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# 1. Introduction

## With globalization, industrialization and manufacturing is expanding at an alarming rate in the past century, and this has caused some serious problems to the world's population. The supplies of natural energy sources such as oil and gas are depleting faster than expected and will be emptied within the next 50 years. The extensive use of these energy sources has also produced tonnes of waste, polluting the environment and altering the climatic conditions. This has brought about a need for renewable sources of clean energy, and also technologies capable of cleaning the environment.<sup>1</sup> Photocatalysts can be the answer to this calamity that is staring mankind in the face. On exposure to sunlight, solar energy can be absorbed by the photocatalyst to produce hydrogen $(H_2)$ from photocatalytic water splitting<sup>2</sup> and also degrade organic pollutants,<sup>3</sup> paving the way to a clean and renewable source of energy in a cleaner environment.

 $TiO_2$  is a photocatalytic material that has been used for a long time.<sup>4</sup> It is stable, non-toxic, environmentally friendly, cheap and easily synthesized at low temperatures.<sup>2,5,6</sup>

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TiO<sub>2</sub>-based photocatalysts, being inexpensive and abundant, in conjunction with having high photostability and environmentally friendly characteristics, are the most extensively studied photocatalytic material for hydrogen production and pollutant degradation. However, its existing issues, such as wide bandgap, high overpotential and rapid recombination of photogenerated carriers limit its photocatalytic properties. The opportunities for structural development of a TiO<sub>2</sub> nanomaterial towards highly efficient and pragmatic photocatalysis applications are evidently plentiful. Hence, in this review, we will look into critical structural engineering strategies that give favorable physicochemical properties such as improved light absorption, photostability, charge-carrier dynamics, increase surface area *etc.* that benefit photocatalysis functionalities. Amongst the various structural engineering options, we will be covering the most prevalent and elegant core-shell and hierarchical structural designs, which rationally combine the advantages of structural manipulation and multi-material composition engineering. This review aims to provide a comprehensive and contemporary overview, as well as a guide of the development of new generation TiO<sub>2</sub> based photocatalysts *via* structural design for improved solar energy conversion technologies.

> However, it has a wide bandgap, limiting its photocatalytic functionality to the UV region of the spectrum. Nonetheless, TiO<sub>2</sub> based photocatalysts are still the most extensively studied materials for the photocatalytic production of H<sub>2</sub> and degradation of pollutants. The enhancement of TiO<sub>2</sub> materials for photocatalytic application lies heavily on the catalyst design and hence warrants a fundamental understanding of all the key objectives of various structural designs for photocatalysis.<sup>7,8</sup> Here, we will review the various structural engineering strategies employed to overcome the drawbacks of TiO<sub>2</sub> for improved photoactivity. The review will cover the least to the most elaborate structural design *i.e.* basic nanoscale structures, core-shell structures and lastly hierarchical structures. We will focus our attention on the effects of various structural designs on the chemical and physical properties of TiO<sub>2</sub>, ranging from light absorption, surface area and charge-carrier dynamics to photostability. Our goal is to provide a comprehensive background towards rational structural engineering of photocatalysts and provide a guide for future structural design of a nanoscale catalyst for photocatalytic H<sub>2</sub> production and degradation applications.

### Photocatalytic reactions on TiO<sub>2</sub>

When  $TiO_2$  is illuminated with UV light, the absorbed photons excite the negatively-charged electrons from the valence band (VB) to the conduction band (CB), leaving behind a



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positively-charged hole in the VB as shown by the following expression:

$$\operatorname{TiO}_2 + h\nu \to \operatorname{TiO}_2(e^-) + \operatorname{TiO}_2(h^+)$$
(1)

A portion of the photogenerated electrons and holes will undergo recombination in the bulk and at the surface.9 However, the electrons and holes that managed to reach the surface of TiO<sub>2</sub> without recombination will reduce and oxidize the reactants adsorbed on the TiO<sub>2</sub> surface. The reduction and oxidation reactions are the basis of photocatalytic H<sub>2</sub> production and photodegradation of organic pollutants, respectively (Fig. 1). For water splitting, the CB level should be more negative than the redox potential of  $H^+/H_2$ , while the VB level should be more positive than the redox potential of O<sub>2</sub>/H<sub>2</sub>O. The photogenerated holes oxidise H<sub>2</sub>O to form O<sub>2</sub> gas while the electrons reduce the  $H^+$  ions to produce  $H_2$ , as shown by eqn (2) and (3), respectively. In the photodegradation of organic compounds, the generated electrons react with dissolved oxygen molecules and produce oxygen peroxide radicals (eqn (4)), while the positively charged holes (h<sup>+</sup>) react with OH<sup>-</sup> derived from H<sub>2</sub>O to form hydroxyl radicals OH' (eqn (5) and (6)). O2' and OH' are powerful oxidizing agents capable of degrading most pollutants.<sup>10,11</sup> The organic compounds can be photodegraded by the  $O_2$  and OH' radicals to  $CO_2$ ,  $H_2O$ , or other mineralization (eqn (7)).

$$4h^{+} + 2H_{2}O \rightarrow O_{2} + 4H^{+}$$
(2)

$$2e^{-} + 2H^{+} \rightarrow H_{2} \tag{3}$$

$$e^- + O_2 \to O_2^{*-} \tag{4}$$

$$h^+ + OH^- \to OH' \tag{5}$$

$$h^+ + H_2O \rightarrow OH' + H^+ \tag{6}$$

 $O_2$  or OH + organic pollutants  $\rightarrow$  degradation products (7)



Fig. 1 Schematic representation of the position of CB and VB of  $TiO_2$  and the redox potentials vs. NHE at pH 0.

# 2. Basic structures of TiO<sub>2</sub>

Many studies have focused on modifying the structures of  $TiO_2$  on the nanoscale in order to improve its photocatalytic activities. Fig. 2 shows that nanostructured  $TiO_2$  can exist in various dimensions and morphologies, namely zero-dimensional  $TiO_2$  nanoparticles; one-dimensional  $TiO_2$  nanofibers, nanorods, nanowires, nanobelts and nanotubes; two-dimensional  $TiO_2$  nanosheets and nanoplates; and three-dimensional hierarchical and interconnected architectures. These  $TiO_2$  materials of various morphologies do not only improve their photocatalytic properties, but also provide suitable platforms to incorporate other materials such as noble metals,<sup>12–18</sup> transition metals or metal oxides,<sup>19–27</sup> carbon-based materials<sup>28–34</sup> and semiconductors<sup>1,35–39</sup> for maximizing the photocatalytic efficiency.

There are a few parameters of TiO<sub>2</sub> basic structures that affect the photocatalytic performance, which include size, crystallinity, surface to volume ratio and surface chemistry. Optimizing the size of TiO<sub>2</sub> nanoparticles has been shown to maximize photocatalytic activities due to their specific sizerelated properties.<sup>40</sup> The energy band structure becomes discrete for nanometer-scale TiO<sub>2</sub> with its photophysical, photochemical, and surface properties being quite different from those of the bulk counterpart, due to the quantum size effect.41 Moreover, smaller photocatalysts reduce electronhole recombination due to shorter charge transfer distances.<sup>42</sup> The diffusion length of charge carriers has to be longer than the particle size to achieve efficient chargecarrier dynamics. The size-dependent stability of various TiO<sub>2</sub> phases has been reported.<sup>4,43</sup> The TiO<sub>2</sub> rutile structure is relatively stable in nanoparticles larger than 35 nm, while the anatase structure is more stable in nanoparticles larger than 11 nm.<sup>44,45</sup> On the other hand, the photocatalytic activity is compromised when the nanoparticles are decreased to less than several nanometers due to the dominant electron-hole



Fig. 2 Schematic diagram of  $TiO_2$  nanostructures according to structural dimensionality.

recombination on the  $TiO_2$  surfaces.<sup>43</sup> Moreover,  $TiO_2$  of higher crystallinity is adopted to facilitate photogenerated charge transfer. Therefore, calcination at appropriate ambient temperature is often carried out to improve the crystallinity and hence induce lower defect density.

Furthermore, a higher surface to volume ratio of nanostructured materials can help to increase photocatalytic efficiency. A larger surface area increases the number of surface sites available to catalyze the reaction, thus enhancing reactant adsorption and product desorption. Compared to the most common nanostructured TiO<sub>2</sub>, such as the commercial TiO<sub>2</sub> nanoparticles (P25), TiO<sub>2</sub> with modified morphologies, such as nanotubes,<sup>46-49</sup> nanofibers,<sup>50,51</sup> nanorods,<sup>52-55</sup> foams,<sup>56,57</sup> and mesoporous structures<sup>58-61</sup> have larger surface area. It has been demonstrated that the photoconversion efficiency of TiO<sub>2</sub> nanotubes is almost twice that of spherical nanoparticles.<sup>62</sup> However, a large surface with dangling bonds may have different potential states, which cause it to act as a recombination center of the excited carriers.<sup>63</sup> Therefore, an increase in the surface area is also possible, leading to a decrease in the photocatalytic activity.

In addition, two-dimensional nanoplate and nanosheet structures have also been explored for improved photocatalytic activity by maximizing the active facets of TiO<sub>2</sub>. Both theoretical and experimental studies indicate that the {001} of anatase TiO<sub>2</sub> is much more reactive than the thermodynamically stable {101} facet.<sup>64,65</sup> Yang et al.<sup>66</sup> developed a method to synthesize high-purity anatase TiO<sub>2</sub> single crystals with a high percentage (47%) of {001} facets using hydrofluoric acid as a morphology controlling agent. Subsequently, synthesis of sheet-like anatase TiO2 single crystals with as much as 90% exposed {001} facets has been demonstrated.67-69 Surface area is another important parameter in optimizing the number of reaction sites available for photocatalysis. Thus, increasing both the surface area and active crystal facet are considered for the design of efficient photocatalysts. Hu et al.<sup>70</sup> reported ultrathin highly active {001} facets and high specific surface area (162.4 m<sup>2</sup> g<sup>-1</sup>) TiO<sub>2</sub> nanosheet superstructures, which has shown a two times increase in photodegradation efficiency as compared to P25.

Other three-dimensional TiO<sub>2</sub> structures based on intrinshape-dependent sic properties, such as hollow structures,<sup>71-76</sup> interconnected structures,<sup>28,77-80</sup> and hierarchical superstructures<sup>81-84</sup> built up from lower-dimensional building blocks have also been reported as an efficient photocatalyst. These structures not only possess a high surface area to volume ratio due to the formation of voids amongst the nanobuilding blocks,85 but also possess unique optical and carrier transfer properties, which will be discussed in detail later. A new generation photocatalyst based on nanoscale structural manipulation is of particular interest as many of these architectures have distinctive physicochemical properties favorable for photocatalysis applications. Amongst the structural engineering strategies, coreshell and hierarchical structuring of a photocatalyst is a prevailing approach for overcoming the drawbacks of pure TiO<sub>2</sub> in photocatalysis. Hereafter, we will be focusing on structural designs and functions of core–shell and hierarchical TiO<sub>2</sub>-based nanostructures for photocatalysis and provide an overview of designing next generation highly efficient TiO<sub>2</sub>-based photocatalysts.

# 3. Core-shell structures

Among the numerous structural designs, core-shell nanocomposites have attracted considerable attention and developed into an increasingly important research area for photocatalytic applications. Core-shell structures generally feature a chemical composition on the surface that is different from the core, thus exhibiting improved photocatalytic properties as compared to their single-component counterparts. The major functions of the core-shell structure for improving the performance of photocatalysts are shown in Fig. 3. They comprise of (i) prevention of undesired migration or dissolution to improve physical structure stability, (ii) deterrence of undesirable aggregation or corrosion during photocatalytic reactions, (iii) activation of unique optical properties, (iv) provision of three-dimensional contact between the shell and the core, which maximizes the core-support interaction in terms of charge transfer and localized surface plasmonic effect, (v) encapsulation of magnetic materials for recycling, and (vi) design of multi-functional photocatalysts.

Depending on the different functions of each material in a core-shell photocatalyst, controlled synthesis over shell thickness, porosity and uniformity is important to produce efficient core-shell photocatalysts. The photocatalytic TiO<sub>2</sub> shell is designed with high active surface area, controlled porosity, and optimized thickness for desired purposes.



Fig. 3 Schematic diagram of core-shell structured photocatalysts according to their functions.

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Different morphologies of TiO<sub>2</sub> can be adopted to further improve its surface area, crystallinity, ratio of active facets and accessibility to the reactants. The inner layers of shell can be used as either an interactive layer or isolation layer, and sometimes both. In the case of the interactive layer, the three-dimensional confinement of the shell allows stronger interaction between different materials for either charge transfer, photon transfer, or energy transfer. When the inner shell is used as an isolation layer, it provides perfect insulation to prevent interaction between different materials, or to protect the inner material from photocorrosion and improve stability. The thickness of this layer also needs to be well controlled so that it achieves its desired function, at the same time not diminishing the functionality of other composition. When the inner layer has dual functions, it is critical to control the shell thickness, as the coating thickness can be used to tune the properties of the inner core that consists of plasmonic metals, upconversion crystals and magnetic materials. Moreover, various structures beyond simple core-shell configuration, such as yolk-shell, hollow multiple shells, multicore-shell and multicomponent core-shell structures allow many other functions to be incorporated, such as unique optical properties, synergistic effects and recycling of the photocatalysts. Core-shell structures have the flexibility to systematically tune the structures, and thus the functions of the photocatalysts. Through rational design and controlled synthesis of TiO<sub>2</sub> composite core-shell structures with multiple components and well-controlled interactions, they are likely to bring many novel and enhanced benefits to photocatalytic reactions.

### 3.1 Structural stability

Core-shell structures provide a platform for synthesizing well-controlled structures with high stability.  $TiO_2$  shells can be synthesized on sacrificial template or catalyst materials to form either core-shell (Fig. 4a), hollow (Fig. 4b), yolk-shell (Fig. 4c and d) or double-shell (Fig. 4e and f) structures. Various shapes of cores have also been used, such as nanoparticles (Fig. 4g and h), nanorods (Fig. 4i–l) and nanocubes (Fig. 4m). Moreover, more complex core-shell structures have also been synthesized, such as multiple-shell structures with (Fig. 4n) and without an inner cavity (Fig. 4o and p).

**3.1.1 Controlled synthesis.** Hollow spheres become an intensive area of research for the structural design of photocatalysts. The porous shell of  $TiO_2$  hollow structures possesses a high specific surface area with a large number of active reaction sites, reduced diffusion distance of photogenerated charge carriers, and improved accessibility to reactants through the porous shell. The challenge for developing efficient  $TiO_2$  hollow photocatalysts lies in the precise control of its structural properties. There are two synthetic approaches, namely template-free and template-assisted methods. Although the template-free method is simple and convenient from a synthetic point of view, they are usually carried out under high temperature and pressure, and it is



**Fig. 4** TEM images of various TiO<sub>2</sub>-based core-shell nanostructured photocatalysts. (a) SiO<sub>2</sub>@TiO<sub>2</sub> core-shell structures, (b) mesoporous TiO<sub>2</sub> hollow nanostructures, (c) SiO<sub>2</sub>@TiO<sub>2</sub> yolk-shell structures, (d) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@TiO<sub>2</sub> yolk-shell nanoparticles, (e) double-shell anatase-rutile TiO<sub>2</sub> hollow spheres, (f) hollow SnO<sub>2</sub>/TiO<sub>2</sub> coaxial nanofibers, (g) Au@TiO<sub>2</sub> core-shell particles, (h) Au<sub>multi</sub>@TiO<sub>2</sub> multiple core-shell particles, (i) gold nanorod@TiO<sub>2</sub> yolk-shell nanostructures, (j) NaYF<sub>4</sub>: Yb,Tm,Gd microrods@TiO<sub>2</sub> core-shell composite, (k) NaYF<sub>4</sub>:Yb,Tm,Gd nanorods@TiO<sub>2</sub> core-shell composite, (l) TiO<sub>2</sub> coated Au/Ag nanorods, (m) cubic Pd@TiO<sub>2</sub> core-shell structures, (n) ellipsoidal  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@TiO<sub>2</sub> yolk-shell structures, (o) SiO<sub>2</sub>-Ag-SiO<sub>2</sub>-TiO<sub>2</sub> triplex-shell structures, (p) Ag@Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@TiO<sub>2</sub> multiple-shell structures. Adapted from ref. 91, 104, 105, 115, 118, 129, 132 and 133 with permission. Copyright Royal Society of Chemistry and WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

quite difficult to control the thickness, porosity and crystallinity of the shells.<sup>60</sup> On the other hand, template-assisted methods are more common and universal processes for synthesizing TiO<sub>2</sub> hollow photocatalysts with well-controlled structural properties.<sup>76,86,87</sup> The basic process involves preparing a sacrificial template and depositing the nanoscale TiO<sub>2</sub> shell layers to form the core-shell structure, followed by post-crystallization and selective etching to remove the sacrificial template to form hollow TiO<sub>2</sub> shell nanostructures (Fig. 5a). Zhang et al.<sup>76</sup> and Joo et al.<sup>72</sup> both synthesized hollow TiO<sub>2</sub> structures based on this process by using carbon nanospheres and SiO<sub>2</sub> colloid as sacrificial templates, respectively. They both demonstrated the crystallinity and phase of hollow TiO<sub>2</sub> spheres with optimized crystallinity, which outperforms P25 in photocatalytic dye decomposition. Lu and co-workers<sup>88</sup> reported a method to fabricate mesoporous anatase TiO<sub>2</sub> nanocup crystals through further etching treatment of hollow TiO<sub>2</sub> spheres using NaOH (Fig. 5b). The assynthesized cup-like anatase TiO2-based photocatalyst exhibits relatively high conversion efficiency of solar energy to photodegradation compared with hollow TiO<sub>2</sub> spheres and conventional P25, due to its high surface area, mesoporous



**Fig. 5** Different synthesis methods to create hollow TiO<sub>2</sub> structures: (a) hollow spheres; (b) nanocups; (c) hollow spheres with surfaceprotected etching method; (d) double-shell hollow spheres; (e) coreshell structure; (f) yolk-shell structure (PAN: polyacrylonitrile).

 $TiO_2$  shell structure, the highly active anatase {101} facet and improved light harvesting ability. Other template-assisted methods have also been developed to produce hollow TiO<sub>2</sub> spheres that aim to provide a more controllable way to retain their structures. For example, the surface-protected etching method (Fig. 5c), in which an additional silica layer was coated onto the TiO<sub>2</sub> surface to prevent breakage of the shell and inhibit extensive structural changes.<sup>60</sup> Another example is the nanoparticle-mediated approach, which has high synthetic flexibility for tailoring complex shelled nanostructures with different architectural designs (Fig. 5d).<sup>89</sup> These various forms of hollow structures show the highly active surface area, high crystallinity and porous shell that are responsible for improved photocatalytic performance. The core-shell scheme provides a simple method to synthesize these hollow TiO<sub>2</sub> structures with high surface area and well-controlled structural properties, which are beneficial for photocatalytic applications.

3.1.2 Anti-migration and dislodging of catalysts. A typical synthesis of core-shell structures involves coating a layer of  $TiO_2$  onto the catalyst particles (Fig. 5e), while an additional sacrificial intermediate layer is needed for making yolk-shell structures (Fig. 5f). Both core-shell and yolk-shell nanostructures, with nanoparticles encapsulated and protected by an

outer shell, can be used to isolate the catalyst nanoparticles and prevent their migration and dislodging during the photocatalytic reactions. Many groups have demonstrated the advantages of structural stability in these core-shell structures towards improving photocatalytic activities.<sup>60,90,91</sup> Our group<sup>91</sup> investigated the photocatalytic stability of three samples (Fig. 6a) of Au on TiO<sub>2</sub> and Au@TiO<sub>2</sub> single (Fig. 4g) and multiple (Fig. 4h) core-shell nanospheres through three cycles of a two hour sacrificial water splitting experiment. The Au on TiO<sub>2</sub> shows a decrease of 33% in H<sub>2</sub> evolution due to leaching, whereas the Au@TiO2 single and multiple coreshell nanospheres exhibit ±5% variation in H<sub>2</sub> evolution (Fig. 6b). Moreover, having a controllable porosity in the TiO<sub>2</sub> shells becomes an extremely important requirement in these cases in order to guarantee the accessibility of the reactant molecules to the encapsulated catalysts. Other works on metal@TiO2 core-shell photocatalysts have been reported, where metallic nanoparticles including Pt,<sup>16</sup> Pd,<sup>90</sup> Au<sup>91</sup> and Ag<sup>92</sup> have been used to enhance the photocatalytic activity on the TiO<sub>2</sub> surfaces by suppressing the electron-hole recombination. The photo-induced electrons migrate to the metal due to the relatively low Fermi level of metals, which make the photoinduced holes stable on the TiO<sub>2</sub> surfaces by increasing the lifetime of charge carriers. Porous TiO<sub>2</sub> shells are a promising structural design, since the porous shells not only prevent the aggregation of core metal nanoparticles but also allow the reactants through the pores to react with inner cores.

### 3.2 Catalytic stability

**3.2.1 Active surface area protection.** One of the major challenges in the use of nanostructured materials as photocatalysts is the stability of the active catalyst particles. As



Fig. 6 (a) Schematic of the three different designs of  $TiO_2$  nanospheres synthesized with/without Au nanoparticles, as well as surface loaded or spatially confined Au nanoparticles. (b) Photocatalytic H<sub>2</sub> evolution cycles of Au on  $TiO_2$  and Au@TiO<sub>2</sub> (single and multiple) core-shell nanospheres. Adapted from ref. 91 with permission. Copyright Royal Society of Chemistry.

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discussed earlier, core-shell or yolk-shell structures offer advantages of structural stability of the catalyst against dislodging and migration. In this section, the catalytic stability of the photocatalyst will be discussed. During both the preparation process of photocatalysts and the photocatalytic reaction, nanoparticles may rapidly grow larger and sinter into large clusters due to their high surface energy (Fig. 7a). This will result in reduction of the active surface area and loss of photocatalytic activity over time. This is illustrated in Fig. 7b, where well-dispersed Pt nanoparticles of 2-3 nm were seen to sinter into a few large crystalline particles of ~10 to 20 nm after calcination Fig. 7c.<sup>28,93</sup> Both Ge et al.<sup>94</sup> and Zhang et al.95 demonstrated a surface-protected etching method for fabricating core-satellite nanoreactors, in which metal nanocatalysts are stabilized by a porous SiO<sub>2</sub> shell, and the procedures involved are shown in Fig. 7d. Metal nanocatalysts are loaded onto the SiO<sub>2</sub> colloid surface through electrostatic interactions or chemical bonding. Another SiO<sub>2</sub> layer is coated onto the metal nanoparticles to affix them onto the initial SiO<sub>2</sub> support (Fig. 7e). Finally, the surfaceprotected etching scheme is applied to transform the outer shell into a mesoporous structure (Fig. 7f), exposing the catalyst particles to outside chemical species. Compared to unprotected metallic nanocatalysts, the as-fabricated structure has consistently shown excellent thermal stability during the catalytic reactions.95 They have also demonstrated that the TiO<sub>2</sub> coated SiO<sub>2</sub>/Au core-shell photocatalyst shows high efficiency in catalyzing the decomposition of organic compounds under the illumination of UV, visible light, and natural sunlight. The structural design of the photocatalyst takes advantage of the synergistic interaction between adsorbed Au and implanted N, and produces stable nonmetal-doped



Fig. 7 Illustration of the use of mesoporous silica layers for protection against sintering of dispersed metal nanoparticles. As shown schematically in panel (a), the original small Pt nanoparticles supported on SiO<sub>2</sub> beads (b) coalesce into a few larger structures (c) upon calcination at 1075 K. (d) Schematic illustration of the synthetic procedure used for the formation of SiO<sub>2</sub>/Au/SiO<sub>2</sub> sandwiched nanoreactor structures. (e, f) TEM images of the sandwiched structures (e) before, and (f) after surface-protected etching. Note that superparamagnetic Fe<sub>3</sub>O<sub>4</sub> particles were included at the core of the samples in (e) and (f) for enhanced recyclability. Adapted from ref. 93 and 95 with permission. Copyright American Chemical Society and WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

anatase nanoparticles with precisely controlled Au nanoparticle decoration.  $^{\rm 96}$ 

3.2.2 Corrosion/oxidation inhibition. Rational design of core-shell structures can prevent corrosion and oxidation of the photocatalyst, since the shell can function as a passivation layer. Photocorrosion occurs when the photogenerated holes do not react quickly with water molecules or organic pollutant; as a result, the holes will react with the photocatalysts, which leads to oxidation of the photocatalysts.97 Many materials suffer from the drawback of having low photocorrosion resistance in most electrolytic media, such as ZnO, CdS, WO<sub>3</sub> and ZnS. This stability issue hinders the use of these materials for long-term photocatalytic applications. Hernández et al.98 addressed this issue through coating of the anatase TiO<sub>2</sub> shell on ZnO nanowires for photocorrosion protection (Fig. 8a). Fig. 8b shows that photocorrosion is evidently observed for the ZnO nanowire photoanodes in contrast to a photostable core-shell nanowire photoanode at a macroscopic level. Moreover, long-term stability photoelectrochemical characteristics of ZnO@TiO2 core-shell photoanodes for water-splitting are obtained (Fig. 8c). In the case of ZnO, it undergoes photocorrosion through selfoxidation and tends to dissolve in the acidic solution. The photogenerated holes have strong oxidation properties. On



**Fig. 8** (a) Scheme of the prepared photoelectrodes, consisting of ZnO nanowires and ZnO@TiO<sub>2</sub> core-shell heterostructures and their band diagrams, which represent the charge carrier transport at the different water-splitting PEC cell interfaces. (b) Picture of the ZnO nanowires (Z-air-A) and the ZnO@TiO<sub>2</sub> core-shell sample (ZT-air-A), treated in air atmosphere, after the PEC test. (c) Chrono-amperometry measurement (*I*-*t*) curves at 0.2 V vs. Ag/AgCl (1.2 V vs. RHE) over light ON-OFF cycles, of the ZnO@TiO<sub>2</sub> core-shell samples annealed in air (ZT-air-A (one-step annealing) and ZT-air-B (two-step annealing)) and in N<sub>2</sub> (ZT-N<sub>2</sub>-A), under dark and under simulated AM 1.5G solar illumination. Adapted from ref. 98 with permission. Copyright 2014 American Chemical Society.

one hand, the photogenerated holes can react with water adsorbed on the ZnO surface to form highly reactive hydroxyl radicals (OH') to perform photocatalysis. On the other hand, the holes may also be trapped on the ZnO surface and react with the surface  $O^{2-}$  ion of ZnO to form  $O_2$ , leading to the dissolution of ZnO. However, with the presence of the TiO<sub>2</sub> shell, an efficient channel for the photogenerated holes from the ZnO surface to the heterosystem/ electrolyte boundary is formed. The holes at the boundary preferentially react with water to give the OH radicals to perform photocatalysis. Hence, with the coating of TiO<sub>2</sub>, the photocorrosion can be efficiently suppressed and the photostability is significantly improved. Li and co-workers<sup>99</sup> reported the synthesis of VO2@TiO2 core/shell nanoparticles, which exhibit enhanced chemical stability of VO<sub>2</sub> against oxidation due to the protective layer of TiO<sub>2</sub>. Coreshell nanostructures provide an attractive approach for the protection of catalytic active nanoparticles. There are many possibilities to engineer the core-shell structure in order to protect the chemical stability of the catalysts and at the same time not compromise its photocatalytic activity. The design of a porous protective layer is also an important factor to consider for the reactant to reach the active sites of the catalysts.

### 3.3 Light absorption

3.3.1 Light scattering. In order to improve light absorption, nanostructures that can reflect and scatter light internally are designed. Unlike the nanoparticles, which allow the light to pass through (Fig. 9a), a core-shell structure formed with materials of different refractive indices allows internal reflection (Fig. 9b),<sup>100,101</sup> thus improving light absorption capability. Moreover, a core-shell structure has been adopted as an intermediate step to create interior cavities within particles, which further enhanced scattering and optical localization within the particles.<sup>102</sup> These structures do not only have a large surface area, but also allow incident light to undergo multiple light scattering and reflection within the hollow cavities. Such a multiple reflection mechanism has been proposed in hollow (Fig. 9c),<sup>103</sup> double-shell hollow (Fig. 9d)<sup>104</sup> and yolk-shell (Fig. 9e)<sup>105,106</sup> structured photocatalysts, as illustrated in Fig. 9.

In order to design an efficient light absorbing photocatalyst through structural modification, there are a few factors that need to be considered. Firstly, the  $TiO_2$  shell thickness of these nanostructures must be thin enough for the UV light to penetrate. Unlike nanoparticles, which allow light to directly pass through (Fig. 9a), the transmitted UV light through the shell will reflect in the hollow channels. This leads to multiple reflection effects as shown in Fig. 9b–e, thus enhancing the light harvesting. It has been reported that UV light, with intensity of 1 mW cm<sup>-2</sup>, can be completely absorbed by a porous  $TiO_2$  film, until its thickness goes beyond several microns.<sup>107</sup> The penetration depth can vary depending on different synthesis methods, particle sizes and



Fig. 9 Schematic diagrams of light pathways in (a) nanoparticles; (b) core-shell spheres (c) hollow spheres; (d) double-shell hollow spheres and (e) yolk-shell spheres. (f) Performance of photocatalytic activities, in terms of the experimental measurement of degradation rate constant-value, for hollow sphere nanoparticles of different diameters (marked by  $\Delta$ ). Numerical simulations of the total absorption power,  $W_{tot}$ , are shown for different incident wavelengths:  $\lambda = 350$  nm (solid-line) and 388 nm (dashed-line), with a shell thickness of 50 nm. A reference sample, made by crushing the original hollow sphere particles into a powder with the same weight, is shown for comparison, with the experimental data marked by  $\bullet$  and its numerical simulations as a dotted-line. Adapted from ref. 109 with permission. Copyright 2013 Elsevier.

the porosity of the TiO<sub>2</sub> shell. On the other hand, the thicknesses of hollow TiO<sub>2</sub> spheres ranging from tens to hundreds of nanometers are reported for improved light harvesting.<sup>104,106,108</sup> Secondly, the size of the hollow spheres can significantly affect the photocatalytic behavior. Based on the extended Mie's scattering theory, Tsai et al.<sup>109</sup> have investigated the light absorption power for hollow TiO<sub>2</sub> spheres with a shell thickness of 50 nm, but of different particle diameters (365 to 930 nm) under different incident wavelengths of 350 nm (solid-line) and 388 nm (dashed-line) as shown in Fig. 9f. The numerical results show higher absorption power for hollow spheres of less than 500 nm. Thirdly, when multiple hollow channels or yolk-shell structures are designed, the size of the interior cavities and the inner scattering center (inner shell or core) will also affect light scattering. Li et al.<sup>106</sup> designed a sphere-in-sphere structure, and showed that with an appropriate inner sphere diameter, the light is used more efficiently, thus offering an improved catalytic activity. Yoo et al.<sup>105</sup> also claimed that the yolk-shell structure with a TiO<sub>2</sub> shell and SiO<sub>2</sub> yolk (Fig. 4c) enhances photocatalytic H<sub>2</sub> production, as a result of multiple reflections of UV light within the interior cavities between SiO<sub>2</sub>

and TiO<sub>2</sub>. The SiO<sub>2</sub> core acts as a scattering center, which also facilitates internal reflections of light (Fig. 9e) and enhances the photocatalytic activity. Lastly, the refractive indices in different regions due to various materials also affect the scattering, transmitted and internal refracted waves, which contribute to total light absorption. Complex hollow structures with multiple shells are highly desirable, as the inner shell can scatter and absorb the light at the same time. Li and co-workers<sup>104</sup> produced a novel double-shell TiO<sub>2</sub> structure (Fig. 4e) with an inner anatase layer and an outer rutile shell using a silica protection layer method. The structural effect on photocatalysis was investigated to show higher light absorption than hollow TiO<sub>2</sub>, and resulted in enhanced photodegradation.

The structural engineering of interior design of hollow  $TiO_2$ , together with optimized size and shell thickness has a significant effect on the light absorption power of these hollow spheres, which in turn affects their photocatalytic properties. This multiple light reflection and absorption concept may be generically applied to the design and fabrication of novel nanomaterials with enhanced optical properties for microelectronics, optoelectronics, and other applications.

3.3.2 Upconversion. Another way to improve light absorption of the photocatalyst is to carry out structural design of core shell structures that encompasses upconversion nanocrystals. The basic mechanism for upconversion materials used in NIR-light active photocatalysis is illustrated in (Fig. 10a). In brief, the NIR light is absorbed by the upconversion nanocrystal itself, which then emits the upconverted UV/visible light. The neighboring UV/visibleactive photocatalysts absorb the emitted light from the upconversion nanocrystals to generate electron-hole pairs, which can be used to complete the photocatalytic cycle. However, the light conversion efficiency is low because only specific wavelengths of sunlight (800 nm or 980 nm) are used to activate the upconversion crystal. In order to fully utilize the converted light and reduce internal scattering and absorption by upconversion crystal, core-shell structures have been adopted to design efficient NIR-light active photocatalysts. Tang and co-workers<sup>110</sup> designed a core-shell structured NaYF<sub>4</sub>:Yb,Tm@TiO<sub>2</sub> for NIR-driven photocatalytic degradation and its performance is two times higher compared to the physical mixture of NaYF<sub>4</sub>:Yb,Tm and TiO<sub>2</sub> sample. This is because the core-shell structured particles allow NaYF<sub>4</sub>:Yb, Tm and TiO<sub>2</sub> to attach closely to each other and form compact interfaces, which benefit the photon energy migration process (Fig. 10a) and hence enhance photocatalytic activity. Other researchers also revealed similar results of a core-shell structure having superior photocatalytic properties when making efficient use of the converted NIR light for photocatalysis.<sup>111-113</sup> Su et al.<sup>114</sup> reported an interconnected porous network of a three-dimensional heterostructure, consisting of upconversion nanoparticles@TiO2@CdSe coreshell spheres as shown in Fig. 10b. This architecture also provides a close contact between the upconversion particles and photon-absorbing dye that ensures immediate absorption of Catalysis Science & Technology



**Fig. 10** (a) Schematic diagram of the mechanism of upconversion crystal( $aTiO_2$  core-shell structure. (b) SEM images of  $TiO_2$  deposited on upconversion nanoparticle coupled  $TiO_2$  inverse opals. (c) Schematic of energy flow in the as-prepared hetero-nanostructures from upconversion nanoparticles to visible light-absorbing CdSe nanoparticles to  $TiO_2$  Inverse Opals upon near-infrared photoexcitation. (d) Energy diagram illustrating the charge injection from the excited CdSe into  $TiO_2$  and the transport of photoinjected electrons to the electrode surface for H<sub>2</sub> generation. Adapted from ref. 110 and 114 with permission. Copyright American Chemical Society and Royal Society of Chemistry.

the emitted light and reduces transmission loss (Fig. 10c). Moreover, the inverse opal structure is known to improve the light-matter interaction due to the strong light scattering effect, which results in a remarkable increase in light path length. The interconnected structure optimally conducts electrons with minimal carrier losses due to its continuous electron conducting pathway (Fig. 10d). By using the asfabricated three-dimensional core-shell heterostructure, H<sub>2</sub> generation via a photoelectrochemical process driven by near-infrared irradiation has been demonstrated. The shell thickness is also a key parameter, as it will affect the light intensity for exciting the inner upconversion crystal core, and hence the photocatalytic activity. Zhang et al.115 demonstrated that a highly crystalline TiO<sub>2</sub> shell with different thicknesses can be uniformly coated onto lanthanide-doped NaYF<sub>4</sub> microrods (Fig. 4i) and nanorods (Fig. 4k). However, the incident NIR light was attenuated by the shell, which resulted in a decrease in the excitation light intensity arriving at the NaYF4:Yb,Tm core. The results showed that a shell with moderate thickness possesses excellent photocatalytic activity under near-infrared irradiation.

The upconversion materials have shown great promise in extending the optical response of photocatalysts from UV/visible to NIR. However, similar to the previous work, the upconversion efficiency is limited by the narrow excitation bands of upconversion nanoparticles, namely 800 and 980 nm. In view of such a limitation, the design of upconversion particles with higher efficiency under low light irradiance is needed, and this can be potentially achieved through nanophotonic manipulation with improved photon capturing and confinement abilities to enhance light absorption utilizing a hierarchical core–shell structure.

### 3.4 Interface engineering

Besides enhanced stability, another major advantage that makes core-shell structured catalysts superior to a single component catalyst is the possible synergies derived from interactions between the core and shell materials.

3.4.1 Surface plasmonic effect. Noble metal nanoparticles such as Au and Ag have been utilized to enhance the photocatalytic efficiency under visible light. Three primary mechanisms have been discussed according to previous works.<sup>33-35</sup> The first mechanism claims that the enhancement is due to the localized surface plasmon resonance (LSPR) effect, where hot electrons are generated and transferred to the semiconductor photocatalyst upon visible light irradiation.<sup>14</sup> Another mechanism is based on the plasmon resonance enhanced local electric field of the incident light, which causes plasmon resonance energy transfer from metal nanoparticles to TiO<sub>2</sub>.<sup>116</sup> The last one is based on efficient scattering mediated by LSPR (far field effect), which leads to longer optical path lengths for photons in TiO<sub>2</sub>, that boost the excitation of electron-hole pairs.<sup>117</sup> Zhou et al.<sup>118</sup> demonstrated that TiO<sub>2</sub> coated Au/Ag nanorod core-shell structures (Fig. 4l) have improved the photocatalytic activity under visible light irradiation, as compared to the mixture of Au/Ag nanorods and P25. This result validates the close contact between the



**Fig. 11** (a) Schematic representation for the mechanism of photocatalytic degradation of dyes upon visible light excitation. Photocatalytic degradation study of MB, (b) photocurrent study and (c)  $\ln(C_0/C)$  versus time on Ag@SiO<sub>2</sub>@TiO<sub>2</sub> (20 nm) with different SiO<sub>2</sub> interlayer thickness. (d) Simulated electric field intensity on the outer surface of Au nanoparticles (up) and Au/SiO<sub>2</sub> core-shell nanoparticles (down) at plasmonic wavelength on the logarithmic scale. The wavelength of incident light is 540 nm (up) and 545 nm (down). (e) Simulation of electric field intensity under *x*-polarized illumination of gold nanoparticles only (up) and gold nanoparticles covered with 3 nm SiO<sub>2</sub> (down) on TiO<sub>2</sub> in the *x*-*z* plane (in arbitrary units). The diameter of nanoparticles is 35 nm (without SiO<sub>2</sub>) and 65 nm (with 3 nm SiO<sub>2</sub>). Adapted from ref. 118–120 with permission. Copyright American Chemical Society and Royal Society of Chemistry.

plasmonic metal and TiO<sub>2</sub> in the core-shell structure, which allows efficient electron transfer from Au/Ag nanorods to the TiO<sub>2</sub> shell. This prevents direct electron-hole recombination and consequently enhances the photocatalytic efficiency (Fig. 11a). In addition, the core-shell structure can also be used to tune the LSPR frequency to the desired range, as the surface plasmons of noble metals are very sensitive to the surrounding media. Zhang et al.119 fabricated a welldispersed triplex Ag@SiO2@TiO2 core-shell photocatalyst, which shows a photocurrent density 38 times larger than that in P25 under visible light due to the plasmonic field of the inner Ag core (Fig. 11b). The SiO<sub>2</sub> interlayer coated on the Ag core plays dual vital roles in this case. The LSPR undergoes a blue shift from 497 nm (Ag@TiO2) to 447 nm (Ag@SiO<sub>2</sub>@TiO<sub>2</sub>) for a 2 nm SiO<sub>2</sub> shell. As the thickness of the shell increases, the LSPR continues to blue shift, which is beneficial for the energy coupling for the plasmonic catalysis mechanism, as the tuned LSPR wavelength is now closer to the energy bandgap of  $TiO_2$  (Fig. 11c).<sup>119</sup> Not only can the

### Minireview

SiO<sub>2</sub> shell tune the LSPR peak to the desired wavelength, it also protects the Ag nanoparticles from oxidation, thus improving the LSPR intensity.<sup>119</sup> This effect has also been observed for Au nanoparticles by Chen and co-workers through both experiments and simulations. Different plasmonic photocatalysts consisting of Au@SiO2/TiO2, Au/ TiO<sub>2</sub>, and TiO<sub>2</sub> were investigated for photodegradation, which gave 95%, 80%, and 44% efficiency, respectively, after 5 h of UV and visible light irradiation. Shell-isolated plasmonic photocatalyst Au@SiO2/TiO2 shows the best performance, which is verified by the simulation results, where a SiO<sub>2</sub> coating is seen to significantly increase the LSPR effect of Au nanoparticles (Fig. 11d). The electromagnetic field of Au@SiO2/TiO2 improved nearly 9 times compared with Au/ TiO<sub>2</sub> (Fig. 11e).<sup>120</sup> In plasmonic core-shell structures, the absorption band is highly dependent on the path length of the shell layer. It is noted that increasing the shell thickness may cause a reduction in penetration depth, thus lowering the intensity of plasmon resonance. Moreover, the exact position of the plasmon absorption band is sensitive to other factors, such as the particle size and shape, and the dielectric constant of the surrounding medium.<sup>121</sup>

3.4.2 Charge separation & transportation. As mentioned earlier for plasmonic core-shell photocatalysts, the encapsulation increases the contact area between the two different materials in the core-shell matrix, thus allowing more efficient electron transfer. This spatial confinement has also been used to design composite core-shell photocatalysts for improving charge separation through incorporating either cocatalyst<sup>90,91,122-124</sup> or sensitizer<sup>22,125</sup> into the core-shell matrix. Our group has demonstrated the effectiveness of the Au/TiO<sub>2</sub> core-shell structure for interfacial chargetransfer in reducing the recombination of electron-hole pairs in photocatalytic water splitting. We also proved the enhanced and prolonged photocatalytic activity of spatially confined metal cores over conventional surface loaded metal particles, which originates from the structural stability and optimized contact interface for heterojunctioninduced charge transfer (Fig. 12a).91 Zhang et al.125 reported that carbon sensitized TiO2@C core-shell nanofibers exhibited enhanced photocatalytic degradation efficiency as compared to the pure TiO<sub>2</sub> nanofibers under visible light irradiation. The high separation efficiency of photogenerated electrons and holes is based on the synergistic effect between carbon as a sensitizer and TiO<sub>2</sub> with one dimensional structure (Fig. 12b). Charge separation is one of the key factors that determine the efficiency of photocatalytic reaction. Although photoillumination and transient absorption measurements have been used to study the dynamics of the electron-hole pairs,<sup>91,126</sup> it is still not very well understood, due to the complexity of many processes that may actually occur at the same time, such as charge carrier generation, electron trapping, inter-band transition, recombination and transportation. Therefore, the use of complementary spectroscopy measurements to understand the dynamics of the electron-hole pairs in



Fig. 12 (a) Proposed photocatalytic mechanism and energy band diagram of the Au@TiO<sub>2</sub> core-shell nanospheres under sunlight irradiation. (b) Visible light-induced photodegradation with the TiO<sub>2</sub>@C core-shell nanofibers. Adapted from ref. 91 and 125 with permission. Copyright Royal Society of Chemistry.

core-shell photocatalysts during catalytic reaction is essential for designing efficient photocatalysts.

### 3.5 Photocatalyst recycling

Considering that most photocatalytic processes are conducted in solution using the suspension form of TiO<sub>2</sub> photocatalysts, separating or collecting these nanosized particles from the solution after photocatalytic reaction becomes difficult. Conventional separation methods, including centrifugation and filtration, may lead to loss of the photocatalysts and an increase in the practical running costs. Thus, it is important to develop a simple way to recycle photocatalysts so that the deactivated photocatalysts can be recovered and reused in order to reduce excessive use of photocatalysts. Magnetic separation provides a convenient approach for separating and recycling nanoparticles from solution by applying an external magnetic field. This approach is feasible for separating and recovering TiO<sub>2</sub> photocatalysts through the integration of magnetic components.<sup>127,128</sup> A core-shell or yolk shell configuration is favorable in the integrated nanocomposites, as the TiO<sub>2</sub> shell can protect the magnetic core



Fig. 13 (a) Schematic illustration of the synthetic strategy to produce Fe<sub>3</sub>O<sub>4</sub>@TiO<sub>2</sub> yolk-shell nanostructures (a-TiO<sub>2</sub> denotes amorphous TiO<sub>2</sub>). (b) Recyclability of the Fe<sub>3</sub>O<sub>4</sub>@TiO<sub>2</sub> nanoparticles for the degradation of RhB solution *via* magnetic separation. (c) Magnetic hysteresis loops and (d) the enlarged view of the central loops of a) Fe<sub>3</sub>O<sub>4</sub>@TiO<sub>2</sub> microspheres, b) Fe<sub>3</sub>O<sub>4</sub>@TiO<sub>2</sub> microspheres, and c) Ag-coated Fe<sub>3</sub>O<sub>4</sub>@TiO<sub>2</sub> microspheres. (e) Photographs of (left) a 1 × 10<sup>-5</sup> M methylene blue (MB) solution after UV irradiation for *ca.* 35 min with dispersed Ag-coated Fe<sub>3</sub>O<sub>4</sub>@TiO<sub>2</sub> microspheres, (middle) the solution after magnetic separation using an external magnetic field, and (right) the 1 × 10<sup>-5</sup> M MB aqueous solution with redispersed Ag-coated Fe<sub>3</sub>O<sub>4</sub>@TiO<sub>2</sub> microspheres after shaking. Adapted from ref. 129 and 130 with permission. Copyright Royal Society of Chemistry and WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

from dissolution and contamination. Su and co-workers129 synthesized well-defined yolk-shell Fe3O4@TiO2 nanoparticles (Fig. 13a and 4d) and its photocatalytic activity was assessed by photodegradation under UV irradiation. These nanoparticles not only exhibit improved photocatalytic performance, but can also be conveniently separated using a magnet and reused. Fig. 13b shows good photocatalytic recyclability and sustainability due to the superparamagnetic behavior of the Fe<sub>3</sub>O<sub>4</sub> core. Zhang et al.<sup>130</sup> demonstrated Agcoated Fe<sub>3</sub>O<sub>4</sub>@TiO<sub>2</sub> core-shell microspheres as recyclable photocatalysts that outperform P25 for photodegradation. It is worth noting that the magnetic saturation (Ms) value of the  $Fe_3O_4$  (77.5 emu g<sup>-1</sup>) microspheres is significantly higher than that of the  $Fe_3O_4$  (a)TiO<sub>2</sub> microspheres (38.7 emu g<sup>-1</sup>) and Ag-coated Fe<sub>3</sub>O<sub>4</sub>@TiO<sub>2</sub> microspheres (36.8 emu g<sup>-1</sup>) as shown in Fig. 13c. Moreover, it can be seen that there are no significant changes in the coercivity (Fig. 13d). Such excellent magnetic properties imply strong magnetic responsivity of the core-shell structure, which enables them to be separated easily from solution with an applied external magnetic force (Fig. 13e). These core-shell photocatalysts recycled by the external magnetic field facilitate easy reuse and regeneration of photocatalysts. Other materials structures that can be fabricated for easy recycling include thin films and hydrogel matrix. However, the reactivities of such photocatalysts are considerably reduced since the effective surface area and

light absorption are significantly decreased. Although some effort has been made in designing and fabricating magnetic core–shell structures as convenient and recyclable photo-catalysts, the stability of such photocatalysts must be further improved.<sup>131</sup>

### 3.6 Multi-functional core-shell photocatalysts

The synergetic effects of multiple semiconductor photocatalysts have been extensively exploited for photocatalytic applications. The core–shell design, whereby each shell layer can be defined within a regulated scale to introduce a specific feature and with the multiple core–shell structural engineering, a range of unique characteristics associated with physical and chemical stability, light absorption, electron and hole separation and transport and recyclability can be realized.<sup>131</sup>

The core-shell design provides a platform for incorporating different materials with isolated functions into one integral design. By coating an inert layer, which separates the two different materials, each individual material can function independently without undesired interference with each other. Zhou and co-workers<sup>132</sup> designed and synthesized  $SiO_2$ -Ag-SiO\_2-TiO\_2 multi-shell photocatalysts (Fig. 14a and 40) with wide-spectral-response. The photocatalytic activity tests showed enhanced photocatalytic efficiency under both UV and visible light irradiation. The main reasons for the enhancement of the photocatalytic activity are (Fig. 14b) (1) the dense Ag nanoparticles covering the SiO<sub>2</sub> core form many "hot spots" and induce a stronger excited localized surface electromagnetic field. (2) The N-doped anatase TiO<sub>2</sub> enhances light absorption in the visible light region. (3) The silica



Fig. 14 (a) Synthesis process of the SiO<sub>2</sub>-Ag-SiO<sub>2</sub>-TiO<sub>2</sub> multi-shell structure. (b) Mechanism of the photocatalytic processes of SiO<sub>2</sub>-Ag-SiO<sub>2</sub>-TiO<sub>2</sub> sample. (c) Schematic illustration of the fabrication of Ag@Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@TiO<sub>2</sub> nanospheres. (d) Mechanism of the photocatalytic processes of the Ag@Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@TiO<sub>2</sub> sample. Adapted from ref. 132 and 133 with permission. Copyright Royal Society of Chemistry.

interlayers between Ag and the  $\text{TiO}_2$  shell prevent electron transfer and increase the stability of Ag. (4) The precise thickness control of the  $\text{SiO}_2$  interlayers that tunes the distance between Ag and  $\text{TiO}_2$  layers is beneficial to adjust the coupling between the LSPR of Ag nanoparticles and the TiO<sub>2</sub>.

Moreover, multiple functions can be integrated into one single design through the core-shell structure. Su et al.<sup>133</sup> demonstrated the design and fabrication of the well-defined triple-shelled Ag@Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@TiO<sub>2</sub> nanospheres with burrshaped hierarchical structures (Fig. 14c and 4p), in which the multiple distinct functional components are integrated into this single nanostructure (Fig. 14d). The Ag core is used to extend the photo-response of TiO2 to the visible region through inducing electromagnetic field magnification and efficient resonance photon scattering. The compact Fe<sub>3</sub>O<sub>4</sub> shell facilitates the modulation of LSPR of Ag nanoparticles and provides efficient magnetic separation. The SiO<sub>2</sub> interlayer protects Ag and Fe<sub>3</sub>O<sub>4</sub> from corrosion and oxidation, which improves the stability of the catalyst. This SiO<sub>2</sub> interlayer between the Fe<sub>3</sub>O<sub>4</sub> nanoparticles and TiO<sub>2</sub> hierarchical structure also inhibits the direct transfer of electrons-holes from TiO<sub>2</sub> to the Fe<sub>3</sub>O<sub>4</sub> layer, which favorably prevents pronounced Fabry-Perot oscillations. Finally, the outermost TiO<sub>2</sub> hierarchical shell assembled by super-thin nanosheets with high surface area is beneficial to promote the adsorption of pollutants, allowing more effective transport of the reactant molecules or ions to the active sites. In comparison with P25, the triple-shelled Ag@Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@TiO<sub>2</sub> nanospheres exhibit outstanding adsorption and degradation of pollutant under visible light or natural sunlight irradiation.

# 4. Hierarchical structures of TiO<sub>2</sub>

Single constituent or basic nanostructures of TiO<sub>2</sub> are known to exhibit photocatalytic properties for energy and environmental applications. However single constituent TiO<sub>2</sub> nanostructures generally lack the necessary properties and tend to aggregate during material processing and photocatalytic reaction, thus limiting their photocatalytic performance. One strategy to overcome the aforementioned limitations is to engineer TiO<sub>2</sub> into hierarchical nanostructured materials. A hierarchical nanostructured material is defined here as a higher dimension of a micro- or nanostructure composed of numerous low-dimensional basic structures. In essence, it consists of nanosized entities that integrate various nanoscale building blocks of dissimilar dimensionality, morphologies and compositions etc. Rather than just geometrical assembly consideration to prevent aggregation, combination of disparate entities can potentially improve or multiply the functional characteristics of a single constituent material. Furthermore, the accomplishment of hierarchical nanostructured materials represents a valuable means of materials manipulation at an unprecedented length scale, to enable probing of specific structure to elucidate structural influence on photocatalytic properties.

Hierarchical TiO<sub>2</sub> composite material is a hot topic in recent years and diverse hierarchical structures have been designed and applied to photocatalysis. The design of TiO<sub>2</sub> hierarchical structures commonly involves growth of nanoscale building blocks on the inner and/or outer surfaces of host materials. These building blocks can be zerodimensional nanoparticles,134 one-dimensional nanostructures such as nanorods,<sup>135</sup> nanowires,<sup>136</sup> nanotubes<sup>137</sup> etc. and two-dimensional structures such as nanosheets<sup>138</sup> and nanoflakes.<sup>139</sup> The composition of secondary structures can be similar or different from the host matrix to form a hierarchical assembly of homogeneous or heterogeneous composite structures, respectively. The hierarchical design concept makes it possible to engineer functional TiO<sub>2</sub> composite materials in which not only are the excellent properties of the host matrix preserved, but also additional functionalities of secondary structures, such as enhanced surface area, improved solar absorption and utilization, fast electron transport and efficient charge collection, and so on, are integrated, forming multi-functional materials. In light of all these functional attributes, we have focused on the designing and engineering of hierarchical TiO<sub>2</sub> materials for advanced photocatalysis applications, where key factors such as specific surface area, light harvesting ability, exposed facet, mixed phase and heterojunction will be discussed (Fig. 15).

### 4.1 High specific surface area

It is known that photocatalysis takes place at a material surface, hence the accessibility to reactants must be high. Surface accessibility is directly related to the porosity of a material. A high specific surface area increases the exposure of active sites and solid–liquid interfaces for a photocatalytic reaction. It is noted that effort to enhance photocatalysis by



Fig. 15 Schematic diagram of hierarchical structured photocatalysts according to their functions.

increasing surface area through the decrease of particle sizes down to several nanometers is often set back by the attractive Van der Waals forces that lead to large agglomerates. As a result, the diffusion of reactant into the interior of the large aggregates is ineffective due to the small pores, long diffusion length, and tortuous pathways. A promising way to overcome the limitation is to compose a hierarchical structure that consists of non-agglomerated entities that do not compromise its surface area. In contrast to the agglomerated structures, hierarchical nanostructured materials can be assembled either in irregular fashion with variable pore size distribution or in periodic fashion with uniform pore-size distribution. With a highly organized structure, the accessibility to reactant molecules, the rate of mass transfer for reactant adsorption as well as other attributes (to be discussed later) can be significantly improved.

In recent years, hierarchical TiO<sub>2</sub> catalysts with interesting morphologies and of high specific surface area have been designed and fabricated for photocatalysis applications, ranging from hierarchical spheres to a mesoporous film matrix. For the case of hierarchical TiO<sub>2</sub> spheres, various building blocks ranging from zero-dimensional, one-dimensional to two-dimensional nanostructures have successfully been assembled and applied to photocatalysis (Fig. 16). Ming et al.<sup>140</sup> have prepared hierarchical TiO<sub>2</sub> spheres that are made up of zero-dimensional nanoparticles. The obtained hierarchical TiO<sub>2</sub> spheres possess high specific surface area (234 m<sup>2</sup> g<sup>-1</sup>), large pore volume (0.36 cm<sup>3</sup> g<sup>-1</sup>), and uniform pore size (11 nm) distribution. Similar hierarchical spheres consisting of zero-dimensional nanoparticles of high surface area of 277 m<sup>2</sup> g<sup>-1</sup> were fabricated.<sup>141,142</sup> Both structures show excellent organic and inorganic pollutant degradation under UV and visible light irradiation. An added advantage of using such a hierarchical TiO<sub>2</sub> sphere for photocatalysis is the ability to separate and recycle them by a simple filtration process due to their overall large particle size. This is verified by repeated photocatalysis reaction that displayed a stable



**Fig. 16** SEM images of various TiO<sub>2</sub>-based hierarchical nanostructured photocatalysts with different building units (a) particles, (b) nanosheets, (c) nanoflakes, (d) nanowires, (e) nanothorns and (f) nanorods. Adapted from ref. 104, 134–136, 138 and 139 with permission. Copyright Royal Society of Chemistry, Elsevier and American Chemical Society.

and nearly constant photo-decomposition rate. On the other hand, Bai and co-workers<sup>143</sup> have synthesized hierarchical TiO<sub>2</sub> spheres that are made up of a one-dimensional nanowire and nanoribbon. The specific surface area is ~100  $m^2$  g<sup>-1</sup>, relatively higher than that of P25 (34 m<sup>2</sup> g<sup>-1</sup>). The hierarchical structures show not only enhanced photodegradation of organic pollutants but also high permeation flux owing to high surface area and fairly dense packing of one-dimensional nanostructures, which poses less resistance to water penetration as compared to compact nanoparticles. Other designs of hierarchical TiO<sub>2</sub> spheres that are made up of two-dimensional nanosheet building blocks have also been synthesized for photocatalysis applications. These high surface area (~170 to 400 m<sup>2</sup> g<sup>-1</sup>) hierarchical spheres with flower-like morphology were assembled from nanosheets or nanoflakes. Similarly, the hierarchical TiO<sub>2</sub> photocatalysts show excellent adsorption ability and high photodegradation rate.144,145

Another type of high surface area TiO<sub>2</sub> hierarchical structure that is of great interest is the mesoporous material. Mesoporous materials have many fascinating properties such as tunable pore sizes, high surface areas, large pore volumes, variable pore shapes, and controllable framework compositions. TiO<sub>2</sub> mesoporous structures of well-defined pores give large surface-to-volume ratios and efficient diffusion pathways for guest species, such as water and organic pollutants, to support efficient photocatalysis. In general, ordered mesoporous TiO<sub>2</sub> can be synthesized using soft or hard templates.<sup>146</sup> More commonly, soft templates based on sol-gel methods using a variety of surfactants and block co-polymers have been employed to synthesize a tailored TiO<sub>2</sub> hierarchical structure. The hierarchical structures composed of zerodimensional nanoparticles showed enhanced adsorption capacity, water permeability and photocatalytic performance.<sup>147–149</sup> Du *et al.*<sup>149</sup> have employed a confinement self-assembly method to create regular voids of a threedimensional periodic colloidal crystal, using Pluronic P123 and polystyrene spheres as a mesostructured template and a macro-structure scaffold, respectively (Fig. 17a). Macromesoporous titania films possess a well-ordered two-dimensional hexagonal (p6mm) mesostructure and wellinterconnected periodic macropores as well as high specific surface area (299  $m^2 g^{-1}$ ) and large pore volume of (0.57 cm<sup>3</sup> g<sup>-1</sup>), (Fig. 17b and c). Incorporation of interconnected macropores in mesoporous films significantly improves the mass transport through the film, reduces the length of the mesopore channel, and enhances the accessible surface area throughout the matrix. The unique macro to mesoporous structures showed enhanced capacity of rapid adsorption and photodegradation of organic dyes.

Other methods of synthesizing exquisite hierarchical structures can be offered by Mother Nature and borrowed as bio-templates. Bio-templates such as butterfly wing and leaf architectures have been used for synthesizing TiO<sub>2</sub> replicas.<sup>150–152</sup> These templates show complex morphology consisting of lamellas and columns, which are in turn



**Fig. 17** (a) Illustration for the preparation of macro-mesoporous  $TiO_2$ graphene composite film. (b and c) TEM images of macro-mesoporous titania films. (d) Photograph of the entire wings. (e-g) SEM and (h) TEM image of butterfly wing architecture  $TiO_2$ . (i) Cross section of a *Saccharum officinarum* Linn. leaf observed using an optical microscope; the inset shows an illustration of the Kranz-type anatomy and digital picture of leaf. (j) Cross-sectional SEM image of leaf morph- $TiO_2$ ; the inset shows a magnification of the corresponding areas contained the white panes: the scale bars are 2 mm. Adapted from ref. 149–152 with permission. Copyright Royal Society of Chemistry, Elsevier, American Chemical Society and WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

arranged into highly ordered architectures forming pores. Based on the prototype of the hierarchical architecture of butterfly wing (Fig. 17d–h) and leaf (Fig. 17i and j), mimic TiO<sub>2</sub> hierarchical structures were produced by a simple immersion/infiltration-calcination method. The biotemplated TiO<sub>2</sub> hierarchical structures have demonstrated high surface area and enhanced photocatalytic properties.

Hence, the design of the  $TiO_2$  hierarchical structure needs to take into account the porous structure formation, not only at the surface but also throughout the bulk of the materials to ensure high specific surface area and pore volume material. With the presence of pores, preferably open, homogenous, ordered and interconnected pores network, physical and chemical properties, as well as extended reactant adsorption and interaction will greatly enhance the photocatalysis reactivity.

### 4.2 Enhanced light harvesting

Photocatalysis is initiated by light absorption. As such it is initially restricted by the number and energy of photons harvested and absorbed by the photocatalyst. One approach to increase the number of photons harvested is to trap light inside a photocatalyst by using wavelength-scale textured nanostructures that minimize reflection losses at the front surface, as well as structures that are designed to trap the light within the photocatalyst. A well-designed hierarchical structure strongly favors efficient harvesting of light. When the hierarchical structure is designed to have a regularly assembled architecture, a series of optimized processes, from multiple light scattering and absorption within the porous structure to light propagation in the presence of periodic columnar structure acting as light guides, can be activated. It is noted that multiple light scattering and increase in optical path length can also be attained with less regularly arranged hierarchical structures.

Spherical hierarchical structures that are designed to be hollow and partially open favor light collection and multiple light scattering to improve the photocatalytic activity. Liu *et al.*<sup>153</sup> reported such TiO<sub>2</sub> hierarchical structures shaped like bowls, ink-bottles, and rings. These hierarchical structures consist of small nanoparticles or polygons with a diameter of *ca.* 10–20 nm that are tightly packed to form mesoporous structures. Furthermore, the diameter of spherical hierarchical structures has been reported to affect photocatalysis performance. Yang and co-workers<sup>154</sup> have fabricated and optimized hierarchical TiO<sub>2</sub> microspheres with diameters ranging from 0.5 to 10  $\mu$ m (Fig. 18a and b). The



Fig. 18 (a and b) SEM images of hierarchical inverse opal  $\text{TiO}_2$  photonic crystal spheres. (c) Light scattering schematic diagram of asprepared  $\text{TiO}_2$  spheres. (d) SEM and TEM images of porous cubic  $\text{TiO}_2$  cages. (e-f) SEM and TEM images of the anodic  $\text{TiO}_2$  nanotubes. (g) Schematic description and (h) corresponding SEM images of branched nanorods. (i) TEM image of a single nanorod. Adapted from ref. 154–158 with permission. Copyright Royal Society of Chemistry, Elsevier and American Chemical Society.

enhanced photodegradation of the microscale inverse opal spheres made up of hexagonally ordered pores was attributed to the synergetic effect of the Mie scattering (Fig. 18c). The angular scattering showed a favorable decrease in forward light scattering and increase in side angle scattering with smaller TiO<sub>2</sub> hierarchical spheres. Nonetheless, the particle should not be so small that it compromises the light scattering intensity. Other than the spherical hierarchical structures that are designed to be hollow and partially open, Tsai et al.<sup>155</sup> have synthesized a hollow hierarchical TiO<sub>2</sub> cube consisting of anatase nanoparticles (Fig. 18d). Cube shaped NaF salt was adopted as the template, where TiO<sub>2</sub> preferentially grew on the edges and corners of the cube to form an open cube framework (Fig. 18d insets). These hierarchical structures with nano-sized anatase particles and a micro scaled cage architecture markedly enhance the light harvesting by multiple-light scattering, resulting in improved photodegradation of the organic compound.

The important role of the meso-macroporous hierarchical structure has been discussed earlier for its high surface area. In fact, periodic assembly of bimodal meso-macroporous TiO<sub>2</sub> also contributes to beneficial light absorption and scattering within such a hierarchical porous system. The existence of macrochannels can increase photoabsorption efficiency and allow efficient diffusion of reactant molecules. In essence, the microchannel can act as a light transfer path for directing incident photon flux into the inner surface of mesoporous TiO2. This efficient light harvester configuration allows light waves to penetrate deep inside the bulk photocatalyst. Chen et al.<sup>156</sup> have fabricated hierarchical mesomacroporous TiO<sub>2</sub> nanostructures with wire-in-tube architectures via anodization and hydrothermal methods (Fig. 18e). The hierarchical wire-in-tube structure is composed of TiO<sub>2</sub> nanoparticles with diameter around 10 nm (Fig. 18f). The periodic wire-in-tube microchannel tube structure exhibited better absorption, attributed to light illumination and scattering throughout the bulk of the hierarchical structure.

In the case of one-dimensional hierarchical structures, branched TiO<sub>2</sub> nanorod structures have been synthesized as efficient photoelectrochemical anodes (Fig. 18g-i).<sup>157,158</sup> The hierarchical structure offers increased light absorption path length due to enhanced light scattering between the branched nanorods. The incident photon-to-current conversion efficiency reaches 67% at 380 nm with an applied bias of 0.6 V versus RHE, nearly two times higher than the bare branches.158 nanorods without Furthermore, onedimensional nanostructures offer the additional benefit of augmented charge transport and reduced electron-hole pair recombination by providing a direct conduction pathway for the photogenerated electrons.

Other than the large surface area rendered by the biotemplates as discussed previously, butterflies exhibit brilliant colors due to their wonderful skills of light manipulation, originating intrinsically from their elaborate architectures. The delicate architectures of butterfly compound eyes and wings are primarily based on nipple arrays, regular network and photonic crystal structures, all of which demonstrate the exquisite physical manipulation of light. The bio-templates structures derived via a simple immersion-calcination method can broaden the horizon of designing an efficient light harvesting photocatalyst. For instance, the inverse V-type ridges dominant in black wing scales of the butterfly Ornithoptera goliath display antireflection and angle regulation of incident light. Furthermore, the TiO<sub>2</sub> photocatalyst applying black butterfly wings as templates displayed 30% light absorption enhancement and shifting of light absorption to a shorter wavelength to complement the TiO<sub>2</sub> bandgap. The polycrystalline structures with different oriented gyroid subdomains in some butterflies exhibit omnidirectional colors with different spectral properties. With appropriate lattice parameters, filling fractions and refractive indices, the gyroid domains can obtain omnidirectional light within particular frequencies around the band gap of the photocatalyst. This introduces more interactions of photons with the photocatalyst and favourably improves catalytic efficiency.159

Hence, it is rational to design hierarchical structured materials composed of a nano/meso to macro scale structure that can reinforce the light harvesting efficiency through a strong light scattering effect, while the nanobuilding blocks including zero-dimensional nanoparticles, one-dimensional nanorods, nanowires *etc.*, that can effectively improve the surface area and simultaneously enhance the light scattering ability within the subdomains of the hierarchical structure.

### 4.3 Exposed high-energy facets

The average surface energies of anatase TiO<sub>2</sub> have been calculated to be 0.90 J m $^{-2}$  for {001}, 0.53 J m $^{-2}$  for {100} and 0.44 J m<sup>-2</sup> for {101}.<sup>160</sup> Based on the Wulff construction, surface energy minimization is the driving force towards optimal formation of a crystal shape and facet. Unfortunately, the majority of the external surface (more than 94%) of a thermodynamically stable shape anatase crystallites consists of less reactive {101} facets. On the contrary, the {001} facet, known for its high photoreactivity characteristics, has low stability, meaning that the {001} facet will diminish quickly during the crystal growth stage, resulting in a crystal that is dominated by the less reactive {101} facet. The origin of the high reactivity properties of {001} have been attributed to high density of surface undercoordinated Ti atoms and, probably more importantly, the strained configuration of the surface atoms. In particular, the existence of large Ti-O-Ti bond angles suggests unstable and highly reactive 2p state oxygen atoms. Evidently, the {001} high-energy facet has shown higher quantum efficiency of surface-mediated photocatalytic redox reactions due to the favorable dissociative adsorption of water and reactant molecules and the separation of photoexcited holes/electrons.<sup>161</sup> Hence, the preparation of a TiO<sub>2</sub> hierarchical structure that is largely made up of reactive facet {001} is pursued in anticipation of high photocatalytic performance.

The synthesis of various nanobuilding blocks with exposed {001} facets and their self-assembly into hierarchical architectures have garnered a lot of interest, since it is noted that P25 possesses only <5% exposed {001} facets.<sup>162</sup> It was found that the {001} facets of anatase TiO<sub>2</sub> with fivecoordinate Ti atoms are tunable by controlling the surface adsorbates. Accordingly, additive/capping agents that selectively bind to specific crystalline facets are chosen as an effective approach to control the crystal shape. The adsorbed species change the relative stability of the different crystal facets, or inhibit the crystal growth in high index facets, thus altering the equilibrium shapes of anatase TiO<sub>2</sub>, resulting in a shape that is ideally controlled by the nature and concentration of the additives. Through experiments and first principles calculations, it has been established that F-terminated surfaces of anatase  $TiO_2$  are largely dominated by  $\{001\}$ facets. 66,163

The hydrothermal method is frequently used to prepare a spherical hierarchical TiO<sub>2</sub> structure with exposed {001} facets, since the addition of hydrofluoric acid aqueous solution to induce fluoride-mediated crystal growth can be conveniently implemented. Here, Liu *et al.*<sup>164</sup> reported the preparation of spherical hierarchical TiO<sub>2</sub> nanostructures that are composed of large numbers of truncated tetragonal pyramidal TiO<sub>2</sub> nanocrystals (*ca.* 100–200 nm) that expose {001} and {101} facets (Fig. 19a–c). By calculations, it is derived that these F-terminated TiO<sub>2</sub> nanostructures contain about 10–30% of highly reactive {001} facets. Owing to their chemically active {001} facets, these TiO<sub>2</sub> nanostructures exhibited enhanced photocatalytic efficiency. Besides this work, Li *et al.*<sup>165</sup> also synthesized similar spherical TiO<sub>2</sub> made up of



Fig. 19 (a, d, g and i) SEM and (b, e and h) TEM images of the TiO<sub>2</sub> nanospheres with dominant exposed {001} facets. (c and f) The corresponding FFT patterns. Adapted from ref. 164–166 with permission. Copyright Royal Society of Chemistry and WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

truncated tetragonal-pyramidal nanocrystals, however with a much higher percentage of exposed {001} facets of ~78% (Fig. 19d-f). The top square surfaces and four isosceles trapezoidal surfaces consist of {001} and {101} facets, respectively. Here, the influences of reaction temperature, amount of hydrofluoric acid, and reaction time were optimized for increased  $\{001\}$  facet exposure. Consequently, the TiO<sub>2</sub> nanospheres exhibited a greatly enhanced photocatalytic organic degradation efficiency. In order to further increase the percentage of the exposed {001} facet of a spherical hierarchical structure, efforts to synthesize structures composed of twodimensional interconnected nanoflakes have been demonstrated (Fig. 19g-i).166 The individual square nanoflake is connected closely with its neighbors, resulting in the complete exposure and surface coverage of the high energy {001} facets up to 90%. The as-prepared spherical hierarchical structure was generated in situ using hydrofluoric acid, through hydrolysis of titanium tetrafluoride (TiF<sub>4</sub>) as a capping and stabilizing agent. Such high exposure of reactive {001} faceted crystal and with F atom termination structures yields excellent photodegradation of toxic organic contaminants, as well as photocatalytic production of H<sub>2</sub> under UV light irradiation.

Aside from this, few attempts have been made towards creating a TiO<sub>2</sub> spherical hierarchical structure that is hollow and has a high surface area and exposed {001} facets. Liu and co-workers<sup>162</sup> reported a hollow hierarchical structure that consists of small TiO<sub>2</sub> polyhedra, typically truncated bipyramids or decahedra, having sizes between 50 and 100 nm (Fig. 20a–c). With the adsorption of active F ions and the dissolution of the interior space, a hollow hierarchical structure of *ca.* 20% exposed {001} facets is formed. Selective adsorption and photocatalytic decomposition of dye molecules were accomplished by using the TiO<sub>2</sub> spherical hierarchical structure with exposed {001} facets and tailored surface chemistry.

In previous work, nanocrystals dominated with exposed {001} facets are used as the building block for TiO<sub>2</sub> hierarchical structures, which still impose some limitations on the specific surface area. Fang *et al.*<sup>167</sup> reported a solvothermal process for synthesizing flowerlike three dimensional hierarchical structures (Fig. 20d). The hierarchical structure is predominantly made up of 97% single-crystalline anatase TiO<sub>2</sub> nanosheets of {001} facets with a thickness of around 10–20 nm. The two-dimensional anatase TiO<sub>2</sub> nanosheets is unique, since it only contains a few tens of layers of crystal units along the [001] crystallographic direction.

Most of the mentioned work is based on powdered hierarchical  $\text{TiO}_2$  nanosheets or granular supported nanosheets, which are difficult to recycle from aqueous solution after photocatalytic reactions and will cause secondary pollution. To solve this problem, an ideal method is to grow these monodispersed nanosheets on a carbon fiber support (Fig. 20e). Compared to the traditional stiff substrate, carbon fibers are flexible, conductive, and stable in corrosive conditions, and they enable radial growth around each individual



**Fig. 20** SEM images of the fluoride-mediated TiO<sub>2</sub> samples: (a) image of a few microspheres; (b) a single microsphere showing its hollow nature; (c) a portion of the microsphere shell composed of nanosized polyhedra with exposed {001} facets. (d) SEM images of the flowerlike TiO<sub>2</sub> nanosheets. (e) Schematic representation of the growth of TiO<sub>2</sub> nanosheet arrays on carbon fibers. (f-g) SEM top-view images at different magnifications of uniform and dense arrays of TiO<sub>2</sub> nanosheets grown on carbon fibers. (h) TEM image of a TiO<sub>2</sub> nanosheet grown on a carbon fiber. Inset: Low-magnification image. (i–j) SEM images of TiO<sub>2</sub> nanosheets grown on carbon fibers. Adapted from ref. 71, 162, 167 and 168 with permission. Copyright Royal Society of Chemistry, American Chemical Society and WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

fiber without agglomeration, thus resulting in a high exposure area and a large surface area, which is critical for photocatalysis applications. Guo and co-workers<sup>71</sup> have reported such a synthetic strategy of highly-reactive facet dominated TiO<sub>2</sub> hierarchical structures (Fig. 20f-h). The carbon fibers are uniformly and compactly covered by a large number of tetragonal nanosheets with a thickness of 40-65 nm and side length of 500-800 nm. The percentage of {001} facets in TiO<sub>2</sub> nanosheets was calculated to be 40-92%, depending on the concentration of fluorine ions. The TiO<sub>2</sub> nanosheet on carbon fiber structure exhibited improved photocatalytic degradation and stability under light irradiation. Besides this work, Weng et al.<sup>168</sup> also reported the synthesis of {001} facet dominated TiO<sub>2</sub> nanosheets on a carbon fiber support (Fig. 20i and j). These hierarchical TiO<sub>2</sub> composite catalysts show enhanced photodegradation properties, notably because of the high reactivity of {001} facets. Moreover, the authors remarked that such a hierarchical structure has been shown to improve its reusability and, more importantly, provide a large surface area to fully expose the reactive facets.

Despite the rapid development of anatase TiO<sub>2</sub> with high energy facets for photocatalysis, challenges in the synthetic route and reactivity prediction still persist. By and large, the synthesis methods reported for anatase TiO<sub>2</sub> crystals with high-energy facets are hazardous since they involve capping agents of F-based compounds, which are highly corrosive. Thus it is desirable to develop a new synthesis method that uses a non-toxic and mild capping agent. Also, although a general consensus was reached on the enhancement of photocatalytic reactivity with exposed {001} crystal facets, there are some conflicting reports on the photocatalytic reactivity order of {010} > {101} > {001}.<sup>169,170</sup> Importantly, various interrelated crystal variables should also be considered to predict the photocatalytic reaction of a selective crystal facet. Nonetheless, the assembly of anatase building blocks into a well-organized structure with highly exposed active crystal facets is crucial to the design of high photoredox reactivity of the photocatalyst.

### 4.4 Mixed phase

The phase structure of TiO<sub>2</sub> is another important factor determining its photocatalytic performance. TiO<sub>2</sub> has mainly four polymorphs in nature, including anatase, rutile, brookite, and TiO<sub>2</sub>(B). All four types of TiO<sub>2</sub> consist of TiO<sub>6</sub> octahedra, but differ in the distortion of the octahedron units and share edges and corners in different manners.<sup>171</sup> The photocatalytic activities of these different phases of TiO<sub>2</sub> are quite distinctive. Phase mixtures of different polymorphs are known to have a synergistic effect on increasing the photocatalytic activity as compared to pure phases. However, for pure phases it is generally accepted that anatase exhibits a higher photocatalytic activity compared to rutile TiO<sub>2</sub>. Few explanations have been proposed for this phenomenon. Anatase has a VB edge at a higher energy level relative to redox potentials of adsorbed molecules, which enhances the oxidation capability of holes by effective transfer of holes from the TiO<sub>2</sub> to adsorbed molecules.<sup>172</sup> Another explanation is that, for a typical thermodynamically stable crystal, the dominant anatase {101} facet is of higher reactivity than the dominant rutile {110} facets.<sup>173</sup> Yet another explanation is the difference in the charge diffusion length between the phases, i.e. anatase having a longer diffusion length promotes longer life-time of charge excitations and/or higher charge carrier mobilities in anatase than in rutile.<sup>174</sup> Evidently, it has been shown that P25 made up of a mixed phase of about 70% anatase and 30% rutile was indeed found to be more active than the pure anatase or rutile phase. For this purpose, various combinations of mixed phases were synthesized to increase photocatalytic activity. Construction of hierarchical structures is a rational means to realize mixed phases of TiO<sub>2</sub> photocatalysts. Thus far, numerous hierarchical TiO<sub>2</sub> nanocatalysts with mixed phases have been synthesized to enhance the photocatalytic property.

Among the mixed phases, the anatase and rutile phases are the most frequently studied photocatalysts of  $TiO_2$ . Hierarchical anatase-rutile  $TiO_2$  has been prepared in a threedimensional nanowire-nanoparticle array for photoelectrochemical water splitting.<sup>175</sup> The photoelectrode is



Fig. 21 (a) Cross-sectional-view SEM image of TiO<sub>2</sub> ND/RNP/ANP arrays. (b) TEM image of TiO<sub>2</sub> NW/RNP/ANP. (c) Schematic diagram illustrating the respective band positions and photogenerated charge separation in the hierarchical anatase/rutile TiO<sub>2</sub> nanostructured arrays. Adapted from ref. 175 with permission. Copyright 2013 American Chemical Society.

composed of a one-dimensional rutile nanowire array with anatase nanoparticles (1.3-7.0 nm diameter) formed on the surface (Fig. 21a and b). The hierarchical TiO<sub>2</sub> structure of the mixed phase enhances charge separation and suppresses charge recombination at the interfacial region between the electrode and water. The difference in the energy levels of anatase and rutile CB acts as an effective charge separator. Electron and hole transfer between the two phases can induce increased lifetimes of electrons and holes, as verified by the electrochemical impedance spectroscopy measurements, leading to higher photocatalytic activity (Fig. 21c). As explained, the photogenerated electrons in the CB preferentially transfer to the rutile nanostructure in the absence of a space charge region under flat band conditions. Through both hierarchical morphology and mixed phase interfacial energetics, a remarkable improvement in photocurrent density and high photoconversion efficiency are attained. Another anatase-rutile mixed-phase hierarchical structure consisting of zero-dimensional building blocks has been reported for its high photocatalytic activity.<sup>176</sup> The hierarchical structure of interconnected nanoparticles forms a relatively high surface area porous network. The mixed-phase titania photocatalysts in this work feature a tunable rutile ratio via sol-gel and controlled calcination processes. As compared to conventional TiO<sub>2</sub> aggregates, such coexistence of the anatase and rutile phase hierarchical structures has shown superior photocatalytic performance, relative to either individual phase photocatalyst.

Among the crystalline TiO<sub>2</sub> phases, TiO<sub>2</sub>(B) is far less common compared to the other three phases. Owing to the lack of facile synthesis methods, TiO<sub>2</sub>(B) and TiO<sub>2</sub>(B) containing mixed phases are rarely studied, as compared to the wellknown anatase–rutile mixed phases. Recently, an effective method to synthesize TiO<sub>2</sub>(B) containing mixed phases has been demonstrated for photocatalytic applications. Wang *et al.*<sup>177</sup> reported hierarchical TiO<sub>2</sub> microspheres assembled by ultrathin nanoribbons of anatase-TiO<sub>2</sub>(B) mixed phase. Upon increasing thermal treatment, the as-obtained nanoribbon (Fig. 22a and b) is transformed to TiO<sub>2</sub>(B) at 400 °C



Fig. 22 (a) SEM and (b–f) TEM images of hierarchical  $\rm TiO_2$  microspheres. (g–k) TEM and HRTEM images of  $\rm TiO_2(B)/anatase/rutile$  nanobelts with branch structures. Adapted from ref. 177–178 with permission. Copyright Royal Society of Chemistry and American Chemical Society.

(Fig. 22c and d), then into mixed phases of anatase at 500 °C (Fig. 22e and f) and finally to the pure anatase phase (>500 °C). According to the crystallographic orientations in Fig. 22e and f, it can be further deduced that an intimate interface is formed between the (020) plane in anatase and the (020) plane of TiO<sub>2</sub>(B). A coherent interface is observed between anatase and TiO<sub>2</sub>(B) phases with closely matched lattice spacing of only 1.14% difference (0.3785 nm vs. 0.3741 nm). Therefore, it is believed that the epitaxial relationship between anatase and TiO<sub>2</sub>(B) phases ensures a well-matched atomic arrangement of these mixed phases. Interestingly, besides the above lattice-match induced epitaxial relationship, the high energy facet of the anatase  $TiO_2$  {001} is wellexposed. Such a unique structure exhibits a considerably high photocatalytic activity for organic degradation, due to coexistence of exposed reactive facets and the offset of the band energy levels between different phases, which facilitates charge transfer and thus enhances the photocatalytic activity.

Furthermore, a hierarchical structure of TiO<sub>2</sub> nanobelts with branched nanorods consisting of three mixed phases, anatase-rutile-TiO<sub>2</sub>(B), was reported by Sarkar et al. (Fig. 22g-k).<sup>178</sup> In detail, the nanobelt has uniform nanorod branches of 15 nm and width of about 8 nm, consisting of tri phases. The phase of the nanostructure was controlled precisely by adjusting the amount of titanium butoxide precursor and the annealing temperature. The band bending effect at the interfaces of mixed-phase TiO<sub>2</sub>(B), anatase, and rutile has been used to explain the improved photocatalytic effect. The CB of the anatase phase is positioned at a higher energy level than that of the rutile phase by about 0.20 eV, while the CB of the anatase phase is at a lower energy level than that of  $TiO_2(B)$ . When the three phases are in contact, the band edge differences aid interphase charge migration where the photogenerated electrons accumulate in the CB of rutile, with the holes in the  $TiO_2(B)$ . This process reduces the recombination

of the photogenerated charges and consequently improves the photocatalytic efficiency. The photocatalytic activity of these triphase nanobelts far exceeds that of single phase nanobelts.

A phase mixing approach is a promising strategy for enhancing charge separation in  $TiO_2$  and hence increasing photocatalytic reactivity. The origin of the improved photocatalysis performance is due to the potential difference established between disparate phases that promote efficient charge separation across the phase junction. The ability to synthesize and tailor both the  $TiO_2$  phase type and composition ratio through precursor and temperature control has enabled systematic study of the phase junction effect on photocatalysis. Various complementary time-resolved spectroscopies and electron paramagnetic resonance can be used to study the dynamics of photogenerated charge transfer to better understand the mechanism of the phase junction in photocatalysis.<sup>179–184</sup>

### 4.5 Heterostructure

Hierarchical structures of two or more materials forming a heterostructure are often used to exploit the strengths of individual materials and compensate their respective short-comings to improve the photocatalytic properties. The construction of well-defined heterostructures by appropriate coupling of foreign components to host a  $TiO_2$  matrix is capable of improving the photocatalysis through (i) extension of the light absorption spectral range, (ii) enhancement of charge separation and (iii) suppression of charge recombination. Hierarchical heterostructures are usually fabricated by two main strategies, namely direct/secondary assembly and loading/deposition of foreign components onto  $TiO_2$  structures.

In regard to the assembly of disparate materials onto TiO<sub>2</sub> structures, direct electrospinning or secondary growth by hydrothermal synthesis on electrospun nanofiber are commonly used to fabricate one-dimensional heterostructures with controllable hierarchical features. Another attractive feature of using the electrospinning method is its capability to prepare large scale mat or membrane nanofibers with potential for recycling. Different nanobuilding blocks, ranging from nanoparticles to nanocubes, nanosheets, nanorods and nanoflakes have been reported as a TiO<sub>2</sub> heterostructure with a hierarchical design. TiO2 nanofibers with SrTiO3 nanocubic heterostructures are fabricated using the electrospinning and secondary hydrothermal technique (Fig. 23a).<sup>185</sup> The uniform distribution of SrTiO<sub>3</sub> cubic nanocrystals on the surface of TiO<sub>2</sub> nanofibers and their interfacial contact leads to beneficial separation of photogenerated carriers. The solar H<sub>2</sub> evolution test shows five times more than bare TiO<sub>2</sub> nanofibers. Our research group has recently reported a TiO<sub>2</sub> heterostructure of nanofibers with nanoparticles (Fig. 23b).<sup>39</sup> Unlike previous reports on conventional surface loading or growth of co-catalyst nanoparticles, direct amalgamation of the co-



Fig. 23 SEM images of one-dimensional TiO<sub>2</sub> hierarchical structures (a) TiO<sub>2</sub> nanofiber with SrTiO<sub>3</sub> nanocubes heterostructures. (b) Wheatgrain textured TiO<sub>2</sub>/CuO nanofibers. (c) Electrospun TiO<sub>2</sub> nanofiber with MoS<sub>2</sub> nanosheets. (d–f) SnO<sub>2</sub>/TiO<sub>2</sub> heterostructures with SnO<sub>2</sub> nanoparticle, nanocrystal and nanorod architectures. (g–i)  $\beta$ -FeOOH/TiO<sub>2</sub> heterostructures with particles, needles and flakes. Adapted from ref. 39, 185–187 and 194 with permission. Copyright Nature Publishing Group, Elsevier, and American Chemical Society and WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

catalyst during electrospinning of TiO<sub>2</sub> nanofibers in our work ensures good stability and recyclability, due to the resistance of the co-catalyst against leaching. The resultant wheat grain-like textured heterostructure with an embedded cocatalyst ensures high surface contact and an intimate interface for enhanced photocatalytic H<sub>2</sub> generation 16.8 times higher than that of bare TiO2 nanofibers. Zhou et al.186 reported an electrospun TiO<sub>2</sub> nanofiber with hydrothermal growth of two dimensional building blocks of MoS<sub>2</sub> nanosheets that self-assembled on the surface of the nanofiber (Fig. 23c). The as-prepared heterostructures show high photocatalytic H<sub>2</sub> production and organic degradation as well as strong adsorption capabilities. Aside from the versatility of secondary hydrothermal growth on TiO<sub>2</sub> nanofibers, hierarchical heterostructures of various morphologies were reported by simply adjusting the reaction parameters.187 SnO<sub>2</sub>/TiO<sub>2</sub> heterostructures with SnO<sub>2</sub> nanoparticles, nanocrystals and nanorod architectures were fabricated by changing the SnCl<sub>4</sub> precursor concentration and reaction temperature (Fig. 23d-f). The photocatalytic studies demonstrated enhanced photocatalytic efficiency of photodegradation of SnO<sub>2</sub>/TiO<sub>2</sub> heterostructures compared to bare TiO<sub>2</sub> nanofibers. Other hierarchical TiO<sub>2</sub> heterostructures with dissimilar materials and of various structures were synthesized using similar methods. SnS<sub>2</sub> nanosheets/TiO<sub>2</sub> nanofibers,<sup>188</sup> ZnO nanocrystals/TiO2 nanotube arrays,189 WO3 nanoparticles/ TiO<sub>2</sub> nanotube,<sup>190</sup> ZnO nanorods/TiO<sub>2</sub> nanofibers,<sup>191</sup> NiO<sub>2</sub>/ TiO<sub>2</sub> flowerlike spheres<sup>192</sup> and reduced graphene oxide (RGO)

nanosheet/TiO<sub>2</sub> nanowire<sup>193</sup> hierarchical TiO<sub>2</sub> nanocomposites have been reported.

Other than the metal oxide based hierarchical heterostructure of dissimilar materials that could only be activated by UV light, the synthesis of more efficient visible-light driven multicomponent oxide photocatalysts with hierarchical heterostructure is a subject of considerable research interest. Our research group has recently reported hierarchical heterostructures of oxyhydroxide nanostructures on electrospun TiO<sub>2</sub> nanofibers. This work presented the versatility of tuning β-FeOOH structural design that cuts across zerodimensional particles, one-dimensional needles and twodimensional flakes (Fig. 23g-i). In addition, synthesizing such oxyhydroxide nanostructures presents the advantage of exhibiting similar functional performance to their oxide counterparts, without the need to undergo an annealing step that could lead to undesirable structural collapse or sintering. The as-obtained hierarchical branched nanostructures possess the combined advantages of rapid charge transfer pathway for carrier collection, large surface area for a greater number of reaction sites, and excellent light trapping, which are all favorable characteristics for enhanced photocatalytic degradation under visible light.<sup>194</sup> Similarly, Shang et al.<sup>82</sup> presented the preparation of a hierarchical nanofibrous mat, that consists of heterostructure Bi<sub>2</sub>WO<sub>6</sub> nanoplates growing aslant on the primary TiO<sub>2</sub> nanofibers. The hierarchical heterostructure exhibited enhanced visible photocatalytic activity of organic compounds in air and water. In general, when TiO<sub>2</sub> and the semiconductor are irradiated by light, the photoinduced electron would be injected from the semiconductor with a more positive CB level to the other, while holes would be transferred from the semiconductor with a more negative VB level across to the one that is more positive. Thus, a spatial separation of photoinduced charges and suppression of charge recombination is achieved, which consequently enhances their lifetime. Furthermore, TiO<sub>2</sub> has limited UV light absorption, while the narrow band gap semiconductor has a wider spectral light absorption. Hence, coupling of TiO2 with a narrow band gap semiconductor can achieve an extension of light absorption.

Another popular method of synthesizing a heterostructure involves straightforward and simple loading of the co-catalyst onto a hierarchical TiO<sub>2</sub> structure. The mass loading and thickness of the deposited co-catalyst onto the TiO2 surface are usually optimized, since high mass loading or too thick co-catalyst film could block the light incident onto TiO<sub>2</sub>, as co-catalysts are typically opaque. In general, noble metals, such as Pt,<sup>195</sup> Pd,<sup>196</sup> Au,<sup>197</sup> Rh,<sup>198</sup> Ru,<sup>199</sup> and Ag (ref. 200), have often been used as efficient co-catalysts. The work function of most metals is larger than that of  $TiO_2$  (4.2 eV), and hence readily promotes the electron transfer from the CB of TiO<sub>2</sub> to the metal. The electron trapping ability of the metal increases with work function, and as such Pt, with the highest work function, is noted as the best proton reduction co-catalyst amongst the noble metals. A Schottky barrier is formed at the interface when the TiO<sub>2</sub> semiconductor is



**Fig. 24** (a) SEM and (b and c) TEM images of TiO<sub>2</sub> spheres decorated with 2.43 wt% of Au nanoparticles (d) possible photocatalytic H<sub>2</sub> production mechanism of TiO<sub>2</sub>-Au under full spectrum light (left image) and visible light ( $\lambda > 420$  nm), where the middle image is TiO<sub>2</sub>-Au and the right image is TiO<sub>2</sub>-Au and Pt nanoparticles. Adapted from ref. 201 with permission. Copyright 2015 Royal Society of Chemistry.

coupled with the metal. The Schottky barrier will drive electron migration from TiO<sub>2</sub> to the noble metal until a thermodynamic equilibrium state is reached, that is, when the Fermi levels are aligned. Subsequent exposure to light irradiation will cause a shift of the TiO<sub>2</sub> Fermi level to a new quasi-Fermi level in which photogenerated electrons are rapidly transferred from TiO2 to Pt particles while the holes remained on the TiO<sub>2</sub>, thus decreasing the recombination rate of electron-hole pairs. Zhang et al.<sup>201</sup> reported hierarchical heterostructure TiO<sub>2</sub> spheres composed of nanosheets that were loaded with Au nanoparticles through anchor molecules (Fig. 24a-c). Different light irradiation scenarios were discussed wherein under UV light photoinduced electrons migrate to Au nanoparticles of higher work function than TiO<sub>2</sub> (Fig. 24d, left), while under visible light, the hot electrons generated in Au nanoparticles due to localized surface plasmon resonance effect will inject electrons to the TiO<sub>2</sub> (Fig. 24d, middle). Furthermore, dual co-catalyst loading of Pt and Au nanoparticles on the TiO<sub>2</sub>, which further improves the photocatalytic H<sub>2</sub> production rates observed under UV to visible light irradiation, is greatly enhanced in the presence of heterojunctions (Fig. 24d, right).

# Conclusions

As discussed, wide band gap semiconductor  $TiO_2$  is low cost and stable but inherently exhibits ineffective visible light absorption. Furthermore, charge recombination is another crucial factor that limits the solar energy conversion efficiency of  $TiO_2$  photocatalysts. Despite these challenges,  $TiO_2$ based photocatalysts continue to be the focus of photocatalytic studies, since the aforementioned drawbacks are surmountable with a synergistic combination of structural and electronic strategies. Here we have reviewed the background of critical design of photocatalyst/photoelectrode materials, a key towards marked improvement in solar energy conversion efficiency of  $TiO_2$  based photocatalysts. We have highlighted TiO<sub>2</sub> photocatalysts with well-defined structural design and the material composition exploitations that contribute to significant improvement in vital processes and attributes such as light absorption, photostability, charge-carrier dynamics, surface area etc. In our opinion, future generation photocatalysts will be of increasing complexity in terms of structural architecture as well as materials constituents. Sophisticated structural and materials hybridization can possibly be achieved through controlled synthesis and solid solution (alloying) of intrinsically narrow-band-gap materials for tunable band gaps, as shown in our recent publications. These efforts should coincide with the exploration of green and facile synthesis along with earth-abundant materials usage of appropriate energy alignment to address the ubiquitous cost and sustainability issues. Other fundamental gaps to be bridged include in-depth understanding of kinetics and dynamics of photoreactivity and other photocatalytic mechanistic studies at the nanometer and atomic levels using complementary computation, spectroscopy, microscopy and electrochemical techniques. With all the challenges of the TiO<sub>2</sub> photocatalyst overcome, we can expect TiO<sub>2</sub>-based photocatalysis to play an important role in the future clean fuel H<sub>2</sub> production and environmental remediation applications.

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