Recent Developments of Advanced Ti$^{3+}$-Self-Doped TiO$_2$ for Efficient Visible-Light-Driven Photocatalysis

Siyoung Na 1, Sohyeon Seo 1 and Hyoyoung Lee 1,2,3,*

1 Department of Chemistry, Sungkyunkwan University, 2066 Seoburo, Jangan-gu, Suwon 16419, Korea; sydizimon@gmail.com (S.N.); sshyeon@skku.edu (S.S.)
2 Center for Integrated Nanostructure Physics (CINAP), Institute for Basic Science (IBS), 2066 Seoburo, Jangan-gu, Suwon 16419, Korea
3 Department of Biophysics, Sungkyunkwan University, 2066 Seoburo, Jangan-gu, Suwon 16419, Korea
* Correspondence: hyoyoung@skku.edu; Tel.: +82-10-3636-9714

Received: 30 April 2020; Accepted: 13 June 2020; Published: 17 June 2020

Abstract: Research into the development of efficient semiconducting photocatalytic materials is a promising approach to solving environmental and energy problems worldwide. Among these materials, TiO$_2$ photocatalysts are one of the most commonly used due to their efficient photoactivity, high stability, low cost and environmental friendliness. However, since the UV content of sunlight is less than 5%, the development of visible light-activated TiO$_2$-based photocatalysts is essential to increase the solar energy efficiency. Here, we review recent works on advanced visible light-activated Ti$^{3+}$-self-doped TiO$_2$ (Ti$^{3+}$–TiO$_2$) photocatalysts with improved electronic band structures for efficient charge separation. We analyze the different methods used to produce Ti$^{3+}$–TiO$_2$ photocatalysts, where Ti$^3+$ with a high oxygen defect density can be used for energy production from visible light. We categorize advanced modifications in electronic states of Ti$^{3+}$–TiO$_2$ by improving their photocatalytic activity. Ti$^{3+}$–TiO$_2$ photocatalysts with large charge separation and low recombination of photogenerated electrons and holes can be practically applied for energy conversion and advanced oxidation processes in natural environments and deserve significant attention.

Keywords: Ti$^{3+}$-self-doping; photocatalysts; modification of TiO$_2$; visible light application; modification of electronic structures

1. Introduction

Environmental pollution and sustainable energy development are controversial issues we all face today [1]. In keeping with the pace of technological development, the development of renewable energy technologies must be studied in depth. Solar energy is the most abundantly available energy source. An amount as large as almost 99.9% of the energy used on Earth is produced by the sun [2–4]. Harnessing this enormous amount of solar energy would provide sustainable and environmentally friendly energy. It is also a promising option for economically feasible technology development.

Semiconducting photocatalysts are an eco-friendly and promising technology that converts solar energy into chemical energy. It can be used in various fields such as photolysis of harmful chemicals [5–8], artificial photosynthesis [9–12], photocatalytic water splitting [1,13–17] and electrochemical energy conversion [18–23]. Semiconducting photocatalysts using solar energy can solve environmental problems and have been actively researched around the world; as such, they have the
potential to become a sustainable energy source [24–26]. Recently, various materials have been studied, including conjugated polymers (CPs) [27–30], 2D-layered materials [25,26,31–34], semiconductor quantum dots (QDs) [35–39], graphene quantum dots (GQDs) [40,41], isolated single-atom site catalyst (ISAS-catalyst) [42–45] and MOF-based materials [46–48]. However, semiconducting photocatalysts containing TiO$_2$ remain the most popular. There are several advantages of TiO$_2$ photocatalysts, including their low cost, good chemical and physical stability, lack of toxicity to humans and high photoreactivity [49–53].

However, there are also disadvantages that limit the practical application of TiO$_2$. First, the recombination of light-generated electrons and holes easily occurs, hindering the efficient use of absorbed energy [54–56]. Second, the TiO$_2$ surface is generally hydrophilic, so its absorption capacity for aromatic organic pollutants is low, limiting its responsiveness [54,57–60]. Though there are many other issues to overcome, the wide bandgap (~3.2 eV) of TiO$_2$ requires ultraviolet light for photoactivity [24,54]. Only 5% or less of sunlight is UV light [24,53,59]. This means that TiO$_2$ cannot use the visible-near IR energy that comprises most sunlight. Therefore, great efforts have focused on research to improve charge separation, surface reactivity and light absorption to overcome the disadvantages of TiO$_2$ [12,61–64]. Increasing solar energy efficiency and using more energy are major challenges for expanding the light-activated region into the visible region.

Adjusting the band structure to harness visible light can result in higher photon harvesting. To achieve this goal, attempts have been made to understand and modify the physical and chemical properties of TiO$_2$, such as the slow-light effect in periodic TiO$_2$ photonic crystals [65] and the multi-reflection effect in semi-hollow TiO$_2$ spheres [66]. Attempts have also been made to improve TiO$_2$ by classic chemical element doping [67–71], dye sensitizing [72,73], formation of semiconducting junctions [74–77], localized surface plasmon resonance (LSPR) photosensitization [78,79], stoichiometric adjustment or coordination of surface atoms or surface oxygen vacancies [61,80–83] and tuning inter-particle interactions of TiO$_2$ nanocrystals [84,85]. In particular, Ti$^{3+}$-self-doped TiO$_2$ (Ti$^{3+}$–TiO$_2$) such as blue-black TiO$_2$ has been found to induce high efficiency in visible-light-driven photocatalysis [86–94]. Nonetheless, improvements in photogenerated charge separation in Ti$^{3+}$–TiO$_2$ remain challenges for a high photon harvesting efficiency. Thus, Ti$^{3+}$–TiO$_2$ has been developed with modifications of the electronic structures to extend TiO$_2$ photocatalyst to highly efficient visible light harvesting.

In this review, we focus on the development of advanced Ti$^{3+}$–TiO$_2$: for efficient solar energy harvesting of TiO$_2$ photocatalysts. Ti$^{3+}$–TiO$_2$ is oxygen-deficient (TiO$_{2-x}$) and was first reported in 2011 by Chem et al. They produced defects on the TiO$_2$ surface and called the resulting material ‘disorder-engineered black TiO$_2$.’ This method reduced the light absorption band gap of to 1.5 eV, suggesting the possibility of using it for visible light catalysis by increasing solar absorption efficiency. [92] Since then, TiO$_2$ has been reduced to produce blue TiO$_2$ [87], and great efforts have been put into developing blue–black TiO$_2$ to use visible light, and much progress has been made. Figure 1 shows the schematic of the nanoparticle structure of Ti$^{3+}$–TiO$_2$ and the band location for the insertion of each dopant.
Figure 1. Schematic structures of (a) TiO₂ and (b) Ti³⁺–TiO₂ according to band positions of (c) TiO₂ and (d) Ti³⁺–TiO₂ modified with heterogeneous materials.

We provide the latest reports on synthesis methods of Ti³⁺–TiO₂-based photocatalysts and their application efficiencies. First, we analyze the physical concept of Ti³⁺–TiO₂ photocatalysts and their production and advancement. We discuss the shortcomings in the production of Ti³⁺–TiO₂ and recent reports on the use of other materials to enhance the absorption of visible light. Moreover, many efforts have been discussed to overcome the disadvantages of photocatalytic efficiencies of Ti³⁺–TiO₂ due to low charge separation and high recombination of photogenerated electrons and holes. Finally, we present some perspectives on the future of modified Ti³⁺–TiO₂ photocatalysts.

2. Preparation of Ti³⁺–TiO₂

Ti³⁺–TiO₂ (TiO₂−x) has been demonstrated to enhance visible light absorption [95]. Ti³⁺ self-doping causes defect levels due to oxygen vacancies in the lattice structure of self-doped TiO₂. The defect levels overlap the conduction band of TiO₂ and can induce vacancies in the electronic state just below the conduction band [96]. As a result, the band gap is reduced, resulting in enhanced visible light absorption. Methods for producing Ti³⁺–TiO₂ have been a focus of many studies. In general, high pressure and high temperature are used to reduce oxygen to form oxygen vacancies. Ti³⁺–TiO₂ doped with high oxygen vacancies is super hydrophilic. Thus, Ti³⁺–TiO₂ on hydrophilic substrates can result in strong bonding to the surface, thus increasing the coating ability.

According to recent trends, there are many reduction methods of TiO₂, which we divide into five main branches: hydrogenation, hydrothermal reaction, alkaline metal reduction, sol–gelation and phase-selective reduction. As generations go through, the preparation method of Ti³⁺–TiO₂ is not always superior, but it is considered to be a little more relaxed and more sophisticated.

2.1. Hydrogenation

Hydrogenation using hydrogen gas to react with oxygen atoms in the lattice of TiO₂ is the most common method for Ti³⁺ doping. Ti³⁺ is self-doped in an abundance of TiO₂ by high thermal or electromagnetic energy [97,98]. Hydrogenation requires harsh synthetic conditions and dangerous production processes (i.e., high heat and pressure, risk of explosion of hydrogen gas) [92,97–99]. To
overcome this, other reducing agents that can provide hydrogen such as NaBH₄ and TiH₂ have been introduced as alternatives to hydrogen gas [98,100–102]. Additionally, increasing the rich Ti³⁺ doping involves higher heat, higher pressure and longer reaction times. Well-crystallized samples can effectively enhance visible and infrared absorption and exhibit hydrophilicity by oxygen doping with H in the lattice. However, in hydrogenated TiO₂, a high concentration of hydrogen atoms was required for efficient photocatalytic activity [103].

Additionally, if the temperature increases under firing conditions, phase conversion from anatase to rutile may occur. This can result in a band gap shift from anatase (~3.2 eV) to rutile (~3.0 eV). Phase transformation requires 600 to 700 degrees of energy in the absence of impurities, but the presence and amount of oxygen vacancies can lower the firing temperature. The increased oxygen deficiency causes relaxation of the large oxygen sublattice and facilitates the rearrangement and modification of atoms from anatase to rutile. In a high-pressure reducing atmosphere, heat transfer is also advantageous because of the high material density. Fast heat transfer will further promote anatase-to-rutile phase transformation [104]. However, the abundant doping of Ti³⁺ results in an irregular crystalline phase, called a disordered phase. Disordered crystals may behave differently from the normal physicochemical properties of anatase and rutile crystals.

2.2. Hydrothermal Reaction

A method of manufacturing Ti³⁺–TiO₂ with abundant defects has been reported using TiCl₃ and TiF₄ as precursors. Ti³⁺ can easily be oxidized under high heat and pressure conditions. Introduction of Ti⁴⁺ can inhibit oxidation of Ti³⁺ in this reaction, leading to abundant doping [105]. In addition, Fang et al. synthesized various reduced TiO₂ samples using Zn powder as a reducing agent and HF as a solvent in a simple one-pot hydrothermal process. However, Ti³⁺ introduced by Zn reduction is not stable in air and can be easily oxidized [106].

This method, which has been slightly improved under hydrogenation conditions, still requires high heat and pressure. It has an advantage in that the reaction proceeds in a liquid state that is easier to handle than hydrogen gas. However, it is unstable in the air and hydrogen saturation is not effective. A new solvent is needed to overcome this stability issue.

2.3. Alkaline Metal Reduction

Researchers tired of using high heat and pressure gases and liquids. In general, attempts have been made to reduce TiO₂ by using alkali metal, the most commonly used solid reducing agent. It is possible to obtain Ti³⁺–TiO₂ by simply replacing the high heat and pressure and simply mixing the powder. In 2013, Yin et al. produced gray TiO₂ rutile nanowires by reducing the TiO₂ surface by directly introducing aluminum metal at a temperature of 700 °C [107]. There have also been attempts to generate Ti³⁺ under milder conditions. In 2017, Zhang et al. sufficiently reduced TiO₂ using Na/NaCl powder under room temperature and an argon atmosphere and treated it with Ru to synthesize nanoparticles of TiO₂ with Ti³⁺ and Ru. Crystalline TiO₂ was milled with Na and NaCl powder at room temperature for 0.25 to 4 h under an argon atmosphere. It can be seen from Figure 2 that the color of P25 becomes darker as it undergoes harsh reaction conditions. Ti³⁺-rich TiO₂ nanocrystals can be used as effective support for Ru particles and the Ru/Ti³⁺–TiO₂ catalysts showed excellent performance in catalytic hydrogenation of N-methyl pyrrole [108].
Figure 2. Scheme of the route for the preparation of Ru/TiO$_2$-$x$. (a–i) Photographs of P25 nanocrystals and TiO$_2$-$x$ prepared by Na/NaCl reduction corresponding to reaction times from 1 to 4 h. Reproduced from [108]. Copyright (2017), The Royal Society of Chemistry.

2.4. Sol-Gelation

Since then, people have shown how to synthesize TiO$_2$ doped with Ti$^{3+}$ abundantly, starting with the precursor building block, rather than doping Ti$^{3+}$ into the already prepared TiO$_2$. Zhang et al. synthesized TiO$_2$ single-crystal nanorods using a sol–gelation method and succeeded in obtaining Ti$^{3+}$-self-doped blue TiO$_2$ single-crystal nanorods by further annealing at 350 °C. Blue TiO$_2$ showed a 97.01% higher decomposition rate of RhB than did white TiO$_2$ under visible light, and the photocatalytic hydrogen generation rate increased. As a result of these investigations, the band gap was reduced to 2.61 eV due to the synergistic effect of the 1D-shaped single crystal structure and this increased the photocatalyst’s visible light absorption ability and photocatalytic reactivity [109]. In 2018, Yao et al. synthesized N/Ti$^{3+}$-doped TiO$_2$ in one step using TiN. Additionally, using BiOBr, N/Ti$^{3+}$-doped TiO$_2$ and heterojunctions were formed to enhance sonocatalytic activity. Doping of BiOBr and N/Ti$^{3+}$ leads to effective charge separation of electron–electron pairs, increasing the methylene blue removal efficiency by 1.81 times [110].

In general, the grown TiO$_2$ crystal phase is anatase. However, depending on the reaction conditions, rutile anatase may also be present. Among the synthetic conditions, there is a possibility that BiOBr promoted rutile growth [110]. Optimal performance is achieved by mixing anatase and rutile in appropriate proportions (85:15). However, it is generally found that the photocatalytic efficiency of anatase is higher. Due to the high density of localized states in anatase, it is used for surface adsorbed hydroxyl radicals and slow charge carrier recombination. Rutile has a high charge recombination rate and consequently has a reduced ability to adsorb functional species, which is detrimental to photocatalytic performance [104].

2.5. Phase-Selective Reduction

There are many ways to produce Ti$^{3+}$–TiO$_2$, but almost all of these require high temperature and high pressure. In addition, it is not yet possible to selectively reduce anatase and rutile phase on TiO$_2$ crystals in harsh conditions of high temperature and high pressure. In 2016, Zhang et al. first developed a method for selectively reducing the crystal phase of Degussa P25 TiO$_2$ nanoparticles at room temperature and atmospheric pressure using a simple Li–Ethylene diamine (EDA) solution. They melted Li metal in EDA solution at room temperature and pressure to produce a blue electride solution of a strong reducing agent to reduce TiO$_2$ nanocrystals. The Li–EDA solution is unique in reducing only the rutile phase while the anatase phase remained the same as in the composition of Degussa P25. They confirmed that Ti$^{3+}$ was selectively introduced into TiO$_2$ to significantly improve visible and near-infrared absorption and increase the charge–hole charge separation efficiency through type II band gap alignment (Figure 3). These effects promoted a strong hydrogen-generating
surface reaction. Therefore, when using phase-selective disorder engineering, 0.5 wt% Pt and 3.46-mmol were used to show high stability and a high hydrogen generation rate of 13.89 mmol·h⁻¹·g⁻¹ [87]. In addition, in 2019, Hwang et al. discovered that when P25 is treated with Na-EDA solution, only the anatase phase is reduced. Engineered Ad/Rt TiO₂ selectively treated with Na-EDA to reduce the anatase phase contained only Ti³⁺ defect sites in the anatase phase and the internal energy band gap was narrowed. This indicates enhanced visible light activity. Hwang et al. subsequently reduced CO₂ using Ti³⁺-self-doped Ad/Rt TiO₂ that selectively reduced only the anatase phase to produce CH₄ using light in the visible region [111]. The phase-selective method of reducing TiO₂ using a metal–EDA electride solution has attracted attention as a promising method of self-doping rich Ti³⁺ on the surface of TiO₂ at room temperature and atmospheric pressure to improve the visible light activity of TiO₂. The developed Blue TiO₂ (BTO) was used for organic arylation reactions, the yield of which was supported with untreated P25 (40%) and BTO (63.4%) [112]. In addition, the BTO had excellent reactive oxygen species (ROS) generation and showed strong efficacy in decomposing algae (Chlamydomonas) under sunlight [113].

The phase-selective reduction of P25 does not require heat or pressure. In addition, while selectively reducing rutile and anatase TiO₂ crystal phases, it became possible to impart selectivity [114]. With the selective reduction of rutile and anatase, their physicochemical properties are clearly different. We expect to pioneer new applications in various fields by applying this method.

Figure 3. (A) Photographs of P25 (left), disordered anatase–TiO₂ (middle) and disordered rutile TiO₂ (right) suspensions (0.05 g L⁻¹) after Li–Ethylene diamine (EDA) treatment for 6 days; (B) x-ray diffraction (XRD) patterns of the Li–EDA-treated P-25 crystals with different treatment times for the (A) anatase phase and the (R) rutile phase. (C) HR-TEM images and selected area electron diffraction pattern of P-25; scale bar: 10 nm; (D) HR-TEM images and the selected-area electron diffraction pattern of blue P-25; scale bar: 10 nm. Enlarged TEM images of the junction area (red squares: P-25 and green squares: blue P-25); (E) calculated bandgap diagrams of P25 (left) and blue P-25 (right). Reproduced from [1]. Copyright (2016), The Royal Society of Chemistry.
3. Enhancement of Photogenerated Charge Separation and Photocatalytic Activity in Advanced Ti$^{3+}$–TiO$_2$

Photocatalysts exhibit catalytic activity when introduced to light. The photogenerated electrons and holes move to the photocatalytic surface. The moved electrons and holes react with adsorbed electron acceptors and donors, respectively, to complete the catalytic reaction. Abundant Ti$^{3+}$ doping can lead the excitation region from ultraviolet to visible light. Ti$^{3+}$-doped TiO$_2$ can narrow the wide band gap of TiO$_2$ for harvesting visible light and can provide an increase in electronic conductivity due to doped Ti$^{3+}$ defects. However, after photoexcitation, the generated electrons and holes may undergo significant electron recombination in the depletion region of Ti$^{3+}$-doped TiO$_2$ [115–117].

To overcome this and ultimately enhance photocatalytic activity in all applications, deformation studies with several different materials have been conducted. Performance can be improved by using Ti$^{3+}$–TiO$_2$ in combination with other materials or elements. Studies using various other materials have been conducted to overcome the previously mentioned limitations of Ti$^{3+}$–TiO$_2$ deformation.

We focus on the synthetic methods of advanced Ti$^{3+}$–TiO$_2$ with high photogenerated charge separation and efficiency and classify them into four categories according to recent developments. Ti$^{3+}$–TiO$_2$ modification has been extensively studied, including metal and nonmetal doping, semiconducting coupling, and stoichiometry modification to prepare and stabilize composites with other materials.

3.1. Metal-Doping

It has long been a major concern to increase the efficiency of TiO$_2$ photocatalysts and expand their use in the visible region using easily accessible metal dopants. Metal dopants can be mixed with Ti$^{3+}$ atoms or replaced by Ti atoms, and the band gap can be adjusted in such a state. Moreover, a new band was produced as a conduction band to help better separate photogenerated charges after photoexcitation. Metal dopants act as an electron acceptor as well as a hole acceptor in the valence band. The introduction of metal dopants is still a promising option for Ti$^{3+}$–TiO$_2$. We summarized these efforts in Table 1.

| Catalysts                        | Light          | Application Target                  | Efficiency          | Ref.   |
|---------------------------------|----------------|-------------------------------------|---------------------|--------|
| Plasmonic Ni/Ti$^{3+}$ TiO$_2$/SiO$_2$ nanospheres | 300 W Xe lamp | Methylene blue                      | 0.11 ± 0.04         | [69]   |
| Pt single atom–anatase(001) Ti$^{3+}$ TiO$_2$ nano sheets | 325 nm, 365 nm, 500 W | Hydrogen evolution reaction | 400 µmol·h$^{-1}$·g$^{-1}$ | [89] |
| Zn-assisted Ti$^{3+}$ TiO$_2$: Tungsten halogen lamp | | Formic acid | 100% 90 min$^{-1}$ | [106] |
| Li–EDA TiO$_2$–Pt: Xenon lamp | | Hydrogen evolution reaction | 350 µmol·h$^{-1}$·g$^{-1}$ | [114] |
| Bi$^{3+}$/Ti$^{3+}$ TiO$_2$: Flumequine under HSO$_5^-$ | | | 65% | [118] |
| Co$^{3+}$/Ti$^{3+}$ TiO$_2$: Acid Orange 7 | 300 W Xe lamp | | 100% 5 h$^{-1}$ | [119] |
| Cu/Ti$^{3+}$ TiO$_2$: F. graminearum and B. dothidea spores | 300 W Xe lamp | Orange G | 72% | [121] |

3.1.1. Surface plasmon effects on Ti$^{3+}$–TiO$_2$

LSPR-based photosensitization can promote the absorption of visible or near infrared rays [122,123]. If the frequency of the incident photon coincides with the natural frequency of the vibrating surface electrons, resonant group oscillations of the valence electrons can occur to promote absorption of Ti$^{3+}$-self-doped TiO$_2$ visible light [124]. Usually, LSPR excitation occurs in the visible region when Au [125], Ag [126], and Pt [127] are combined with TiO$_2$ [128]. Attempts to combine Ti$^{3+}$-
self-doped TiO$_2$ and LSPR metals have continued. However, in almost all cases, noble metals should be used for plasmon resonance [125–127]. The use of precious metals is still valid. In 2019, phase-selective room-temperature solution engineering was used to enhance HER performance by attaching Pt particles to TiO$_2$ richly doped with Ti$^{3+}$ [114]. This indicates that the simple phase-selective room-temperature solution engineering method does not lag behind TiO$_2$ manufactured in other harsh conditions of different reducing conditions.

Recently, He et al. used Ti$^{3+}$ and Ni for plasmon-mediated carrier transfer to enhance the degradation of methylene blue in visible light. They deposited Ni–TiO$_2$ structures on SiO$_2$ spheres based on the modified nanosphere lithography method. It was found that plasmon-generated hot electrons and Ni holes can be transferred to TiO$_2$ in a heterogeneous structure (Figure 4). The transferred hot electrons and holes occupy oxygen vacancies or produce Ti$^{3+}$. TiO$_2$ self-doped with Ti$^{3+}$ showed enhanced removal performance of methylene blue of 0.11 ± 0.04 μmol·L$^{-1}$·min$^{-1}$ in visible light [69].

Furthermore, it is valuable to be able to achieve the same effect as LSPR by using inexpensive non-precious metal transition metals other than Ni. We believe that developing a method of applying transition metals will become the main approach to metal-doped Ti$^{3+}$ TiO$_2$ in the future.

![Figure 4](image_url) Fabrication and morphology of plasmonic Ni–TiO$_2$ substrates. (A) Spin-coating silica nanospheres on glass or a Si wafer; (B) deposition of TiO$_2$ on (A); (C) deposition of Ni on (B); (D–F) False-colored SEM images of the sample surfaces described in (A–C); (G) monitoring PMCT in Ni–TiO$_2$ heterostructures by X-band EPR spectroscopy; (H) illustration of PMCT in Ni–TiO$_2$. Hot electrons (red) are transferred from Ni to TiO$_2$ upon the LSPR excitation of Ni and spatially separated.
3.1.2. Single Atom Site Doping Effects on Ti$^{3+}$–TiO$_2$

Isolated single atom site (ISAS) catalysts are a new approach in the field of catalysis due to their increased catalytic activity and excellent selectivity. Hejazi et al. created a stable platinum single atom site by grafting Pt single atoms to the Ti$^{3+}$-self-doped TiO$_2$ anatase (001) nanosheet by hydrogenation [89]. After reducing the thin Ti$^{3+}$ layer in the surface Ar/H$_2$ environment, it was used as a Pt single atom support and tightly adhered from the diluted aqueous Pt solution. The amount of Pt deposition can be adjusted by considering the heat treatment temperature in Ar/H$_2$. This showed a 150-fold improvement in hydrogen generation rate over that observed using the same amount of platinum nanoparticles (Figure 5) [89]. Despite many issues, including the stability of ISAS catalysts, this is a very attractive approach. With a small amount of metal, a photocatalytic performance of tens to hundreds of times improvement is observed. In addition, we believe that a single atom leads to a widely applicable approach for many. The development of the ISAS catalyst using Ti$^{3+}$ as support can provide a new approach for Ti$^{3+}$-self-doped TiO$_2$ for absorbing visible light.

![Figure 5](image_url)

**Figure 5.** (a) Schematic of the sputtered layer, (b) top-surface SEM image and (inset) optical image of the TiO$_2$ layer deposited on SiO$_2$–Si TEM grid; (c) HAADF-TEM image and (d) EDS map of Pt-SA-decorated TiO$_2$ layer; (e) surface density of atomic Pt for different samples; (f) schematic of Pt-SA-decorated TiO$_2$ for H$_2$ evolution application. Reproduced from [89]. Copyright (2020). Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2020.

3.1.3. Transition or Rare Metal Grafting on Ti$^{3+}$–TiO$_2$

In general, the bonding of transition metals and TiO$_2$ is a classic method. Similarly, much effort has been put into grafting transition metals into Ti$^{3+}$–TiO$_2$. Recently, research on photocatalysts for removing microorganisms and viruses was actively conducted in addition to the removal of existing classical organic or inorganic contaminants. Zhang et al. reported cell lysis of *E. coli* and agropathogenic fungal spores by preparing classical Cu and Ti$^{3+}$–TiO$_2$ in a new way. It was reported
that anhydrous ethanol can be used as a reducing agent in the hydrothermal process leading to the formation of metallic copper and Ti\(^{3+}\). They confirmed the photocatalytic disinfection effect on five agricultural pathogenic fungal spores, including *F. graminearum* and *B. dothidea* spores, by fluorescence staining using a FungaLight CFDA-AM/propidium iodide yeast vitality kit. Almost all bacteria were killed upon irradiation for 3 h. In Figure 6, killed bacteria are identified by fluorescent staining. Both copper and other metals are expected to be effective in bacterial and viral cell lysis when combined with Ti\(^{3+}\)-self-doped TiO\(_2\) [120].

![Figure 6](image-url)

**Figure 6.** Fluorescent images showing cell viability of the *F. graminearum* macroconidia after illumination for 100 min: without photocatalyst (a and b) or treated with the 10% Cu/Ti\(^{3+}\)-TiO\(_2\) composite (c and d); (b, d) are the enlarged observations of macroconidia in (a, c). The cell was stained by CFDA-AM/propidium iodide and the live cells appear green, while the dead ones are red in the images. (e) is ESR spectrum of the pure TiO\(_2\) and Cu/Ti\(^{3+}\)-TiO\(_2\). Reproduced from [120]. Copyright (2020), Elsevier.

Recently, grafting of rare earth metals such as Bi (rather than classic commercially available metals such as Cu, Zn and Co) into Ti\(^{3+}\)-TiO\(_2\) has been reported. Gul et al. increased the solar reactivity by grafting Bi to Ti\(^{3+}\)-TiO\(_2\). They performed extensive doping with Ti\(^{3+}\) and Bi-by-Bi doping and sol–gel technology and showed better photocatalytic performance than undoped TiO\(_2\) for flumequine decomposition [118].

As shown in Figure 7, Zhou et al. introduced doping with six rare earth metals (i.e., La, Ce, Pr, Nd, Eu and Gd) and sepiolite with Ti\(^{3+}\)-TiO\(_2\) to improve visible light activity and provide low band gap energy. In addition, this strategy resulted in a high adsorption capacity of contaminants through the sepiolite and improved the photocatalytic performance. Figure 7 shows the schematic structure...
for modification of the conduction band maximum and the photodegradation effect of Orange G for each metal. They found that, upon doping of rare earth metal ions, the structure and chemical properties of the nanocomposite of TiO$_2$ depended heavily on the radius of the rare earth metal ion. Rare-earth ions with a valence of +3 (i.e., RE$^{3+}$) can be abundantly doped with Ti$^{3+}$ because the rare earth metal ions are much larger than that of Ti$^{4+}$. However, this can cause a charge imbalance that can contribute to the adsorption of OH$^-$ and it is also reported that the empty 4f level of rare earth metals can act as a scavenger for light-generating electrons. Of the six rare earth metals, the Eu complex showed the best photocatalytic performance [121]. The combination of common transition metals and rare earth metals with Ti$^{3+}$-self-doping can be an excellent way to enhance photocatalytic performance, and promising materials for cell lysis of viruses and bacteria can be developed.

Figure 7. (a) Proposed visible-light-induced photocatalytic mechanism over the RE–TiO$_2$/Sep nanocomposites and (b) photocatalytic degradation rate of orange G under visible light irradiation for 10 h over various types of photocatalysts. Reproduced from [121]. Copyright (2018), Elsevier.

3.2. Nonmetal Doping

Much effort has been made to expand the applications of TiO$_2$ photocatalysts with metal and nonmetal based dopants into the visible light regime and increase the photocatalytic efficiency. In particular, many common elements such as nitrogen, carbon, sulfur and phosphorus have been used for grafting. The grafting of nonmetallic elements such as these can lower the surface energy for adsorption of the photocatalytic surface [129]. Unlike metal dopants, nonmetal dopants can be directly involved in the band of TiO$_2$. In addition, nonmetallic elements with a different electronic environment from oxygen can have positive and negative effects on the band gap energy. We believe that such modification through band engineering is a unique possibility for nonmetal dopants. We summarize the recent Ti$^{3+}$ and nonmetallic dopant grafting in Table 2.
Table 2. Summary of nonmetal doped Ti\textsuperscript{3+}-self-doped TiO\textsubscript{2} photocatalysts.

| Catalysts                  | Light               | Application Target | Efficiency | Ref. |
|----------------------------|---------------------|--------------------|------------|------|
| N/Ti\textsuperscript{3+}/C TiO\textsubscript{2} | 500 W Xe lamp       | Rhodamine B        | 100% 1 h\textsuperscript{-1} | [70] |
| N/Ti\textsuperscript{3+} TiO\textsubscript{2} nanotube | 400 W Halogen lamp | Rhodamine B        | 100% 4 h\textsuperscript{-1} | [130] |
| N/Ti\textsuperscript{3+} TiO\textsubscript{2} spheres | 300 W Xe lamp       | Methylene orange   | 100% 3 h\textsuperscript{-1} | [131] |
| S/Ti\textsuperscript{3+} TiO\textsubscript{2}   | 150 W Xenon lamp    | Hydrogen evolution reaction | 22.5 μL∙h\textsuperscript{-1}∙cm\textsuperscript{2} | [132] |
| S/Ti\textsuperscript{3+} TiO\textsubscript{2}–Ag nanorods | Xe lamp             | Hydrogen evolution reaction | 209.2 μmol∙h\textsuperscript{-1}∙g\textsuperscript{-1} | [133] |
| C–N–S-tridoped Ti\textsuperscript{3+} TiO\textsubscript{2} | 300 W Xe lamp       | Hydrogen evolution reaction | 149.7 μmol∙h\textsuperscript{-1}∙g\textsuperscript{-1} | [134] |

3.2.1. N-Doped Ti\textsuperscript{3+}–TiO\textsubscript{2}

Nitrogen is one of the most frequently used nonmetal elements for adjusting the valence band of TiO\textsubscript{2}. Doping with nitrogen may cause the maximum upward movement of the valence band, and visible light absorption may also be improved by controlling the red-shift of the absorption edge. Nitrogen can improve both carrier density and electron conductivity in the neutral region [129]. Additionally, it can act as an absorption site for organic pollutants. Recently, efforts have been made to enhance visible light absorption and enhance photocatalytic performance using Ti\textsuperscript{3+} and N dopants together. By doping N and Ti\textsuperscript{3+} together, Ti\textsuperscript{3+} in the band decreases the conduction band, and N increases the valence band to reduce the band gap energy and enhance the photocatalytic performance. Jia et al. improved the charge separation by introducing carbon after N doping, introducing carbon components, and using carbon as a site to accept the separated charge after photoexcitation. This showed a significantly faster Rhodamine B decomposition rate than conventional nitrogen-doped Ti\textsuperscript{3+}-self-doped TiO\textsubscript{2} (Figure 8) [70].

![Figure 8. Schematic diagram of the charge transfer and the proposed reaction mechanism over N-doped TiO\textsubscript{2}/C nanocomposites under visible light irradiation. Reproduced from [70]. Copyright (2017), Elsevier.](image)

3.2.2. Sulfur-Doped Ti\textsuperscript{3+}–TiO\textsubscript{2}

Among nonmetal dopants, sulfur has the same valence as oxygen, has adequate energy, and may not cause charge imbalance in TiO\textsubscript{2}. The energy band occupied by the charge imbalance can act as a carrier recombination site and degrades the carrier transport process [129,135]. Based on these advantages, sulfur has been noted as another promising nonmetallic dopant to drive the performance
of TiO$_2$ photocatalysts. Active research with Ti$^{3+}$ is ongoing. Ji et al. introduced S$^-$ into anatase TiO$_2$ together with Ti$^{3+}$, which significantly lowered the band gap energy and increased photocatalytic hydrogen production. They confirmed that, by introducing sulfur and Ti$^{3+}$, the band gap decreased from 3.2 eV for the existing anatase TiO$_2$ to 2.0 eV after co-doping [132]. As shown in Figure 9, Meng et al. added plasmonic Ag particles to TiO$_2$ nanorods introduced with sulfur and Ti$^{3+}$ to synergistically reduce the band gap through impurity dopants and expand LSPR into the visible light regime. These are photocatalytic reactions where phenol’s visible-light-driven photocatalytic decomposition rate and hydrogen production rate are as high as 98.67% and 209.2 μmol∙h$^{-1}$∙g$^{-1}$, approximately 2 and 5 times higher than TiO$_2$ alone [133].

![Figure 9. Schematic diagram for the formation of Ag/S–TiO$_{2-x}$ nanorods. Reproduced from [133]. Copyright (2017), Elsevier.](image)

3.2.3. Multi-Doped Ti$^{3+}$–TiO$_2$

Several elemental dopants can be introduced at the same time. Yan et al. reported black TiO$_2$ nanosheets with Ti$^{3+}$ by doping nitrogen, carbon and sulfur. The doped C, N, S elements can result in additional impurity levels above the valence band. The mass concentrations of doped C, N and S are 14.20%, 4.80% and 3.30%, respectively, and these worked synergistically with Ti$^{3+}$. They used visible light to photocatalytically decompose methyl orange up to 92.13%. The amount of hydrogen generated by the photocatalyst was 149 μmol∙h$^{-1}$∙g$^{-1}$ [134]. An attempt to use multiple materials without being limited to a single material may provide a new way to improve photocatalytic performance.

3.3. Semiconducting Coupling

Semiconducting heterogeneous catalytic junction enhances various properties by adding a new band to Ti$^{3+}$–TiO$_2$. The newly added band may additionally absorb visible light, promote optical junction carrier separation and transfer and enhance interactions with the target material. Semiconducting heterojunctions are advantageous for absorbing visible light of photocatalysts and increase photocatalytic activity by promoting separation and transfer of photojunction carriers of semiconductors [136,137]. Previous bands of semiconductor materials such as CdS [138], Ag$_3$PO$_4$ [139], Cu$_2$O [140] and WO$_3$ [141], have been combined with TiO$_2$. Recently, g–C$_3$N$_4$ has shown overall water splitting band potential and high visible light response, leading to the current trend [142,143]. Likewise, when Ti$^{3+}$–TiO$_2$ is combined with semiconducting materials, better synergy can be expected than before. We looked at the recent trends of Ti$^{3+}$–TiO$_2$ and organized them in Table 3.
### Table 3. Summary of semiconducting coupling with Ti₃⁺ self-doped TiO₂ photocatalysts.

| Catalysis | Light | Application Target | Efficiency | Ref. |
|-----------|-------|---------------------|------------|------|
| Ti³⁺ TiO₂/g-C₃N₄ | Xe lamp | Hydrogen evolution reaction | 3748.46 μmol∙h⁻¹∙g⁻¹ | [90] |
| Ti³⁺ TiO₂/WO₃/Ag | Solar | CO₂ to CO | 1166.72 μmol∙h⁻¹∙g⁻¹ | [91] |
| Ti³⁺ TiO₂/meso-g-C₃N₄ | 500 W Xe lamp | Methylene blue | 100% 2 h⁻¹ | [93] |
| Ti³⁺ TiO₂/WO₃ | 420 nm cutoff | Toluene | 100% 60 min⁻¹ | [94] |
| Ti³⁺ TiO₂ nanowires/rGO | 300 W Xe lamp | Waste oil | 100% 5 h⁻¹ | [103] |
| N/Ti³⁺ TiO₂/BiOBr | 120 mW lamp | Methylene blue | 100% 50 min⁻¹ | [110] |
| Ti³⁺ TiO₂/MoS₂/Ag | 500 W Xe lamp | Bisphenol A | 100% 2 h⁻¹ | [144] |
| Ti³⁺ TiO₂/AgPO₄ QD | 300 W Xe lamp | Methylene orange | 100% 100 min⁻¹ | [145] |
| Ti³⁺ TiO₂/CdS QD | 300 W Xe lamp | Methylene blue | 100% 150 min⁻¹ | [146] |
| Ti³⁺ hollow TiO₂/MoS₂/CdS | 300 W Xe lamp | Hydrogen evolution reaction | 8950 μmol∙h⁻¹∙g⁻¹ | [147] |
| N/Ti³⁺ TiO₂/MoS₂ | 300 W Xe lamp | Methylene orange | 100% 2 h⁻¹ | [76] |
| Ti³⁺ TiO₂/Ce³⁺ CeO₂ | 300 W Xe lamp | Methylene blue, Methylene orange | 100% 3 h⁻¹ | [148] |
| Ti³⁺ TiO₂/FeOₓ | 420 nm LED | Oxygen evolution reaction | 410 μmol∙h⁻¹∙g⁻¹ | [149] |
| Ti³⁺ TiO₂/g-C₃N₄ hollow nanosphere/MoS₂ QD | 300 W Xe lamp | Hydrogen evolution reaction | 1524.37 μmol∙h⁻¹∙g⁻¹ | [150] |
| Ti³⁺ TiO₂/g-C₃N₄ nanospheres/Ag | 300 W Xe lamp | Methylene orange | 100% 3 h⁻¹ | [151] |
| Ti³⁺ TiO₂/g-C₃N₄ | Xe lamp | NOₓ | 75% | [152] |

### 3.3.1. Transition Metal Dichalcogenide or Quantum Dot/Ti³⁺–TiO₂

Transition metal dichalcogenide (TMD) materials based on quasi-dimensional (2D) structures have recently attracted attention because of their excellent electronic and optical properties. These materials have great potential for high-tech applications and have different properties compared to conventional bulk counterpart materials. The state density of the TMD material increases in a semi-continuous stepwise fashion. Therefore, TMD materials can exhibit new electronic and optical properties [25,26]. MoS₂ is a representative TMD material, and it is a popular material in HER photocatalysts and electrocatalysts. This is because the sandwiched MoS₂ atomic layer can provide various unsaturated bonds at the edge of the layer. There have been attempts to enhance the photocatalytic performance with recent Ti³⁺–TiO₂ using these new electronic and optical properties. There have been attempts to dope the MoS₂ layer and other semiconducting or metal materials over spear-shaped black Ti³⁺–TiO₂. Attempts have been made to bond N/Ti³⁺–TiO₂ with spear and MoS₂ and to apply hollow Ti³⁺–TiO₂ and MoS₂/CdS together [76,147]. All of the materials were able to clearly identify the vertically grown layer and showed excellent performance in removing HER and Methylene orange. Figure 10 shows the schematic structure and mechanism of action of hollow black TiO₂/MoS₂/CdS. In addition to TMD metal, there have been attempts to combine Ti³⁺–TiO₂ with a layered material represented by bismuth oxyhalides. Yao et al. confirmed the well-grown TiO₂ and BiOBr nanostructures by synthesizing N/Ti³⁺–TiO₂ and BiOBr in one step. These materials showed high efficiency in removing methylene blue due to increased visible light absorption [110].
In addition to 2D-based layered materials, zero-dimensional quantum dots using TMD materials are also attracting attention because of their small size, large specific surface area and shortened charge travel distance. Many recent TiO$_2$ quantum dot complexes have attracted considerable attention. Coupling of TiO$_2$ and semiconducting quantum dots can improve the charge separation of photo-generated electron-electron pairs and smaller quantum dot materials are uniformly dispersed on the TiO$_2$ surface, preventing aggregation of quantum dots and providing more active sites [153,154]. However, the synergy of the existing TiO$_2$/QD materials was not satisfactory [155,156]. Therefore, a catalyst using visible solar energy was achieved with the introduction of Ti$^{3+}$–TiO$_2$. Likewise, there have been recent attempts to modify the MoS$_2$ and CdS QDs through conjugation of Ti$^{3+}$–TiO$_2$ as shown in Figure 11[146,150]. Abundant Ti$^{3+}$self-doping sufficiently improves the visible light response, and QD MoS$_2$ and CdS can promote photocatalytic carrier separation through a built-in electric field to provide a rich specific surface area to improve photocatalytic performance.
In addition to TMD materials, there have also been attempts to integrate Ti$^3+$–TiO$_2$ with QD. Ag$_3$PO$_4$ attracted attention because of its high quantum yield and band gap energy (2.45 eV) suitable for absorbing visible light. However, Ag$_3$PO$_4$ was only used as a photocatalyst due to fast charge recombination and relatively large particle size. Overcoming these shortcomings with QD Ag$_3$PO$_4$ and bonding with Ti$^3+$–TiO$_2$ increased visible light responsiveness and improved photocatalytic performance (Figure 12).[145] The introduction of quantum dots suggests a new paradigm to solve problems that could not be solved with the existing classical materials. Richly doped Ti$^3+$ can serve as an effective support for quantum dot materials and as an electron carrier delivery site. Thus, richly doped Ti$^3+$ has very promising and potential possibilities, requiring more in-depth research into this area.

Figure 11. Process diagram of the preparation and photocatalytic hydrogen evolution reaction (HER) mechanism of the MoS$_2$ QDs modified black Ti$^3+$–TiO$_2$/g–C$_3$N$_4$ hollow nanosphere heterojunction. Reproduced from [150]. Copyright (2019), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
3.3.2. Carbon-Based Nonmetallic Semiconductors/Ti³⁺–TiO₂

Carbon-based nonmetallic semiconducting materials are attracting great attention in the energy industry because of their attractive properties such as high conductivity and easy accessibility. The two-dimensional electronic network of sp² carbon atoms exhibits high electron mobility and conduction [157]. In the past few years, carbon-based materials have been extensively explored as photocatalysts. Recently, graphitic-carbon nitride (g–C₃N₄) has attracted much attention as a visible light active catalyst due to its appropriate band gap (2.69 eV). In particular, TiO₂ and Z-structure photocatalyst band alignments are similar to the plant photosynthesis process and can provide high photocatalytic activity through more powerful charge separation than type I and type II band alignment [158,159]. Ti³⁺–TiO₂ can strengthen this Z-structure with abundant Ti³⁺ doping in the conduction band. Figure 13 shows the Z structure diagram between TiO₂ and g–C₃N₄. Recently, studies on enhancing the performance of visible light-activated photocatalysts have been actively conducted through the combination of Ti³⁺–TiO₂ and g–C₃N₄. There have been attempts to improve charge separation by doping plasmon metal between Ti³⁺–TiO₂/g–C₃N₄. Cao et al. introduced Ag-doped black TiO₂ nanosphere structures and g–C₃N₄. Figure 14 shows a schematic of the Ti³⁺–TiO₂/Meso-g–C₃N₄ manufacturing method. They showed that Ag could act as an electron-conducting bridge between TiO₂ and g–C₃N₄, contributing to electron donors and acceptors in the Z-structure [151].

![Schematic of the Ag₃PO₄ QDs–TiO₂ nano spheres (NS) composite and its energy diagram and photocatalytic mechanism under visible light irradiation. Reproduced from [145]. Copyright (2016), The Royal Society of Chemistry.](image_url)
3.3.3. Metal Oxide/Ti$^{3+}$–TiO$_2$

Heterojunctions of metal oxide and TiO$_2$ are a classic (and the easiest) method to enhance TiO$_2$ photocatalytic activity after metal doping. To date, new heterojunctions of various metal oxides and TiO$_2$ have been studied. Heterojunctions of Ti$^{3+}$–TiO$_2$ and metal oxides are also of great interest. Although many metal oxides are candidates, heterojunctions of WO$_3$ and Ti$^{3+}$–TiO$_2$ have recently been developed. WO$_3$ can achieve Z-structure band alignment with Ti$^{3+}$–TiO$_2$. The resulting Z-structure has a band structure similar to natural photosynthesis [158,159]. This can strongly increase the charge separation efficiency. In addition, two different redox sites can suppress the reverse reaction of radical production. In 2020, Nguyen et al. developed a catalyst that introduced blue Ti$^{3+}$–TiO$_2$ and WO$_3$ produced by lithium (Li–EDA) of ethylenediamine, a strong reducing agent of the previous superbase. They showed 100% selectivity in reducing CO$_2$ to CO, and that blue Ti$^{3+}$–TiO$_2$/WO$_3$ formed a perfect Z-structure (Figure 15) [91]. Consequently, the introduction of a complete Z-structure can be a powerful modification of Ti$^{3+}$–TiO$_2$. This is a direct way to overcome the weakness of charge separation and recombination and dramatically enhance the performance of photocatalysts.
Figure 15. Band alignments of P25 and blue TiO2 NPs and the proposed electron transfer mechanism of the 7BT/W1–A1 HNPs photocatalyst. The photoelectrons generated and excited electrons from the CB of WO3 to migrate to trap holes at the VB of blue TiO2 sites through a Z-scheme system. After separation, the excited electrons rapidly jump from the CB of blue TiO2 onto Ag NPs acting as active sites for conversion of CO2 into CO, while all of the photogenerated holes directly oxidize H2O to form O2 from the VB of the WO3 site. Reproduced from [91]. Copyright (2019) Elsevier.

There have also been attempts to make heterojunctions with CeO2, which has a band gap energy similar to TiO2. CeO2 has recently attracted attention due to the special redox properties between Ce (III) and Ce (IV) oxidation states, which include high thermal stability, excellent oxygen storage capacity and easy conversion. Xiu et al. developed Ti3+/Ce3+ self-doped TiO2/CeO2 nanosheets by reducing TiO2 and CeO2 together. They showed that Ti3+ and Ce3+ complement each other and enhance electron separation (Figure 16) [148].

Figure 16. Visible-light-driven photocatalytic mechanism for Ti3+-TiO2/Ce3+-CeO2 nanosheet heterojunctions. Reproduced from [148]. Copyright (2017), Elsevier.

3.4. Stoichiometry Modification

There have been attempts to change the stoichiometry of materials beyond controlling Ti3+-self-doped intrinsic defects to enhance the visible light absorption of TiO2 photocatalysts. Introduction of
defect states such as Ti$^{3+}$ is sensitive to the chemical state and spatial distribution of electronic structure modifiers. Therefore, photocatalytic activity may be reduced through the formation of an undesirable band structure. It is important to create favorable defects at the atomic level to improve absorption in the visible light band. However, it is still difficult to correct structural defects at the atomic level and produce an optimal TiO$_2$ material. A study on correcting atomic-level structural defects is ongoing beyond the recent Ti$^{3+}$–TiO$_2$ work. Efforts have been made to replace hydrogen vacancies in Ti$^{3+}$–TiO$_2$ with atomic levels of hydrogen [81], carbon [82] and nitrogen [82,83]. We summarized in table 4.

In general, reduced Ti$^{3+}$–TiO$_2$ has a blue-black color, whereas substituted TiO$_2$ has a different color. Red TiO$_2$ appears when the space for a single oxygen atom is filled with two hydrogen atoms, called Ti$^{3+}$:TiO$_2$ [81]. As shown in Figure 17, the color and atomic/band structure of TiO$_2$ was changed according to the vacancies in the crystal structure. In addition, the introduction of heterogeneous elements results in a new band state. The band gap is reduced due to changes in the conduction band and valence band, and both show excellent activity in visible light.

**Figure 17.** The color change of anatase TiO$_2$ powder from white to blue by introducing hydrogen-free oxygen vacancies and from white to red by introducing atomic hydrogen-mediated oxygen vacancies. The top panel shows digital images of the samples and the bottom panel shows the atomic structures of anatase TiO$_2$ and oxygen-deficient TiO$_2$ with and without atomic hydrogen. Blue and red spheres indicate titanium and oxygen atoms, respectively and green spheres represent hydrogen. The calculated band structures of TiO$_2$ with (a) OV-2H, (b) 4 (OV-2H) and (c) a neutral OV. Reproduced from [81]. Copyright (2018), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
We believe that engineering the oxidation state of Ti atoms (beyond Ti³⁺, which is simply reduced) and the surrounding electronic environment through complete stoichiometric control is a new paradigm for developing effective TiO₂ visible photocatalysts. In the future, we can expect to expand and improve the photocatalytic performance through visible light for TiO₂ photocatalysts via uniformly controlled stoichiometric modifications.

Table 4. Summary of stoichiometry modification of Ti³⁺-self-doped TiO₂ photocatalysts.

| Catalyst | Color       | Application Target             | Efficiency          | Ref. |
|----------|-------------|--------------------------------|---------------------|------|
| Ti³⁺2H₂TiO₂ | Red        | –                              | –                   | [81] |
| Ti³⁺CN TiO₂  | –          | Oxygen evolution reaction       | 4.125 μmol·h⁻¹·g⁻¹ | [82] |
| Ti³⁺N TiO₂   | Yellow-green | Methylene orange               | 100% 2 h⁻¹          | [83] |

4. Conclusion and Outlook

TiO₂-based photocatalytic reactions were first reported in the early 1930s. They were first used to bleach dye using reactive oxygen species generated under UV light. TiO₂ photocatalyst (called a “photosensitizer”) has been studied extensively, and it is expected to play a role in solving the limited energy problem [24]. In particular, efforts have been made to improve the absorption band of TiO₂ photocatalyst into the visible light regime to efficiently use solar energy. These efforts continued to Ti³⁺–TiO₂, and since the report of black Ti³⁺–TiO₂ reduced by Ward et al. in 2011, Ti³⁺–TiO₂ research has made great progress [92]. We first studied the development of TiO₂ reduction to produce abundant Ti³⁺ for overcoming the high heat and pressure of the hydrogenation reaction (as the first generation of Ti³⁺–TiO₂-based photocatalysts). Then, due to their long reaction times and risks, increasing mild and easy to handle methods have been developed as the next generation. A lithium-ethylenediamine solution (Li–EDA) has been introduced for self-doping Ti³⁺ effectively at room temperature and atmospheric pressure, as well as controlling the crystalline phase of reduced TiO₂. Selective reduced crystal phases with different physicochemical properties will pioneer photocatalytic utilization for several properties [87]. However, although Ti³⁺ is abundantly doped such that the band region for visible light is expanded, there are still limitations. The interaction and reactivity between target materials and photocatalysts, as well as effective suppression of charge separation and recombination, are still challenges that need to be overcome. The best way to improve the limited performance of these single materials is with several different composite materials.

In this review, we focused on the types and methods of Ti³⁺–TiO₂ and the materials introduced and categorized them into four categories according to recent developments. Ti³⁺ doping can be used as sufficient support for an isolated single-atom site catalyst and can stabilize the catalyst atom. The isolated single-atom catalyst has excellent selectivity and reactivity with a small amount of catalyst [89]. Introducing metals other than plasmonic precious metals will make commercialization easier. The introduction of LSPR using isolated single atom site catalysts and non-precious metals in metal dopants is the most effective modification method. Going further, bimetallic sites, which have been extensively studied recently, are being proposed as a new way to solve the selectivity and stability issues that a single atom catalyst cannot. There are different advantages depending on the metal combination, and there are even advantages to not using precious metals. It has recently been shown that bimetallic site catalysts can also be applied with TiO₂ [160]. However, this approach requires more research of bimetal sites.

The introduction of nonmetal dopants is a way to engineer the fundamental band structure of TiO₂. Modification of the band structure can make it easier to expand this approach to visible photocatalysts, and most nonmetal dopants can improve the decomposition of harmful substances through strong interactions with organic harmful substances. Another approach is doping two or three heterogeneous elements beyond single element nonmetallic doping. The introduction of a suitable semiconducting material can be used to overcome the shortcomings of the aforementioned TiO₂ photocatalysts. Beyond the classic 3D dopant, the introduction of 2D TMD and 0D QD materials shortens both the large specific surface area and charge travel distance. Because of this, it is possible to improve the charge separation of electron–electron pairs, which could not be solved before. The
improved charge separation has high expectations for HER and water splitting. The introduction of metal oxides can also be a great alternative. Due to their excellent accessibility and stability, carbon-based materials can be promisingly combined with Ti$^{3+}$ TiO$_2$. The Z-structure has a structure similar to that of photosynthesis. The formation of Z-structures through the introduction of metal oxides and carbon-based materials is a powerful approach to improving photocatalytic performance. Similar to a plant’s photosynthetic structure, the photocatalyst can replace various functions of plants in the future. This research field has potential in the energy industry.

Furthermore, advances in material engineering technology can dominate atomic defects. This presents a new base of TiO$_2$ photocatalysts through heteroatom insertion into the TiO$_2$ grid beyond Ti$^{3+}$ single atom doping [81–83]. It is expected that the next generation of Ti$^{3+}$–TiO$_2$ is in stoichiometric modification. If the electronic environment is completely controlled by controlling the oxidation state of the Ti atom and the surrounding atoms rather than simply doping the reduced Ti$^{3+}$, there is a possibility to produce a TiO$_2$ photocatalyst suitable for each application method. TiO$_2$ has been studied as a practical photocatalytic material. However, in addition to applications that can be directly applied, in-depth studies on the electron environment, oxidation state of various dopants in the crystal structure, enhanced charge separation, and defect-level band energy are feasible. By investigating the atomic state and bonding level in the final crystal structure, it is possible to identify the principles and mechanisms of theoretical photocatalytic applications. Such an understanding is essential to improving photocatalytic performance.

Advanced Ti$^{3+}$–TiO$_2$ approaches have recently been extended to visible light in solar energy harvesting and air purification. In particular, we believe that by applying air purification [152], diseases caused by viruses and bacteria [120] in the air—that have emerged as among the biggest problems faced by humanity—can be prevented by using Ti$^{3+}$–TiO$_2$:based photocatalysts, a visible photocatalyst that is harmless to humans. For this, it is necessary to study the interactions of cells with photocatalysts in a view point of biochemistry, as well as conduct theoretical studies about classical interactions between organic and inorganic and their mechanisms. Nonetheless, the application of visible light photocatalysts in this industry is still insufficient. It is essential to explore sufficient functions required for commercialization,[91] further study of Ti$^{3+}$–TiO$_2$:based materials and the development of more effective heterogeneous materials. This makes Ti$^{3+}$–TiO$_2$: a viable option for visible photocatalysts in the future.

Author Contributions: S.N. wrote the original draft. S.S. and H.L. edited the draft and supervised it. All authors have read and agreed to the published version of the manuscript.

Acknowledgments: This work was supported by the Institute for Basic Science (IBS-R011-D1). This work was partially supported by the Korea Evaluation Institute of Industrial Technology (20004627) and the INNOPOLIS Foundation (2019-DD-SB-0602).

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Ran, J.; Zhang, J.; Yu, J.; Jaroniec, M.; Qiao, S.Z. Earth-abundant cocatalysts for semiconductor-based photocatalytic water splitting. *Chem. Soc. Rev.* **2014**, *43*, 7787–7812.
2. Dickinson, R.E. Land Surface Processes and Climate—Surface Albedos and Energy Balance. In *Theory of Climate. Proceedings of a Symposium Commemorating the Two-Hundredth Anniversary of the Academy of Sciences of Lisbon*; Saltzman, B., Ed.; Elsevier: Amsterdam, The Netherlands, 1983; Volume 25, pp. 305–353.
3. Dines, W.H. The heat balance of the atmosphere. *Q. J. R. Meteorol. Soc.* **1917**, *43*, 151–158.
4. Stephens, G.L.; Li, J.; Wild, M.; Clayson, C.A.; Loeb, N.; Kato, S.; L’Ecuyer, T.; Stackhouse, P.W.; Lebsock, M.; Andrews, T. An update on Earth’s energy balance in light of the latest global observations. *Nat. Geosci.* **2012**, *5*, 691–696.
5. Kumar, A. A Review on the Factors Affecting the Photocatalytic Degradation of Hazardous Materials. *Mater. Sci. Eng. C* **2017**, *7*, 106–114.
6. Santhosh, C.; Malathi, A.; Daneshvar, E.; Kollu, P.; Bhatnagar, A. Photocatalytic degradation of toxic aquatic pollutants by novel magnetic 3D-TiO2@HPGA nanocomposite. *Sci. Rep.* **2018**, *8*, 15531.
7. Panthi, G.; Park, M.; Kim, H.-Y.; Lee, S.-Y.; Park, S.-J. Electrospun ZnO hybrid nanofibers for photodegradation of wastewater containing organic dyes: A review. J. Ind. Eng. Chem. 2015, 21, 26–35.
8. Gupta, V.K.; Jain, R.; Nayak, A.; Agarwal, S.; Shrivastava, M. Removal of the hazardous dye—Tartrazine by photodegradation on titanium dioxide surface. Mater. Sci. Eng. C 2011, 31, 1062–1067.
9. Zhang, T.; Lin, W. Metal–organic frameworks for artificial photosynthesis and photocatalysis. Chem. Soc. Rev. 2014, 43, 5982–5993.
10. Hoffmann, M.R.; Moss, J.A.; Baum, M.M. Artificial photosynthesis: Semiconductor photocatalytic fixation of CO2 to afford higher organic compounds. Dalton Trans. 2011, 40, 5151–5158.
11. Lee, S.H.; Kim, J.H.; Park, C.B. Coupling Photocatalysis and Redox Biocatalysis Toward Biocatalyzed Artificial Photosynthesis. Chem. Eur. J. 2013, 19, 4392–4406.
12. Ong, W.-J.; Tan, L.-L.; Ng, Y.H.; Yong, S.-T.; Chai, S.-P. Graphitic Carbon Nitride (g–C3N4)-Based Photocatalysts for Artificial Photosynthesis and Environmental Remediation: Are We a Step Closer to Achieving Sustainability? Chem. Rev. 2016, 116, 7159–7329.
13. Osterloh, F.E. Inorganic nanostructures for photoelectrochemical and photocatalytic water splitting. Chem. Soc. Rev. 2013, 42, 2294–2320.
14. Takanabe, K. Photocatalytic Water Splitting: Quantitative Approaches toward Photocatalyst by Design. ACS Catal. 2017, 7, 8006–8022.
15. She, X.; Wu, J.; Xu, H.; Zhong, J.; Wang, Y.; Song, Y.; Nie, K.; Liu, Y.; Yang, Y.; Rodrigues, M.-T.F.; et al. High Efficiency Photocatalytic Water Splitting Using 2D α-Fe2O3@g–C3N4 Z-Scheme Catalysts. Adv. Energy Mater. 2017, 7, 1700025.
16. Lin, L.; Yu, Z.; Wang, X. Crystalline Carbon Nitride Semiconductors for Photocatalytic Water Splitting. Angew. Chem. Int. Ed. 2019, 58, 6164–6175.
17. Zhu, M.; Zhu, C.; Wu, D.; Wang, X.; Wang, H.; Gao, J.; Huang, H.; Shi, C.; Liu, Y.; Kang, Z. Efficient photocatalytic water splitting through titanium silicalite stabilized CoO nanodots. Nanoscale 2019, 11, 15984–15990.
18. Collins, G.; Armstrong, E.; McNulty, D.; O’Hanlon, S.; Geaney, H.; O’Dwyer, C. 2D and 3D photonic crystal materials for photocatalysis and electrochemical energy storage and conversion. Sci. Technol. Adv. Mater. 2016, 17, 563–582.
19. Rangan, K.; Arachchige, S.M.; Brown, J.R.; Brewer, K.J. Solar energy conversion using photochemical molecular devices: Photocatalytic hydrogen production from water using mixed-metal supramolecular complexes. Energy Environ. Sci. 2009, 2, 410–419.
20. Bard, A.J. Inner-Sphere Heterogeneous Electrode Reactions. Electrocatalysis and Photocatalysis: The Challenge. J. Am. Chem. Soc. 2010, 132, 7559–7567.
21. Zhang, P.; Lou, X.W. Design of Heterostructured Hollow Photocatalysts for Solar-to-Chemical Energy Conversion. Adv. Mater. 2019, 31, 1900281.
22. Shiraiishi, Y.; Toi, S.; Ichikawa, S.; Hirai, T. Photocatalytic NH3 Splitting on TiO2 Particles Decorated with Pt–Au Bimetallic Alloy Nanoparticles. ACS Appl. Nano Mater. 2020, 3, 1612–1620.
23. Misra, M.; Chowdhury, S.R.; Singh, N. TiO2@Au@CoMn2O4 core–shell nanorods for photo–electrochemical and photocatalytic activity for decomposition of toxic organic compounds and photo reduction of Cr6+ ion. J. Alloys Compd. 2020, 824, 153861.
24. Xu, H.; Ouyang, S.; Liu, L.; Reunchan, P.; Umezawa, N.; Ye, J. Recent advances in TiO2-based photocatalysis. J. Mater. Chem. A 2014, 2, 12642–12661.
25. Rao, C.N.R.; Ramakrishna Matte, H.S.S.; Maitra, U. Graphene Analogues of Inorganic Layered Materials. Angew. Chem. Int. Ed. 2013, 52, 13162–13185.
26. Sun, Z.; Talreja, N.; Tao, H.; Texter, J.; Muhler, M.; Strunk, J.; Chen, J. Catalysis of Carbon Dioxide Photoreduction on Nanosheets: Fundamentals and Challenges. Angew. Chem. Int. Ed. 2018, 57, 7610–7627.
27. Sprick, R.S.; Bonillo, B.; Clowes, R.; Guiglion, P.; Brownbill, N.J.; Slater, B.J.; Blanc, F.; Zwijnenburg, M.A.; Adams, D.J.; Cooper, A.I. Visible-Light-Driven Hydrogen Evolution Using Planarized Conjugated Polymer Photocatalysts. Angew. Chem. Int. Ed. 2016, 55, 1792–1796.
28. Wang, S.; Hai, X.; Ding, X.; Jin, S.; Xiang, Y.; Wang, F.; Jiang, B.; Ichihara, F.; Oshikiri, M.; Meng, X.; et al. Intermolecular cascaded π-conjugation channels for electron delivery powering CO2 photoreduction. Nat. Commun. 2020, 11, 1149.
Catalysts 2020, 10, 679

29. Zhao, P.; Wang, L.; Wu, Y.; Yang, T.; Ding, Y.; Yang, H.G.; Hu, A. Hyperbranched Conjugated Polymer Dots: The Enhanced Photocatalytic Activity for Visible Light-Driven Hydrogen Production. *Macromolecules* **2019**, *52*, 4376–4384.

30. Lan, Z.-A.; Ren, W.; Chen, X.; Zhang, Y.; Wang, X. Conjugated donor-acceptor polymer photocatalysts with electron-output “tentacles” for efficient hydrogen evolution. *Appl. Catal. B* **2019**, *245*, 596–603.

31. Hasani, A.; Tekalgne, M.; Le, Q.V.; Jang, H.W.; Kim, S.Y. Two-dimensional materials as catalysts for solar fuels: Hydrogen evolution reaction and CO₂ reduction. *J. Mater. Chem. A* **2019**, *7*, 430–454.

32. Di, J.; Yan, C.; Handoko, A.D.; Seh, Z.W.; Li, H.; Liu, Z. Ultrathin two-dimensional materials for photo- and electrocatalytic hydrogen evolution. *Mater. Today* **2018**, *21*, 749–770.

33. Li, J.; Zhan, G.; Yu, Y.; Zhang, L. Superior visible light hydrogen evolution of Janus bilayer junctions via atomic-level charge flow steering. *Nat. Commun.* **2016**, *7*, 11480.

34. Bao, W.; Cai, X.; Kim, D.; Sridhara, K.; Fuhrer, M.S. High mobility ambipolar MoS₂ field-effect transistors: Substrate and dielectric effects. *Appl. Phys. Lett.* **2013**, *102*, 042104.

35. Lian, S.; Kodaimati, M.S.; Dolzhnikov, D.S.; Calzada, R.; Weiss, E.A. Powering a CO₂ Reduction Catalyst with Visible Light through Multiple Sub-picosecond Electron Transfers from a Quantum Dot. *J. Am. Chem. Soc.* **2017**, *139*, 8931–8938.

36. Li, X.-B.; Gao, Y.-J.; Wang, Y.; Zhan, F.; Zhang, X.-Y.; Kong, Q.-Y.; Zhao, N.-J.; Guo, Q.; Wu, H.-L.; Li, Z.-J.; et al. Self-Assembled Framework Enhances Electronic Communication of Ultrasmall-Sized Nanoparticles for Exceptional Solar Hydrogen Evolution. *J. Am. Chem. Soc.* **2017**, *139*, 4789–4796.

37. Wu, L.-Z.; Chen, B.; Li, Z.-J.; Tung, C.-H. Enhancement of the Efficiency of Photocatalytic Reduction of Protons to Hydrogen via Molecular Assembly. *Acc. Chem. Res.* **2014**, *47*, 2177–2185.

38. Zrazhevskiy, P.; Sena, M.; Gao, X. Designing multifunctional quantum dots for bioimaging, detection, and drug delivery. *Chem. Soc. Rev.* **2018**, *39*, 4326–4354.

39. Smith, A.M.; Nie, S. Semiconductor Nanocrystals: Structure, Properties, and Band Gap Engineering. *Acc. Chem. Res.* **2010**, *43*, 190–200.

40. Zheng, L.; Su, H.; Zhang, J.; Walekar, L.S.; Vafaee Molamahood, H.; Zhou, B.; Long, M.; Hu, Y.H. Highly selective photocatalytic production of H₂O₂ on sulfur and nitrogen co-doped graphene quantum dots tuned TiO₂. *Appl. Catal. B* **2018**, *239*, 475–484.

41. Dao, S.; Zhang, X.; Shao, Z.; Ding, K.; Jie, J.; Zhang, X. 12.35% efficient graphene quantum dots/silicon heterojunction solar cells using graphene transparent electrode. *Nano Energy* **2017**, *31*, 359–366.

42. Di, J.; Chen, C.; Yang, S.-Z.; Chen, S.; Duan, M.; Xiong, J.; Zhu, C.; Long, R.; Hao, W.; Chi, Z.; et al. Isolated single atom cobalt in Bi₃O₄Br atomic layers to trigger efficient CO₂ photoreduction. *Nat. Commun.* **2019**, *10*, 2840.

43. Wang, A.; Li, J.; Zhang, T. Heterogeneous single-atom catalysis. *Nat. Rev. Chem.* **2018**, *2*, 65–81.

44. Liu, J. Catalysis by Supported Single Metal Atoms. *ACS Catal.* **2017**, *7*, 34–59.

45. Li, X.; Bi, W.; Zhang, L.; Tao, S.; Chu, W.; Zhang, Q.; Luo, Y.; Wu, C.; Xie, Y. Single-Atom Pt as Co-Catalyst for Enhanced Photocatalytic H₂ Evolution. *Adv. Mater.* **2016**, *28*, 2427–2431.

46. Dhakshinamoorthy, A.; Li, Z.; Garcia, H. Catalysis and photocatalysis by metal organic frameworks. *Chem. Soc. Rev.* **2018**, *47*, 8134–8172.

47. Nasalevich, M.A.; van der Veen, M.; Kapteijn, F.; Gascon, J. Metal–organic frameworks as heterogeneous photocatalysts: Advantages and challenges. *CrystEngComm* **2014**, *16*, 4919–4926.

48. Corma, A.; Garcia, H.; Llabrés i Xamena, F.X. Engineering Metal Organic Frameworks for Heterogeneous Catalysis. *Chem. Rev.* **2010**, *110*, 4606–4655.

49. Baloiy, J.; Seadira, T.; Raphulu, M.; Ochieng, A. Preparation, Characterization and Growth Mechanism of Dandelion-like TiO₂ Nanostructures and their Application in Photocatalysis towards Reduction of Cr(VI). *Mater. Today* **2015**, *2*, 3973–3987.

50. Goodeve, C.F.; Kitchener, J.A. The mechanism of photosensitisation by solids. *J. Chem. Soc. Faraday Trans.* **1938**, *34*, 902–908.

51. Jiang, L.; Wang, Y.; Feng, C. Application of Photocatalytic Technology in Environmental Safety. *Procedia Eng.* **2012**, *45*, 993–997.

52. Hashimoto, K.; Irie, H.; Fujishima, A. TiO₂ Photocatalysis: A Historical Overview and Future Prospects. *Jpn. J. Appl. Phys.* **2005**, *44*, 8269–8285.
53. Dong, H.; Zeng, G.; Tang, L.; Fan, C.; Zhang, C.; He, X.; He, Y. An overview on limitations of TiO2-based particles for photocatalytic degradation of organic pollutants and the corresponding countermeasures. Water Res. 2015, 79, 128–146.

54. Schneider, J.; Matsuoka, M.; Takeuchi, M.; Zhang, J.; Horiiuchi, Y.; Anpo, M.; Bahnemann, D.W. Understanding TiO2 Photocatalysis: Mechanisms and Materials. Chem. Rev. 2014, 114, 9919–9986.

55. Higashimoto, S. Titanium-dioxide-based visible-light-sensitive photocatalysis: Mechanistic insight and applications. Catalysts 2019, 9, 201.

56. Etacheri, V.; Di Valentin, C.; Schneider, J.; Bahnemann, D.; Pillai, S.C. Visible-light activation of TiO2 photocatalysts: Advances in theory and experiments. J. Photochem. Photobiol. C 2015, 25, 1–29.

57. Torimoto, T.; Okawa, Y.; Takeda, N.; Yoneyama, H. Effect of activated carbon content in TiO2-loaded activated carbon on photodegradation behaviors of dichloromethane. J. Photochem. Photobiol. C 1997, 103, 153–157.

58. Bhattacharyya, A.; Kawi, S.; Ray, M.B. Photocatalytic degradation of orange II by TiO2 catalysts supported on adsorbents. Catal. Today 2004, 98, 431–439.

59. Szczepanik, B. Photocatalytic degradation of organic contaminants over clay–TiO2 nanocomposites: A review. Appl. Clay Sci. 2017, 141, 227–239.

60. Yang, J.; Du, J.; Li, X.; Liu, Y.; Jiang, C.; Qi, W.; Zhang, K.; Gong, C.; Li, R.; Luo, M. Highly hydrophilic TiO2 nanotubes network by alkaline hydrothermal method for photocatalysis degradation of methyl orange. Nanomaterials 2019, 9, 526.

61. Pan, X.; Yang, M.-Q.; Fu, X.; Zhang, N.; Xu, Y.-J. Defective TiO2 with oxygen vacancies: Synthesis, properties and photocatalytic applications. Nanoscale 2013, 5, 3601–3614.

62. Wang, Y.; Wang, Q.; Zhan, X.; Wang, F.; Saifdar, M.; He, J. Visible light driven type II heterostructures and their enhanced photocatalysis properties: A review. Nanoscale 2015, 3, 8326–8339.

63. Lazar, M.A.; Daoud, W.A. Achieving selectivity in TiO2-based photocatalysis. RSC Adv. 2013, 3, 4130–4140.

64. Liu, L.; Liu, Z.; Liu, A.; Gu, X.; Ge, C.; Gao, F.; Dong, L. Engineering the TiO2–Graphene Interface to Enhance Photocatalytic H2 Production. ChemSusChem 2014, 7, 618–626.

65. Chen, J.L.; von Freymann, G.; Choi, S.Y.; Kitaev, V.; Ozin, G.A. Amplified photochemistry with slow photons. Adv. Mater. 2006, 18, 1915–1919.

66. Li, H.; Bian, Z.; Zhu, J.; Zhang, D.; Li, G.; Huo, Y.; Li, H.; Lu, Y. Mesoporous Titania Spheres with Tunable Chamber Stucture and Enhanced Photocatalytic Activity. J. Am. Chem. Soc. 2007, 129, 8406–8407.

67. Zhu, J.; Deng, Z.; Chen, F.; Zhang, J.; Chen, H.; Anpo, M.; Huang, J.; Zhang, L. Hydrothermal doping method for preparation of Cr3+-TiO2 photocatalysts with concentration gradient distribution of Cr3+. Appl. Catal. B 2006, 62, 329–335.

68. Mathew, S.; Ganguly, P.; Rhatigan, S.; Kumaravel, V.; Byrne, C.; Hinder, S.J.; Bartlett, J.; Nolan, M.; Pillai, S.C. Cu-doped TiO2: Visible light assisted photocatalytic antimicrobial activity. Appl. Sci. 2018, 8, 2067.

69. He, S.; Huang, J.; Goodsell, J.L.; Angerhofer, A.; Wei, W.D. Plasmonic Nickel–TiO2 Heterostructures for Visible-Light-Driven Photocatalytic Reactions. Angew. Chem. Int. Ed. 2019, 58, 6038–6041.

70. Jia, T.; Fu, F.; Yu, D.; Cao, J.; Sun, G. Facile synthesis and characterization of N-doped TiO2/C nanocomposites with enhanced visible-light photocatalytic performance. Appl. Surf. Sci. 2018, 430, 438–447.

71. Zhou, F.; Song, H.; Wang, H.; Komarneni, S.; Yan, C. N-doped TiO2/sepiolite nanocomposites with enhanced visible-light catalysis: Role of N precursors. Appl. Clay Sci. 2018, 166, 9–17.

72. Romero Saez, M.; Jaramillo, L.; Saravanan, R.; Benito, N.; Pabón, E.; Mosquera, E.; Gracia Caroca, F. Notable photocatalytic activity of TiO2-polyethylene nanocomposites for visible light degradation of organic pollutants. EXPRESS Polym. Lett. 2017, 11, 899–909.

73. Saravanan, R.; Aviles, J.; Gracia, F.; Mosquera, E.; Gupta, V.K. Crystallinity and lowering band gap induced visible light photocatalytic activity of TiO2/CS (Chitosan) nanocomposites. Int. J. Biol. Macromol. 2018, 109, 1239–1245.

74. Raziq, F.; Sun, L.; Wang, Y.; Zhang, X.; Humayun, M.; Ali, S.; Bai, L.; Qu, Y.; Yu, H.; Jing, L. Synthesis of Large Surface-Area g–C3N4 Comodified with MnOx and Au–TiO2 as Efficient Visible-Light Photocatalysts for Fuel Production. Adv. Energy Mater. 2018, 8, 1701580.

75. Delsouz Khaki, M.R.; Shafeeyan, M.S.; Raman, A.A.A.; Daud, W.M.A.W. Evaluating the efficiency of nano-sized Cu doped TiO2/ZnO photocatalyst under visible light irradiation. J. Mol. Liq. 2018, 258, 354–365.
76. Liu, X.; Xing, Z.; Zhang, Y.; Li, Z.; Wu, X.; Tan, S.; Yu, X.; Zhu, Q.; Zhou, W. Fabrication of 3D flower-like black N–TiO2-x@MoS2 for unprecedented-high visible-light-driven photocatalytic performance. *Appl. Catal. B* 2017, 201, 119–127.

77. Zhang, L.; Qin, M.; Yu, W.; Zhang, Q.; Xie, H.; Sun, Z.; Shao, Q.; Guo, X.; Hao, L.; Zheng, Y. Heterostructured TiOx/WOx nanocomposites for photocatalytic degradation of toluene under visible light. *J. Electrochem. Soc.* 2017, 164, H1086.

78. Yao, G.-Y.; Liu, Q.-L.; Zhao, Z.-Y. Studied Localized Surface Plasmon Resonance Effects of Au Nanoparticles on TiO2 by FDTD Simulations. *Catalysts* 2018, 8, 236.

79. Lin, Z.; Wang, X.; Liu, J.; Tian, Z.; Dai, L.; He, B.; Han, C.; Wu, Y.; Zeng, Z.; Hu, Z. On the role of localized surface plasmon resonance in UV-Vis light irradiated Au/TiO2 photocatalysis systems: Pros and cons. *Nanoscale* 2015, 7, 4114–4123.

80. Schaub, R.; Wahlström, E.; Rennau, A.; Læsgaard, E.; Stensgaard, I.; Besenbacher, F. Oxygen-Mediated Diffusion of Oxygen Vacancies on the TiO2(110) Surface. *Science* 2003, 299, 377.

81. Yang, Y.; Yin, L.C.; Gong, Y.; Niu, P.; Wang, J.Q.; Gu, L.; Chen, X.; Liu, G.; Wang, L.; Cheng, H.M. An Unusual Strong Visible-Light Absorption Band in Red Anatase TiO2: Photocatalyst Induced by Atomic Hydrogen-Occupied Oxygen Vacancies. *Adv. Mater.* 2018, 30, 1704479.

82. Wu, T.; Niu, P.; Yang, Y.; Yin, L.-C.; Tan, J.; Zhu, H.; Irvine, J.T.S.; Wang, L.; Liu, G.; Cheng, H.-M. Homogeneous Doping of Substitutional Nitrogen/Carbon in TiO2: Plates for Visible Light Photocatalytic Water Oxidation. *Sci. Rep.* 2019, 29, 1901943.

83. Cao, Y.-Q.; Zhao, X.-R.; Chen, J.; Zhang, W.; Li, M.; Zhu, L.; Zhang, X.-J.; Wu, D.; Li, A.-D. TiOxNy Modified TiO2 Powders Prepared by Plasma Enhanced Atomic Layer Deposition for Highly Visible Light Photocatalysis. *Sci. Rep.* 2018, 8, 12131.

84. Ismail, A.A.; Bahnemann, D.W.; Bannat, I.; Wark, M. Gold nanoparticles on mesoporous interparticle networks of titanium dioxide nanocrystals for enhanced photocatalytic efficiencies. *J. Phys. Chem.* 2009, 113, 7429–7435.

85. Forsyth, M.; MacFarlane, D.R.; Best, A.; Adebahr, J.; Jacobsson, P.; Hill, A.J. The effect of nano-particle TiO2 fillers on structure and transport in polymer electrolytes. *Solid State Ion.* 2002, 147, 203–211.

86. Xiu, Z.; Guo, M.; Zhao, T.; Pan, K.; Xing, Z.; Li, Z.; Zhou, W. Recent advances in Ti3+ self-doped nanostructured TiO2: visible light photocatalysts for environmental and energy applications. *Chem. Eng. J.* 2020, 382, 123011.

87. Zhang, K.; Wang, L.; Kim, J.K.; Ma, M.; Veerappan, G.; Lee, C.-L.; Kong, K.-J.; Lee, H.; Park, J.H. An order/disorder/water junction system for highly efficient co-catalyst-free photocatalytic hydrogen generation. *Energy Environ. Sci.* 2016, 9, 499–503.

88. Naldoni, A.; Allieta, M.; Santangelo, S.; Marelli, M.; Fabbri, F.; Cappelli, S.; Bianchi, C.L.; Psaro, R.; Dal Santo, V. Effect of Nature and Location of Defects on Bandgap Narrowing in Black TiO2 Nanoparticles. *J. Am. Chem. Soc.* 2012, 134, 7600–7603.

89. Hejazi, S.; Mohajerinia, S.; Osagwbu, B.; Zoppellaro, G.; Andryskova, P.; Tomanec, O.; Kment, S.; Zbořil, R.; Schmuki, P. On the Controlled Loading of Single Platinum Atoms as a Co-Catalyst on TiO2 Anatase for Optimized Photocatalytic H2 Generation. *Adv. Mater.* 2020, 32, 1908505.

90. Yu, X.; Fan, X.; An, L.; Liu, G.; Li, Z.; Liu, J.; Hu, P. Mesocrystalline Ti3+TiO2: hybridized g–C3N4 for efficient visible-light photocatalysis. *Carbon* 2018, 128, 21–30.

91. Nguyen, C.T.K.; Quang Tran, N.; Seo, S.; Hwang, H.; Oh, S.; Yu, J.; Lee, J.; Anh Le, T.; Hwang, J.; Kim, M.; et al. Highly efficient nanostructured metal-decorated hybrid semiconductors for solar conversion of CO2 with almost complete CO selectivity. *Mater. Today* 2020, doi:10.1016/j.mattod.2019.11.005.

92. Chen, X.; Liu, L.; Yu, P.Y.; Mao, S.S. Increasing Solar Absorption for Photocatalysis with Black Hydrogenated Titanium Dioxide Nanocrystals. *Science* 2011, 331, 746.

93. Wang, S.; Cai, J.; Mao, J.; Li, S.; Shen, J.; Gao, S.; Huang, J.; Wang, X.; Parkin, I.P.; Lai, Y. Defective black Ti3+ self-doped TiO2 and reduced graphene oxide composite nanoparticles for boosting visible-light driven photocatalytic and photoelectrochemical activity. *Appl. Surf. Sci.* 2019, 467, 45–55.

94. Tan, S.; Xing, Z.; Zhang, J.; Li, Z.; Wu, X.; Cui, J.; Kuang, J.; Zhu, Q.; Zhou, W. Ti3+-TiO2/g–C3N4 mesostructured nanosheets heterojunctions as efficient visible-light-driven photocatalysts. *J. Catal.* 2018, 357, 90–99.
95. Sasikala, R.; Shirke, A.; Sudarsan, V.; Sakuntala, T.; Sudakar, C.; Naik, R.; Bharadwaj, S.R. Highly dispersed phase of SnO2 on TiO2 nanoparticles synthesized by polyol-mediated route: Photocatalytic activity for hydrogen generation. Int. J. Hydrog. Energy 2009, 34, 3621–3630.

96. Justicia, I.; Ordejón, P.; Canto, G.; Mozos, J.L.; Fraxedas, J.; Battiston, G.A.; Gerbasi, R.; Figueras, A. Designed Self-Doped Titanium Oxide Thin Films for Efficient Visible-Light Photocatalysis. Adv. Mater. 2002, 14, 1399–1402.

97. Buso, D.; Pacifico, J.; Martucci, A.; Mulvaney, P. Gold-nanoparticle-doped TiO2 semiconductor thin films: Optical characterization. Adv. Funct. Mater. 2007, 17, 347–354.

98. Zhu, G.; Shan, Y.; Lin, T.; Zhao, W.; Xu, J.; Tian, Z.; Zhang, H.; Zheng, C.; Huang, F. Hydrogenated blue titania with high solar absorption and greatly improved photocatalysis. Nanoscale 2016, 8, 4705–4712.

99. Qiu, J.; Li, S.; Gray, E.; Liu, H.; Gu, Q.-F.; Sun, C.; Lai, C.; Zhao, H.; Zhang, S. Hydrogenation Synthesis of Blue TiO2 for High-Performance Lithium-Ion Batteries. J. Phys. Chem. 2014, 118, 8824–8830.

100. Sun, L.; Li, Z.; Li, Z.; Hu, Y.; Chen, C.; Yang, C.; Du, B.; Sun, Y.; Besenbacher, F.; Yu, M. Design and mechanism of core–shell TiO2 nanoparticles as a high-performance photothermal agent. Nanoscale 2017, 9, 16183–16192.

101. Wang, J.; Wang, Y.; Wang, W.; Peng, T.; Liang, J.; Li, P.; Pan, D.; Fan, Q.; Wu, W. Visible light driven Ti\textsuperscript{3+} self-doped TiO2 for adsorption-photocatalysis of aqueous U(VI). Environ. Pollut. 2020, 262, 114373.

102. Cheng, D.; Li, Y.; Yang, L.; Luo, S.; Yang, L.; Luo, X.; Luo, Y.; Li, T.; Gao, J.; Dionysiou, D.D. One-step reductive synthesis of Ti\textsuperscript{3+} self-doped elongated anatase TiO2: nanowires combined with reduced graphene oxide for adsorbing and degrading waste engine oil. J. Hazard. Mater. 2019, 378, 120752.

103. Li, J.-J.; Weng, B.; Cai, S.-C.; Chen, J.; Jia, H.-P.; Xu, Y.-J. Efficient promotion of charge transfer and separation in hydrogenated TiO2/WO3 with rich surface-oxygen-vacancies for photodecomposition of gaseous toluene. J. Hazard. Mater. 2018, 342, 661–669.

104. Hanaor, D.A.H.; Sorrell, C.C. Review of the anatase to rutile phase transformation. J. Mater. Sci. 2011, 46, 855–874.

105. Zhu, Q.; Peng, Y.; Lin, L.; Fan, C.-M.; Gao, G.-Q.; Wang, R.-X.; Xu, A.-W. Stable blue TiO\textsubscript{2-x} nanoparticles for efficient visible light photocatalysts. J. Mater. Chem. 2014, 2, 4429–4437.

106. Fang, W.; Dappozze, F.; Guillard, C.; Zhou, Y.; Xing, M.; Mishra, S.; Daniele, S.; Zhang, J. Zn-Assisted TiO\textsubscript{2-x} Photocatalyst with Efficient Charge Separation for Enhanced Photocatalytic Activities. J. Phys. Chem. 2017, 121, 17068–17076.

107. Yin, H.; Lin, T.; Yang, C.; Wang, Z.; Zhu, G.; Xu, T.; Xie, X.; Huang, F.; Jiang, M. Gray TiO2 Nanowires Synthesized by Aluminum-Mediated Reduction and Their Excellent Photocatalytic Activity for Water Cleaning. Chem. Eur. J. 2013, 19, 13313–13316.

108. Zhang, M.; Pei, Q.; Chen, W.; Liu, L.; He, T.; Chen, P. Room temperature synthesis of reduced TiO2: and its application as a support for catalytic hydrogenation. RSC Adv. 2017, 7, 4306–4311.

109. Zhang, Y.; Xing, Z.; Liu, X.; Li, Z.; Wu, X.; Jiang, J.; Li, M.; Zhu, Q.; Zhou, W. Ti\textsuperscript{3+} Self-Doped Blue TiO2(B) Single-Crystalline Nanorods for Efficient Solar-Driven Photocatalytic Performance. ACS Appl. Mater. Interfaces 2016, 8, 26851–26859.

110. Yao, Y.; Sun, M.; Yuan, X.; Zhu, Y.; Lin, X.; Anandan, S. One-step hydrothermal synthesis of N/Ti3+ co-doping multiphasic TiO2/BiOBr heterojunctions towards enhanced sonocatalytic performance. Ultrason Sonochem 2018, 49, 69–78.

111. Hwang, H.M.; Oh, S.; Shim, J.-H.; Kim, Y.-M.; Kim, A.; Kim, D.; Kim, J.; Bak, S.; Cho, Y.; Bui, V.Q.; et al. Phase-Selective Disordered Anatase/Ordered Rutile Interface System for Visible-Light-Driven, Metal-Free CO\textsubscript{2} Reduction. ACS Appl. Mater. Interfaces 2019, 11, 35693–35701.

112. Bak, S.; Lee, S.M.; Hwang, H.M.; Lee, H. Phase-selective modulation of TiO2: for visible light-driven CH arylation: Tuning of absorption and adsorptivity. J. Mol. Catal. B Enzym. 2019, 171, 71–76.

113. Kim, Y.; Hwang, H.M.; Wang, L.; Kim, I.; Yoon, Y.; Lee, H. Solar-light photocatalytic disinfection using crystalline/amorphous low energy bandgap reduced TiO2. Sci. Rep. 2016, 6, 25212.

114. Kim, N.Y.; Lee, H.K.; Moon, J.T.; Joo, J.B. Synthesis of Spherical TiO2 Particles with Disordered Rutile Surface for Photocatalytic Hydrogen Production. Catalysts 2019, 9, 491.

115. Zhang, C.; Chen, S.; Mo, L.; Huang, Y.; Tian, H.; Hu, L.; Huo, Z.; Dai, S.; Kong, F.; Pan, X. Charge Recombination and Band-Edge Shift in the Dye-Sensitized Mg\textsuperscript{2+}-Doped TiO2 Solar Cells. J. Phys. Chem. 2011, 115, 16418–16424.
116. Cao, J.; Zhang, Y.; Tong, H.; Li, P.; Kako, T.; Ye, J. Selective local nitrogen doping in a TiO₂ electrode for enhancing photoelectrochemical water splitting. ChemComm 2012, 48, 8649–8651.
117. Cao, J.; Zhang, Y.; Liu, L.; Ye, J. A p-type Cr-doped TiO₂ photo-electrode for photo-reduction. ChemComm 2013, 49, 3440–3442.
118. Gul, I.; Sayed, M.; Shah, N.S.; Ali Khan, J.; Polychronopoulou, K.; Iqbal, J.; Rehman, F. Solar light responsive bismuth doped titanita with Ti³⁺ for efficient photocatalytic degradation of flumequine: Synergistic role of peroxymonosulfate. Chem. Eng. J. 2020, 384, 123255.
119. Liu, H.; Shen, B.; Xing, M.; Zhang, J.; Tian, B. Vacuum-activated Co³⁺ and Ti³⁺ co-modified TiO₂ with stable and enhanced photocatalytic activity. Res. Chem. Intermed. 2016, 42, 3459–3471.
120. Zhang, J.; Yuan, M.; Liu, X.; Wang, X.; Liu, S.; Han, B.; Liu, B.; Shi, H. Copper modified Ti³⁺ self-doped TiO₂ photocatalyst for highly efficient photodisinfection of five agricultural pathogenic fungus. Chem. Eng. J. 2020, 387, 124171.
121. Zhou, F.; Yan, C.; Sun, Q.; Komarneni, S. TiO₂/Sepiolite nanocomposites doped with rare earth ions: Preparation, characterization and visible light photocatalytic activity. Microporous Mesoporous Mater. 2019, 274, 25–32.
122. Wang, P.; Huang, B.; Dai, Y.; Whangbo, M.-H. Plasmonic photocatalysts: Harvesting visible light with noble metal nanoparticles. Phys. Chem. Chem. Phys. 2012, 14, 9813–9825.
123. Wang, Z.; Liu, Y.; Huang, B.; Dai, Y.; Lou, Z.; Wang, G.; Zhang, X.; Qin, X. Progress on extending the light absorption spectra of photocatalysts. Phys. Chem. Chem. Phys. 2014, 16, 2758–2774.
124. Linic, S.; Christopher, P.; Ingram, D.B. Plasmonic-metal nanostructures for efficient conversion of solar to chemical energy. Nat. Mater. 2011, 10, 911–921.
125. Hu, M.; Chen, J.; Li, Z.-Y.; Au, L.; Hartland, G.V.; Li, X.; Marquez, M.; Xia, Y. Gold nanostructures: Engineering their plasmonic properties for biomedical applications. Chem. Soc. Rev. 2006, 35, 1084–1094.
126. Rycenga, M.; Coble, C.M.; Zeng, J.; Li, W.; Moran, C.H.; Zhang, Q.; Qin, D.; Xia, Y. Controlling the Synthesis and Assembly of Silver Nanostructures for Plasmonic Applications. Chem. Rev. 2011, 111, 3669–3712.
127. Bigall, N.C.; Härtling, T.; Klose, M.; Simon, P.; Eng, L.M.; Eychmüller, A. Monodisperse Platinum Nanospheres with Adjustable Diameters from 10 to 100 nm: Synthesis and Distinct Optical Properties. Nano Lett. 2008, 8, 4588–4592.
128. Hutter, E.; Fendler, J.H. Exploitation of Localized Surface Plasmon Resonance. Adv. Mater. 2004, 16, 1685–1706.
129. Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y. Visible-Light Photocatalysis in Nitrogen-Doped Titanium Oxides. Science 2001, 293, 269.
130. Zhao, Y.; Zhu, L.; Yu, Y.; Gao, F.; Wang, W.; Chen, D.; Zhao, X. Facile one-pot preparation of Ti³⁺ N co-doping TiO₂: nanotube arrays and enhanced photodegradation activities by tuning tube lengths and diameters. Catal. Today 2019, doi:10.1016/j.cattod.2019.06.051.
131. Cao, Y.; Xing, Z.; Shen, Y.; Li, Z.; Wu, X.; Yan, X.; Zou, J.; Yang, S.; Zhou, W. Mesoporous black Ti³⁺/N–TiO₂ spheres for efficient visible-light-driven photocatalytic performance. Chem. Eng. J. 2017, 325, 199–207.
132. Ji, L.; Zhou, X.; Schmuki, P. Sulfur and Ti³⁺ co-Doping of TiO₂ Nanotubes Enhance Photocatalytic H₂ Evolution Without the Use of Any co-catalyst. Chem.: Asian J. 2019, 14, 2724–2730.
133. Li, M.; Xing, Z.; Jiang, J.; Li, Z.; Yin, J.; Kuang, J.; Tan, S.; Zhu, Q.; Zhou, W. Surface plasmon resonance–enhanced visible-light-driven photocatalysis by Ag nanoparticles decorated S–TiO₂–x nanorods. J. Taiwan Inst. Chem. Eng. 2018, 82, 198–204.
134. Yan, X.; Xing, Z.; Cao, Y.; Hu, M.; Li, Z.; Wu, X.; Zhu, Q.; Yang, S.; Zhou, W. In-situ C-N-S-tridoped single crystal black TiO₂ nanosheets with exposed {001} facets as efficient visible-light-driven photocatalysts. Appl. Catal. B 2017, 219, 572–579.
135. Irie, H.; Watanabe, Y.; Hashimoto, K. Nitrogen-Concentration Dependence on Photocatalytic Activity of TiO₂-xNₓ Powders. J. Phys. Chem. B 2003, 107, 5483–5486.
136. Wang, X.; Cui, Y.; Li, T.; Lei, M.; Li, J.; Wei, Z. Recent Advances in the Functional 2D Photonic and Optoelectronic Devices. Adv. Opt. Mater. 2019, 7, 1801274.
137. Wei, H.; McMaster, W.A.; Tan, J.Z.Y.; Chen, D.; Caruso, R.A. Tricomponent brookite/anatase TiO₂/g–C₃N₄ heterojunction in mesoporous hollow microspheres for enhanced visible-light photocatalysis. J. Mater. Chem. 2018, 6, 7236–7245.
138. Li, S.-Y.; Liu, Z.-L.; Xiang, G.-X.; Ma, B.-H.; Meng, X.-D.; He, Y.-L. Influence of calcination temperature on the photocatalytic performance of the hierarchical TiO2 pinecone-like structure decorated with CdS nanoparticles. Ceram. Int. 2019, 45, 767–776.

139. Zhao, F.-M.; Pan, L.; Wang, S.; Deng, Q.; Kou, J.-J.; Wang, L.; Zhang, X. Ag3PO4/TiO2: composite for efficient photodegradation of organic pollutants under visible light. Appl. Surf. Sci. 2014, 317, 833–838.

140. Zhang, Y.-H.; Li, Y.-L.; Jiu, B.-B.; Gong, F.-L.; Chen, J.; Fang, S.; Zhang, H. Highly enhanced photocatalytic H2 evolution of CuO microcube by coupling with TiO2 nanoparticles. Nat. Nanotechnol. 2019, 30, doi:10.1088/1361-6528/aafcccb.

141. Chen, X.; Ye, J.; Ouyang, S.; Kako, T.; Li, Z.; Zhou, Z. Enhanced Incident Photon-to-Electron Conversion Efficiency of Tungsten Trioxide Photoanodes Based on 3D-Photonic Crystal Design. ACS Nano 2011, 5, 4310–4318.

142. Yang, Y.; Qiu, M.; Li, L.; Pi, Y.; Yan, G.; Yang, L. A Direct Z-Scheme Van Der Waals Heterojunction (WO3∙H2O/g–C3N4) for High Efficient Overall Water Splitting under Visible-Light. Sol. RRL 2018, 2, 1800148.

143. Pan, J.; Jiang, Z.; Feng, S.; Zhao, C.; Dong, Z.; Wang, B.; Wang, J.; Song, C.; Zheng, Y.; Li, C. The enhanced photocatalytic hydrogen production of the fusiform g–C3N4 modification CaTiO3 nano-heterojunction. Int. J. Hydrog. Energy 2018, 43, 19019–19028.

144. Zhao, T.; Xing, Z.; Xi, Z.; Li, Z.; Chen, P.; Zhu, Q.; Zhou, W. Synergistic effect of surface plasmon resonance, Ti3+ and oxygen vacancy defects on Ag/MoS2/TiO2-x ternary heterojunctions with enhancing photocatalysis for low-temperature wastewater degradation. J. Hazard. Mater. 2019, 364, 117–124.

145. Ma, L.; Han, H.; Pan, L.; Tahir, M.; Wang, L.; Zhang, X.; Zhou, J.-J. Fabrication of TiO2 nanosheets via Ti3+ doping and Ag3PO4 QD sensitization for highly efficient visible-light photocatalysis. RSC Adv. 2016, 6, 63984–63990.

146. Zhao, T.; Xing, Z.; Xu, Z.; Li, Z.; Shen, L.; Cao, Y.; Hu, M.; Yang, S.; Zhou, W. CdS quantum dots/Ti3+-TiO2 nanobelts heterojunctions as efficient visible-light-driven photocatalysts. Mater. Res. Bull. 2018, 103, 114–121.

147. Sun, B.; Zhou, W.; Li, H.; Ren, L.; Qiao, P.; Li, W.; Fu, H. Synthesis of Particulate Hierarchical Tandem Heterojunctions toward Optimized Photocatalytic Hydrogen Production. Adv. Mater. 2018, 30, 1804282.

148. Xiu, Z.; Xing, Z.; Li, Z.; Wu, X.; Yan, X.; Hu, M.; Cao, Y.; Yang, S.; Zhou, W. Ti3+-TiO2/Ce3+-CeO2 Nanosheet heterojunctions as efficient visible-light-driven photocatalysts. Mater. Res. Bull. 2018, 100, 191–197.

149. Wang, Y.; Cao, X.; Hu, Q.; Liang, X.; Tian, T.; Lin, J.; Yue, M.; Ding, Y. FeOx Derived from an Iron-Containing Polyoxometalate Boosting the Photocatalytic Water Oxidation Activity of Ti3+-Doped TiO2. ACS Appl. Mater. Interfaces 2019, 11, 23135–23143.

150. Pan, J.; Dong, Z.; Jiang, Z.; Zhao, C.; Wang, B.; Zhao, W.; Wang, J.; Song, C.; Zheng, Y.; Li, C. MoS2:Quantum Dots Modified Black Ti3+-TiO2/g–C3N4 Hollow Nanosphere Heterojunction toward Photocatalytic Hydrogen Production Enhancement. Solar RRL 2019, 3, 1900337.

151. Cao, Y.; Xing, Z.; Li, Z.; Wu, X.; Hu, M.; Yan, X.; Zhu, Q.; Yang, S.; Zhou, W. Mesoporous black TiO2-x/Ag nanospheres coupled with g–C3N4 nanosheets as 3D/2D ternary heterojunctions visible light photocatalysts. J. Hazard. Mater. 2018, 343, 181–190.

152. Huang, Y.; Wang, P.; Wang, Z.; Rao, Y.; Cao, J.-j.; Pu, S.; Ho, W.; Lee, S.C. Protonated g–C3N4/Ti3+ self-doped TiO2 nanocomposite films: Room-temperature preparation, hydrophilicity, and application for photocatalytic NOx removal. Appl. Catal. B 2019, 240, 122–131.

153. Ye, M.-Y.; Zhao, Z.-H.; Hu, Z.-F.; Liu, L.-Q.; Ji, H.-M.; Shen, Z.-R.; Ma, T.-Y. 0D/2D Heterojunctions of Vanadate Quantum Dots/Graphitic Carbon Nitride Nanosheets for Enhanced Visible-Light-Driven Photocatalysis. Angew. Chem. Int. Ed. 2017, 56, 8407–8411.

154. Huo, N.; Gupta, S.; Konstantatos, G. MoS2–HgTe Quantum Dot Hybrid Photodetectors beyond 2 μm. Adv. Mater. 2017, 29, 1606576.

155. Tian, Z.; Xu, P.; Wang, W.; Zhang, D.; Xiao, S.; Li, X.; Li, G. C60-Decorated CdS/TiO2: Mesoporous Architectures with Enhanced Photostability and Photocatalytic Activity for H2 Evolution. ACS Appl. Mater. Interfaces 2015, 7, 4533–4540.

156. Huo, Y.; Yang, X.; Zhu, J.; Li, H. Highly active and stable CdS–TiO2 visible photocatalyst prepared by in situ sulfurization under supercritical conditions. Appl. Catal. B 2011, 106, 69–75.

157. Yu, X.; Li, Z.; Liu, J.; Hu, P. TaOC chemical bond enhancing charge separation between Ta3+ doped Ta2O5 quantum dots and cotton-like g–C3N4. Appl. Catal. B 2017, 205, 271–280.
158. Zhou, P.; Yu, J.; Jaroniec, M. All-Solid-State Z-Scheme Photocatalytic Systems. *Adv. Mater.* 2014, 26, 4920–4935.

159. Zhang, L.J.; Li, S.; Liu, B.K.; Wang, D.J.; Xie, T.F. Highly Efficient CdS/WO₃ Photocatalysts: Z-Scheme Photocatalytic Mechanism for Their Enhanced Photocatalytic H₂ Evolution under Visible Light. *ACS Catal.* 2014, 4, 3724–3729.

160. Liu, L.; Zhou, X.; Liu, L.; Jiang, S.; Li, Y.; Guo, L.; Yan, S.; Tai, X. Heterogeneous Bimetallic Cu–Ni Nanoparticle-Supported Catalysts in the Selective Oxidation of Benzyl Alcohol to Benzaldehyde. *Catalysts* 2019, 9, 538.