strategies which are using an organic dye as photosensitizer and doping with ions or other oxides. Both these two methods can directly modify the chemical composition of semiconductors; therefore, the photocatalytic response can be altered by chemical contents. Besides chemical methods, tuning physical morphology has also emerged as an efficient method to provide strongly enhanced photocatalytic properties by adjusting the size or structure of semiconductors.

In recent years (within the past 20–30 years), micro-/nanomaterials have drawn great attention worldwide and many efforts have been applied in a vast number of fields ranging from magnetic, electrical, optical, especially to photocatalytic activity [20–24]. Merging the micro-/nanoscience and photocatalysis fields attracted continued interest because of their contributions to light energy harvesting compared with the bulk counterpart, and are expected to provide the basis for developing new and effective devices [25–27]. Various revolutionary research studies in both scientific and engineering fields have been reported focusing on the mechanisms and methodologies of the augment of photocatalytic activities [28–32]. In this review, we discuss the relationship between structure-induced photocatalytic properties of semiconductors, through summarizing the species of the structure types of semiconductors to highlight the special photocatalytic properties that are provided by nano-/microstructure, such as size quantization effects, structure-dependent crystallization, structure-induced multi-reflection effects and so on. The structure types of semiconductor materials can be sorted as zero-/two-dimensional, one-dimensional and multi-dimensional materials, according to their structural characteristics with the order from simple to complicated. The original generation (zero-dimensional) are solid membranes, films or powders, which initially gained researchers’ attention because of their facile fabrications and easier utilization. Meanwhile, by further advancing such planar morphology involving porous or particle structures at the nanoscale, the band gap and the position of conducting and valence bands are strongly influenced, which is generally described as ‘quantum size effect’ [33–37]. The second generation can be considered as the semiconductor materials with one-dimensional well-organized geometrical shapes, such as nanorods, nanoparticles, nanowires (NWs), etc. Also hollow, porous or particle structures can be involved, which not only largely augment the surface area of the materials but also exhibit special characteristics such as higher efficiency of electron transport or easier substrate diffusion [38–41]. The third generation are semiconductors with hierarchical assemblies that combine the two- or three-dimensional structures. Such complicated structures further increase the surface area of semiconductor materials, and also show structure-induced characteristics such as multiple reflection of incident light, etc.

In this review, we will describe the synthetic techniques, the structure morphology and the structure-induced physical properties of semiconductors with photocatalytic activities. For better explanation, we categorize the semiconductors into three sorts by their structure type, and the benefits of each structure type are also illuminated. Table 1 presents the outline of this review.

## 2. Zero-/two-dimensional semiconductor materials

Basically, films and membranes are the most common and useful structures providing a two-dimensional planar morphology that can be easily covered on various substrates, and thereby
Figure 1. (a) TiO$_2$ thin films with microscaled pore structure; (b) scanning electron microscopy (SEM) image of the TiO$_2$ films composed of small nanoparticles; (c) typical SEM microphotograph of undoped TiO$_2$ particle. (Online version in colour.)

Table 1. The structure classification of photocatalytic semiconductors and their structure-enhanced photocatalytic types.

<table>
<thead>
<tr>
<th>Dimensional classification</th>
<th>Significant structures</th>
<th>Structure-induced contributions of photocatalysis</th>
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<tbody>
<tr>
<td>zero-/two-dimensional</td>
<td>powder, film, membrane</td>
<td>quantum confinement effect, easier for doping and application</td>
</tr>
<tr>
<td>with simple structure</td>
<td></td>
<td></td>
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<tr>
<td>one-dimensional</td>
<td>nanotube, nanofibre, nanorod, etc.</td>
<td>augment of surface area, quantum confinement effect</td>
</tr>
<tr>
<td>multi-dimensional</td>
<td>micro-/nano-composite structures</td>
<td>material composition, augment of surface area, multiple reflections of UV light, inner trap of pollutant</td>
</tr>
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have been widely investigated by many researchers as the fundamental model. There are several techniques to form films coated on substrates, and can be generally categorized as dry processes (including reactive pulsed laser deposition [42], magnetron sputtering deposition and physical [43] or chemical vapour deposition [44,45]) and wet processes (including sol–gel technique [46–51], hydrothermal method [52] and micro-arc oxidation [53]). Among those preparation techniques, the sol–gel technique attracted lots of attention because of its simple operating process, low cost and it being able to effect large area coating [54,55]. The initial investigation of TiO$_2$ thin-film photocatalyst took place in the early 1990s, when Fujishima’s group prepared a semitransparent TiO$_2$ film on a glass substrate by sintering a TiO$_2$ sol at 450°C. The prepared film showed extraordinarily high photocatalytic activity, even higher than that of one of the most active commercial TiO$_2$ powders, Degussa P-25 [56]. Owing to the development of special synthetic techniques, some micro-/nanostructures are being introduced into the film or membrane structures of semiconductors. For example, as shown in figure 1a, Zainal and Lee investigated the photoelectrocatalytic behaviour of sol–gel-derived TiO$_2$ thin films. The microscaled pore structures were obtained during the losing process of polyethylene glycol by heating treatment, and such sol–gel dip-coating method is effective to form well-covered and homogeneous films on the substrates [55].

Yu and Hu also prepared TiO$_2$ thin films on fused-SiO$_2$ substrates, by the sol–gel method and spin-coating technique. After calcinations, the continuous thin film was observed to consist of uniformly distributed small nanoparticles (as shown in figure 1b). Although the TiO$_2$ thin films were calcined at different temperature, the thickness of all the films was around 80 nm, and therefore showed transparent characteristics. The photocatalytic results also showed that the TiO$_2$ films prepared at 600 and 800°C possess the highest photocatalytic ability, owing to coarsening, crystal growth and spheroidizing of the TiO$_2$ grains in the films [54].

As the composition of the precursors for synthesizing films or membranes is easily controlled, transition metals [57,58] or other inorganic elements can simply be doped into films or membranes.
to further adjust the photocatalytic activities of semiconductors. For example, Sayikan and co-workers synthesized Sn-doped and undoped nano-TiO$_2$ particles by hydrothermal process at low temperature, and transparent and smooth TiO$_2$-based thin films were further prepared by spin-coating technique. The photocatalytic performance of Sn-doped TiO$_2$ thin film is higher than that of undoped TiO$_2$ film (figure 1c) [59]. Kamat and co-workers have used nanostructured semiconductor films of SnO$_2$, TiO$_2$ and SnO$_2$/TiO$_2$ for the electrochemically assisted photocatalytic degradation of the textile azo dye naphthol blue black [60]. Recently, Yu’s group synthesized a new family of lamellar transition-metal (Ni, Co) molybdate–cetyltrimethylammonium mesostructured composites by a simple chemical precipitation method, and these lamellar mesostructured composites displayed enhanced capability in decomposition of acid fuchsin [61]. Therefore, nanostructure as well as metal elements were involved in planar film forming porous or particle structures. Inorganic elements can also be doped into semiconductor materials for the potential better utilization of solar energy [62–65]. For example, Li et al. reported the synthesis of N-doped, F-doped and N–F-doped TiO$_2$ powders by spray pyrolysis and found that the N–F-doped TiO$_2$ demonstrated the highest visible-light activity [66]. Also due to the fact that films are easier to be synthesized and used, researchers usually choose such planar structures to examine the relationship between the crystal structure and photocatalytic property. For example, Yu and Hu investigated the relationship between the temperature-affected crystal structure and photocatalytic activities, finding that the anatase crystallites grow in size linearly with calcination temperature ranging from 600 to 1200$^\circ$C, and the TiO$_2$ films prepared at 600–800$^\circ$C possess higher photocatalytic ability than those prepared at 1000–1200$^\circ$C [54]. Therefore, zero-dimensional planar bulk film or membrane provides a great contribution from fundamental researches of element-doping and crystal morphology of photocatalytic semiconductors to commercial products [67–69].

The above-mentioned nanostructured semiconductors can largely promote photocatalytic activity because of their unique properties derived from low dimensionality and quantum confinement effect. Indeed, the nano-sized materials with high surface areas exhibited enhanced photoactivities, because the photo-generated electron–hole pairs could move effectively to the surface to increase the number of active sites, and therefore the photocatalytic reaction would be enhanced markedly. On the other hand, the nanoscaled structure-induced quantum size effect will also promote the photocatalytic activity. For example, Hyeon and co-workers synthesized TiO$_2$ nanorods at a large scale via a non-hydrolytic ester elimination reaction of titanium(IV) alkoxide and oleic acid. After removing the stabilizing surfactants from the TiO$_2$ nanorods without aggregation, the naked nanorods were successfully prepared, and the photocatalytic inactivation was investigated. The results showed that the band gap shift of the TiO$_2$ nanorods should be attributed to the quantum size effect governed by the diameter of the nanorods (3.4 nm) rather than by their length (38 nm). The increased band gap of the TiO$_2$ nanorods partially enhanced photocatalytic activity [70]. Therefore, the introduction of nanosize into the conventional bulk semiconductors benefits their photocatalytic behaviour in a physical aspect. When downsizing the crystallite dimension of semiconductor particles up to several nanometres, the charge carriers appear to behave quantum mechanically [71–79], resulting in the increase of band gap and the shift of band edges to generate larger redox potential. Several studies have already found that using size-quantized semiconductors can enhance photoefficiencies [80–84], although other works showed that photoactivities of size-quantized semiconductors decreased compared with their bulk-phase counterparts [81,85]. Such phenomenon should be attributed to the competition relationship between the positive effects of increased potential on quantum yields and the unfavourable surface speciation and surface defects formed during the preparation processes of semiconductor particles [86–88].

3. One-dimensional semiconductor materials

Since the development of modern synthetic technologies and morphology observation equipment, various novel morphologies of nano-/microstructured semiconductors have been
prepared [89–92]. One-dimensional semiconductors, which possess nanoscaled section diameter and micro- or macroscaled length, have attracted considerable attention recently owing to their enhanced photocatalytic activities.

The basic category should be solid nanostructured semiconductor materials that are composed of the simplest units such as NWs and nanorods. For example, Yoshikawa’s group synthesized TiO$_2$ NWs by the hydrothermal treatment of commercial TiO$_2$ powders (the scanning electron microscopy (SEM) structure is shown in figure 2a); meanwhile, the effect of post-heat-treatment temperature on the phase structure, morphology and photocatalytic activity for hydrogen evolution was investigated. Although the apparent one-dimensional morphology of TiO$_2$ NWs was thermally stable at any post-heat-treatment temperature, they presented different crystal structures from TiO$_2$(B) NWs (at approx. 300°C), to anatase-type (at approx. 500°C) to rutile-type (at more than 900°C). The order of the photocatalytic activity for H$_2$ evolution is: TiO$_2$ anatase > TiO$_2$ rutile ≥ TiO$_2$(B) > hydrogen titanate [93]. Recently, Yu’s group prepared ultralong orthorhombic silver trimolybdate NWs with well-dispersed Ag nanoparticles by a simple hydrothermal process [94].

Hafez reported the large-scale synthesis of pure anatase TiO$_2$ nanorods (figure 2c) using a simple and low-cost modified hydrothermal method. The porous single-crystal TiO$_2$ nanorods have a good size distribution (approx. 4–16 nm) with the dimensions of 200–300 nm in length and of 30–50 nm in diameter, which resulted in high Brunauer–Emmett–Teller (BET) specific area of 85.2 m$^2$ g$^{-1}$, and showed better environmental photocatalysis compared with their precursor nanostructures: (anatase/rutile) TiO$_2$ nanoparticles and titanate nanotubes (figure 2b) [95].

Various novel structures were introduced recently, because the nanostructures can largely enhance the photocatalytic activities of semiconductors. Wang’s group reported a nanosheet morphology of titanium acid H$_2$Ti$_2$O$_5$·H$_2$O prepared by doping Zn$^{2+}$ into Ti–O crystal structure through the hydrothermal method (figure 3a). Although the decomposition ratio of methyl orange solution with H$_2$Ti$_2$O$_5$·H$_2$O is slightly lower than that with TiO$_2$, the unique layer structure may still find much wider potential applications [96]. Xu and co-workers prepared uniformly sized anatase TiO$_2$ nanocrystallites with cuboidal morphology by changing titanium hydroxide precipitates into their corresponding ethanol gels, and then dried in supercritical ethanol and calcined at high temperature (figure 3b). This work also demonstrated that good crystallization of the material is crucial to photocatalytic ability, which was proved by the fact that increasing the calcination temperature up to 800°C improved the crystallization and further increased the photocatalytic activities [97]. Chen and co-workers synthesized pure brookite TiO$_2$ nanoflowers consisting of single crystalline nanorods by using a facile one-step hydrothermal process (figure 3c). The anatase, brookite and titanate can be adjusted by the concentration of NaCl during the hydrothermal treatment process, and the brookite nanoflowers exhibited remarkable photoactivity [98]. Caruso and co-workers demonstrated the novel use of a polymer gel template to produce TiO$_2$ networks with high porosity, which can be adjusted by the polymer gel properties from tens of nanometres to micrometres in diameter (figure 3d). Such open ‘coral-like’ network structure allows high access of the TiO$_2$ surface to the reaction medium, and shows high photocatalytic activity [99].
Furthermore, hollow structures were involved in one-dimensional morphology; therefore, nano-/microtubes, hollow spheres and core–shell structures were widely investigated. Chen’s group prepared long TiO$_2$ hollow fibres with mesoporous walls by the sol–gel two-capillary spinneret electrospinning technique (figure 3e(i)-(ii)). The porous fibres were as long as 30 cm with diameters of 0.1–4 µm and wall thicknesses of 60–500 nm, giving a BET surface area of 200–208 m$^2$ g$^{-1}$ and an average pore size of 6.7 nm. These TiO$_2$ hollow fibres with mesoporous walls showed higher photocatalytic activities than commercial TiO$_2$ nanoparticles and corresponding mesoporous TiO$_2$ powders [100]. Crittenden’s group also reported the preparation of a novel TiO$_2$-based p–n junction nanotube which combines the hollow structure and core–shell structure together. Platinum was contained in the hollow inner space of the

**Figure 3.** (a) Transmission electron microscopy (TEM) image and selected area electron diffraction pattern of as-prepared H$_2$Ti$_2$O$_5$·H$_2$O with nanosheet structure. (b) TEM image of TiO$_2$ nanocuboids. (c) Field emission SEM image of brookite TiO$_2$ nanoflowers. (d) SEM image of TiO$_2$ networks with homogeneous pores. (e) SEM images of xerogel (i) and TiO$_2$ (ii) hollow fibres. (f) SEM images of hollow TiO$_2$ microsphere structures synthesized with the aerosol-assisted flow synthesis method: (i) B-doped and (ii) Ni-doped.
TiO$_2$-based nanotubes by a template and removing process. In this case, a p–n junction was built, and the electrons can move more freely in the platinum leaving more valence band holes in the TiO$_2$ [101].

Lee’s group synthesized highly effective B-doped, Ni-doped and B–Ni-codoped TiO$_2$ microsphere photocatalysts via an aerosol-assisted flow synthesis method. The hollow structure (figure 3f(i)(ii)) was attributed to the escape of gas phase HBO$_2$ from the interior part of the TiO$_2$ microspheres during the pyrolysis reaction. The photocatalysis was enhanced, because the doping samples showed obvious red shift in their absorption edges [102].

Semiconductor materials of one-dimensional structure such as nanofibres and NWs, especially those with hollow structures such as nanotubes and hollow spheres, can also provide physical-enhanced photocatalytic activities besides enlarged photocatalytic surface area [38–41]. Tachikawa et al. have prepared titania nanotubes by digesting titania nanoparticles (e.g. P-25) under strong conditions in an autoclave [103]. Laser flash photolysis results showed that the half-life of the photo-generated holes was obviously longer for titania nanotubes compared with nanoparticle structures. Homoplastically, Yanagida et al. also claimed that the electron transport in titania nanotube electrodes was efficiently higher than in electrodes prepared with nanoparticles [104]. This should be attributed to the low dimensionality of the nanotube structures which resulted in the higher diffusion length of charge carriers. The results of parallel photocatalytic experiments in the presence or the absence of air revealed that the nanotube structures can generate more trapped electrons [103]. Schmuki and co-workers also claimed that the ordered tubes provide higher photocatalytic efficiency compared with P-25 films, and suggested that such a difference is due to an optimized photocatalyst geometry that favours substrate diffusion and diminishes the charge carriers [105]. Schmuki and co-workers reported that the potential of low dimensional hollow morphology in photocatalysis is very good, although more evidence is desirable. Therefore, improving the photocatalytic activities of semiconductors simply by changing the shape and dimension of materials has prodigious investigation values [106].

4. Multi-dimensional semiconductor materials

With the further development of synthetic techniques, hierarchical semiconductors with multi-dimensional morphology were fabricated with the expectation of better photocatalytic activities. The primary structure of these materials is based on nano- or microscaled aggregations, and then nanoparticle, nanoporous or other nanoscaled units comprise of the secondary structure. Therefore, the multi-dimensional semiconductor materials usually have micro-/nanocomposite structures, which will definitely further improve the surface area to promote the photocatalytic activities. Recently, many scientists focused their attention on the formation of multi-dimensional semiconductors and demonstrated that the catalytic process would occur more efficiently in hierarchical structures.

Through an electrospinning-assisted route, Wang and co-workers synthesized a three-dimensional Bi$_2$WO$_6$/TiO$_2$ hierarchical heterostructure. The Bi$_2$WO$_6$ nanoplates consist of nanoparticles with a size of less than 20 nm grown slantingly on the primary TiO$_2$ nanofibres. Compared with the bulk Bi$_2$WO$_6$/TiO$_2$ powder, the Bi$_2$WO$_6$ nanoparticles and the TiO$_2$ sample, the as-prepared hierarchical nanofibrous mat exhibited enhanced visible photocatalytic activity due to the structure–property relationships, including the surface area, grain size and hierarchical heterostructure (figure 4a) [107].

Yu and co-workers synthesized hierarchical nanoporous F-doped TiO$_2$ spheres by a one-step low-temperature hydrothermal approach. Therein, titanium tetrafluoride was used as both a source of fluorine doping and a precursor of titanium. During the hydrothermal process, HF was generated and created a localized HF-rich zone around the TiO$_2$ particles, which provided the nucleation centre and the chemical etching of the hydrolysis products; therefore, the hierarchical porous F-doped TiO$_2$ spheres were obtained. The as-prepared F-doped TiO$_2$ porous spheres
showed high photocatalytic activities, not only because the fluorine dopant shifted the optical absorption edge of TiO$_2$ to lower energies to enhance the photoactivities under visible light, but also it provided excellent adsorptive properties of chemical reactant, because the porous structure made it easy for molecules to move into or outside (figure 4b) [108].

Kale and co-workers prepared pretty marigold-like CdIn$_2$S$_4$ nanostructures and nanotubes using a hydrothermal method. The formation of the spherical (marigold flower) structure was mainly attributed to the geometric building blocks, because a simple array of such crystals (petals) will easily generate curvature and develop into a marigold-like structure. After the CdIn$_2$S$_4$ nanotube was formed in the methanol-mediated reaction, the curvature of the petals was further accelerated by the hydrothermal conditions. As the fascinating structure showed good crystallinity, H$_2$ production under visible-light irradiation was quite excellent and higher than those reported previously (figure 4c) [109].

Highly hierarchical plate-like FeWO$_4$ microcrystals have been synthesized by Yu and co-workers through a simple solvothermal route. The as-prepared product was composed of uniform hexagonal plate-like microcrystals, each of which was composed of six nearly equal petals. Both the ethylene glycol and the concentration of CH$_3$COONa used in the preparation played an important role in the formation of plate-like FeWO$_4$ microcrystals, because the former can affect the solubility, reactivity and diffusion behaviour of the reagents, and the latter provides a basic environment for the formation of FeWO$_4$ microcrystals. The hierarchical FeWO$_4$ microstructures showed excellent photocatalytic activity in the degradation of organic contaminants under exposure to UV and visible-light irradiation (figure 4d) [110].

Zhang and co-workers reported hierarchical BiOX (X = Cl, Br, I) nanoplate microspheres that were synthesized by a general one-pot solvothermal process. The formation process of such hierarchical BiOX nanoplate microspheres was proposed to have three steps: first, the formation of BiOX nanoparticles; second, the ethylene glycol-induced self-assembly of primary nanoplates to form loose microspheres; third, the formation of regular hierarchical microspheres. Compared with TiO$_2$ (Degussa, P-25) under UV–visible light irradiation and C-doped TiO$_2$ under visible light, BiOI exhibited the most excellent activity under both UV–visible and visible-light irradiation because of its suitable band gap (figure 4e) [111].

Wu and co-workers synthesized facile and bioinspired ZnO hierarchical architectures, including prism-like and flower-like structures and crystalline and non-crystalline hollow microspheres, with the assistance of the amino acid histidine (His) under mild conditions. It is well known that histidine coordination to Zn$^{2+}$ is a structural motif of zinc finger proteins [112–116], and histidine molecules play different roles in the formation and self-assembly of ZnO hierarchical architectures, owing to the competitive coordination between the histidine and OH$^-$ to Zn$^{2+}$ when the reactant molar ratios were adjusted. When Zn$^{2+}$/NaOH molar ratio is 1:22, OH$^-$ plays the crucial role in controlling the growth, resulting in the formation of the anisotropic prism-like ZnO (figure 4f(i)). When Zn$^{2+}$/NaOH molar ratio is changed to 1:10 and 1:2.5, histidine molecules, as the competitive ligand of OH$^-$ to Zn$^{2+}$, adsorb on the surface of ZnO nuclei and result in the formation of flower-like structures and nanoparticles (figure 4f(iii)), which further self-assembled into the hollow microspheres (figure 4f(iii)). When the Zn$^{2+}$/His molar ratio is changed to 1:2, ZnO nuclei are covered by the histidine molecules, which prevents further crystallization and results in the formation of the non-crystalline hollow microspheres (figure 4f(iv)). The as-prepared ZnO hierarchical architectures could photocatalyse the reaction of HCHO and CO$_2$ [117].

Xie’s group synthesized a nanoplate-built hierarchical nest-like structure of Bi$_2$WO$_6$ by a facile and economical method in the presence of polyvinyl pyrrolidone, which acts as a selective crystal face inhibitor to align the nanoplates. During the formation of submicroscaled solid spheres by the aggregation of small primary nanocrystals, the free polymer molecules absorbed on the face of the submicroscaled solid spheres, which may provide many high-energy sites for further growth with prolonged hydrothermal treatment. Then, the hollow structures formed by growing of the submicroscaled solid spheres gradually inside the unstructured polymer aggregates.
The hierarchical nest-like structure Bi$_2$WO$_6$ not only showed high photocatalytic activity but also exhibited a favourable discharge capacity in a lithium-ion battery [118].

Yu’s group prepared a hierarchical macro/mesoporous titania using a micelle-templated method by the dropwise addition of tetrabutyl titanate to distilled water [119]. By hydrolyzation of tetrabutyl titanate in pure water, the water channels and the microphase-separated regions of TiO$_2$ particles were spontaneously radially patterned. The as-prepared hierarchical TiO$_2$ materials were calcined at different temperature, and the photocatalytic activities were evaluated. The results revealed that the hierarchical titania calcined at 300°C showed the most effective photocatalytic activity because of the best hierarchical macro-/mesoporous morphology and the largest specific surface area.

The major causation of the enhanced photoactivities of such complicated multi-dimensional semiconductors is still the augment of BET values compared with zero- or one-dimensional structures. However, besides surface area growth, such complicated structure of the multi-hierarchical materials also provides additional structure-induced properties such as extending the light absorption area into the visible region. For example, photonic crystals have been reported to promote light absorption by increasing the reflection of the light path when the incident light
passes through the material [120–124]. The regularly ordered photonic crystals meant that it was difficult for the incident light to escape but was easily trapped inside the crystals when entering through them, and resulted in a multitude of reflections and diffractions. Therefore, the photonic crystal arrangement increased the probability of light absorption and charge separation by increasing the incident light contact time. On the other hand, inverse opals were reported to slow down photons and enhance the photocatalytic activities, because the dimension of the monodisperse empty spheres caused a light stop band at the wavelength relevant to the dimensions of the spheres [125]. Correspondingly, Jiang’s group synthesized submicrosized multichannel TiO₂ fibres by multifluidic compound-jet electrospinning (figure 5a), which contain immiscible multichannel inner fluids and outer fluids. By removing the inner fluids through calcinations, the hollow multichannel structure was formed with controllable channel numbers by controlling the channel number of inner fluids. The photocatalytic activity evaluation revealed that the hollow structure can largely enhance the photoactivity because of the augmentation of surface area, and the hollow structure can also offer a cooperative effect of trapping more gaseous molecules inside the channels and multiple reflection of incident light [126]. Lu and Li reported the synthesis of hollow titania spheres with tunable interior structure and urchin-like morphology by a template-free approach (figure 5b), in which a titania precursor solvothermally reacted in glycerol, alcohol and ethyl ether. The photocatalytic activity results revealed that such unique structure can largely enhance the catalytic ability, because the sphere interior voids induced multiple reflections of UV light [127].

5. Conclusions

With the development of synthetic technology, several modification techniques and chemical additives have been developed to prepare semiconductors with various morphology from simple zero-dimensional to multi-dimensional. In addition, the research focuses experienced a transition from chemical doping to physical morphology designing to obtain better photocatalytic ability. In this review, the relationship between the photocatalytic properties of semiconductors and their physical microstructures was mainly discussed. An increasing amount of research has indicated that micro-/nanostructures can induce enhanced photocatalytic properties owing to their special configuration characteristics, revealing that one of the most important research areas in the future is the construction of micro-/nanocomposite materials. With the development of designing complicated structures of semiconductors, photocatalytic properties will be improved correspondingly; therefore, both experimental research and industrial applications will be benefited accordingly.

Funding statement. The authors thank the National Natural Science Foundation of China (grant nos. 21101010, 21222309, 21134003, 21004002), 973 Programme (nos. 2012CB933200, 2010CB934700, 2009CB30404) for continuing financial support.
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