Review
Photocatalytic Carbon Dioxide Conversion by Structurally and Materially Modified Titanium Dioxide Nanostructures

Tarek Fawzi 1, Sanju Rani 2, Somnath C. Roy 3 and Hyeonseok Lee 1,*

1 Department of Photonics, National Sun Yat-sen University, No. 70, Lien-Hai Rd, Kaohsiung 80424, Taiwan; t@g-mail.nsysu.edu.tw or tarekfawzi8@gmail.com
2 Department of Physics, SRM Institute of Science and Technology, Ramapuram Campus, Chennai 600089, Tamil Nadu, India; sanjur@srminst.edu.in
3 Semiconducting Oxide Materials, Nanostructures and Tailored Heterojunction (SOMNaTH) Lab, Functional Oxides Research Group (FORG) and 2D Materials and Innovation Centre, Department of Physics, IIT Madras, Chennai 600036, Tamil Nadu, India; somnath@iitm.ac.in
* Correspondence: hslee611@mail.nsysu.edu.tw; Tel.: +886-7-525-2000 (ext. 4473)

Abstract: TiO₂ has aroused considerable attentions as a promising photocatalytic material for decades due to its superior material properties in several fields such as energy and environment. However, the main dilemmas are its wide bandgap (3–3.2 eV), that restricts the light absorption in limited light wavelength region, and the comparatively high charge carrier recombination rate of TiO₂, is a hurdle for efficient photocatalytic CO₂ conversion. To tackle these problems, lots of researches have been implemented relating to structural and material modification to improve their material, optical, and electrical properties for more efficient photocatalytic CO₂ conversion. Recent studies illustrate that crystal facet engineering could broaden the performance of the photocatalysts. As same as for nanostructures which have advantages such as improved light absorption, high surface area, directional charge transport, and efficient charge separation. Moreover, strategies such as doping, junction formation, and hydrogenation have resulted in a promoted photocatalytic performance. Such strategies can markedly change the electronic structure that lies behind the enhancement of the solar spectrum harnessing. In this review, we summarize the works that have been carried out for the enhancement of photocatalytic CO₂ conversion by material and structural modification of TiO₂ and TiO₂-based photocatalytic system. Moreover, we discuss several strategies for synthesis and design of TiO₂ photocatalysts for efficient CO₂ conversion by nanostructure, structure design of photocatalysts, and material modification.

Keywords: photocatalysis; CO₂ reduction; TiO₂; nanostructures and hydrogenation

1. Introduction

Plants preserve carbon cycle in nature via photosynthesis process as they convert CO₂ into carbohydrates, but several activities such as industrialization, urbanization, deforestation and excessive consumption of fossil fuels affected this cycle considerably [1]. The accumulation of CO₂ in the atmosphere, beyond the capacity of the nature to handle, has created severe global warming phenomena that result in climate change. Now, the devastating effects from unusual weather patterns are visible all around us. In the recent years, therefore, CO₂ capturing and utilization is a focal subject for the scientific community [2,3], as it addresses the energy crisis and global warming without hindering the development plans or urbanization [4]. In particular, recycling of CO₂ into carbon containing and value-added chemicals regenerates fuel within the present hydrocarbons-based energy infrastructure.

CO₂ is a linear molecule, with weak electron affinity, chemically stable and the nucleophilic approach at the carbon atom governs its conversion reaction [5]. C=O bond dissociation requires more than 750 kJ/mol of energy [6]. Thermodynamically, this reaction
is an uphill one, hence input of energy is required to break C=O bond. In nature, the photosensitizers (e.g., chlorophyll) capture energy from sunlight to use it in the endothermic reactions.

To mimic these natural solar energy conversion, several techniques such as photoelectrochemical (PEC) [7], biochemical [8], photocatalysis [9], radiolysis [10], thermocatalysis [11], and electrocatalysis [12] have been proposed for CO\textsubscript{2} conversion into useful chemicals. Photocatalytic (PC) methods has been identified as one of the most suitable approaches to convert CO\textsubscript{2} into different gaseous (ethane, methane, etc.) and liquid (ethanol, methanol, formate etc.) products under solar light irradiation at ambient temperature and pressure [13]. The most attractive aspect of such approach is the utilization of renewable solar radiation to draw the energy required for driving the catalytic process. In the case of a pure photocatalytic approach (without any electric field), this is called artificial photosynthesis that imitates the energy cycle of nature [14]. In addition, use of renewable solar energy brings in associated advantages such as environmental compatibility, economic feasibility, and product selectivity [15].

Up to now, several different types of materials such as metal complexes, organic molecules, precious metals, ions, organic molecules, and semiconductors have been explored to enhance the efficiency of photocatalytic processes. Among these materials, semiconductors in general and metal oxides in particular have shown immense potential over the others with regard to stability, toxicity, and feasibility of the fabrication etc., which makes them desirable in photocatalytic applications [16].

The general understanding for an efficient photocatalytic process by semiconductor materials, the electrons and holes in the semiconductor materials should have sufficient energy to ionize the CO\textsubscript{2} and H\textsubscript{2}O, respectively. In other words, energies of the photogenerated electron and hole (e\textsuperscript{-}/h\textsuperscript{+}) must be higher than the overpotential of H\textsubscript{2}O/O\textsubscript{2} (0.82 vs. NHE at pH 7) and lower than the overpotential of CO\textsubscript{2}/HCOOH (−0.61 V vs. NHE at pH 7), respectively [17,18]. Performing photo-assisted redox reactions such as CO\textsubscript{2} reduction or water oxidation therefore requires a photocatalyst with an optimum bandgap (at least 2.88 eV) [19] so as to generate electrons and holes with sufficient energies. Simultaneously, the photocatalyst must be able to absorb large fraction of the solar spectrum even from visible and near IR light absorption (in addition to UV) [20].

Historically, TiO\textsubscript{2} is the most extensively investigated semiconductor material for photocatalytic CO\textsubscript{2} conversion since the successful demonstration of the photoelectrochemical CO\textsubscript{2} conversion by Inoue et al. in 1979 [21]. Moreover, owing to superior advantages such as material robustness, chemical and thermal stability, nontoxicity, corrosion resistance, and ease of synthesis, TiO\textsubscript{2}-based photocatalytic systems became popular and related applications have been focal target for researchers due to its tremendous potential in different solar driven processes such as water splitting, pollutant degradation and CO\textsubscript{2} conversion [21,22]. It is well known TiO\textsubscript{2} has three crystalline phases, anatase, rutile, and brookite possessing the bandgap values in the range of 3.0–3.6 eV. However, the bandgap is relatively large to absorb whole solar spectrum and this limits the light absorption of TiO\textsubscript{2} only to UV region, which is ~5% of total solar energy available. Moreover, the charge recombination in TiO\textsubscript{2} is a serious issue and this makes the photocatalytic reaction by TiO\textsubscript{2} inefficient. Hence, increasing the optical absorption and decreasing the charge recombination of the TiO\textsubscript{2} are of another prime importance. To overcome these limitations, lots of research has proposed on material modification, low dimensional introduction, and design of photocatalytic structure for TiO\textsubscript{2} to achieve highly efficient photocatalytic CO\textsubscript{2} conversion.

Therefore, in this review, we summarize the works that have been carried out for the enhancement of photocatalytic CO\textsubscript{2} conversion by material and structural modification of TiO\textsubscript{2} and TiO\textsubscript{2}-based photocatalytic system. We provide several strategies and their details: (1) crystal facet engineering (2) nanostructures (3) junction formation (4) material modification, in particular, by hydrogenation (5) single atom photocatalysts (6) metal-organic framework.
2. Strategy I: Crystal Facet Engineering of TiO$_2$ Photocatalyst

Titanium dioxide is a multifunctional material that has attracted researchers due to its applicability to various fields such as photocatalysis, photovoltaics, and biomedical applications [23,24]. TiO$_2$ nanoparticles and nanocrystals have been obtained via different preparation methods such as flame spray pyrolysis, hydrothermal treatment and sol-gel method. In particular, crystallites with selective facets are helpful in catalysis. In addition to wet chemistry approaches, powders produced from flame pyrolysis resulted in nanocrystals with thermodynamically stable (101) surface [25,26] and (100)/(010) surface planes, and some reactive (001) facets (Figure 1 shows the different types) [27,28].

While, the size of TiO$_2$ nanoparticles differs remarkably depending on the synthesis process [29], the preparation techniques affect the crystal shapes significantly [30]. Choosing a specific synthesis method depends on the required morphology of TiO$_2$ material, which further depends on the target application. The methods of synthesis significantly affect the morphology, crystallinity, and phase, which have their influence on the physical and chemical properties. The synthesis strategies are chosen, considering the ability to tailor particle-size, the integration with other structures or phases [31], flexibility of self-assembly [32], possibility of doping with other elements [33,34], also inlaying heteroatoms, heterostructures or quantum dots [35,36] in order to manipulate the electronic and optical properties.

Anatase is the most investigated photoactive polymorph of TiO$_2$, with its thermodynamically stable (101) facets (>94%), dominating in consonance with the Wulff construction. The morphology, crystal growth, and facets can be controlled by using a shape and growth controller such as HF [28]. In addition, in another approach, a mixture of HF/alcohol has been employed for establishing metastable surfaces reaching 98.7% of (001) and 1.3% of (100) facets [37]. Using F$^-$ along with citric acid or hydroxyl acids results in continuous curvature of rutile and anatase, where F$^-$ ions play not only the role of a stabilizer for (001) facets growth but also as an etching reagent [38,39]. The morphology of the anatase nanoparticles can be manipulated via the relative concentrations of OH$^-$ and F$^-$ [40]. Hydroxyl groups boost the isotropic growth, whereas F$^-$ eliminates (001) surfaces supporting the TiO$_2$ crystals lateral growth. However, an excessive concentration of F$^-$ reduces the size of particles significantly as a result of TiOF$_2$ formation.

The facet engineering effect was reported by Wang et al. [41]; where they found that the Schottky barrier height of Au/TiO$_2$ (101) interface is lower than its counterparts from the interface (001). Which enhanced the electrons transfer from CB of TiO$_2$ to Au and significantly enhances the photocatalytic performance in producing CO and CH$_4$ in comparison with other samples containing Au/TiO$_2$ (001) interfaces. In another study, Dong et al. [42] showed that crystal facets engineering of TiO$_2$ loaded with Cr$_2$O$_3$, (2HF-
Although TiO$_2$ in its bulk form has been investigated for decades, its nanostructured morphologies also have been investigated for photocatalysis and other applications [55], focusing on one dimensional (1D) [56], two dimensional (2D) [57], or three dimensional (3D) structures [58]. Nanostructures or nanomaterials are defined as features where at least one dimension is smaller than 100 nm [59]. However, in a more technically elaborated way, a nanomaterial is defined as where charge carriers are quantum-mechanically confined as evidenced by the consequent modifications in electronic and optical properties. How-

TiO$_2$/0.2Cr$_2$O$_3$) exhibited 30-fold increment in CO$_2$ conversion compared to the TiO$_2$ without facet engineering.

Studies and theories illustrated that (101) facets are the most stable facets thermodynamically for anatase TiO$_2$, whilst other facets (100) and (001) are active and possess high surface energy [43]. Anatase crystal has an equilibrium shape consisted of slightly truncated tetragonal bipyramid enclosed with two (001) and eight (101) facets [44]. Tetragonal nanorods of anatase crystals consisted of high ratio of lateral (100) facets have been fabricated via immersing alkali titanate nanotubes in basic solution followed with hydrothermal transformation [45]. In addition, Anatase crystals with elongated truncated tetragonal bipyramids that contains high ratio of (100) facets; enclosed via different types of facets (001), (100) and (101) were fabricated via hydrothermal reaction in aqueous HF solution [46]. However, still a dilemma to fabricate tetragonal cuboid of anatase crystals enclosed only with (001) and (100) facets. Keeping in mind that anatase nanosheets were fabricated by using solvothermal route in 1-butanol solvent containing HF; these nanosheets consists of (100) and (001) facets, 1.3% and 98.7, respectively [47,48]. Preparing anatase cuboids and manipulating facets percentage (100) and (001) may help in evaluating facet reactivity throughout the photocatalytic reactions. Hence, it is for crucial significance to synthesize anatase cuboids enclosed by (001) and (100) facets over a wide size range, as in lithium-ion batteries and solar cells where several studies [49–52] relied on the exposed facets of anatase effect on its optical and electrochemical features to be applied in such applications. Photocatalytic materials can be formed via the integration of multiple components, adjusting the facet of each component. This method enables to boost the photocatalytic performance but, since the facet engineering in the multiple component system, in general, are complicated for its delicate control, the combination of two pre-synthesized components is more preferable for its usage, rather than a new component on the one pre-synthesized material [53]. For example, tailoring the surface facets of TiO$_2$ seeds into nanocrystals with graphene oxide can be seen in Figure 2a. capping agent deficiency results in octahedral TiO$_2$ nanocrystals enclosed by TiO$_2$-101-G. TiO$_2$-001-G nanosheets and TiO$_2$-100-G nanorods were formed on graphene with F$^-$ and SO$_4^{2−}$ employed as capping agents, as shown in Figure 2b–g).

![Figure 2](image-url)

**Figure 2.** (a) Schematic illustrating the synthesis of TiO$_2$-graphene nanocomposites with controllable TiO$_2$ crystal facets. (b–g) transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of the as-prepared (b,e) TiO$_2$-101-G, (c,f) TiO$_2$-001-G, and (d,g) TiO$_2$-100-G. (Taken with permission from [54]).

### 3. Strategy II: Nanostructured TiO$_2$

Although TiO$_2$ in its bulk form has been investigated for decades, its nanostructured morphologies also have been investigated for photocatalysis and other applications [55], focusing on one dimensional (1D) [56], two dimensional (2D) [57], or three dimensional (3D) structures [58]. Nanostructures or nanomaterials are defined as features where at least one dimension is smaller than 100 nm [59]. However, in a more technically elaborated way, a nanomaterial is defined as where charge carriers are quantum-mechanically confined as evidenced by the consequent modifications in electronic and optical properties. How-
ever, even before the electronic or optical properties are investigated, the nanomaterials are characterized by a huge enhancement in the surface to volume which enhances the interaction with the surrounding environment [60]. Each of these nanostructures have their own characteristics in terms of light scattering, aspect ratio, recyclability, major surface area, stability, and directional transfer of photogenerated charges that decreases recombination rate. Synthesis method for 1D nanostructures involves tailored and directional growth, which is achieved either by the structure directing agents or by the use of templates. The directional growth is not required for 2D and 3D morphologies, but the synthesis process may involve multiple steps and highly optimized conditions to obtain structures with minimal defects. In the case of 0D nanostructures such as quantum dots, although there have been studies reported in the literature, the enhancement in band gap caused by the quantum confinement effect reduces the effectiveness of use in photocatalysis. Following chapters provide fundamental features of each nanostructure and its application for CO₂ conversion.

3.1. Zero-Dimensional Nanostructured TiO₂

The nanoparticles or 0D nanostructures offer a lot of advantages and a high degree of flexibility in terms of use in photocatalysis. In particular, nanoparticles can be used to functionalize various surfaces of materials that help in forming either heterojunctions or modifying light absorption. Further, tailoring the size of the nanoparticles changes the surface area, which, in turn, influence the catalytic reactions. Moreover, when formed into quantum dots, the optical and electronic properties are modified drastically to help in catalytic reactions. These nanostructures are cheap, stable, recyclable, and biocompatible [61]. TiO₂ nanoparticles with their special morphology and acid-base sites have been useful in many catalytic reactions under mild conditions compared to other metal oxides (e.g., CuO, ZnO, etc.) [62]. Liu et al. [63] constructed 0D nanoparticles/2D CoP nanosheets heterojunction and the results showed improvement in photocatalytic H₂ evolution rate in comparison to pure TiO₂. Another study [64] reported that In-doped TiO₂ nanoparticles improved the photocatalytic activity for CO₂ reduction where CO was detected and CH₄ yield increased remarkably. In addition, Wada et al. [65] employed rutile TiO₂ nanoparticles as a modifier to enhance the charge transfer, where RuRe/TiO₂/NS-C₃N₄ showed capability in converting CO₂ into CO with high selectivity under visible light (λ > 400). Tseng et al. [66] used sol-gel method in synthesizing Cu/TiO₂ nanoparticles and measured the photoreduction that showed methanol yield much higher than those resulted from sol-gel TiO₂ and Degussa P25, as well. Moreover, Pt/TiO₂ nanoparticles composites yield CH₄, H₂ and C₂H₆ under visible light irradiation with increment of 3.7 times in comparison with Pt/P25 [67]. Perovskite quantum dots also showed its potential for photocatalytic CO₂ conversion with TiO₂ [68,69].

3.2. One-Dimensional Nanostructured TiO₂

The one-dimensional morphologies such as nanowires, nanorods, nanobelts and nanotubes have several interesting properties including directional charge transport, improved light absorption by high aspect ratio and widen surface area [70]. A lot of research reports further modified properties of nanostructures through doping or decoration of other materials such as graphene derivatives or noble metals to enhance photocatalytic CO₂ conversion with high aspect ratio [71,72]. The integration of the specific geometry and the high aspect ratio yield dramtical enhancement in charge carrier generation, separation, and transport which boost the conversion efficiency [73]. For instance, TiO₂ nanorods (TNRs) have a single-crystalline structure and small boundary resistance [74], that reduces the impact from grain boundaries and supplies fast electron transportation [75,76]. It was reported that TNRs as shown in Figure 3 shows higher photocatalytic activity than the nanoparticles because of the increment in active sites and the influence of the crystal plane [77]. Moreover, the comparison between TiO₂ nanorods and the counterparts of nanoparticles showed that the recombination rate of the nanorods are lower than enhanced the photocatalyst photocatalytic activity [78].
belts (TNB) forming heterostructures with ZnFe$_2$O$_4$ nanoparticles [89], and TNT covered with rGO sheets with embedded TiO$_2$ nanoparticles [90]. All the techniques and materials implemented onto 1D TiO$_2$ nanostructures enhanced the photocatalytic performance by improving the product (CO, CH$_4$, CH$_3$OH, CH, CF) yield under light irradiation because of all or some of these factors: (i) increasing active surface area, (ii) increasing CO$_2$ adsorption on the surface (iii) trapping electrons via oxygen defects (iv) enhancing charge separation.

3.3. Two-Dimensional Nanostructured TiO$_2$

Ultrathin two-dimensional nanomaterials possess sheet-like structure with a thickness of few atoms (less than 5 nm), their widths are larger than several hundred nanometers [91,92]. Their superb physical and chemical properties have led significant attention for diverse lateral structured applications [93]. In comparison with 0D and 1D, 2D...
nanomaterials have extraordinary advantages; support them with optimistic potential for photocatalytic applications.

- First and foremost, 2D materials possess larger surface-to-volume ratio over their bulk counterparts [94]. Hence, 2D materials have more active sites on their surface that can enhance their photocatalytic performance significantly.
- Second, their atomic thickness benefits mass transport and light energy harvest [93]. The ultrathin structure minimizes the distance of the charge migration from the bulk to the surface, decreasing carrier recombination and enhancing the photocatalytic activity [95].
- Third, the high fraction of coordinated unsaturated centers can work as active centers and interact with the substrate intimately [96].

Hence, they perform stellar platforms to prepare multicomponent photocatalysts. The aforementioned extraordinary properties provide diversified number of opportunities with high activity and selectivity for CO$_2$ reduction. In particular, synthesizing fine-tuned and strong photocatalysts that fulfill the requirements of CO$_2$ reduction applications [97]. These properties encouraged Tu et al. to fabricate 2D sandwich-like hybrid nanosheet out of graphene and TiO$_2$ in Figure 4, where TiO$_2$ nanoparticles uniformly were loaded onto graphene nanosheet to prevent their breakdown and restacking.

![Figure 4. SEM image of 2D nanosheet sandwich-like graphene/TiO$_2$. (a) The typical G2-TiO$_2$ with remarkable structural flexibility. (b) The TiO$_2$ nanoparticles intimate contact with graphene. (Taken with permission from [98]).](image)

2D structures provide large active surface area, enhanced surface adsorption, enhanced interfacial charge transfer, and selectivity caused by the band edge alignment. Zhou et al. loaded with TiO$_2$ nanoparticles onto layered nanosheets of g-C$_3$N$_4$ for CO$_2$ conversion [99]. Urea served as a source of N doping as well as g-C$_3$N$_4$ precursor. Low urea formed an N-doped TiO$_2$ and resulted in CH$_4$ during the photocatalytic CO$_2$ reduction while high urea formed composite of g-C$_3$N$_4$ and N-TiO$_2$ that produced CO. The reason behind the selectivity of products is alignment of band edges with respect to the redox potentials of the possible products. The photocatalytic yield increased due to average surface area, enhanced light absorption, promoted charge transfer and well-aligned band edges with respect of product redox potentials. Likewise, TiO$_2$-g-C$_3$N$_4$ nanosheets heterostructure (TNS-CNN) has been synthesized via in situ pyrolysis approach [100]. TNS-CNN used H$_2$O and H$_2$ as reducing agents in CO$_2$ conversion process where its CO yield was very high compared to pristine TNS. This performance is attributed to the surface area increment, enhanced charge transfer kinetics, role played by H$_2$ and light absorption. Ultrathin TiO$_2$ nanosheets also play an essential role for efficient photocatalytic CO$_2$ conversion, when prepared from the lamella structure of TiO$_2$-Octylamine [101]. The conversion efficiency is a result of several factors such as increasing CO$_2$ adsorption sites, enormous increasing in surface area, which in turn, increased the light absorption. Moreover, the fluorescence lifespan of the generated charges into the ultrathin TiO$_2$ nanosheets is higher when compared to their counterparts in
bulk material. Thus, these ultrathin nanosheets provide efficient charge separation within its 2D channels. In another report, TiO₂ ultrathin nanosheets (TiO₂-U) were synthesized by hydrothermal method followed by photochemical deposition of Pt nanoparticles [102]. Moreover, an interesting study suggested growing the photocatalytic material onto a 2D conductive substrate. Recently, Ti₃C₂ MXenes (TT) has been synthesized and covered with TiO₂ nanoparticles [103]. Upon calcinating TT at 550 °C, the TiO₂ nanoparticles formed at the edges and the surfaces of TT layers which improves the surface area by making it rougher. Applying higher temperature than 550 °C decreased the photocatalytic performance due to the decreased proportion of the conductive TT. Hence, TT offers an efficient charge separation that improves the performance and the surface area contributed significantly in providing more reactive sites for CO₂ adsorption for conversion process, as well. Another report described the 2D nanostructure of Bi₂WO₆-TiO₂ bi-nanosheet (BT) for CO₂ conversion into CH₄ and CO [104]. This report provided an approach concerning carbonaceous intermediates or surface species in the value-added chemicals generation. It was found that BT resulted in improved CO and CH₄ yield compared to pristine material due to the enhanced charge transfer and the Z-scheme mechanism.

As known, TiO₂ has three common polymorphs anatase, brookite, and rutile. Brookite is the least used one while rutile is the most common one. It is well known that TiO₂ has a wide bandgap of 3.0 eV for rutile. In addition to this, it was reported that the bandgap of anatase is about 3.2 eV, while that of the brookite is anywhere between 3.0–3.6 eV. Anatase nanoparticles with grain size (5–10 nm) shows a blue shift in the absorption edge of 10 nm, and their bandgap is about 3.3–3.4 eV in comparison with the commercial sample with a crystal size 39 nm which bandgap is about 3.2 eV [105]. Another study reported that the bandgap of pure TiO₂ nanoparticles is 3.7–3.9 eV, as shown in Figure 5a [106].

![Figure 5. Tauc plots of (a) TiO₂ nanoparticles (b) Titanate nanotubes and rutile.](image)

Figure 5. Tauc plots of (a) TiO₂ nanoparticles (b) Titanate nanotubes and rutile.

Studies proved that as the material shrinks to the nanometer scale, the bandgap starts to increase due to the quantum size effect [107]. Hence, TiO₂ nanowires (TNWs) have higher bandgap compared to the bulk materials, for instance growing the TNWs along with (001) direction results in a blue shift and this shift depends on the size of the TNRs [107]. In addition, the bandgap of titanate nanotubes is almost 3.84 eV ascribed to quantum confinement effect, shown in Figure 5b [60]. Moreover, in a comparison between TiO₂ nanosheets (TNSs) and bulk materials, the spectrum of the TNSs showed significant blue-shift that indicates increasing in the bandgap [108].

4. Strategy III: Formation of the Junction with TiO₂

Photocatalysis CO₂ conversion is closely related to the management of charge carriers, namely, electrons and holes, that are necessary for CO₂ reduction and water oxidation, mainly governed by photon absorption, photocarrier generation, and charge separation and transfer. These reactions rely on several factors: bandgap, E₆ of photocatalyst, photo carrier generation rate, charge transfer kinetics, and recombination rate. Photocarrier generation rate depends on the conditions of the irradiation and the optical absorption properties of
photocatalysts while the charge transfer depends on the reaction occurrence whether it takes place at the surface or within photocatalysts. The recombination can be minimized by improving the crystallinity, increasing transfer kinetics, or the control of the crystallite size [109]. Highly crystallized material minimizes the presence of impurities, surface or bulk defects. Crystallite size control stimulates the point defects of particles that trap e− or h+ which in turn delays the recombination for a few micro or nanoseconds [95]. In addition, the reaction efficiency can be enhanced by increasing the adsorption capability of the surface [110].

To achieve these improvement and enhancement in properties and performance of TiO2 photocatalysts, we can make an effective junction with other materials. As mentioned, since TiO2 has disadvantages for efficient light absorption and charge transfer, making a junction with efficient light absorbers or/and charge transporting materials would be beneficial for the enhancement of the performance. The subchapters below provide the features and examples of several junctions that can be made with TiO2.

4.1. A Semiconductor-Semiconductor Heterojunction

The most typical semiconductor-semiconductor heterojunction can be formed in p-n junction. The p-n junction, where an n-type and a p-type semiconductor are in intimate contact (for charge transport across the interface), has several advantages in photocatalysis. When two such semiconductors make a junction, a depletion layer is formed at the interface and internal electric field is established at the interface due to the relative positions of the Fermi levels. This built-in electric field at this junction helps in separating the photo-generated electron-hole pairs thus minimizing the recombination. Further, the junction can be designed in such a way that the light absorption range of one semiconductor can be extended by choosing the other semiconductor with a smaller band gap. Therefore, two fundamental challenges, light absorption and charge carrier separation, in TiO2-based photocatalysts n photocalysis- can be tackled by creating p-n junction with materials that have suitable band gaps and intimate energy band structure [111].

Moreover, non-p-n junction, that is, n-n junction between the materials also helps in photocatalysis in a similar manner. In such a heterostructure, the band edge offsets at conduction and valance bands endow a driving force for charge transfer and separation and, with a proper selection of materials, enhanced light absorption can be expected. Such a configuration, called a type II heterojunction is highly useful in photocatalysis [112].

These semiconductor-semiconductor heterojunction structure has been demonstrated in lots of work in the field of photocatalysts. Guo et al. [113] reported that Bi2WO6/TiO2 heterojunction photocatalysts showed strong adsorption ability and improved visible light photocatalytic activities. Shang et al. [114] also studied Bi2WO6/TiO2 photocatalytic activity as it demonstrated enhanced photocatalytic activity by 8 orders compared to the bare Bi2WO6. MgO− covered TNT via alkaline hydrothermal reaction also demonstrated for CO2 conversion [115]. This heterojunction enhanced the CO2 photoreduction as indicated by higher amounts of CO and CH4 compared to that from sole TNT photocatalysts. This enhancement is attributed to the chemisorption of CO2 and subsequent conversion into MgCO3 which is more reactive than the linear molecules of CO2. Li et al. [83] fabricated TNT via hydrothermal reaction followed by constructing CdS/TiO2 and Bi2S3/TiO2, the photocatalytic performance of both of them enhanced CO2 reduction into CH3OH under visible light irradiation. In addition, Li et al. [115] presented a study showing the development of MgO/TNTs films in CO2 photoreduction activity into methane in comparison with TiO2 films where MgO played a crucial role in CO2 methanization.

4.2. Semiconductor-Metal Heterojunction

TiO2 photocatalysts forms a junction with various metal materials to enhance the photocatalytic performance. A metal in contact with a semiconductor creates Schottky or ohmic contact and these contacts influence on electric field or charge concentration distribution at interface. As in the semiconductor-semiconductor junction above, the metal
materials can affect the electrical properties of the photocatalytic structures for charge separation and transfer of the semiconductor materials forming a junction together. In addition, some special metals such as Ag, Au, or Cu help in extending light absorption with suitable plasmonic effect when they make a junction with TiO$_2$ [116–119]. Further, metals with suitable surface energies also help in enhancing the adsorption of the gaseous/liquid species under catalytic reaction [18]. Wang et al. [120] successfully fabricated Au/TiO$_2$ heterojunction that resulted in reduction products CH$_4$ and CO, with 80% CH$_4$ selectivity. Saraev et al. [121] modified TiO$_2$ with Pt and Cu/CuO, and reported that this design is an efficient photocatalyst for CO$_2$ conversion as it shifted the working range to the visible light and produced CH$_4$. Another study reported that Au$_{0.25}$Pt$_{0.75}$/TiO$_2$ nanofiber showed higher activity of CO$_2$ photoreduction into CH$_4$ under UV-vis irradiation [122]. In addition, Mankidy et al. [123] reported that Ag-Pt bimetallic and core sell Ag@SiO$_2$ onto TiO$_2$ showed a significant development in the photoreduction of CO$_2$ with H$_2$O into CH$_4$.

4.3. Semiconductor-Carbon Heterojunction

Similarly, to the metal-semiconductor junctions, carbon materials are also used to form heterostructures with photoactive semiconductors. Several carbon materials such as activated carbon, graphene, and graphene oxide have been employed in heterojunctions preparation. These materials demonstrate high surface area that improves molecules adsorption and the photocatalysis performance of the material [124]. The porous morphology demonstrated by carbon materials adsorbs gaseous species for catalytic reactions. Further, graphene and carbon nanotube (CNT) have a metallic structure and forms a Schottky barrier with a semiconductor material at the interface that improve charge transfer and alleviate the recombination rate by the established built-in electric field. Simultaneously, the metallic nature of graphene or CNTs efficiently collect photogenerated charges from the semiconductor [125,126]. Photogenerated electrons move by the built-in electrical field from conduction band of semiconductor to CNTs in order to balance Fermi levels, while holes exist in the semiconductor share in redox reaction [127]. Padmanabhan et al. [128] prepared a study showing that TiO$_2$/graphene is more active for photocatalysis than sole TiO$_2$. In the report, the graphene sheet acted similar to an electron acceptor facilitating the transfer and separation of the generated electrons during irradiation, thus reducing the e/h recombination. Carbon quantum dots also led the improvement for photocatalytic reaction with TiO$_2$. A CQD/TNT nanocomposite yields more than two times higher production rates both for CO and CH$_4$ compared to those of bare TNTs [129]. Another study presented by Morawski et al. [130] stated that combining commercial P25 with carbon spheres then depositing this composite on glass fiber fabric showed high efficiency and selectivity in CO$_2$ reduction into CO.

5. Strategy IV: Modified TiO$_2$ Nanostructures by Hydrogenation

The next strategy applicable for efficient TiO$_2$ photocatalysts is to modify its properties. Several approaches have been explored to modify properties of TiO$_2$ through conventional doping process. Doping of metal ions (Cr, Sn, Zn, W, etc.) and nonmetallic ions (C, P, I, N etc.) into TiO$_2$ to create discrete or midgap energy states within its bandgap has been attempted to enhance its electro- and photo-response [131,132]. However, the doping elements are also known to create recombination center simultaneously [131]. While, nonmetallic ion doping is difficult due to the diverse chemical properties of the dopant ions and the existence of O$_2^-$ in TiO$_2$. Nitrogen is one of the elements that has been extensively doped into TiO$_2$ for visible light absorption [133,134].

Another way of modifying the properties of TiO$_2$ is hydrogenation that is different from the conventional doping method. The hydrogenation is the way of introducing oxygen vacancy by hydrogen element that results in the incorporation of Ti$^{3+}$ to TiO$_2$ [135,136]. Namely, Hydrogenation reduces TiO$_2$ through the conversion of Ti$^{4+}$ to Ti$^{3+}$ or other states. Depending on the degree or method of hydrogenation, the colors of the hydrogenated TiO$_2$ can be varied: black, blue, or brown [137]. Hydrogenation generally results in surface
modifications in few nm and leads to the modification of energy band structure of TiO$_2$, forming additional energy states located under the conduction band edge [137]. These modified properties of TiO$_2$ by the hydrogenation can contribute to many advantageous characteristics for more efficient photocatalytic performance: enhanced light absorptions and control of bandgap. To implement the hydrogenation to TiO$_2$, a number of techniques such as electrochemical reduction, metal reduction, NaBH$_4$ reduction, laser ablation, microwave radiation, ultrasonication, ion thermal process, and oxidation have been carried out [138,139]. The characteristics of the modified TiO$_2$ are affected by various factors, including not only experiment conditions such as reactants, temperature, concentration and pressure of hydrogen and reaction time but also material conditions such as the surface morphology, defect content, shape, and size [140–142]. Here this section provides the examples of hydrogenated TiO$_2$ synthesis and characteristics, and investigates its applicability to TiO$_2$ nanostructures.

The several approaches are valid for the formation of the hydrogenated TiO$_2$ to modify nanotubes. The hydrogenated TiO$_2$ is basically a reduced form of TiO$_2$ and can have extended light absorption region due to the creation of midgap states. In one of the reports, black TiO$_2$ has been synthesized via solvothermal method using ethylenediamine followed with calcination of the nanotubes (NT) at 600 $^\circ$C in a hydrogen atmosphere [143]. The photoelectron spectra of the surface showed Ti$^{3+}$ and oxygen deficiencies (it is also named as self-doping defects) which contributed in bandgap reduction [143]. In another report, 2D TiO$_2$ nanosheets have been synthesized via evaporation-induced self-assembly, followed by solvothermal treatment and ethylenediamine reflux [144]. Further, TiO$_2$ nanospheres has been obtained via combining hydrogenation with surfactant-induced solvothermal method [145] to achieve reduced TiO$_2$ in a controlled manner. These helped the morphology of TiO$_2$ to mitigate aggregation and to have low surface energy [145]. Furthermore, 1D TiO$_2$ nanotubes have been fabricated via applying hydrogenation and facile solvothermal method [146]. All these reports indicate that controlled hydrogenation leads to the formation of the reduced TiO$_2$ that helps in photocatalytic processes [146].

To obtain decent hydrogenation, the experimental conditions in the synthesis process play a significant role in controlling properties of the materials. It has been found that the reactor materials impact the properties: stainless-steel reactor resulted in black powder, while in quartz reactor blue powder was obtained indicating different extents of reduction [147,148]. The initial powder was prepared via mixing 2 g of TiO$_2$ in 50 mL NaOH at 120 $^\circ$C for 48 h, then washed in water and HCl followed by drying overnight at 110 $^\circ$C to yield titanate nanotubes [142]. Moreover, hydrogen in the atmosphere can easily reduce TiO$_2$, and processing in hydrogen ambient resulted in gray TiO$_2$. Depending on the degree of hydrogenation and processing conditions, various colors appear on TiO$_2$. In another report, the color of protonated titanates converted into brown through calcination at 500 $^\circ$C in H$_2$ atmosphere (N$_2$:5%) for 4 h [142]. Hydrogenation of anatase nanowire microspheres demonstrated high visible light absorption and contained Ti-H and O-H bonds which in turn leads to stabilization of surface disordered layer [142]. In addition, the pressure can be also an important factor for the hydrogenation. The hydrogenation of TiO$_2$ was implemented using H$_2$ pressure at lower temperature with small amount of Pt. In this hydrogenation, hydrogen flow was directed from platinum to TiO$_2$, which is known as an advanced reduction procedure [149].

Hydride processes are also applied for the hydrogenation of TiO$_2$. When hydrogenation process leads to reduced TiO$_2$, the annealing and thermal conditions may pose safety hazards. To avoid these problems, hydride processing has been proposed, in which, hydrides are used in modest conditions to release molecular hydrogen that works as a safe reductant to obtain black TiO$_2$ [150]. Both dry and sol-gel methods can be used in hydride reduction. In the dry method, pristine TiO$_2$ and hydride are mixed and annealed in Ar and N$_2$ atmosphere [151]. In the sol-gel process, NaBH$_4$ is used as the reduction agent. NaBH$_4$ is added to a mixture of two solutions that is made of (EtOH/HNO$_3$) and (EtOH/titanium tetra butoxide), until the gel is reformed. The gel is calcined in a muffle furnace for 3 h to
obtain hydrogenated TiO$_2$ nanoparticles [152]. Although a completion of hydrogenation may lead to black TiO$_2$, other colors is also obtainable by adjusting the temperature and the reduction duration [153]. The synthesized black TiO$_2$ nanoparticles were able to absorb > 80% of the sunlight [145]. Nevertheless, the reaction between CaH$_2$ and TiO$_2$ may result in TiO$_3$ and Magneli phase if process is allowed to continue for 240 h. Table 1 summarize hydrogenated TiO$_2$ materials by various techniques, their features fabrication, and performance measure for CO$_2$ conversion.

Table 1. Various techniques for the synthesis of hydrogenated TiO$_2$ materials and their features in the synthesis processes.

| Catalyst                          | Treatment                           | Note                                                                 | H$_2$ Evolution Rate/Removal Efficacy | Reference |
|-----------------------------------|-------------------------------------|----------------------------------------------------------------------|---------------------------------------|-----------|
| Black TiO$_2$ nanoparticles       | Thermal plasma furnace              | The absorption increases promptly and monotonously in visible spectrum, when the wavelength is >400 nm | Visible light: 83%                      | [154]     |
| Black TiO$_2$ nanotubes           | Hydrogen plasma method              | NaOH solution (10M, 50 mL), to be used in heating 2g of P25 for 12 h, then being washed with water and HCL. | 7 µmol h$^{-1}$ cm$^{-2}$              | [155]     |
| Black TiO$_2$ nanoparticles       | Electron beam treatment             | Electron-beam-assisted high energy electron used in changing the composition of TiO$_2$. Electron beam maximum energy 0.7 MeV. Electron beam maximum power 28 kW | Visible light: 85%                      | [156]     |
| TiO$_2$ nanotubes with black appearance for the proton-implanted layer | Proton implantation                 | The top of the nanotubes is being modified via high energy proton ion-implantation strategy. Then implanting the substrate with Varian 350D ion implanter. The resulted nanotubes showed high performance in aqueous solution. | UV: 38%                              | [157]     |
| Defective TiO$_2$                 | Metal reduction                     | Metals like Zn, Al, Mg are excellent reductants that for being cheap, safe and convenient in comparison with hydrogen. | Solar light: 95%                        | [142]     |
| Black TiO$_2$ and TiO$_2$ nanotubes | Aluminum reduction                 | TiO$_2$ and Al are being processed in a dual tube furnace below 0.5 Pa | 3.9 mmol g$^{-1}$ h$^{-1}$              | [158,159] |
| Gray TiO$_2$ nanowires            | Aluminum reduction                  | Titanate nanowires are being processed in double zone furnace in Al atmosphere for 4 h | Solar light: 95%                        | [160]     |
| Black brookite TiO$_2$ nanoparticles | Aluminum reduction                | Brookite TiO$_2$ and Al powder are being placed in dual vacuum furnace and heated for 4 h at 300–600 and 800 °C. This process promoted the absorption of visible spectrum and IR of brookite TiO$_2$ | Solar light: 92%                        | [159]     |
Table 1. Cont.

| Catalyst                     | Treatment                      | Note                                                                                                                                                                                                 | H$_2$ Evolution Rate/Removal Efficacy | Reference |
|------------------------------|--------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------|-----------|
| Black rutile TiO$_2$ Nanoparticles | Molten Aluminum               | The sample is being heated at 550–800 °C at a pressure of $6 \times 10^{-4}$ Pa in a vacuum-double-zone furnace. And the results showed enhanced absorption.                                                     | 932 µmol h$^{-1}$ g$^{-1}$           | [161]     |
| Black TiO$_2$-x nanoparticles | Al powder                      | Al powder and P25 (0.5 g) are being processed in a two-zone vacuum furnace. Then using thermal plasma furnace to apply hydrogen plasma for 5 h.                                                              | 15 mmol h$^{-1}$ g$^{-1}$             | [162]     |
| Black TiO$_2$-N nanoparticles | Zn reduction                   | The material is being heated in a gas stream of NH$_3$-Ar Solar light: 85%                                                                                                                         |                                       | [162]     |
| Rutile TiO$_2$ nanoparticles  | Zn reduction                   | Mixing aqueous TiCl$_2$ (1 mL) and isopropanol (30 mL) at 180 °C in existence of Zn powder for 6 h.                                                                                                   | 1.4 mmol h$^{-1}$ g$^{-1}$            | [163]     |
| Black TiO$_2$ photocatalyst   | Mg reduction                   | Mixing TiO$_2$ with Mg powder resulted black TiO$_2$. But Mg and H$_2$ resulted in highly stable and active reduced black TiO$_2$.                                                                   | 440 µmol h$^{-1}$ g$^{-1}$            | [164]     |
| Porous amorphous Vo-TiO$_2$   | Organic reduction              | 300-Xe lamp has been used as a light source. The target is aqueous methanol solution (25 vol%, 120 mL) for 8 h in UV and visible light: 5.67 mmol h$^{-1}$ g$^{-1}$ For 14 h, in visible light radiation: 115 µmol h$^{-1}$ g$^{-1}$ | Visible light and UV: 5.67 mmol h$^{-1}$ g$^{-1}$ | [165]     |
| Ti$^{3+}$ doped TiO$_2$       | Organic reduction              | 300 W Xe lamp, aqueous methanol solution (25 vol%, 120 mL), for 4 h in visible light irradiation: 50 µmol h$^{-1}$ g$^{-1}$                                                                           | Visible light: 115 µmol h$^{-1}$ g$^{-1}$ | [166]     |
| Defective TiO$_2$-x           | Organic reduction              | Imidazolxy and 2-ethylimidazole                                                                                                           |                                       | -         |
| Gray TiO$_2$                  | Organic reduction              | A TiO$_2$ precursor exposed to UV for one hour then annealed with hydrochloric acid, and imidazole (1 g) in a muffle furnace at 450 °C                                                              | 115 µmol h$^{-1}$ g$^{-1}$            | [165]     |
| Black defective TiO$_2$ nanotubes | Electrochemical reduction | TiO$_2$ were synthesized via Ti foil anodization in (4 mA for 3000 s or 80 V for 7200 s), then calcined in air.                                                                                 | Visible light: 72%                    | [168]     |
| Ti$^{3+}$ self-doped TiO$_2$-x nanoparticles | Chemical oxidation | The light source used is 300 W Xe lamp. Target and concentration are aqueous methanol solution (100 mL, 20%) MB (120 mL, 5 × 10$^{-4}$ mol/L), for 4 h.                                           | 250 µmol h$^{-1}$ g$^{-1}$            | [169]     |
### Table 1. Cont.

| Catalyst | Treatment | Note | H₂ Evolution Rate/Removal Efficacy | Reference |
|----------|-----------|------|------------------------------------|-----------|
| Ti³⁺ self-doped rutile TiO₂ | Chemical oxidation | Using solar simulator, MB (30 mL, 10⁻⁵ M), for 1 h | - | [170] |
| Ti³⁺ self-doped TiO₂₋ₓ anatase nanoparticles | Chemical oxidation | Light source: 300 W Xe arc lamp MB (100 mL, 1.5 × 10⁻⁵ mol/L) aqueous methanol solution (20 vol%) for 30 min | 147 µmol h⁻¹ g⁻¹ | [171] |

#### 6. Strategy V: Single Atom Photocatalysts

In the past few years, single atom catalysts (SACs) have nominated as potent photocatalysts that can be employed in CO₂ reduction efficiently, owing to their compelling properties. First, SACs have high activity and selectivity caused by their distinctive electron structure and unsaturated coordination sites. Second, they have a notable reduction in metal usage brought by the maximum atom utilization. Third, they possess clear reaction mechanisms endowed by the well-defined active sites. Fourth, they help in understanding and realizing the structure and activity relationship due to their atomic scale structure [172,173]. Theoretically, the valence of a single-atom on a support surface supposed to be zero; but practically the value is different. These atoms are being stabilized depending on the covalent coordination or ionic interaction with the supporting surface atoms, hence it possesses partial charge provided via the metal support interactions. In photocatalytic systems, the photogenerated electrons reduces the stabilized ions into metal ions during the photocatalytic reaction [33]. However, Zhang et al. [174] reported a mass production method of a single atom cobalt to be used in photocatalytic CO₂ reduction. As well as, Xiong et al. [175] presented a study of CO₂ reduction over Ni single atoms supported on defect-rich ZrO₂. This strategy requires further studies to define its influencing factors. It is true that throughout the past decades, physicochemical characteristics and functions of these photocatalysts have been attained. Still, more studies required to tailor the electronic and chemical structures in order to widen its use in photocatalytic applications.

#### 7. Strategy VI: Metal Organic Framework

Metal organic frameworks (MOFs) are microporous or mesoporous crystalline solid where the lattice is being formed via linking metallic nodes with rigid organic linkers possessing two or more coordination positions; the metallic nodes comprise of metal cations or clusters of few ions of metals. In addition, they can be called porous coordination polymers (PCPs) attributed to the nature of the interaction between the metallic nodes and the organic linkers. MOFs includes almost all the di-, tri- and tetra-positive ions mentioned in the periodic table. The materials that can be used in structure and binding groups of the organic linkers are abundant, as well. Yet, the most renowned ones are organo-phosphorous compounds, aromatic polycarboxylates and nitrogenated heterocycles [176].

MOFs has shown promising potentials in photocatalysis applications and energy conversion [177]. Titanium-based MOFs (Ti-MOFs) are attractive for practical applications, especially tetravalent cation due to its good redox activity, rigid framework and strong metal-ligand bonding [178]. Ti-MOFs represent an exemplary role in MOF family for their rich content, low toxicity, excellent structural topologies, and fascinating photocatalytic activity [179]. The variety of Ti-MOFs has been expanded by manipulating the synthesis parameters of organic ligands and titanium precursors. Nowadays, Ti-MOF derived materials showed high capability in the fields of energy conversion because of their stability, porosity, and regular component arrangement [177]. For instance, preparing Au/TiO₂ by pyrolyzed Au/NH₂-MIL-125 boosted CO₂ reduction into CH₄ [180]. It was reported that NH₂-MIL-125 (Ti) reduced CO₂ into HCOO⁻ in presence of TEOA as electron donor [181].
Zhang et al. synthesized Cu-NH2-MIL-125 (Ti) that showed improved light absorption and ameliorated the charge separation, supported with an extended stability throughout four photocatalysis cycles [182]. The photocatalytic conversion rate of CdS-MIL-125 (Ti) was enhanced by the improved light absorption and e/h pairs separation [183]. Moreover, the reports showed that coupling narrow band-gap semiconductors with Ti-MOFs boosts the photosensitive impact and enhances light absorption capacity [184]. Yang et al. proposed a study about ternary heterostructured MIL-125/Ag/g-C3N4 nanocomposites that showed efficient photoreduction in visible light [185]. Many other applications in different fields of renewable energy have received extensive attention due to the promising results via reducing the recombination centers, controlling reactive sites and enhancing the light absorption.

8. Conclusions

TiO2 has been one of the most investigated materials in photocatalysis and studies are in progress among the scientific community to address the unresolved issues. Crystal facet engineering is an important strategy for optimizing both reactivity and selectivity. Researchers have investigated several fabrication routes to control the crystal facets’ type and density. Studies have been able to synthesize photocatalysts with defined facets and their effects on selectivity of product formation have been investigated both theoretically and experimentally, controlling the ratio of different facets and achieving a dominant orientation still remains a challenge.

The nanostructures of TiO2 in its several types and morphologies have been fabricated to explore the novel electronic and the optical properties. Anodization is the most common technique to synthesize vertically aligned nanotubes, however, several other of the 1D and 2D structures have been synthesized using various chemical approaches such as solution growth, hydrothermal and sol-gel process. In particular, designing anatase nanocrystals with the most active facet of (001) helped in scrutinizing catalytic activity in a systematic way.

These morphologies and preparation methods directly control the photocatalytic performance of the synthesized nanomaterials in the form of band gap, electronic structure, light absorption, and surface adsorption. These property enhancements have been explained by the existence of Ti3+, oxygen vacancies, active surface area, charge separation and photocatalysis response. Moreover, owing to the reduction of the e-h recombination, the subsequent lifetime enhancement, the charge transfer kinetics is enhanced as well.

Nevertheless, there are still several challenges remain with the TiO2 nanostructures to achieve higher and better efficiency in photocatalysis. Taking into consideration the different modification approaches of these structures through the synthesis via different methods, there is no unambiguous approach to achieve all properties in the best possible values and hence the synthesis approaches depend on desired morphology or application. However, more investigations are required to achieve in-depth understanding of the structure-property relationships in various types and forms of TiO2, and to address the issues such as recombination of photo generated charges and extending the light absorption. The heterojunction approach is expected to play a big role in scaling up and commercially viable technologies. By a suitable selection of the heterojunction component (metal or semiconductor), several drawbacks of TiO2 such as narrow light absorption, higher recombination, surface area for molecular adsorption can be addressed. Further, the regeneration of the photocatalysts and slowing the rate of degradation are severe challenges for practical and scalable implementation. Hence, more theoretical and experimental studies are required to reach comprehensive understanding of TiO2 nanostructures and further research needed to promote its properties.

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