Shape Tailored TiO₂ Nanostructures and Their Hybrids for Advanced Energy and Environmental Applications: A Review

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Shape tailored TiO₂ nanostructures with various dimensionality (zero to three dimension) have unique physicochemical and functional properties that facilitates its efficient energy and environment applications, e.g., solar light driven photocatalytic hydrogen generation and decontamination of organic/inorganic toxic pollutants, CO₂ reduction into the hydrocarbon fuels, solar cells, supercapacitors and lithium-ion batteries etc. However, the wide band gap nature and the fast recombination of the photogenerated charge carriers in TiO₂ usually limit its overall performance under solar light illumination. In this review, we present a state of the art on the fabrication techniques of shape tailored TiO₂ nanostructures and the strategies employed to make the system catalytically more efficient. Though shape tailored TiO₂ nanostructures with large specific surface area and highly energetic (001) facet exposed TiO₂ nanostructures (2D and 3D) can enhance the photocatalytic efficiency to a reasonable extent, further surface engineering is needed for the modification of the electronic band arrangement, visible light sensitization and efficient charge separation. Herein, TiO₂ heterostructures (HSs) with metal/non-metal doping, surface fluorination, plasmonic noble metal nanoparticles (NPs) and coupling with the narrow band gap suitable semiconductor (type-II) are discussed in details covering from zero dimensional to three dimensional heterostructures. The synthesis strategies, charge transfer mechanism and their participation in the photocatalysis are elaborated. Though one dimensional TiO₂ HSs have been widely studied, we present the recent development of critical surface engineering strategies of two and three dimensional systems, which give rise to the excellent properties including the enlargement of surface area, light absorption capability and efficient separation of electrons/holes resulting in the superior performance in advanced applications. Based on recent breakthroughs in the field, future directions and outlook of the field are presented at the end.

Keywords: Shape Tailored TiO₂ Nanostructures, 0D TiO₂, 1D TiO₂, 2D TiO₂, 3D TiO₂, Plasmonic Heterostructure, Type-II Heterostructure, Visible Light Photocatalysis, Hydrogen Production.

1. INTRODUCTION

The rapid industrialization, continuous growth of global economy and population in the past few decades have...

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steadily raised the awareness of potential global crisis of energy because of our rapacious consumption of fossil fuels at an extremely fast rate. Thus, the global warming and climate change becomes the inevitable consequence of various pollution in the environment resulting from the extensive use of fossil fuels.\(^1\)\(^-\)\(^3\) For the sustainable development of our society, the advancement of technologies towards the renewable green energy systems as well as the environmental decontamination becomes the most urgent task. Parallel to the ongoing various renewable energy projects, such as supercapacitors, solar cells and lithium ion (Li-ion) batteries,\(^4\)\(^-\)\(^6\) optical photon induced catalysis or photocatalysis by a suitable semiconductor has attracted great attention and research fascination due to its diverse potential application in the field of energy and environment involving the decomposition of organic and inorganic pollutants,\(^7\) CO\(_2\) reduction into hydrocarbon fuels,\(^8\)\(^,\)\(^9\) and photocatalytic water splitting for hydrogen production.\(^10\)

After the remarkable discovery of photocatalytic water splitting in TiO\(_2\) electrode under the ultraviolet (UV) irradiation by Fujishima and Honda,\(^10\) notable progress has been made in designing the efficient semiconductor photocatalysts. Thus, the semiconductor TiO\(_2\) has been paid great attention, established to be most advantageous and extensively used for the various catalytic and energy applications such as, photocatalytic degradation of industrial pollutants,\(^11\)\(^,\)\(^12\) CO\(_2\) reduction,\(^13\)\(^,\)\(^14\) water splitting for H\(_2\) evolution,\(^15\)\(^,\)\(^16\) solar cells,\(^17\)\(^,\)\(^18\) supercapacitors,\(^19\)\(^,\)\(^20\) lithium ion batteries\(^21\)\(^,\)\(^22\) and biomedical devices,\(^23\)\(^,\)\(^24\) TiO\(_2\) satisfies the prerequisite to be an efficient photocatalyst keeping the redox potential of highly reactive oxygenated species (hydroxyl and superoxide radicals, hydrogen peroxide etc.) in forbidden energy gap. Initially the investigations were concentrated mainly on the TiO\(_2\) nanoparticles (NPs) and an excellent performance was observed only under the UV light irradiation. This is because of the large band gap of TiO\(_2\) (∼3.2 eV for anatase and brookite, ∼3.0 eV for rutile) and thus the threshold of excitation wavelength falls in the UV region of the solar spectrum.\(^25\)

Since, only ∼5% of the incident radiation on the earth’s surface lies in the UV zone and the rest 95% in the visible (∼43%) and infrared zone (∼52%), the performance of TiO\(_2\) nanostructures as a natural solar light photocatalyst is usually not satisfactory and it needs further investigation for lowering the activation energy of TiO\(_2\). Another unavoidable difficulties with the TiO\(_2\) NPs is the high recycling cost after each reaction due to its small size and high dispersion in the aqueous solution. As the photocatalysis is fully a surface property of a semiconductor, enhancement in the specific surface area of TiO\(_2\) nanostructures with various dimensionality such as (i) zero dimensional (0D) quantum dots (QDs), (ii) one dimensional (1D) nanorods (NRs), nanowires (NWs), nanobelts (NBs), nanotubes (NTs), nanoribbons (NRbs), (iii) two dimensional (2D) nanosheets (NSs) and three dimensional (3D) superstructures, nanoflowers (NFs), nanospheres etc.

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have been studied extensively in the last decade resulting in the significant advancement in the field of photocatalysis and energy applications.

In bare homogeneous TiO₂ nanostructure, the recombination process of photogenerated excitons is observed to be random and thus recombination is highly probable before reaching the surface to initiate redox reactions causing low efficiency of photocatalysis. Additionally, TiO₂ nanostructure can utilize only ~5% of the incident solar light 28 and shows slow charge carrier transfer, making it inefficient in the industrial scale.

To overcome these limitations, modification of physico-chemical and optical properties of the shape tailored titania and its heterostructures (HSs) is indispensable. Therefore, enhancement in the efficiency of the photocatalytic process by tuning the electronic band structure and light harvesting range of TiO₂ to the visible and NIR region has been achieved through various strategies, such as coupling with a narrow band gap semiconductor (type-II HSs), 29, 30 doping with metal and non-metal ions, 31–36 co-doping with multiple foreign elements, 37 depositing noble metal NPs 38–40 to form plasmonic HSs, surface sensitization with organic dyes, 41, 42 surface fluorination, 43, 44 etc.

In the last decade, an appreciable development has been made on the fabrication of shape tailored nanoscale TiO₂ HSs with various dimensionality. In this review, we first provide a summary of the crystal structures of TiO₂ in distinct phases followed by the detailed methodologies for the fabrication of shape tailored TiO₂ nanostructures, including OD, 1D, 2D and 3D nanostructures. Next, we focus on the tuning of electronic structure, the range of optical absorption and charge separation efficiency in the TiO₂ HSs fabricated by depositing plasmonic noble metal NPs, coupling with various appropriate narrow band gap semiconductors, doping etc. Finally, we look into their influence on the photocatalytic hydrogen evolution and environmental decontamination properties.

2. CRYSTAL STRUCTURES OF VARIOUS PHASES OF TiO₂

Titania (TiO₂) generally exists in three distinct poly-morphs (phases): rutile, anatase, and brookite, where anatase and rutile phases have tetragonal crystal structure with space groups I41/amd and P42/mmm, respectively and brookite has orthorhombic crystal structure with space group Pbcn. 45 In each polymorph, titanium cations are found to be six-fold coordinated to oxygen anions, which forms distorted TiO₂ octahedra. The crystal structure of TiO₂ differs with phase due to the distinct spatial arrangement of the TiO₂ octahedra building blocks (see Fig. 2). While anatase has corner sharing TiO₂ octahedra, in rutile phase edge sharing is observed and the brookite shows the both. Among the different crystal phases, rutile is considered to be the most thermodynamically stable bulk phase. At the nanoscale, anatase and brookite are generally regarded as more stable due to their low surface energy, although there exists some debate on this issue. 46, 47 Additionally, there exists another exotic crystal phase of pure TiO₂ (space group C2/m), known as TiO₂ (B) (Fig. 2(d)). This phase is generally produced by solution based process, like hydrothermal method. It has a very open framework structure despite having the identical chemical formula. Thus, it possesses a lower density and a larger specific capacity than other phases, which are extremely advantageous in the applications of photocatalysis, solar cells and energy storage, such as lithium-ion batteries. 48–51 The detailed growth studies have revealed that the crystal phases are determined by the experimental conditions and also post growth treatments (synthesis method, pH of the medium, annealing duration and annealing temperature). Zhang et al. 52 have thermodynamically analyzed the limiting crystal size to be stable under a certain crystal phase. Anatase can have the size up to 11 nm, for brookite 11–35 nm and for the bulk phase, rutile, it should be more than 35 nm. Yang et al. 53 obtained different crystal phases (rutile, anatase, and brookite) by a hydrothermal method using different pH values of peroxide titanic acid solution. With pH value lower than 8, only rutile phase was found. When the pH was varied in the range 8–10, brookite and rutile phases were obtained in the mixed phases. However, with the pH value higher than 10, only anatase phase was obtained. Santara et al. 54 discussed the effect of annealing temperature and environment on the crystal phases and surface feature of the TiO₂ nanostructures. Prior to the annealing, no peak was observed in the XRD pattern of the TiO₂ nanoribbon. The growth of TiO₂ (B) phase from hydrogen titanate was observed at annealing temperature 500 °C. When the temperature was increased to 700 °C, the B-phase started converting into anatase and a mixture of these two was obtained. When annealed at 900 °C, the TiO₂ nanoribbons were found in anatase and rutile mixed phase, indicating a partial transformation of anatase into rutile phase. Beyond 900 °C only

Figure 1. A schematic illustration of various steps of photocatalysis by TiO₂: (I) formation of free excitons, (II) photoinduced charge recombination, (III) photoinduced charge transfer to the oxygen or hydroxyl ion (IV, V) oxidation and reduction caused by valence band hole and conduction band electron, respectively. Reproduced with permission from [28], Y. Wang, et al., Nanoscale 5, 8326 (2013). © 2013, RSC.
phase detected was rutile in bulk phase. Tay et al.\textsuperscript{55} synthesized a mixed phase anatase/brookite TiO\textsubscript{2} nanostructure by a simple hydrothermal method, which shows enhanced hydrogen production activity compared to the highly crystalline pure brookite and P25.

\section{3. SYNTHESIS OF SHAPE TAILORED TiO\textsubscript{2} NANOSTRUCTURES}

Distinct morphological feature of semiconductor nanostructures acts as extremely determining factor for the growth of high performance photocatalysts for hydrogen evolution as well as environmental cleaning, Li-ion batteries, solar cells, etc. Thus, shape tailored various surface morphology of TiO\textsubscript{2} including zero dimension (quantum dots), one dimension (nanorods, nanowires, nanoribbons, etc.), two dimension (nanosheets, nanoplates, etc.) and three dimension (flowers, hierarchical architectures) are being extensively investigated to address the challenges of energy crises, environmental issues, etc. of the modern era.

\subsection{3.1. Synthesis of 0D TiO\textsubscript{2} Nanostructure}

0D TiO\textsubscript{2} quantum dots (QDs) based nanostructures are comparatively least studied system among various dimension nano-heterostructures (1D, 2D and 3D) for the energy and environmental applications. To grow the shape tailored nanostructures, hydrothermal method is one of the most widely used methods for its versatility with controllability, repeatability, relatively lower cost and industry based large scale production. Recently, few approaches have been explored to prepare the 0D TiO\textsubscript{2} QDs based various HSs after the breakthrough work by Pan et al.\textsuperscript{16} on the hydrothermal synthesis of (001) facet dominated TiO\textsubscript{2} nanosheet with self-decorated TiO\textsubscript{2} QDs. Their long time hydrothermal strategy and subsequent defect curing by the hydrothermal washing are the key factors to obtain defect-free nanosheets decorated with TiO\textsubscript{2} QDs with sizes 1.5–3 nm, as shown in Figure 3. The band gap enlargement of TiO\textsubscript{2} due to the formation of QDs and its HSs with TiO\textsubscript{2} nanosheet increases photoactivity significantly which is highly promising for photocatalytic performances.

Xu et al.\textsuperscript{57} designed TiO\textsubscript{2} QDs on Cu\textsubscript{2}O octadecahedra (Cu\textsubscript{2}O–O) single crystals with (110) and (100) exposed facets synthesized by a sol gel method. Figures 4(a)–(d) shows the details of the structural and morphological properties of the TiO\textsubscript{2} QDs and Cu\textsubscript{2}O HSs. The Figure 4(e) demonstrates the synthesis pathways of the Cu\textsubscript{2}O octadecahedra, TiO\textsubscript{2} QDs and their HSs. Special technique of coupling the TiO\textsubscript{2} QDs with the Cu\textsubscript{2}O facets to form numerous stable \textit{p}–\textit{n} heterojunctions is used here for the extremely efficient charge migration through the interface of the heterostructures.

\subsection{3.2. Synthesis of 1D TiO\textsubscript{2} Nanostructures}

\subsubsection{3.2.1. Sol–Gel and Template Assisted Method}

One of the key synthesis processes of wet chemistry method is the sol–gel method with low temperature and easy control in surface morphology is generally used to synthesize 1D TiO\textsubscript{2} nanostructures. In general, the TiO\textsubscript{2} sol–gel is prepared by mixing titanium isopropoxide or titanium butoxide in acetic acid followed by a heating to high temperature with vigorous magnetic stirring which allows hydrolysis and condensation reactions. Thus shape tailored TiO\textsubscript{2} nanostructures are obtained. Joo et al.\textsuperscript{58} have prepared 3.4 nm (diameter) × 38 nm (length) sized TiO\textsubscript{2} nanocrystals from sol–gel reaction between titanium(IV) isopropoxide and oleic acid at 270 °C. They have successfully controlled the length of the as-grown NRs between 28–39 nm by adding 1-hexadecylamine to the reaction mixture as a co-surfactant. The template-assisted method is also extensively used to fabricate the 1D TiO\textsubscript{2} nanostructures. An anodic aluminum oxide (AAO) nanoporous membrane consisting of parallel straight array of nanopores with well controllable dimension (diameter and length), is usually considered as a template. Finally, the template is removed by chemical etching and 1D TiO\textsubscript{2} nanostructures remain on the substrate. Sander et al.\textsuperscript{59} have fabricated dense, thermally stable and well-aligned TiO\textsubscript{2} nanotubes by sequential atomic layer deposition (ALD) process with TiCl\textsubscript{4} as the precursor material using template assisted method. A combination of sol–gel and template assisted method produces better control over

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.jpg}
\caption{A schematic representation of various TiO\textsubscript{2} polymorphs: (a) Rutile; (b) anatase; (c) brookite; and (d) TiO\textsubscript{2} (B). Each purple sphere represents Ti atom, and the blue octahedra represent TiO\textsubscript{6} blocks. Oxygen atoms at the corner of the octahedra are omitted for clarity. Reproduced with permission from [45], Y. Zhang, et al., RSC Adv. 5, 79479 (2015). © 2015, RSC.}
\end{figure}
the growth of 1D TiO₂ nanostructures and high performance in the real life applications. For example, Qiu et al.⁶⁰ and Lin et al.⁶¹ synthesized 1D TiO₂ nanorods, nanotube arrays and nanowires, respectively by a combined template-assisted sol–gel method as shown in Figure 5.

### 3.2.2. Hydrothermal Method

Hydrothermal method is the most used chemical method for the fabrication of shape tailored TiO₂ nanostructures including various 1D architectures. Usually the reaction is conducted in a stainless steel chamber with a Teflon liner under high temperature with autogenous pressure.

It is probably the simplest method for tuning the surface morphology at the lowest production cost. Kasuga et al.⁶²–⁶³ discovered a template free new route to fabricate TiO₂ nanotubes with diameter ~8 nm and length ~100 nm considering amorphous TiO₂ as a precursor material treating at high temperatures with concentrated NaOH solvent. Afterwards, many research articles have reported on the growth of TiO₂ nanotubes,⁶⁴–⁶⁵ nanowires,⁶⁶–⁶⁷ nanorods,⁶⁸–⁶⁹ nanobelts,⁷⁰–⁷¹ nanosheets⁷²–⁷⁵ by the hydrothermal method. Depending upon the solvent used, the synthesis procedure can generally be divided into two methods: first, acid hydrothermal method where the reactants are titanium salts and concentrated hydrochloric acid (HCl) and second, alkali hydrothermal method where the reactants are TiO₂ nanoparticles and concentrated sodium hydroxide (NaOH) solution. These two
methods have different reaction mechanism which produces different 1D morphological features of TiO₂. During alkali-hydrothermal process, layered sodium titanate \((\text{Na}_2\text{Ti}_4\text{O}_9)\) is produced in an intermediate reaction stage. As the \(\text{Na}^+\) ions are residing between the edge-shared TiO₆ octahedral layers, it can be easily replaced by protons (H⁺ ion) in a dilute acidic medium. Thus, hydrogen titanate \((\text{H}_2\text{Ti}_5\text{O}_{11} \cdot \text{H}_2\text{O})\) is formed and the interlayer distance becomes enlarged because of the larger intercalated size effect of H₂O molecules causing weaker static interaction between neighboring TiO₆ octahedral sheets. Thus, hydrogen titanate can easily be exfoliated to form nanosheets which in turn curl up from the edges to form TiO₂ nanotubes to minimize the high surface tension.\(^{76,77}\)

Additional hydrothermal conditions like type of precursor, its size, concentration of NaOH solvent, temperature and reaction duration may affect the structure and morphology of the nanostructures.

Morgan et al.\(^{78}\) showed the effect of concentration of NaOH and the reaction temperature on the formation of various nanostructure from P25 (TiO₂) through alkaline hydrothermal treatment (see Fig. 6). Similar results have been reported by Tanaka\(^{79}\) and Peng et al.,\(^{80}\) an investigation of the effect of concentration of NaOH, temperature and reaction time duration on the nanostructure formation.

For further modification and improvement in the nanostructures, several approaches like microwave assisted heating process, ultrasonication and magnetic rotation of the reactants during the hydrothermal treatment were adopted. Stirring based hydrothermal method has been proved to be an extremely beneficial for the growth of much longer nanotube (up to tens of micrometers) (see Fig. 7). The optimized nanotubes with very high aspect ratio exhibit ultrafast rechargeable Li-ion battery materials with high stability.\(^{81,82}\)

### 3.2.3. Solvothermal Method

Similar to the hydrothermal process, the solvothermal method is also a common growth process for various TiO₂ nanostructures. The only difference between the hydrothermal and the solvothermal method is the use of organic solvent (ethanol, ethylene glycol, \(n\)-hexane, etc.) in solvothermal method, while only water is used as reaction solution in hydrothermal method.\(^{83-87}\) Wang,\(^{88}\) Santara et al.\(^{53,89}\) have grown nanowires, nanotubes and nanoribbons by a solvothermal method considering ethanol, glycerol and ethylene glycol as solvents, respectively, see Figures 8(a), (b), (e)–(h). The as-grown nanowires and nanotubes are suitable for the high performance Li-ion battery materials, whereas the nanoribbons with modified effective band gap and optical absorption window are promising for the photocatalysis under solar light. Nitrogen and fluorine co-doped TiO₂ nanobelts have also been reported for high performance photocatalysis, see Figure 8(c).\(^{88}\) Selection of appropriate solvent is the

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**Figure 6.** Morphological shape evolution of P25 (TiO₂) to (a) nanotube and (b) nanoribbon after hydrothermal treatment at 160 °C and 220 °C, respectively. Reproduced with permission from [78], D. L. Morgan, et al., *Chem. Mater.* **20**, 3800 (2008). © 2008, ACS.
key factor for the growth and various surface modifications of the nanostructures.

Despite its versatility and advantages of the hydrothermal and solvothermal method over the other growth processes, it has still some disadvantages. First, the nanostructures grown by this method are not always uniform in size and shape. Second, the as-grown 1D nanostructures are generally too small for the better performance in the real life applications. Third, the reaction rate is very slow and it takes long time to grow desired materials. Fourth, the growth of monolayer 2D materials (MoS$_2$, MoSe$_2$, WS$_2$, etc.) is not well controllable by this method.

Figure 7. (a) FESEM image of TiO$_2$ nanotubes obtained at 500 rpm. (b) TEM image of (a), the arrow shows nanotubular structure. (c–f) FESEM images of TiO$_2$ nanotubes obtained from the hydrothermal reaction with temperature maintained at 130 °C for 24 hrs at stirring rates of 0, 300, 400, 500 and 1000 rpm, respectively. (g) XRD patterns of TiO$_2$ nanotubes at various stirring speed. Reproduced with permission from [81], Y. Tang, et al., Angew. Chem. Int. Ed. 53, 13488 (2014). © 2014, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Figure 8. SEM micrographs of different TiO$_2$ nanostructures synthesized by the solvothermal method: (a) Nanowires, (b) nanotubes, (c) nanobelts. Reproduced with permission from [88], Q. Wang, et al., Inorg. Chem. 45, 6944 (2006). © 2006, ACS (a, b). Reproduced with permission from [90], Z. He, et al., ACS Appl. Mater. Interfaces 4, 6816 (2012). © 2012, ACS, (c). (d–f) TEM and FESEM images, respectively of TiO$_2$ (B) nanoribbons synthesized at 180 °C for 16 hrs and 500 °C post growth treatment. The inset of (e) shows the EDX spectrum. Reproduced with permission from [54], B. Santara, et al., Nanoscale 5, 5476 (2013). © 2013, RSC. (g) High magnification TEM image of TiO$_2$ nanoribbons calcined at 700 °C showing nanobricks and nanopits on its surface, and the inset shows the corresponding SAED pattern. (h) FESEM images of TiO$_2$ nanoribbons calcined at various temperatures: 500 °C, 700 °C and 900 °C, respectively. Reproduced with permission from [89], B. Santara, et al., J. Phys. Chem. C 117, 23402 (2013). © 2013, ACS.
3.2.4. Electrochemical Anodization Method

In 1984, Assefpour-Dezfuly et al.\textsuperscript{91} reported the growth of porous, well aligned 1D TiO\textsubscript{2} nanotube arrays by two step process: etching in alkaline peroxide and then anodization in chromic acid. Presently, anodization process is commonly used for the synthesis of 1D TiO\textsubscript{2} nanostructured materials on Ti foil substrate. The TiO\textsubscript{2} nanotubes synthesized by this method are very promising for the photoanode material due to its high performance, stability and easy synthesis procedure. Afterwards, Zwilling et al.\textsuperscript{92} made a breakthrough by growing nanoporous titania nanotube in fluoride containing electrolytes on Ti foil. Since then, a lot of attention has been paid to optimize the controlled growth of the 1D TiO\textsubscript{2} nanostructures.\textsuperscript{93–95}

It is now well understood that the nature of electrolyte, it’s pH, applied voltage, reaction duration and temperature of the reaction solution determine the morphology and the dimension of the TiO\textsubscript{2} nanostructures. The as-grown TiO\textsubscript{2} nanotubes of various generations are shown in Figure 9. Even though, a remarkable progress on the optimized growth of 1D TiO\textsubscript{2} nanostructure has been achieved, development is still going on for the further improvement of the length of the nanotubes in F\textsuperscript{-} based organic-inorganic neutral electrolytes.

3.2.5. Electrospinning Method

In 2003, Li et al.\textsuperscript{96} synthesized TiO\textsubscript{2} nanofibers having diameter \(\sim\)55 nm by a electrospinning method for the first time. In this process, a polymer solution is injected from a needle of a syringe like chamber under the influence of strong electric field. Due to the continuous gathering electric charges, the polymer solution starts stretching to form ultralong and hollow nanofibers. More and more attention are being paid to this method due to the easy formation of single-phase and highly crystalline TiO\textsubscript{2} nanofibers. Figure 10(a) shows a schematic of the electrospinning process and the (b) is the FESEM images of TiO\textsubscript{2} nanofibers grown by it. Zhu et al.\textsuperscript{98} reported the growth of porous-shaped anatase TiO\textsubscript{2}, cluster-shaped anatase TiO\textsubscript{2}, hierarchical-shaped rutile TiO\textsubscript{2}, and nano-necklace rutile

![Figure 9](image-url). SEM images of the TiO\textsubscript{2} nanotubes categorized under (a) 3rd generation in ethylene glycol/fluoride electrolytes, (b) shows a inclined view of (a) and (c) is the TEM image of a TiO\textsubscript{2} nanotube corresponding to (a), (d, e) top and cross section view, respectively of 5th generation with multi step anodization in ethylene glycol/fluoride electrolytes, (f, g) top and cross section view, respectively of 5th generation with two-step anodization process with ethylene glycol and fluoride electrolytes. Reproduced with permission from [93], M. Paulose, et al., J. Phys. Chem. C 111, 14992 (2007). © 2007, ACS, (a–c). Reproduced with permission from [94], M. Ye, et al., J. Am. Chem. Soc. 134, 15720 (2012). © 2012, ACS, (d–e). Reproduced with permission from [95], M.-Z. Ge, et al., J. Mater. Chem. A 3, 3491 (2015). © 2015, RSC, (f–g).
TiO$_2$ by the electrospinning method followed by the annealing at temperatures 500, 600, 700 and 800 °C, respectively. It is observed that the diameter of the nanofibers shrink from 200 nm to <100 nm due the effect of annealing at high temperatures though the axial continuity is unaltered. Ag, CuO, ZnO, carbon, etc. can be introduced into the nanofibers to modify the surface features for the improvement in many application like photocatalysis.97–99

3.3. Synthesis of 2D TiO$_2$ Nanostructures

2D faceted TiO$_2$ nanosheets with various surface energies are at the focus of intense research in the field of energy and environmental remediation. The key factor on tuning the exposed crystallographic facets of TiO$_2$ as well as its facet percentage without disturbing its stability is the nature of solvents used, capping and shape controlling agents and impurities introduced into the crystals.100–102

The capping agents used to be adsorbed selectively and interact differently with the different crystalline facets. This strategy is used to design nanocrystals with various dominant reactive facets.103

Several fabrication techniques have been developed for the growth of 2D TiO$_2$ nanocrystals dominated with (001) facets. Among all, most explored and easy method is the surface fluorination to stabilize the highly reactive (001) facets.105

3.3.1. Hydrothermal Method

Recently, researches are focused on the development of 2D anatase single crystals with large percentage of reactive (001) facets due to its extremely high reactivity using a simple facile hydrothermal method.106–110 Various techniques are used to calculate the exposed facets like, FESEM, TEM and XRD simply by assuming the whole surfaces are occupied by the (101) and (001) facets.69

Yang et al.75 reported for the first time the hydrothermal synthesis of anatase TiO$_2$ single crystals with 47% exposed (001) facets considering TiF$_4$ as a precursor material and hydrofluoric acid (HF) as a shape controlling agent. Each single truncated bipyramid shaped anatase TiO$_2$ nanocrystal is composed of two flat square surfaces corresponding to (001) facets while the four isosceles trapezoidal surfaces are ascribed to the (101) facets. The average interfacial angle between these two facets is estimated to be ~68.3° which is consistent with the theoretical value.112 Following this work, synthesis of (001) facet dominated 2D TiO$_2$ nanosheets have been extensively studied with various surface modification for photocatalytic applications. Wen et al.113 synthesized large area highly reactive and purely anatase TiO$_2$ nanosheets fully dominated by (001) and (100) facets with relative amount of 98.7% and 1.3%, respectively which are generally thermodynamically unfavourable due to their...
high surface energy. The as-grown TiO₂ nanosheets are very large in the length ~4.1 μm and (001) facet dominated surfaces are showing appreciably high photocatalytic activity (see Fig. 11). Yu⁻⁄ and Wang et al.¹¹⁵ synthesized (001) facet dominated anatase TiO₂ nanosheets by the hydrothermal method, which are highly beneficial for the photoelectric conversion efficiency in dye-sensitized solar cells as compared to the P25. Han,¹⁰⁶ Yan,¹¹⁶ Tian¹¹⁷ and Liu et al.¹¹⁸ also synthesized (001) faceted TiO₂ nanosheets which behave as good photocatalysts. Wu and co-workers reported a facile non-aqueous synthesis route for the preparation of rhombic-shaped anatase TiO₂ nanocrystals with exposed (001) for the first time.¹¹⁹ Following this work, Gordon et al.¹¹¹ synthesized TiO₂ NCs having size 10–100 nm by a controlled non-aqueous seeded growth considering the precursors TiF₄ and TiCl₄ where the TiF₄ enables the exposure of (001) facets (see Fig. 12). Dinh et al.¹²⁰ demonstrated the TiO₂ nanocrystal growth with various shapes: rhombic, truncated rhombic, spherical, dog-bone, truncated and elongated rhombic, etc. by using a modified hydrothermal route employing both as capping agents (see Fig. 12). In the water vapor
environment a simple variation of oleic acid and oleylamine molar ratio, precursor or the reaction temperature make extremely fine tuning over the shape evolution of the TiO₂ nanocrystals, similar to the works discussed in the Ref. [121].

### 3.3.2. Chemical Vapor Deposition Method

Though the chemical based growth mechanism of TiO₂ is now firmly established, the synthesis of pure TiO₂ nanostructure by physical method is not yet well explored. Lee et al.122 designed high density (001) facet dominated TiO₂ nanosheets both in anatase and rutile phases on silicon and silicon coated substrates via a chemical vapor deposition method, as shown in Figure 13. They have shown that the H₂ autoignition induced below its autoignition temperature (536 °C) could prevent the phase transformation from anatase to rutile.

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**Figure 13.** (A, B) Schematic representation along with the FESEM micrographs of (001) facet dominated anatase and rutile TiO₂ nanosheets by CVD method with H₂ flow. Reproduced with permission from [122], W.-J. Lee and Y.-M. Sung, *Cryst. Growth Des.* 12, 5792 (2012). © 2012, ACS.

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### 3.4. Synthesis of 3D TiO₂ Nanostructures by Hydrothermal/Solvothermal Method

#### 3.4.1. (001) Faceted Nanocubic Structures

Numerous techniques have been explored for the fabrication of 3D TiO₂ architectures with different shapes. Notable progress has been reported for the preparation of (001) facet dominated 3D nanostructures by hydrothermal and modified hydrothermal methods. As the average surface formation energy is maximum for (001) facet (0.90 J m⁻²) which is almost double than that of the (101) facet (0.44 J m⁻²) these facets are highly catalytically active and are very promising for the future generation of energy and environmental cleaning.72 3D TiO₂ single crystal architectures have been synthesized by various precursor materials like TiF₄, TiCl₄, Tetrabutyl titanate, titanium isopropanoxide, TiOSO₄, etc.32,43,123 Yang and co-workers demonstrated a novel solvothermal route for the shape tailored synthesis of 3D single crystals of anatase TiO₂ with dominating

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Figure 15. (a, b) FESEM and TEM images of nearly 100% (001) facet dominated anatase TiO₂ nanosphere, respectively. (c) FESEM image of (001) faceted TiO₂ nanoflowers. (d) FESEM image of etched (001) faceted TiO₂ nanoflowers with size 1.5–2 μm. Reproduced with permission from [21], J. S. Chen, et al., J. Am. Chem. Soc. 132, 6124 (2010). © 2010, ACS, (a, b). Reproduced with permission from [72], M. Liu, et al., Nanoscale 2, 1115 (2010). © 2010, RSC, (c). Reproduced with permission from [73], Q. Xiang, et al., ChemComm. 47, 4532 (2011). © 2011, RSC, (d).

percentage of reactive facets prepared by considering a water-2-propanol as solvent (see Fig. 14).
Wen et al. demonstrated the solvothermal synthesis of single crystalline TiOF2 nanocube and its transformation to anatase TiO2 for the first time by the calcination under various atmospheres such as pure argon, moist argon and pure hydrogen sulfide (H2S). After this breakthrough work, similar reports have been published on the solvothermal synthesis of 3D TiO2 single crystals with cubic morphology for the efficient photocatalysis as well as the energy applications (see Fig. 14). 

3.4.2. (001) Faceted Nanoflower Structures
Chen et al. reported the growth of 3D hierarchical nanoporous spheres of lateral size a few hundred nm composed of ultrathin anatase TiO2 nanosheets (thickness ~3 nm) for the first time with nearly 100% exposed (001) facets, as shown in Figure 15. The nanospheres with high specific surface area (~170 m2 g−1) is reported to be extremely beneficial for the reversible and ultrafast Li-ion battery application. Besides, Liu et al. reported a novel growth process via a simple hydrothermal route of 3D anatase TiO2 nanoflowers composed by truncated tetragonal pyramidal TiO2 nanocrystals. Ti powder was used as precursor material and the hydrofluoric acid (HF) as the shape controlling agent. The size of the nanoflowers are reported to be 300–700 nm while the truncated tetragonal pyramidal TiO2 nanocrystals have size 50–150 nm. Following this work, several reports have been published with tuned (001) facet percentage with various precursor material. Ma et al. considered the shape controlling agents as disodium ethylene diamine tetraacetate (EDTA) along with the HF solution while TiF4 as the precursor material and they observed much larger nanoflowers with length up to 1.2 μm. Numerous studies have been performed thereafter to enhance the photocatalytic performance, dye sensitized solar cell and Li-ion battery application simply by controlling the (001) facet percentage. 

3.4.3. 3D Microspheres
Liu et al. demonstrated a fluoride mediated self-transformation based fabrication of hollow TiO2 microspheres of diameter 1–2 μm, which is composed of anatase polyhedral, as shown in Figure 16. Yu and co-workers also have shown a novel one-step hydrothermal strategy for the growth of surface-fluorinated TiO2 hollow microspheres and tubular-shaped anatase single crystals (001) facets exposed considering ammonium bi-fluoride (NH4HF2) as a shape controlling agent. Recently, Liu et al. showed a new facile method consisting of electrospray and hydrothermal treatment to grow mesoporous core–shell TiO2 microspheres composed of tiny anatase TiO2 nanocrystals and dominated by high-energy facets. It is proposed that the amorphous TiO2 network formed by the electrospray plays a crucial role for the formation of mesoporous TiO2 spheres. The core–shell structure with very specific surface area as well as exposed high energy facets makes the system a very promising candidate for application in photocatalytic hydrogen evolution and DSSCs.

3.4.4. 3D Hierarchical Microstructures
Fabrication of 3D hierarchical flower-like nanostructure has attracted enormous attention due to their large density of active sites, high surface area and greater pore volume, as these properties are extremely beneficial for the adsorption and catalytic application. A glycerol mediated solvothermal technique followed by calcinations under various preselected conditions has been demonstrated by Tian et al. (see Fig. 17). The 3D morphology evolution by dissolution and recrystallization is fully determined by the reaction species, temperature, and duration of nucleation. Further, H2O2 was also employed as a structure-tuning agent to grow purely anatase TiO2 microflowers with (001) facets exposed. As HCl has a tendency to assist the growth in the rutile phase, an interplay between the HCl and H2O2 finally determines the crystal structure, phase, morphology, and facet orientation. The phase evolution of TiO2 has been observed to vary gradually.
from pure rutile to bi-crystalline phases of anatase and rutile and finally to pure anatase with increasing H₂O₂ concentration in the range 0–0.7 M. Recently, titanium glycerolate precursor has been used by Kim et al. as both the TiO₂ precursor as well as the sacrificial templates which discards the requirement of additional surfactants or ionic additives. Similar growth mechanism i.e., nucleation-aggregation-recrystallization of 3D hierarchical anatase superstructures with high percentage of exposed (001) facets has been successfully demonstrated via a simple one-pot solvothermal strategy.

4. SURFACE ENGINEERING OF TiO₂ NANOSTRUCTURE AND ITS APPLICATION IN CATALYSIS

In the last few decades, various photocatalysts have been explored, such as TiO₂, ZnO, WO₃, Bi₂WO₆, ZnWO₄, etc. Among them, TiO₂ nanostructures have proved its extremely high potential as a photocatalyst and a positive sign can be observed in its commercialization as a photocatalyst. The coupling of different semiconductors results in improved photocatalytic activity. TiO₂ shows appreciably good photocatalytic activity irrespective of the nature of the medium of catalytic reaction: in aqueous pollutants, air pollutants or the CO₂ reduction from the hydrocarbon fuels. Energy and environmental problems gradually become more serious with the fast development of technology and economy. Specially, huge amount of waste water and heavily toxic gases from the various factories are destroying the diversity of water life by contaminating it and introduces non-curable disease in the human life. Thus, an urgent as well as effective solution for these problems was needed to maintain the growth of economy and sustainable development of technology. TiO₂ has been established to be an excellent photocatalyst and it can be commercialized due to its abundant availability in the nature, non-toxicity, strong oxidizing as well as reducing power and long-term stability towards the photo and chemical corrosion. The limitations of the bare TiO₂ nanostructures is its UV illumination sensitivity (wide band gap, anatase: 3.2 eV, rutile: 3.0 eV) and weak separation efficiency of the photogenerated charge carriers leading to the efficient recombination which results in low photocatalytic activity under the solar irradiation. After the photo-excitation, electrons at the conduction band may attack the oxygen molecules to produce superoxide radicals, and the valence band holes can react with water to generate hydroxyl radicals simultaneously which in turn degrades the pollutants, see Figure 1, showing a possible simple reaction mechanism of the photocatalysis. In comparison to the photocatalysis, photoelectrocatalysis has been shown to have higher efficiency of catalysis i.e., the degradation pollutants as well as hydrogen generation. In this case, a low bias voltage applied to the TiO₂ electrode can transfer the photocarriers efficiently through the external circuit inhibiting their fast recombination. Thus, plenty of active species (hydroxyl, superoxide radicals) present on the TiO₂ surface accelerates the catalytic efficiency.

Being a wide band gap semiconductor, the optical absorption of TiO₂ fully falls in the UV region (~380 nm). Besides, the excited state average life time of the photo-generated electrons and holes is too short to participate in the redox reaction for bare TiO₂ nanoparticles. However shape tailored 1D, 2D and 3D TiO₂ nanostructures exhibit superior charge transport due to the high specific surface area, exposed high energy facets, low axial resistance (for 1D structures), etc. Though the shape tailored TiO₂ architectures are showing better results in degradation as well as hydrogen evolution it is still necessary to modify the electronic arrangement in the nanostructure by incorporating several techniques to make it industry level efficient. Several modifications have been explored to prevent recombination of electrons/holes and to achieve higher photocatalytic activity such as: (1) doping with metal and non-metal elements, (2) loading noble metal nanoparticles to drive surface plasmon resonance (SPR) and to create hot electrons and (3) fabrication of staggered type (type-II, in general) heterostructure with another semiconductor for synergic absorption and efficient interfacial charge separation for better utilization of solar energy.

4.1. 0D TiO₂ Quantum Dots and Its HSs

The TiO₂ QDs can have even larger band gap than its bulk counterpart making it disadvantageous for the utilization of solar light. As the separation of the photocatalyst from the pollute solution after photocatalysis is an important and inevitable part, use of only TiO₂ QDs for photocatalysis is not recommended. But, a proper heterostructure with different phase or microstructure can be beneficial to create longer life time of charge carriers through the interfacial charge transfer, making the system promising. Pan et al. demonstrated a TiO₂ QD HSs with 2D (001) faceted TiO₂ nanosheet. The band position of narrow band gap 2D TiO₂ and large band gap 0D QDs are suitable enough for the efficient transfer of photogenerated electrons from the 2D to 0D surface and vice versa for the holes. Thus, a uniformly coated TiO₂ nanosheet with TiO₂ QDs (synthesized after 168 hrs of hydrothermal treatment) shows superior degradation efficiency under UV light, see Figures 18(a)–(c). Besides, a highly stable and recyclable p–n heterojunction photocatalyst composed of Cu₂O octadecahedra and TiO₂ QDs has been studied by Xu and co-workers. Incorporation of TiO₂ QDs enhances the visible light sensitization and the charge transfer from the p-type Cu₂O to n-type TiO₂ is thermodynamically favorable leading to high efficiency (97% in 60 min under visible light), see the Figures 18(d)–(g).
4.2. 1D TiO₂ HSs

4.2.1. Doping: Metal and Non-Metal Elements

A controlled incorporation of a suitable secondary element into the TiO₂ lattice may introduce additional energy levels in between the forbidden region of TiO₂ nanostructured materials and thus can sensitize the enhanced visible light absorption and suppressed recombination of the photogenerated electrons and holes. The first report on the successful doping of nitrogen into TiO₂ by sputtering method in a nitrogen rich environment showed extended optical absorption band from UV to visible region, resulting to the superior visible light photodegradation of methyl orange (MO).31 Following this work, several reports have been published on the doping with various non-metal ions such as, sulfur (S)139 and fluorine (F)142 fabricated by various methods including hydrothermal, sputtering and thermal treatment method (see Fig. 19). Introduction of doping element causes the narrowing of the effective band gap of the TiO₂ which facilitates the interfacial transfer of photogenerated carries and thus, dramatically enhanced photocatalytic activity under visible light irradiation.

Besides the individual doping, the existing literature is mainly concentrated on the co-doping with N and F, or N and S (see Fig. 19).90,143 These results mainly demonstrate the incorporation of additional energy band, enhanced visible light absorption, lower recombination rates, making the TiO₂ nanostructures suitable to be commercially used. sp²-hybridized single layer graphene has been widely used for the surface modification of TiO₂ nanostructures due to its unique mechanical, electrical, and thermal properties.138,139,151 Recently, Ge et al.144 showed improved photocatalytic dye degradation and hydrogen evolution by a reduced graphene oxide/TiO₂ nanotube composite fabricated by electrodeposition followed by carbonation technique.95

Doping with the ions of transition metal such as Fe, V and Cu has also been explored for the improvement of the photoelectron conversion efficiency under the solar light illumination suppressing the recombination of photogenerated charge carriers and stability.145–147 Though the doping is beneficial for the improvement of charge separation and photocatalysis, it is observed that the performance of TiO₂ is fully dependent on the doping amount, energy state, electron configuration of the doped element and also on the percentage of doping. Excessively high amount of doping may act as the recombination center rather than the trap centre, resulting in low photocatalytic activity.

4.2.2. Plasmonic 1D TiO₂ HSs with Noble Metals

The most promising approach for the enhancement of visible light absorption, high charge separation at the interface and hence the photocatalytic activity is to decorate the TiO₂ nanostructures with noble metal nanoparticles such as Au, Ag, Pd, Pt, Cu, etc.148–153 In general, Fermi level position of Au, Ag, Pt, etc. noble metals lies just below the conduction band of TiO₂. Thus, the metal NPs can act as trap centers for the photogenerated electrons from valence band to conduction band upon visible light illumination.154 Besides, a properly designed TiO₂ HS with noble metals involves a coupling interaction between the plasmonic oscillations and the electromagnetic radiation incident on the nanostructures with the same frequency. Due to this strong coupling, excitation of extremely intense and highly localized surface plasmon resonance (LSPR) is observed. These plasmonic nanostructures with TiO₂ may be advantageous for the efficient light trapping component integrated in photocatalytic devices. The plasmonic
nanostructures drive the LSPR excitation following the light absorption and eventually the plasmons may decay non-radiatively in a femtosecond time scale, giving its energy to the electrons in the conduction band of TiO$_2$. Thus, highly energetic electrons (1–4 eV for the Ag or Au NPs) are produced in thermal non-equilibrium with the atoms of the TiO$_2$ known as “hot electrons” (see Fig. 20). After the migration of these electrons from the plasmonic material to the TiO$_2$ in contact forms a metal-semiconductor Schottky junction, which may accelerates the rate of photocatalysis.

Among the various existing strategies of fabrication of plasmonic noble metal NPs (photoreduction method, plasma sputtering, electrodeposition, electrospinning and hydrothermal method) on TiO$_2$ nanostructures, the hydrothermal method has been established to be the most easy and versatile method in controlling the shape, size and dispersion over the TiO$_2$ template. Ye et al.$^{94}$ sensitized TiO$_2$ nanotube arrays with Pd QDs (of size $\sim 3.3$ nm) by a facile hydrothermal method (see Fig. 21), which showed a superior photoelectrocatalytic water splitting under UV irradiation. Lin et al.$^{157}$ reported the deposition of Pt NPs of size 1.0–3.0 nm titanate nanotubes by a wet impregnation method. Nam et al.$^{158}$ decorated Ag and Au NPs separately with size 5–10 nm on the TiO$_2$ nanofibers via a one-step electrospinning process which enables the specific capacity to increase up to 20% in Li-ion battery application (see Fig. 21). Recently, our group has reported on the ultrahigh photodegradation efficiency of Ag NPs (size $\sim 17$ nm) decorated anatase TiO$_2$ NRs HSs synthesized by a solvothermal method followed by a UV light induced photoreduction procedure. Almost
100% of degradation efficiency with two sequential rate constants is observed, which was explained on the basis of plasmonic effect induced enhanced visible light absorption, hot electrons generated charge transfer through the interface of the HSs and N-de-ethylation process of RhB. Yang et al. reported 100% photodegradation of RhB by Ag nanocrystal (size 3.8 nm) decorated TiO2 nanotubes under visible light. Zhou et al. and Zhang et al. have incorporated Au encapsulation and Au/Pt NPs, respectively with the TiO2 nanostructures and superior photocatalytic activity has been achieved.

Wang et al. showed a hydrothermally grown TiO2 NWs with a diameter of 100–200 nm anchored with 1 At% of Pt NPs with the average size ∼5 nm exhibit very high photodegradation of MB under UV light. Thus, plasmonic metal NPs modified TiO2 nanostructures can effectively enhance visible light absorption, suppress the recombination of photogenerated electron/hole pairs, and facilitate their transfer through in the interfaces improving the photocatalytic hydrogen production activity, solar cells, supercapacitors and lithium batteries.

4.2.3. TiO2 Type-II HSs

The discovery of semiconductor heterostructure by Herbert Kroemer and Zhores I. Alferov opened up a wide research window in the field of high speed optoelectronics, photocatalysis and energy storage applications. The band position and their alignment at near the interface solely determine the catalytic behavior of a semiconductor heterojunction. Among the various semiconductor heterojunctions, a type-II (staggered type) band arrangement of TiO2 with a suitable semiconductor develops a band bending at the heterojunction resulting to a built-in electric field, which actually drives the photogenerated electrons and holes in two opposite directions (see Fig. 22). The formation of heterojunction by coupling an n-type

![Figure 21](image_url) **Figure 21.** (a, b) SEM and TEM images of Pt/TiO2 nanotube HSs. (c) Amount H2 evolved in photocatalytic water splitting. (d) TEM image of Au NRs encapsulated by TiO2 layers (e) extinction spectra of Au NRs display two SPR bands at 516 and 655 nm, corresponding to their transverse and longitudinal SPR modes, respectively. (f) Shows the normalized degradation curves with irradiation time. (g) TEM image of Ag/TiO2 NRs with 1.5:1 weight ratio and (h) sequential decay kinetics of HSs. (i–k) TEM images of TiO2 nanofibers decorated with Au, Pt and both, respectively. Inset shows the HRTEM lattice fringe patterns. (l) Shows improved H2 evolution by the bi-metal decoration. (m) Schematic diagram showing the LSPR absorption, generation of hot electrons and their transfer to accelerate the photocatalytic reaction. Reproduced with permission from [94], M. Ye, et al., J. Am. Chem. Soc. 134, 15720 (2012). © 2012, ACS, (a–c). Reproduced with permission from [160], N. Zhou, et al., Nanoscale 5, 4236 (2013). © 2013, RSC, (d–f). Reproduced with permission from [68], K. K. Paul and P. K. Giri, J. Phys. Chem. C 121, 20016 (2017). © 2017, ACS, (g, h, m). Reproduced with permission from [161], Z. Zhang, et al., J. Phys. Chem. C 117, 25939 (2013). © 2013, ACS, (i–l).

![Figure 22](image_url) **Figure 22.** Schematic band alignment of staggered type semiconductor heterojunction showing charge separation at the interface.
semiconductor (say, TiO$_2$) with a p-type semiconductor (say, Cu$_2$O, Ag$_2$O)$^{47,163,164}$ develops an electric field from n-type to p-type semiconductor, which increases the carrier separation efficiency at the interface.

Though numerous fabrication techniques have been developed for the synthesis of semiconductor HSs including physical (sputtering, physical vapor deposition) and chemical (hydrothermal, sol gel, sonochemical, electrodeposition, microwave and chemical vapor deposition) approaches, hydrothermal technique is extremely popular due to its low cost, versatility against the shape tuning and multipurpose advantages over the other processes. Liu et al.$^{165}$ synthesized a type-II heterojunction composed of TiO$_2$ (B)/anatase core–shell nanowire (see Fig. 23). As the conduction as well as the valence band of anatase lies above the respective bands of TiO$_2$ (B), an efficient charge transfer may happen at the junction, which is described to be responsible for the enhanced photocatalytic activity towards the decomposition of organic dye, methyl orange (MO). Zhou and co-workers demonstrated the high photocatalytic activity by anatase TiO$_2$ nanobelt designed with Ag$_2$O NPs in the UV irradiation.$^{166}$ Following this work, several reports have been published focusing on the mechanism of photocatalytic degradation of dye with various ionic nature.$^{47,164}$ Zhou et al.$^{167}$ reported a novel synthesis route of TiO$_2$ nanobelt wrapped with few layer MoS$_2$ for the first time via the hydrothermal method (see Fig. 23).

Rough surface of TiO$_2$ nanobelt was used as the template for the growth of few layer MoS$_2$ film. The 50 wt% of MoS$_2$ loaded on TiO$_2$ showed maximum photocatalytic hydrogen production activity at rate of 1.6 mmol h$^{-1}$g$^{-1}$. Following this work, several unique approaches have been reported for the further improvement with MoS$_2$ layered structure.$^{168,169}$ Wang et al.$^{170}$ incorporated wide band gap SnO$_2$ nanocrystals on the TiO$_2$ nanofibers via electrospinning method followed by a facile hydrothermal method. Cadmium sulfide (CdS) is also a commonly used candidate to form a type-II HSs. It has the band gap of $\sim 2.4$ eV which is able to absorb visible light up to 520 nm. Shao et al.$^{171}$ developed a novel route to deposit CdS NPs uniformly on the TiO$_2$ nanotubes via a constant current electrochemical deposition process. Compared to the bare TiO$_2$ nanotube arrays the CdS/TiO$_2$ HSs showed around 11-fold enhancement in photoelectrochemical activity. Similar reports with semiconductors CdS QDs,$^{172}$ CdSe,$^{173}$ CdS/CdSe,$^{174}$ $\text{C}_n\text{N}_x$,$^{175}$ Sn$_2$O$_4$,$^{176}$ RuO$_2$,$^{177}$ Bi$_2$MoO$_6$,$^{178}$ Copper(II) phthalocyanine,$^{172}$ ZnO,$^{180}$ ZnIn$_2$S$_4$ have also explored the development of type-II HSs towards the commercialization of the photocatalysts.

### 4.3. 2D TiO$_2$ HSs

Noble metal NPs loaded highly energetic (001) faceted 2D TiO$_2$ HSs have also been explored extensively.
As discussed earlier, the (001) facets have high average surface energy resulting to the highly active sites for the photocatalytic application towards environmental remediation as well as energy applications. Thus, several strategies have been developed to increase the surface area of exposed (001) facets. The plasmonic noble metal NPs (Ag, Au, Pd, Pt, etc.) anchored with the 2D TiO₂ nanosheets can influence the spectral response, generation of photoinduced carriers, their separation and participation in the redox reactions which actually control the kinetics of photocatalysis, as discussed for the 1D TiO₂ HSs case (Section 4.2.2). Till date, various fabrication techniques have been developed to prepare plasmonic noble metal decorated 2D TiO₂ nanostructures such as, impregnation, UV light induced photodeposition, co-precipitation and sol–gel methods. As, the photocatalytic activity in a plasmonic semiconductor nanocomposites is strongly influenced by the size, shape and the spatial distribution of the NPs, it is important to develop an easily controllable methodology to decorate uniform and well-dispersed metal NPs on the TiO₂ nanosheets. Wang et al. proposed the growth of plasmonic coupling photocatalyst, Au/TiO₂/Au nanostructure directly on a Ti foil. The enhancement in the near-field amplitude of LSPR in the vicinity of metal NPs boosts the kinetics of photocatalysis of the neighboring semiconductor. Here, authors have optimized the thickness (~5 nm) of the middle layer TiO₂ nanosheets to be satisfied the condition of required for the coupling effect. Thus, this system advantageous as a “plasmonic coupling photocatalyst” compared to the bare TiO₂ nanosheet. Besides the Au NPs, Pt NPs loaded TiO₂ nanosheets also reported by several groups for the enhanced H₂ production by the photocatalytic water splitting. Yu et al. reported that the 2 wt% of Pt NPs decorated (001) facet exposed anatase TiO₂ nanosheets exhibit highest H₂ evolution of 333.5 μmol h⁻¹. Following this work, Qi et al. fabricated CdS sensitized Pt/TiO₂ nanosheet HSs with exposed (001) facets via a hydrothermal treatment followed by a photochemical reduction (see Fig. 24). It is observed that the H₂ evolved under the visible and UV irradiation are 265 and 590 μmol h⁻¹, respectively. Pan et al. have synthesized TiO₂ nanosheets by C₃N₄ template method and introduced Pt NPs into it for the higher photocatalytic dye degradation. Jiang and co-workers developed a hybrid nanostructure of TiO₂ nanosheets designed with Au nanocubes and Au nanocages for the sensitization of broad solar spectrum from visible to NIR region and plasmon-mediated photocatalytic hydrogen production. Additionally Pd nanocubes increase the catalytically active sites enormously to enhance the hydrogen production rate.

Doping with metal and non-metal elements in (001) facet exposed TiO₂ nanosheet can improve the optical absorption simply by modifying the band arrangement of the nanostructure and shifting the threshold of the optical response value from UV to the visible region. Introduction of a new element may substitute the lattice oxygen and form interstitial species in the vicinity of near surface regions. Thus, visible light sensitization can effectively be incorporated by narrowing the band gap due to the formation of mid band gap energy levels of doping element. Doping of TiO₂ (001) facets with non-metal elements such as nitrogen was demonstrated by Xiang et al. for the first time (see Fig. 25). They observed superior visible light photocatalytic H₂-production activity by the self-doped TiO₂ nanosheets (exposed facet 67%) with nitrogen. To put the step forward, it was expected that employment
of other non-metal element into the (001) faceted TiO₂ may also boost the optical absorption. S-doping in the TiO₂ lattice may introduce additional states in between the wide spaced optical band gap of TiO₂ facilitating the enhanced visible light sensitivity and thus the solar light driven photocatalysis.

Rather than the single element doping as discussed above, doping by multiple elements in 2D TiO₂ nanosheets may give synergistic effect resulting to the enhanced photocatalytic performance. Xiang et al. reported the hydrothermal preparation of N and S co-doped (001) facet exposed TiO₂ nanosheets considering thiourea as the doping precursor. Compared to the bulk TiO₂, the N-S co-doped TiO₂ nanosheet exhibits the appearance of a new absorption shoulder at \( \sim 390-500 \) nm due to the introduction of localized states near the valence band edge and the improved absorption in the range of 550–750 nm as a result of the combined effect of N and S co-doping, further confirmed by the DFT calculation. An exceptionally advantageous hybrid structure by directly growing 2D anatase TiO₂ nanosheets with (001) exposed facets on the graphene support is useful for the enhanced photocatalytic hydrogen evolution, fast lithium storage, etc.

### 4.4. 3D TiO₂ HSs

Among the various shaped TiO₂ nanostructures, the 3D superstructures and its composites are least studied system in the field of energy and environmental applications. In spite of having several advantageous properties such as high specific surface area, large number of catalytically active sites, easy charge transfer through the interfaces, the 3D nanostructure is not well explored may be because of the tedious synthesis process. But, in 2009 Wu et al. reported the growth of truncated wedge-shaped TiO₂ nanostructures as shell over the Au NPs as core by a simple and flexible hydrothermal route (see Fig. 26). To stabilize the structure, the immediate layer on the Au NPs is of (101) faceted TiO₂ which minimizes the average surface energy of the whole system. Then, epitaxially segmented orientation growth of (001) faceted TiO₂ was observed on the TiO₂ layer. The F⁻ ions hydrolyzed TiF₄ precursor acts as the shape controlling agent to form well defined wedge-like TiO₂ shells and also contributes to the exposed (001) facets. The superior photocatalytic activity of the Au@TiO₂ core–shell HSs was investigated by decomposition of acetaldehyde in gaseous phase. Wu et al. has developed an exceptional strategy for the bottom up synthesis of AuNR/TiO₂ nano-dumbbell like structures with spatially separated Au and TiO₂ regions, by wet-chemistry technique (see Fig. 26). The as prepared Au NRs are exposed in their side wall which acts as the optical window for the incident light as well as it offers a fast lane transfer of the photogenerated hot electrons to the TiO₂ side, making the AuNR/TiO₂ HSs extremely high efficient for the H₂ generation under visible/NIR light. Separation of photocatalysts after the reaction still remains a tedious job for the researchers. Shen and co-workers developed a new magnetically separable plasmonic 3D sandwich-structured Fe₂O₃/SiO₂/Au/TiO₂ photocatalyst, which shows easy magnetic separability, higher absorption in the visible region and thus the enhanced photocatalytic activity towards the decomposition of organic compounds under the illumination of simulated sunlight (see Fig. 26). Following these works, similar reports with other plasmonic NPs like Ag and graphene have also discussed on the enhancement strategy of photocatalysis.

The formation of type-II HS composed of 3D TiO₂ microstructure grown by hydrothermal method and an another semiconductor (Ag₂O NPs) having suitable band position was discussed by Sarkar et al. Uniform
decoration of $p$-type Ag$_2$O NPs on the $n$-type TiO$_2$ forms numerous number of type-II $p$–$n$ heterojunction which promotes an efficient charge separation due to built-in electric field at the junction as shown in Figure 27.

Thus, an enhanced UV light induced photocatalytic activity was demonstrated by the optimized HSs with apparent first-order rate constant of 0.138 min$^{-1}$. Different staggered type HSs of 3D TiO$_2$ demonstrating superior
5. CONCLUSION AND OUTLOOK

Since 1972, intense research efforts have been devoted to the fabrication, properties and surface engineering of TiO2 nanostructures and their influence in various applications has given rise to a rich database for the future developments. The latest breakthrough works on applications has given rise to a rich database for the performances. A proper understanding of the surface chemistry in controlling the morphology of TiO2 and its HSs with distinct facets exposed is necessary for the designing of high quality and atmosphere stable devices. Most of the frequently used fabrication techniques from 0D to 3D nanostructures including hydrothermal/solvothermal method, electrochemical anodization method, sol−gel method, template-assisted method, electrosplinning method and chemical vapor deposition method have been critically reviewed. Among them, the hydrothermal route is found to be the most popular for the fabrication of shape controlled different dimensional TiO2 and its nanoheterostructures. This is because of the easy control over the size, shape and for the low cost. Enhancement of the specific surface area as well as the catalytically active sites, surface modification with the metal/non-metal doping, formation of type-II and plasmonic HSs can accelerate the kinetics of photocatalysis, solar cells, supercapacitors and lithium-ion battery performances.

Even though the shape tailored TiO2 based photocatalysts have evolved to be most promising material and capable enough to solve the future needs for diverse applications, several issues such as efficiency, stability and the secondary contamination by the photocatalysts limits its commercial applications and adequate market presence. The extremely beneficial sulfide based semiconductors like MoS2, Cds etc. allow superior solar energy harvesting when coupled to the TiO2. But the aqueous soluble sulfur easily gets detached from the system and contaminates the solution meant to be decontaminated. Besides, the plasmonic HSs with noble metal NPs are not well stable in the aqueous medium as most of them tend to be oxidized, severely reducing the efficiency as a photocatalysts. Additionally, only 1D TiO2 HSs are observed to be investigated enormously even though the other dimensional (001) faceted 2D TiO2 nanosheet and 3D superstructures nanostructures are also expected to be promising and superior than the 1D structures in some extent (larger specific surface area, active catalytic sites and easy recycling process). We believe that the low cost TiO2 HSs with high atmosphere stability will be realized in future, which will reach the needs of the society in the field of energy and environmental applications.

Acknowledgment: We acknowledge the financial support from MEITY (Grant No. 5(9)/2012-NANO (VOL-II)) for carrying out part of this work.

References and Notes

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Received: 30 September 2017. Accepted: 9 October 2017.