## **Nanoscale**



REVIEW

View Article Online



Cite this: Nanoscale, 2024, 16, 18165

# Structurally and surficially activated TiO<sub>2</sub> nanomaterials for photochemical reactions

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Renewable fuels and environmental remediation are of paramount importance in today's world due to escalating concerns about climate change, pollution, and the finite nature of fossil fuels. Transitioning to sustainable energy sources and addressing environmental pollution has become an urgent necessity. Photocatalysis, particularly harnessing solar energy to drive chemical reactions for environmental remediation and clean fuel production, holds significant promise among emerging technologies. As a benchmark semiconductor in photocatalysis, TiO2 photocatalyst offers an excellent solution for environmental remediation and serves as a key tool in energy conversion and chemical synthesis. Despite its status as the default photocatalyst, TiO2 suffers from drawbacks such as a high recombination rate of charge carriers, low electrical conductivity, and limited absorption in the visible light spectrum. This review provides an indepth exploration of the fundamental principles of photocatalytic reactions and presents recent advancements in the development of TiO<sub>2</sub> photocatalysts. It specifically focuses on strategic approaches aimed at enhancing the performance of TiO2 photocatalysts, including improving visible light absorption for efficient solar energy harvesting, enhancing charge separation and transportation efficiency, and ensuring stability for robust photocatalysis. Additionally, the review delves into the application of photodegradation and photocatalysis, particularly in critical processes such as water splitting, carbon dioxide reduction. nitrogen fixation, hydrogen peroxide generation, and alcohol oxidation. It also highlights the novel use of TiO<sub>2</sub> in plastic polymerization and degradation, showcasing its potential for converting plastic waste into valuable chemicals and fuels, thereby offering sustainable waste management solutions. By addressing these essential areas, the review offers valuable insights into the potential of TiO2 photocatalysis for addressing pressing environmental and energy challenges. Furthermore, the review encompasses the application of TiO<sub>2</sub> photochromic systems, expanding its scope to include other innovative research and applications. Finally, it addresses the underlying challenges and provides perspectives on the future development of TiO<sub>2</sub> photocatalysts. Through addressing these issues and implementing innovative strategies, TiO<sub>2</sub> photocatalysis can continue to evolve and play a pivotal role in sustainable energy and environmental applications.

Received 5th June 2024, Accepted 8th September 2024 DOI: 10.1039/d4nr02342k

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#### 1 Introduction

Photocatalysis stands as a promising solution for addressing a wide array of environmental and energy-related challenges by facilitating photochemical catalytic reactions. This process harnesses the abundant and renewable energy of sunlight to drive chemical transformations without requiring additional energy

input, thereby positioning it as an attractive avenue for diverse applications. Typically, photocatalysis employs a semiconductor photocatalyst that absorbs photons, generating active electron-hole pairs upon exposure to light. This photoexcitation leads to the generation of electrons in the conduction band (CB) and electronic vacancies or holes in the valence band (VB). Among the numerous photocatalysts derived from a variety of semiconducting materials, including metal oxides, oxysulfides, metal sulfides, oxysulfides, and their composites, metal oxides hold particular importance due to their favorable band gap and band edge positions. Notably, TiO<sub>2</sub> has emerged as one extensively studied semiconductor in photocatalysis due to its exceptional optical and electronic properties, as well as its unique chemical and physical character-

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istics facilitating a broad spectrum of reactions under solar irradiation. Since its pioneering role in photo-assisted water splitting in the early 1970s,6 TiO2 has garnered significant attention as a photocatalyst, leading to extensive research into the fabrication, structure, and applications of nanostructured TiO<sub>2</sub>-based photocatalysts.<sup>7,8</sup> These photocatalysts have found widespread consideration for numerous processes, such as environmental purification, 9-12 water splitting, 13,14 carbon dioxide reduction, 15,16 nitrogen fixation, 17,18 hydrogen peroxide generation, 19,20 alcohol oxidation, 21,22 and many more.

However, despite its remarkable properties, the widespread utilization of TiO<sub>2</sub> in photocatalytic applications faces inherent limitations. A primary challenge arises from its relatively large band gap of 3.2 eV, necessitating the use of high-energy photons for activation, primarily in the ultraviolet (UV) region below 400 nm, which represents only a small fraction of the total solar spectrum. Consequently, TiO2 photocatalysts exhibit limited efficiency under natural sunlight conditions, with a substantial portion of solar energy remaining untapped. Moreover, TiO2 is constrained by rapid recombination of electron-hole pairs, resulting in lifetimes typically ranging from 10<sup>-12</sup> to 10<sup>-11</sup> seconds, further diminishing its photocatalytic performance. To overcome these challenges, substantial efforts have been directed towards extending the working spectrum of TiO<sub>2</sub> photocatalysts into the visible light range, which accounts for 45% of total solar energy, and enhancing their charge carrier separation capabilities. Various approaches have thus been explored, aiming to unlock the full potential of TiO<sub>2</sub> photocatalysts for solar-driven processes, including bandgap engineering, surface modification, defect engineering, nanostructuring, and hybridization.

(I) Band gap engineering involves modifying the electronic structure of TiO2 to shift its band gap, typically achieved through doping with metal or non-metal ions. This introduces donor or acceptor states below or above the conduction or valence bands, respectively, enabling electronic transitions with lower energy compared to pure TiO2. As a result, visible light absorption and photocatalytic activity are enhanced. 23 (II) Surface modification of TiO2, through functionalization or nanoparticle deposition, creates localized energy states within the band gap.<sup>24</sup> For instance, deposition of noble metals like Pt or Au can trap visible light and enhance charge separation, thereby improving photocatalytic activity under visible light irradiation.<sup>24</sup> (III) Defect engineering through introducing hydrogen to TiO2 can create oxygen vacancies and modify its electronic structure, narrowing the band gap and improving visible light absorption.<sup>25</sup> (IV) Nanostructuring TiO<sub>2</sub> at the nanoscale can create quantum confinement effects or surface defects, modifying its electronic properties and band gap.<sup>26</sup> With the large surface-to-volume ratio of nanomaterials, abundant surface reaction sites are offered, potentially modulating the catalytic activity of surface atoms and leading to improved catalytic performance. 27-30 (V) Hybridization techniques for TiO<sub>2</sub> involve forming composites with various materials such as graphitic carbon nitride, MXenes, metal-organic frameworks, and aerogels. These materials are integrated with TiO2 to enhance its photocatalytic performance by leveraging their unique properties. For instance, graphitic carbon nitride can improve visible light absorption,31 MXenes can enhance conductivity and charge separation,<sup>32</sup> metal-organic frameworks can provide high surface area and tunable porosity,33 and aerogels can offer lightweight structures with high surface area.<sup>34</sup> By combining TiO<sub>2</sub> with these materials, hybrid composites can achieve superior light absorption, increased charge carrier separation, and improved catalytic activity, addressing the limitations of pure TiO2.

In light of the significant research advancements in the field of TiO2, a brief search of the literature in the Web of Science database for "TiO2" returns over 260 000 results, demonstrating the extensive interest and investigation in this



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tions (h-index 80) and ~300 research highlights. He has been honored as a Fellow of the Royal Society of Chemistry (FRSC) and has been recognized as a highly cited researcher in the Web of Science/Scopus.

material. When specifically searching for "TiO<sub>2</sub> photocatalyst", the results narrow to over 30 000, indicating the focused research on its photocatalytic properties. However, this number may still underrepresent the true scope, as many relevant studies might not explicitly label TiO2 as a photocatalyst. This extensive body of research highlights the critical importance of TiO2 in the field of photocatalysis, underlining its significant role and impact in advancing environmental remediation and energy conversion technologies over several decades.

For a quick overview of the research history, we present a brief timeline of milestones in the development of TiO<sub>2</sub> photocatalysts for various applications (Fig. 1). The first investigation of TiO<sub>2</sub> as a photocatalyst began in the 1970s when it was identified as a semiconductor capable of splitting water under UV light. During the 1980s and 1990s, significant advancements in doping techniques enhanced its photocatalytic efficiency under visible light. The early 2000s introduced engineered nanostructures and facets, which further improved TiO2's performance. In the 2010s, research focused on defect engineering and developing heterojunctions and composite/ hybrid materials, incorporating TiO2 with other semiconductors and noble metals to boost its photocatalytic activity. Recent years have seen progress in single-atom co-catalysts, with atomically dispersed metal atoms on TiO2 tuning active sites, selectivity, and stability. Moving forward, 3D printing technology has enabled the creation of complex TiO2 nanostructures with favorable properties for photochemical reactions. These advancements have expanded TiO<sub>2</sub>'s applications in environmental remediation and energy conversion, with photoreforming waste polymers into sustainable hydrogen fuel and chemical feedstock marking a significant leap in waste-toenergy technology.

This review provides a comprehensive and interdisciplinary perspective on the advancements in TiO2 photocatalysts, brid-



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ing the first yolk-shell nanostructure in lithium-sulfur batteries, which is a licensed technology. He pioneered the first study of sodium dendrites using cryogenic TEM, and the first anode-free magnesium battery with five times the energy density of standard magnesium batteries.

ging materials science, chemistry, environmental science, and engineering to offer a holistic understanding of their diverse applications. Going beyond general advancements, this review offers a detailed analysis of specific techniques such as doping, metal nanoparticle incorporation for surface plasmon resonance, morphological control, and hybridization. These approaches target three main steps: improving visible light absorption for efficient solar energy harvesting, enhancing charge separation and transportation efficiency, and maximizing charge utilization while ensuring good stability for robust photocatalysis. Recent progress includes the development of single-atom co-catalysts, advanced heterojunctions, and sophisticated 3D printing technologies for creating complex TiO2 nanostructures.

These developments have significantly broadened TiO2's applications. In the realm of environmental remediation, TiO2 photocatalysts have shown significant promise in breaking down pollutants under visible light, making them viable for water and air purification processes. Their antibacterial properties also present opportunities for public health improvements. For sustainable energy production, TiO2 has been explored extensively for water splitting, which generates hydrogen as a clean fuel. In addition, it is used for carbon dioxide reduction, converting carbon dioxide into valuable fuels, and nitrogen fixation, which is critical for producing ammonia for fertilizers.

Emerging applications such as hydrogen peroxide generation and alcohol oxidation are also discussed, illustrating the broadening scope of TiO<sub>2</sub> photocatalysis. The review delves into the novel application of TiO<sub>2</sub> in plastic polymerization and degradation processes. Here, TiO2 photocatalysts facilitate the breakdown of plastic waste into valuable chemicals and fuels, offering a sustainable approach to waste management and resource recovery. Recent research highlights the potential of photocatalytic depolymerization of various plastics and the conversion of plastic-derived intermediates into useful products, addressing plastic pollution and promoting circular economy principles (Fig. 2).

Finally, the review presents a summary and outlook on the major challenges and promising perspectives for future research in TiO<sub>2</sub> photocatalysts. Overall, the advancements in TiO2-based photocatalysts are anticipated to provide robust solutions to some of the most pressing energy and environmental challenges facing society today. The review highlights the transformative potential of TiO<sub>2</sub> photocatalysts in addressing these global issues and sets a clear roadmap for future research directions aimed at maximizing their efficiency and practical applicability.

### Photochemical reactions of TiO<sub>2</sub> nanomaterials

TiO<sub>2</sub> occurs in nature in three distinct polymorphs: rutile, anatase, and brookite, with rutile being the most abundant followed by anatase and then brookite. In all three forms of TiO<sub>2</sub>,

Grätzel: Suppression Fuiishima and Kawai and Sakata: Bard: Liquid-Hoffmann: Pichat: Platinized TiO<sub>2</sub> Photocatalytic Honda: phase Z-scheme of charge Photocatalytic Electrochemical photocatalysts photocatalyst for recombination production of H<sub>2</sub>O<sub>2</sub> degradation of photolysis of water hydrogen production through interparticle and organic via photoreforming at a semiconductor electron transfer peroxides in aqueous in aqueous TiO2 electrode of waste polymers suspensions of TiO2. suspensions . ZnÖ, and sand 1972 1979 1981 1984 1988 1990 Zhao: Dye Tada: All-solid-state Zou: Carbon-doped Tatsuma: Multicolor photochromic Rao: Photocatalytic sensitized TiO<sub>2</sub> TiO<sub>2</sub> for pollutants Z-scheme in control in TiO2 films loaded with silver N₂ reduction using CdS-Au-TiO<sub>2</sub> removal nanoparticles metal loaded TiO<sub>2</sub> for visible-light nanojunction driven alcohol system oxidation 2008 2007 2006 2004 Mao: Photocatalysis with black Yu: High-reactive Han: Non-centrosymmetric Janus Au-TiO-Yu: Direct 7-scheme {001} facet-exposed hydrogenated TiO<sub>2</sub> photocatalyst for H2 generation TiO<sub>2</sub>/a-C<sub>3</sub>N<sub>4</sub> anatase TiO<sub>2</sub> photocatalyst for photocatalytic decomposition 2009 2011 2012 2013 Yu: S-scheme photocatalyst for hydrogen production Wang: Defect-Che: CoNi@SiO-N-TiO<sub>2</sub>/a-C<sub>2</sub>N<sub>4</sub> Zhang: Defect-rich TiO2 nanosheets for N2 fixation in water stabilized single @TiO₂ microspheres atomic Au sites on with strong photocatalyst for enhanced catalytic photoreduction absorption performance of CO2 to CO 2019 2018 2016 2014 Lou: Ru atoms over the multi-edged TiO2 Zhang: Floatable Moretti: Defect-engineered nanostructured TiO<sub>2</sub> photocatalyst for sphere for photocatalytic H<sub>2</sub> evolution S-scheme TiO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub> water remediation and solar fuel photocatalyst for Reisner: Chemoenzymatic H<sub>2</sub>O<sub>2</sub> production and photoreforming of plastic alcohol conversion feedstocks for solar fuel generation 2020 2022 2023 Kowalska: TiO<sub>2</sub> Ma: Atmospheric nanoengineering towards efficient pressure conversion 3D-printed of CO and H₂O to mixed-phase plasmonio hydrocarbons TiO<sub>2</sub> foam for photocatalysis using TiO<sub>2-x</sub>/N pharmaceutical photothermal degradation catalyst

Fig. 1 Timeline of milestones in TiO<sub>2</sub> nanomaterials development, highlighting continuous advancements and innovations in the field. 1972, Fujishima and Honda: Electrochemical photolysis of water at a semiconductor electrode. 35 1979, Bard: Liquid-phase Z-scheme photocatalysts. 36 1981, Kawai and Sakata: Platinized TiO<sub>2</sub> photocatalyst for hydrogen production via photoreforming of waste polymers.<sup>37</sup> 1984, Grätzel: Suppression of charge recombination through interparticle electron transfer.<sup>38</sup> 1988, Hoffmann: Photocatalytic production of H<sub>2</sub>O<sub>2</sub> and organic peroxides in aqueous suspensions of TiO<sub>2</sub>, ZnO, and sand.<sup>39</sup> 1990, Pichat: Photocatalytic degradation of organic pollutants in aqueous TiO<sub>2</sub> suspensions.<sup>40</sup> 1994, Rao: Photocatalytic N<sub>2</sub> reduction using metal loaded TiO<sub>2</sub>. 41 2004, Tatsuma: Multicolor photochromic control in TiO<sub>2</sub> films loaded with silver nanoparticles. Reproduced with permission from ref. 42. Copyright 2004, American Chemical Society. 2006, Tada: All-solid-state Z-scheme in CdS-Au-TiO<sub>2</sub> nanojunction system. 43 2007, Zou: Carbon-doped TiO<sub>2</sub> for pollutants removal. 44 2008, Zhao: Dye sensitized TiO<sub>2</sub> as a photocatalyst for visiblelight driven alcohol oxidation. 45 2009, Yu: High-reactive (001) facet-exposed anatase TiO<sub>2</sub>. 46 2011, Mao: Photocatalysis with black hydrogenated TiO<sub>2</sub>. Reproduced with permission from ref. 25. Copyright 2011, American Association for the Advancement of Science. 2012, Han: Non-centrosymmetric Janus Au-TiO2 photocatalyst for H2 generation Reproduced with permission from ref. 13. Copyright 2012, Wiley-VCH. 2013, Yu: Direct Z-scheme TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> photocatalyst for photocatalytic decomposition. 47 2014, Zhao: N-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> photocatalyst for selective photoreduction of CO<sub>2</sub> to CO.<sup>48</sup> 2016, Che: CoNi@SiO<sub>2</sub> @TiO<sub>2</sub> microspheres with strong wideband microwave absorption.<sup>49</sup> 2018, Wang: Defect-stabilized single atomic Au sites on TiO2. 50 2019, Yu: S-scheme photocatalyst for hydrogen production. 51 2019, Zhang: Defect-rich TiO2 nanosheets for N2 fixation in water. Reproduced with permission from ref. 52. Copyright 2019, Wiley-VCH. 2020, Lou: Ru atoms over the multi-edged TiO2 sphere for photocatalytic H<sub>2</sub> evolution. Reproduced with permission from ref. 53. Copyright 2020, American Association for the Advancement of Science. 2022, Zhang: Floatable S-scheme TiO<sub>2</sub>/Bi<sub>2</sub>O<sub>3</sub> photocatalyst for H<sub>2</sub>O<sub>2</sub> Production and alcohol conversion.<sup>54</sup> 2023, Moretti: Defect-engineered nanostructured TiO<sub>2</sub> photocatalyst for water remediation and solar fuel. <sup>55</sup> 2023, Reisner: Chemoenzymatic photoreforming of plastic feedstocks for solar fuel generation. Reproduced with permission from ref. 56. Copyright 2023, Wiley-VCH. 2024, Mattia: 3D-printed mixed-phase TiO<sub>2</sub> foam for pharmaceutical degradation. Reproduced with permission from ref. 57. Copyright 2024, Royal Society of Chemistry. 2024, Ma: Atmospheric pressure conversion of CO and H<sub>2</sub>O to hydrocarbons using TiO<sub>2-x</sub>/Ni photothermal catalyst.<sup>58</sup> 2024, Kowalska: TiO<sub>2</sub> nanoengineering towards efficient plasmonic photocatalysis. Reproduced with permission from ref. 59. Copyright 2024, Elsevier.

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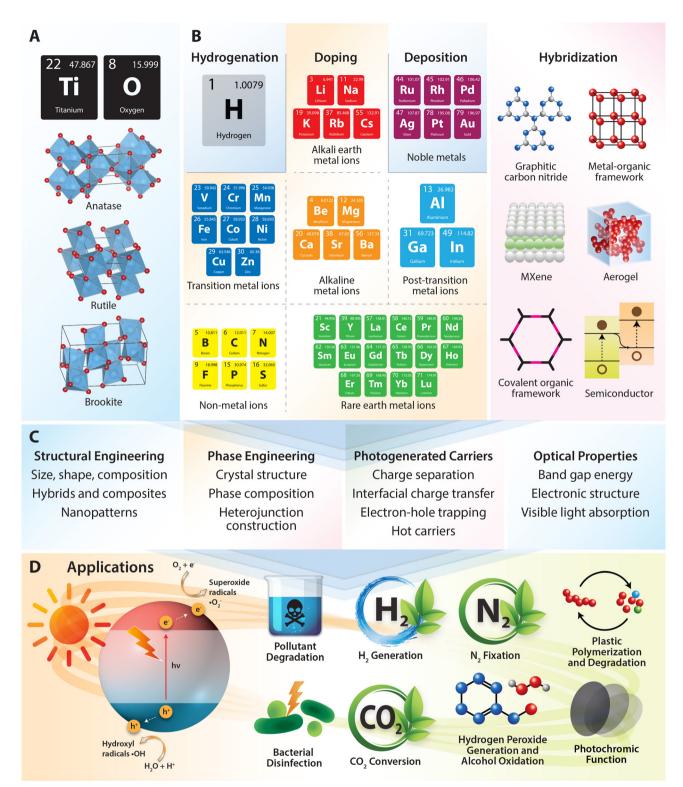


Fig. 2 An overview on modification strategies of TiO<sub>2</sub> for photocatalytic applications. (A) Crystal structures of TiO<sub>2</sub> in anatase, rutile, and brookite phases. (B and C) Modification strategies used to optimize structural, electronic, and surface properties of TiO2 semiconductor. Key techniques include hydrogenation (defect engineering), ion-doping (metal/non-metal), noble metal deposition, and hybridization/compositing with other materials. (D) Schematic illustration of the mechanism of TiO<sub>2</sub> photocatalysis for applications in environmental remediation, bacterial disinfection, hydrogen generation, carbon dioxide reduction, nitrogen fixation, hydrogen peroxide generation, alcohol oxidation, photochromic functions, plastic polymerization and degradation.

Table 1).

Review

the TiO<sub>6</sub> octahedra exhibit distortion, with titanium ions coordinated to six oxygen ions. In anatase, the TiO6 octahedra are arranged in a tetragonal structure where each octahedron shares four edges with neighboring octahedra but lacks corners. This unique configuration results in a lattice with specific characteristics such as high surface area and excellent photocatalytic activity. Rutile also features a tetragonal structure, albeit with a different alignment of the TiO<sub>6</sub> octahedra. In rutile, each octahedron shares two opposing edges to create linear chains in the (001) direction, which are interconnected at their corners, leading to a denser crystal lattice compared to anatase. Brookite's orthorhombic crystal structure is distinguished by octahedra sharing three edges and three corners, resulting in a more intricate lattice structure compared to anatase and rutile. Among these polymorphs, rutile is the most thermodynamically stable phase of TiO2, while anatase and brookite are metastable phases that can transition into rutile at elevated temperatures. 60,61 The varied properties and functionalities of these TiO<sub>2</sub> polymorphs establish them as

 $TiO_2$  photocatalytic reactions rely on the fundamental generation of electron-hole pairs through photoexcitation. When  $TiO_2$  is exposed to UV light, electron-hole pairs are generated between the valence band (VB) and conduction band (CB). These pairs subsequently migrate to the surface of the  $TiO_2$ , where they either undergo recombination and release the energy as heat, become trapped in metastable surface states, or interact with adsorbed electron donors/acceptors. In photodegradation reactions, the holes can directly react with organic compounds or oxidize water to produce hydroxyl radicals ( $^{\circ}OH$ ), initiating an oxidative process that leads to the breakdown of organic compounds. Meanwhile, the electrons can react with organic compounds to form reduction products or with molecular oxygen to generate superoxides ( $^{\circ}O_2^{-}$ ), which can trigger the formation of various reactive oxygen species

essential materials in photochemical reactions (refer to

(e.g., 'O<sub>2</sub><sup>-</sup>, 'OH, H<sub>2</sub>O<sub>2</sub>, etc.).<sup>62</sup> These photogenerated reactive oxidative species play a crucial role not only in degrading organic compounds but also in the photocatalytic inactivation of bacteria by oxidizing their cell walls and inducing cell lysis. In aerobic conditions, bacterial cells are inactivated through oxidation, whereas in anaerobic conditions, bacterial cells are inactivated through reduction, with the cells capable of trapping the electrons to prevent charge recombination.<sup>63</sup>

When a photocatalyst is utilized for water splitting to generate hydrogen, it is essential that the conduction band (CB) level is more negative than the reduction potential of H<sup>+</sup> to H<sub>2</sub> (0 V vs. NHE at pH 0), and the valence band (VB) should be more positive than the oxidation potential of H<sub>2</sub>O to O<sub>2</sub> (1.23 V vs. NHE). This requirement indicates that a minimum photon energy of 1.23 eV is needed to facilitate photocatalytic water splitting, corresponding to a wavelength of approximately 1000 nm. However, an activation barrier exists in the charge transfer process between the solid photocatalyst and water molecules, necessitating a photon energy exceeding the band gap of the photocatalyst to effectively split pure water at a reasonable rate. 14

In the realm of carbon dioxide reduction, the process involves converting carbon dioxide into valuable chemical products like hydrocarbons or synthetic fuels by leveraging the reactivity of electron–hole pairs generated by the photocatalyst. The photocatalytic reduction of carbon dioxide with  ${\rm TiO_2}$  entails a series of steps facilitated by photoexcited charge carriers. Upon light exposure,  ${\rm TiO_2}$  absorbs photons, creating electron–hole pairs that migrate to the semiconductor's surface. Carbon dioxide molecules adsorb onto the  ${\rm TiO_2}$  surface, where photoexcited electrons can reduce them to form various carbon-based products such as carbon monoxide (CO), methane (CH<sub>4</sub>), or formic acid (HCOOH). This reduction process involves multiple proton–electron transfer steps, followed by the release of the newly formed carbon-based products from the  ${\rm TiO_2}$  surface into the environment.<sup>64</sup>

Table 1 Overview of pristine TiO<sub>2</sub> photocatalyst in environmental remediation applications

Photocatalysts	Synthesis methods	Pollutants	Degradation efficiency	Ref.
TiO <sub>2</sub> nanosheets	Solvothermal	Rhodamine B	>90% in 15 min under UV light	250
TiO <sub>2</sub> nanorods	Hydrothermal	<i>p</i> -Cresol	>90% in 75 min under UV-visible light	267
TiO <sub>2</sub> nanostructures	Hydrothermal	Rhodamine B	>90% in 150 min under UV light	251
TiO <sub>2</sub> nanotubes	Hydrothermal	Orange II	89.46% in 2000 min under UV light	392
TiO <sub>2</sub> nanotubes	Electrochemical anodization	Volatile organic compounds	72.1% in 30 min under UV-LED	393
TiO <sub>2</sub> nanotubes	Electrochemical anodization	β-Blocker metoprolol	87.09% (milli-water) and 62.05% (tap water) in 120 min under UV-LED	394
TiO <sub>2</sub> nanotubes	Hydrothermal	$H_2S$	10 ppm to 1.0 ppb in 3 h under UV light	395
Mesoporous TiO <sub>2</sub> nanoshell@	<i>In situ</i> complexation-	Methylene blue	95% in 40 min under UV light	396
polyimide nanofibers	hydrolysis			
Nano flower-like rutile TiO <sub>2</sub>	Hydrothermal	Methylene blue	98.95% in 180 min under solar light	252
Raschig rings-supported TiO <sub>2</sub>	Sol-gel	Rhodamine 6G	91% in 30 min under UV light	397
TiO <sub>2</sub> films	Magnetron sputtering	(i) Methylene blue,	(i) 45% in 8 h under UVB light,	280
		(ii) E. coli bacteria	(ii) >90% in 45 min under UVB light	
TiO <sub>2</sub> sheets	Chemical synthesis/hydrogenation	Rhodamine B	99% in 75 min under simulated solar light	398
TiO <sub>2</sub> hollow spheres	Hard template-based approach	Ciprofloxacin	82% in 6 h under simulated solar light with AM1.5G filter, 100 W Xe arc lamp	55
TiO <sub>2</sub> particles	Ultrasound assisted sol–gel	Metformin	75.4% in 120 min under UV light	61

Similarly, in nitrogen fixation, electron-hole pairs play a pivotal role in catalyzing the reduction of nitrogen molecules to produce ammonia, a critical component in fertilizers and various chemical processes. The thermodynamically non-spontaneous reaction ( $N_2 + 3H_2O \rightarrow 2NH_3 + 1.5O_2$ ), which combines water splitting and nitrogen fixation, can be accomplished with solar energy input. The photocatalytic process of nitrogen fixation can be delineated into multiple stages. Initially, photogenerated electrons are promoted to the CB, creating vacancies (or holes) in the VB. Subsequently, some of these electrons and holes may recombine, while others migrate to the catalyst surface to participate in redox reactions. Specifically, water can be oxidized to oxygen by the holes, whereas nitrogen is reduced to form ammonia through successive transfers of photogenerated electrons and protons sourced from water.17

## Modification of electronic structures by doping

Despite significant advancements in the design and improvement of TiO<sub>2</sub> photocatalysts, challenges persist when using pure TiO<sub>2</sub> due to its low quantum efficiency and limited utilization of visible light. To address these challenges, considerable efforts have been directed towards modifying the electronic structure of TiO2 to shift its absorption into the visible range and enhance its photocatalytic performance. One approach involves doping, which introduces permissible electronic states between the CB and VB by incorporating metal ion (Table 2) and non-metal ion (Table 3) dopants. It is wellknown that metal ions incorporated into the TiO<sub>2</sub> lattice typically introduce donor states below the conduction band, while non-metal ions contribute to the formation of acceptor states above the valence band (Fig. 3A). These donor and acceptor states play crucial roles in altering the electronic structure of TiO2, affecting its band gap and, consequently, its optical and photocatalytic properties. 62,65 In this section, we outline recent progress in fabricating various TiO2 semiconductors to enhance photoconversion efficiency in the visible light region, employing strategies such as doping with metal ions and nonmetal ions.

#### 3.1 Metal ions

Metal-ion doping of TiO2 involves the introduction of metal ions into the TiO2 lattice structure to modify its properties. This helps reduce carrier recombination by creating electron trap centers, ultimately enhancing its photocatalytic activity. 66 Various metal ions such as alkali, alkaline earth, transition, and rare-earth can be incorporate into the TiO2 matrix to alter its electronic structure and tailor its photocatalytic activity.

3.1.1 Alkali earth metal ions. Doping TiO<sub>2</sub> with alkali earth metal ions involves introducing ions like lithium, sodium, potassium, rubidium, and caesium into the TiO2 lattice structure. Alkali metal doping, especially with ions like Li<sup>+</sup>, has demonstrated potential in improving the photocatalytic properties of TiO<sub>2</sub>. This enhancement is attributed to several mechanisms, including the reduction of crystallite size, improved crystallinity, and decreased recombination of generated charges.<sup>67</sup> Sodium doping had been known to cause sodium poisoning which degrades the photocatalytic property of TiO<sub>2</sub>. 68 Accordingly, low sodium content may serve as a recombination center, while higher sodium content favors the formation of brookite or sodium titanate, which are less photoactive than TiO<sub>2</sub> in its anatase form.<sup>69</sup> Report suggested that the poisoning effect may arise from a combination of various contaminants, including calcium, potassium, and magnesium, found on glass surfaces rather than solely from sodium doping.<sup>70</sup> Interestingly, sodium doping has been shown to enhance photocatalytic activity in some reports, compared to both the synthesized TiO<sub>2</sub> nanopowder and commercially available P25 TiO2. The enhancement was made possible through the com-

Table 2 Overview of metal-doped TiO<sub>2</sub> photocatalyst in environmental remediation applications

Photocatalysts	Synthesis methods	Pollutants	Degradation efficiency	Ref.
Na-TiO <sub>2</sub> nano-powder	Sol-gel	Methylene blue	92.5% in 60 min under UV light, peak $\lambda_{\rm max}$ = 365 nm	72
Na-TiO <sub>2</sub> nanotubes	Electrochemical anodization	Methylene blue	97.3% in 180 min under solar light	73
Rb-TiO <sub>2</sub> nanoparticles	Sol-gel	Methylene blue	97% in 60 min under UV light	77
Mg-TiO <sub>2</sub> nanoparticles	Sol–gel	Methyl orange	47.82% in 120 min under UV light	80
Ca-TiO <sub>2</sub> nanofibers	Sol-gel electrospinning	Rhodamine B	95% in 100 min under UV light	399
Ba-TiO <sub>2-x</sub> $(x = 5\%)$	Template assisted synthesis	Rhodamine B	99.4% in 30 min under simulated solar light	400
Ba-TiO <sub>2</sub> quantum dots	Co-precipitation	Methylene blue	99.5% in 120 min under visible light	81
Fe-TiO <sub>2</sub> nanoparticles	Sol-gel	Methyl orange	98% in 60 min under visible light	88
Fe-TiO <sub>2</sub> nanoparticles	Electrospray-assisted flame spray pyrolysis	Escherichia coli	99.4% in 5 h under UV light	87
In-TiO <sub>2</sub> nanoparticles	Sol-gel	$H_2S$	100% in 120 min under UV light	85
Mo-TiO <sub>2</sub> particles	Sol–gel/underwater plasma	Rhodamine B	96% in 60 min under visible light	256
W-TiO <sub>2</sub> particles	Sol–gel/underwater plasma	Rhodamine B	96% in 60 min under visible light	256
Tb-TiO <sub>2</sub> coating	Plasma electrolytic oxidation	Methyl orange	75% in 12 h under simulated sunlight	92
Nd-TiO <sub>2</sub> nanoparticles	Sol-gel	Methyl orange	96.5% in 120 min under simulated sunlight	91
Eu-TiO <sub>2</sub> nanorods	Hydrothermal	Methyl orange	100% in 20 min under simulated sunlight	89
Er–Ce co-doped TiO <sub>2</sub> nanoparticles	Sol-gel	<ul><li>(i) Staphylococcus aureus,</li><li>(ii) E. coli</li></ul>	(i) 91.23% and (ii) 92.8% in 20 min under simulated double solar radiation	281

Table 3 Overview of non-metal doped TiO<sub>2</sub> photocatalyst in environmental remediation applications

Photocatalysts	Synthesis methods	Pollutants	Degradation efficiency	Ref.
B-TiO <sub>2</sub> particles	Sol-gel	(i) Diuron, (ii) <i>o</i> -phenylphenol, (iii) 2-methyl-4-chlorophenoxy-acetic acid, (iv) terbuthylazine	(i) and (ii) 70–80% in 120 min, (iii) >90% in 45 min, (iv) 50% in 120 min under solar light	271
$\operatorname{B-TiO}_2$ nanoparticles	Solvothermal	(i) 2,4-Dichloro-phenol, (ii) bisphenol-A, (iii) ibuprofen & flurbiprofen	(i) 75.1% in 5 h, (ii) 97.7% in 4 h, (iii) 81–85% in 5 h under visible light	275
B-TiO <sub>2</sub> nanocrystals	Electrochemical anodization/hydrothermal	Rhodamine B	>90% in 60 min under visible light	401
B-TiO <sub>2</sub> nanoparticles	Co-precipitation	Rhodamine B	>90% in 90 min under visible light	99
C-TiO <sub>2</sub> particles	Controlled hydrolysis	Caffeic acid	>90% in 120 min under visible light	402
C-TiO <sub>2</sub> core-shell nano-	In situ polymer, Encapsulation–	Methylene orange	>90% in 30 min under UV light	104
structures (TiO <sub>2</sub> @C)	graphitization			
C-TiO <sub>2</sub> single-crystal	Hydrothermal	(i) Methylene blue, (ii) Rhodamine B, (iii)	(i) 98.3% in 60 min, (ii) 99.4% in	403
nanorods	•	<i>p</i> -Nitrophenol	20 min, (iii) 63% in 80 min under visible light	
C-TiO <sub>2</sub> nanoparticles	Vapour-assisted solvothermal	(i) Phenol, (ii) Methyl orange	(i) 94.6% in 75 min, (ii) >90% in 75 min under visible light	404
C-TiO <sub>2</sub> core-shell	Sol-gel	Methylene blue	90.1% in 120 min under visible light	107
nanostructures	TT double and	Physical P	2000/ in 400 min on long TR/ links	400
C-TiO <sub>2</sub> nanoparticles	Hydrothermal Hydrolysis	Rhodamine B Methyl orange	>90% in 120 min under UV light 83.23% in 150 min under UV light	109 405
Biochar–TiO <sub>2</sub> particles C/C-doped TiO <sub>2</sub> hollow	Sol-gel	Rhodamine B	96% in 140 min under UV light	405
microsphere C-nanohorns-TiO <sub>2</sub>	Solvothermal	Methylene blue and methyl orange	90% in 4 h under solar light	407
nanoflowers	Solvoenermar	Methylene blue and methyl olange	30 70 III I II dilaci solai ligite	107
N-TiO <sub>2</sub> nanoparticles	Sol-gel	Rhodamine B	90% in 40 min under visible light	116
N-TiO <sub>2</sub> nanoparticles	Sol-gel	Methyl orange	90% in 200 min under UV-vis light	257
N-TiO <sub>2</sub> nanoparticles	Graft polymerization	Methyl orange	65% in 60 min under visible light	408
N-TiO <sub>2</sub> nanoparticles	Plasma-assisted electrolysis	Methyl orange	91% in 300 min under visible light	409
N-TiO <sub>2</sub> nanoparticles	Co-precipitation Solvothermal	Rhodamine B	99.2% in 540 min under visible light	410
N-TiO <sub>2</sub> nanoparticles P-TiO <sub>2</sub> particles	Post-phosphation	Methylene blue Bisphenol A	92% in 500 min under visible light 92% in 67 min under sunlight	119 411
P-TiO <sub>2</sub> particles P-TiO <sub>2</sub> powders	Microwave-hydrothermal	Methylene blue	>90% in 100 min under visible light	258
P–TiO <sub>2</sub> nano-powders	Emulsion-based sol-gel	Methylene blue	>90% in 30 min under simulated solar light	412
P-TiO <sub>2</sub> nanoparticles	Solvothermal/heat treatment	Ciprofloxacin	>90% in 60 min under visible light	277
Mesoporous P-TiO <sub>2</sub>	Microwave-assisted sol-gel	Sulfamethazine	>90% in 300 min under visible light	413
P–TiO <sub>2</sub> /polyacrylic composite	Sol-gel	Formaldehyde	100% in 60 min under visible light	90
S-TiO <sub>2</sub> nanoparticles	Solvothermal	Phenol	85.4% in 10 h under visible light	139
S–TiO <sub>2</sub> nanorods	Oxidant peroxide method assisted hydrothermal	Methyl orange and phenol	80% in 120 min under visible light	138
S-TiO <sub>2</sub> nanoparticles	Hydrothermal	Rhodamine B	80% in 60 min under visible light	134
S-TiO <sub>2</sub> particles	Flame spray pyrolysis	Acetaldehyde	75% in 300 min under visible light	137
S-TiO <sub>2</sub> nanoparticles Meso-macroporous S-	Sol–gel Ball-milling	Diclofenac (i) Methylene blue, (ii) Methyl orange,	93% in 4 h under visible light (i) 98% in 100 min, (ii) 60% in	136 135
TiO <sub>2</sub> nanoparticles	Ball-Illilling	(iii) 4-Nitro-phenol	100 min, (iii) 50% in 80 min under visible light	133
F-TiO <sub>2</sub> nanorods	Hydrolysis/refluxing process	Methylene blue	90% in 130 min under visible light	414
F–TiO <sub>2</sub> hollow spiny nanocubes	Hydrothermal/ photoreduction	Phenol	58.6% in 60 min under visible light	143
F-TiO <sub>2</sub> nanoparticles	Hydrothermal	4-Methoxybenzyl alcohol	56.4% in 240 min under visible light	142
F-TiO <sub>2</sub> /exfoliated bentonite	Sol-gel	Toluene	11% in 80 min under visible light	144

bined effect of reduced electron-hole recombination rate, increased surface area, and enhanced crystallinity.<sup>71–73</sup>

For the larger alkali ions, potassium doping is considered effective for stabilizing the anatase phase of  ${\rm TiO_2}$ , as alkaline elements promote the formation of anatase crystalline phase. Doping with potassium can control the agglomeration of  ${\rm TiO_2}$  particles, improve photocatalytic efficiency, enhance the

adsorption of reactants on the catalyst, reduce the electron-hole recombination rate, and increase the specific surface area of TiO<sub>2</sub>.<sup>74</sup> For instance, K-doped TiO<sub>2</sub> thin films with a concentration of 10 wt% resulted in a reduction in the optical band gap energy of TiO<sub>2</sub> from 3.5 to 3.0 eV, thereby enhancing light absorption capabilities.<sup>75</sup> Furthermore, the presence of hydroxyl groups on the surface of K-doped TiO<sub>2</sub> is likely to

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A CR Ti 3d CB Ti 3d CB Ti 3d Metal doping **Band** gap Narrowed Non-metal doping **Band** gap O 2p 02p VR O 2p h<sup>+</sup> Pure TiO Metal doped TiO Non-metal TiO

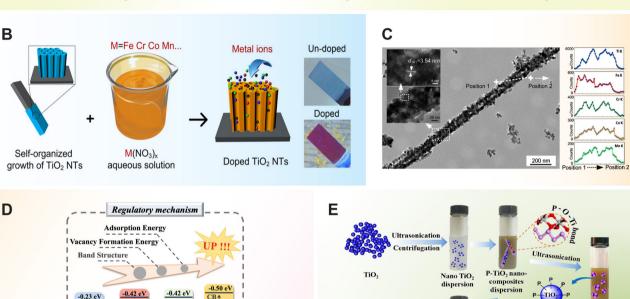


Fig. 3 (A) Schematic diagram of photocatalytic mechanisms of pure, metal and non-metal doped TiO<sub>2</sub> semiconductor. (B) Metal ions doping of transition metal ions (Cr, Co, Fe, Mn) doped TiO<sub>2</sub> nanotubes through anodization in an aqueous solution. (C) Transmission electron microscopy (TEM) image of transition metal ion doped TiO<sub>2</sub> nanotube with corresponding elemental composition line scans. Reproduced with permission from ref. 84. Copyright 2019, American Chemical Society. (D) Band structure position of trivalent metal ions (Al, Ga, In)-doped TiO<sub>2</sub>. Reproduced with permission from ref. 85. Copyright 2024, American Chemical Society. (E) Schematic illustration of fabricating phosphorus doped TiO<sub>2</sub>/polyacrylic composites by using black phosphorous as the phosphate source. Reproduced with permission from ref. 90. Copyright 2024, Elsevier.

enhance its photocatalytic activity and hydrophilic properties.<sup>76</sup> This makes it suitable for various applications such as synthesizing water-dispersible coatings and achieving optimal photovoltaic performance. For rubidium doping, it can induce distortion in the TiO2 lattice, promoting the formation of oxygen vacancies. These vacancies act as traps for capturing photo-generated electron-hole pairs, reducing their recombination rate. Furthermore, rubidium doping converts Ti<sup>4+</sup> into Ti<sup>3+</sup> through charge compensation, potentially forming impurity levels in the titania lattice that restrain

3.04 eV

Ga-TiO.

recombination and extend light absorption. Meanwhile, rubidium oxide on the TiO2 surface can transfer and capture electrons, thereby reducing the recombination rate of photo-generated carriers.<sup>77</sup> Metal dopants with larger ionic radii may not substitute Ti<sup>4+</sup> in the TiO<sub>2</sub> lattice easily, leading them to diffuse on the surface and inhibit the growth of TiO2 grains, ultimately enhancing its photocatalytic properties.78

Ultrasonication

3.1.2 Alkaline earth metal ions. Doping TiO<sub>2</sub> with alkaline earth metal ions involves introducing ions like magnesium,

Polyacrylic/P-TiO, composites

calcium, strontium, or barium into the TiO2 lattice structure. In a comparative study of alkali and alkaline earth metal doping in Mn/TiO2, it was observed that sodium, potassium, and calcium doping led to the deactivation of the photocatalyst, whereas magnesium doping enhanced the photoactivity. This suggests that alkaline earth metal doping, particularly with magnesium, provides a more significant enhancement to the photocatalytic properties of TiO<sub>2</sub>.<sup>79</sup> Specifically, magnesium doping leads to an increase in oxygen vacancies, which can be attributed to the differences in electronegativity and ionic radius between Ti and Mg during the substitution of Ti<sup>4+</sup> by Mg<sup>2+</sup> in the lattice. These oxygen vacancies play an important role in photocatalytic reactions by serving as electron acceptors, thus reducing the recombination rate of electron-hole pairs. 80 Similarly, doping TiO2 with the alkaline earth metals like strontium and barium can alter the oxide's optical absorption characteristics by modifying the band gap energy.81,82 The dopants may act as an electron trap, thereby

inhibiting the recombination rate of electron-hole pairs.

3.1.3 Transition metal ions. Transition metal ions possess multiple valences and unfilled d-electron structures, allowing them to introduce impurity levels within the band gap of TiO<sub>2</sub>. These impurities serve as shallow traps for photogenerated electrons or holes, effectively reducing the recombination of electron-hole pairs. 83 Transition metal ions, such as Cr, Co, Cu, Fe, and Mn, can be introduced into TiO2 nanotubes by anodization (Fig. 3B) while preserving their ordered tubular structures (Fig. 3C). These ions may occupy interstitial or substitutional positions in the lattice, depending on their respective radii compared to Ti<sup>4+</sup>. For instance, Fe<sup>3+</sup> (69 pm) and Cr<sup>3+</sup> (75.5 pm) ions, with smaller radii similar to Ti<sup>4+</sup> (74.4 pm), are likely to occupy substitutional positions in the lattice of TiO<sub>2</sub>, while a larger radius like Co<sup>2+</sup> (79 pm) may occupy interstitial positions. On the other hand, Cu<sup>2+</sup> (88 pm) and Mn<sup>2+</sup> (97 pm) ions, with larger radii than Ti4+, are also expected to occupy interstitial positions, potentially facilitating the separation of electron-hole pairs. This dual doping mechanism enhances the absorption of visible light, contributing to improved photocatalytic performance.<sup>84</sup> Notably, Group IIIA trivalent metal ions like Al<sup>3+</sup> (50 pm), Ga<sup>3+</sup> (60 pm), and In<sup>3+</sup> (81 pm) possess a radius similar to Ti4+, enabling partial substitution within the TiO2 lattice. This substitution leads to doped TiO2 with minimal lattice distortion and no alteration of the crystal structure. In addition, this doping introduces a shallow acceptor level above the valence band in the energy band structure (Fig. 3D), leading to a substantial increase in the carrier concentration of photocatalysts and enhances light quantum efficiency.85

The roles of transition metal ions in charge trapping, recombination, interfacial transfer, and photocatalytic activity were systematically studied by doping six types of transition metal ions, including V, Mn, Fe, Cu, Ce, and W, into the surface lattice of TiO<sub>2</sub> powders. Among these ions, Fe and Cu were found to enhance interfacial charge transfer by inhibiting defect-mediated annihilation, promoting d–d transitions, and inducing thermally induced de-trapping. Conversely, Mn ions

introduced states in the mid-band-gap region, leading to the trapping of charge carriers and significant consumption *via* intra-atomic relaxation. Additionally, Ce and W ions formed strong bonds with O<sup>2-</sup> radicals, thereby limiting charge utilization and photocatalytic performance. Ref Particularly, Fe metal ions are widely studied for doping into the TiO<sub>2</sub> lattice due to their notable effects. However, the efficacy of Fe-doped TiO<sub>2</sub> has been hindered by the formation of an amorphous contamination layer, primarily composed of iron oxide, on the nanoparticle surface. The removal of the contamination layer through acid treatment has proven to be effective in enhancing the photocatalytic activity from 24% to 98%.

3.1.4 Rare earth ions. Rare earth elements constitute of a unique group within the periodic table, comprising 17 elements including scandium, yttrium, and the lanthanides from lanthanum to lutetium. Lanthanides are part of the f-block of the periodic table, characterized by the filling of 4f orbitals. The f-orbitals of rare earth ions are relatively low in energy and spatially diffuse, making them available for bonding with Lewis bases. This interaction can result in the formation of stable coordination complexes where the Lewis base molecule or ion acts as a ligand surrounding the rare earth ion. Doping TiO2 with rare earth ions presents a promising strategy for enhancing its photocatalytic performance by introducing unfilled 4f orbitals into the TiO2 lattice. These unfilled orbitals serve as effective electron traps, capturing photoexcited electrons and preventing their recombination with holes. As a result, the lifetime of charge carriers within the TiO<sub>2</sub> lattice is extended, leading to improved photocatalytic performance. Moreover, the presence of rare earth elements has been observed to increase the temperature at which the anatase to rutile transformation occurs in TiO2.89 This higher transformation temperature is beneficial for maintaining the desired anatase phase, which is typically more favorable for photocatalysis.

Doping TiO2 with 1 mol% neodymium results in modified TiO<sub>2</sub> with solely the anatase phase, demonstrating superior photocatalytic activity. 91 This enhancement is attributed to the formation of bonds between the rare earth element and TiO2, which not only increases photocatalytic reactivity but also restrains the generation of the rutile phase within the TiO2 structure. The exclusive formation of the anatase phase and the facilitation of bonding interactions with the rare earth element led to improved performance in the modified TiO2 composition. The study of Tb-doped TiO2 photocatalytic activity revealed that the substitution of Ti4+ ions with Tb3+ ions induce the creation of oxygen vacancies within the TiO2 lattice, due to a large mismatch in ionic radii and charge imbalance. 92 As the Tb3+ content increases, the absorption edge of the material shifts gradually towards higher wavelengths. This observed red shift is attributed to charge-transfer transitions between the f electrons of Tb3+ ions and either the conduction or valence band of TiO2. The study of different rare earth ions, including Pr3+, Eu3+, Er3+, Y3+, Ho3+, Yb3+, and Nd<sup>3+</sup>, reveals that TiO<sub>2</sub> doping with these ions leads to enhanced photocatalytic activity. 93-95 Among these ions, Ho3+

stands out for its significant absorption in the visible light region, which can contribute to improved photocatalytic performance under visible light irradiation.<sup>96</sup> This finding highlights the importance of selecting appropriate dopants with favorable electronic structures to maximize the utilization of visible light for photocatalysis.

#### 3.2 Non-metal ions

The development of metal-incorporated TiO2 visible light photocatalysts often encounters challenges such as low thermal stability, photo-corrosion, and increased likelihood of serving as recombination centers due to the localized d-states of the dopants deep in the band gap of TiO2. 97,98 To address these drawbacks associated with metal-incorporated photocatalysts, extensive research has focused on modifying TiO2 with non-metal elements to achieve stable visible-light-active TiO2. Non-metal-incorporated TiO2 crystals have shown greater success compared to metal doping because they can introduce mid-gap states acting as electron donors or acceptors within the band gap of TiO2. These mid-gap states effectively reduce the band gap energy and enhance the photoconversion efficiency of TiO<sub>2</sub> in the visible light region.

3.2.1 Boron-doped TiO<sub>2</sub>. Doping with boron represents an effective strategy to reduce the band gap of TiO2 by substituting oxygen atoms in the TiO2 lattice with boron atoms, thereby broadening its visible light absorption. 99 Boron incorporation into the TiO<sub>2</sub> lattice can occur through three mechanisms: (1) substitutional doping, involves the replacement of oxygen atoms; (2) interstitial doping, which entails the addition of boron atoms; or (3) a combination of both types of doping within the TiO2 lattice. Notably, the stability of interstitially doped B-TiO2 is superior to that of substitutional doping due to the high formation energy of the latter. Substitutionally doped B-TiO2, while metastable, tends to decompose into boron oxide. 100,101

3.2.2 Carbon-doped TiO<sub>2</sub>. Carbon is a promising dopant for narrowing the band gap of TiO2 by creating a hybrid orbital above the valence level of TiO2, thereby increasing its capacity for visible light absorption. 102-108 Various carbon sources, including carbon nanotubes, graphene, and natural carbon materials, have been reported to enhance the optical and photocatalytic activities of TiO2 matrices. One crucial aspect for enhancing photocatalytic activity lies in controlling the dopant source during the synthesis process. Carbon doping influences the degree of crystallinity, which in turn governs the photocatalytic sites and activity. For instance, hydrothermal synthesis of titanate precursor with different carbon sources (e.g., resorcinol, phloroglucinol, ethylene glycol, and glycerol) was found to alter the phase structure and influence the ratio of anatase to brookite in mixed phase structures of TiO<sub>2</sub>. <sup>109</sup> These mixed crystal phases exhibited lower band gap energy and reduced photogenerated electron-hole recombination rates. In another example, C-doped TiO2 catalysts prepared via a sol-gel method from titanate precursor and glucose show enhanced anatase to rutile phase transformation due to carbon doping from the glucose source.110 This occurs

through the formation of Ti-O-C bonds, which are positioned within the interstitial locations of the TiO2 lattice at the interfaces of the anatase TiO2 domains. Successful anatase crystallization suppresses the electron-hole recombination rate by reducing the number of defects, thereby improving photocatalytic activity.

In many cases, doping techniques are utilized to enhance visible light absorption in photocatalytic materials, but they often result in the formation of defect sites, which can compromise photocatalytic activity. One strategy to mitigate the probability of charge recombination is to encapsulate C-doped TiO<sub>2</sub> particles with nano-sized graphene. This approach aims to facilitate the effective transfer of photogenerated electrons to surface active sites by reducing the interfacial chargetransfer resistance between C-doped TiO2 and reactants. As a result, the prolonged lifetime of photogenerated charges over the C-doped TiO<sub>2</sub> nanoparticles enables the generation of a large number of hydroxyl radicals with high oxidizing power for photodegradation purposes.

Another approach to modifying TiO2 with carbon involves the formation of core-shell nanostructure photocatalysts. In this method, carbon-modified TiO<sub>2</sub> core-shell nanostructures were fabricated using an acidified sol-gel system with titanium-n-butoxide and a regenerated cellulose membrane. 104 This approach has been shown to enhance the visible light photocatalytic performance. The synergistic effect of the carbon shell and TiO2 promotes the formation of a large number of hydroxyl radicals due to the carbon's photosensitizer behavior, thus supporting higher photocatalytic activity. The enhanced visible light absorption capability is primarily attributed to the incorporation of carbon dopants at interstitial positions in the TiO<sub>2</sub> lattice, forming O-Ti-C or Ti-O-C bonds. In addition, the formation of the carbon core-shell nanostructure occurs through a carbonaceous layer grafted onto the surface of TiO<sub>2</sub> via Ti-O-C and Ti-OCO bonds. In this study, the calcination temperature is identified as an important parameter for controlling the thickness of the carbon shell coating on TiO2, as well as its crystallinity, surface area, and optical properties. Specifically, increasing the calcination temperature from 75 to 500 °C results in a narrowing of the band gap from 2.95 to 2.80 eV, and an increase in the thickness of the carbon shell from 0.40 to 1.20 nm, respectively. However, excessive carbon thickness is found to be detrimental to photocatalysis because it can shield the passage of light and hinder reactant adsorption on the TiO2 surface.

3.2.3 Nitrogen-doped TiO2. Among non-metal dopants, nitrogen emerges as a highly promising candidate for altering the band gap of TiO<sub>2</sub> due to its intrinsic properties, including comparable atomic size to oxygen, small ionization energy, and stability. 112-114 The doping of nitrogen in TiO2 leads to the mixing of N 2p with O 2p states, resulting in a narrower band gap compared to pure TiO2 by shifting the edge of the valence band upward. Several techniques and methodologies have been developed to incorporate nitrogen into TiO2, including direct nitridization, 115 sol-gel, 116 electrochemical methods, 117 hydrothermal, 118 and solvothermal reactions, 119 sputtering, 120

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and ball milling with nitrogenous compounds. 121 In principle, oxygen-rich conditions, such as those employed in wet processes like sol-gel methods, induce the formation of nitrogen atoms in interstitial positions of the TiO2 lattice. In contrast, oxygen-deficient (reducing) conditions favor the incorporation of nitrogen atoms in oxygen lattice sites, resulting in substitutional doping. 120,122 Substitutional doping reduces the band gap of TiO<sub>2</sub> to approximately 3.06 eV, while interstitial doping can further narrow it to ~2.46 eV. The presence of nitrogen promotes a red-shift in absorption spectra and lowers the energy formation of oxygen vacancies, consequently enhancing photocatalytic activity through efficient electron trapping and electron-hole separation. 123,124 The correlation between oxygen vacancies and photocatalytic properties depends on the concentration of nitrogen doping. At low nitrogen concentrations, interstitial doping dominates, promoting oxygen vacancies. Conversely, high levels of nitrogen incorporation encourage substitutional doping, which reduces the concentration of oxygen vacancies. For highly doped anatase, a cubic titanium oxynitride phase was discovered which offers valuable insights into the fundamental shift in absorption wavelength. This shift enables excellent photocatalytic performance using visible light, signifying a significant advancement in the field. 125

**3.2.4 Phosphorus-doped TiO**<sub>2</sub>. The doping of phosphorus into  $TiO_2$  lattices results in absorption in the visible light region due to the impurity energy level in the band gap, typically in the form of  $P^{5+}$  ions. Chemically, it is more favorable to incorporate  $P^{5+}$  ions into the  $TiO_2$  lattice by substituting  $Ti^{4+}$  ions to form Ti-O-P bonds, rather than incorporating  $P^{3+}$  ions by substituting  $O^{2-}$  ions to form Ti-P bonds. This preference is ascribed to the significantly larger formation energy required for phosphorus substituting oxygen in  $TiO_2$  (15.48 eV) compared to phosphorus substituting titanium (1.32 eV).

Early studies on phosphorus-modified TiO2 primarily focused on improving thermal stability and surface area. 127,128 Surface modification of TiO2 with phosphoric acid is a common technique for preparing P-doped TiO2 photocatalysts. Phosphate anions from phosphoric acid adsorb strongly on the surface of TiO2, significantly influencing the interfacial and surface chemistry of TiO<sub>2</sub>. 129 The incorporation of phosphorus into the TiO2 lattice using phosphoric acid as the phosphorus source via a sol-gel method resulted in a redshift in the absorption edge due to the formation of Ti-O-P bonds in the crystal lattice. 130 Furthermore, phosphorus doping affects the crystallization of TiO<sub>2</sub> by inhibiting crystal growth and suppressing the phase transformation from anatase to rutile. Apart from these observed merits, the enhanced visible light activity is primarily attributed to increased hole signal intensity, indicating efficient trapping of photogenerated holes.

Apart from post-treating  $TiO_2$  with phosphoric acid, other methods of introducing phosphorus into  $TiO_2$  include using elemental red phosphorus via a ball milling process<sup>131</sup> or decomposing black phosphorus via high-intensity ultrasonication.<sup>90</sup> In the case of black phosphorus, it can absorb

onto the  ${\rm TiO_2}$  surface through electrostatic interactions, leading to the formation of uniformly dispersed P-TiO<sub>2</sub> composites. These P-TiO<sub>2</sub> composites can then be blended with a polyacrylic matrix to prepare functional coatings with photocatalytic properties (Fig. 3E). During the decomposition process of black phosphorus, P<sup>5+</sup> ions are produced and incorporated into the crystal lattice of TiO<sub>2</sub> to form P-O-Ti bonds. This incorporation leads to the generation of more defects in the P-TiO<sub>2</sub> crystals, which helps trap electrons and suppress the recombination of electron-hole pairs. Consequently, the photocatalytic ability of P-TiO<sub>2</sub> is expected to be superior to both TiO<sub>2</sub> and black phosphorus.

3.2.5 Sulfur-doped  $TiO_2$ . The modification of  $TiO_2$  with sulfur doping results in band-gap narrowing by introducing localized states within the band gap structure of  $TiO_2$ .<sup>132</sup> However, incorporating sulfur into  $TiO_2$  poses challenges due to the larger ionic radius of sulfide ions ( $S^{2-}$ , 1.84 Å) compared to oxide ions ( $O^{2-}$ , 1.22 Å). This discrepancy in size leads to a higher formation energy for the substitution of sulfur to form Ti-S bonding compared to Ti-O bonding. In principle, sulfur doping in  $TiO_2$  can occur through various mechanisms, including the substitution of  $Ti^{4+}$  (0.65 Å) by  $S^{6+}$  and/or  $S^{4+}$  ( $\sim$ 0.51 Å), or the direct incorporation of  $S^{2-}$  into the  $TiO_2$  lattice. The substitution of  $Ti^{4+}$  by  $S^{6+}$  or  $S^{4+}$  ions is more chemically favorable due to their smaller ionic radii compared to  $S^{2-}$  ions.<sup>133</sup> In another words, the sulfur dopant can act as both cationic and anionic substitution in  $TiO_2$  ( $S^{6+}$ ,  $S^{4+}$ ,  $S^{2-}$ ).

The early studies on sulfur doping of TiO2 have shown that the band gap modification is achieved by substituting lattice oxygen with S2- ions to form Ti-S bonds, representing anionic substitution. 133 In this work, S-doped TiO2 was synthesized through the oxidative annealing of titanium disulfide. This doping of sulfur induces a significant shift in the absorption edge towards lower energy by mixing the S 3p states with the VB. 134 The use of titanium disulfide as starting material was later extended in hydrothermal oxidation reaction to prepare anionic S-doped TiO2. 134 Subsequent to thermal annealing, various chemical processes have been developed for synthesizing S-doped TiO2, including ball milling, 135 sol gel, 136 flame spray pyrolysis, 137 oxidant peroxide method, 138 hydrothermal reaction, 134 and solvothermal reactions. 139 The choice of preparation method and sulfur sources significantly influences the ionic form of sulfur doping in TiO2. Studies have shown that thiourea and carbon disulfide as sulfur sources favor the formation of anionic sulfur doping in the TiO2 crystal lattice. When TiS<sub>2</sub> or CS<sub>2</sub> is used, most of the sulfur from TiS<sub>2</sub> or CS<sub>2</sub> is oxidized, leaving residual S as S2-, which replaces oxygen atoms in the O-Ti-O framework. Conversely, using thiourea as the sulfur source promotes the cationic doping of S atoms into the  ${
m TiO_2}$  crystal lattice.  $^{138,140}$ 

**3.2.6 Fluorine-doped TiO<sub>2</sub>.** Fluorine has been utilized in multiple capacities to enhance the photocatalytic performance of TiO<sub>2</sub>. It has been utilized as a capping agent and/or dopant in TiO<sub>2</sub> to modify both their surface and bulk properties. This modification leads to increased specific surface area, creation of surface oxygen vacancies, enhanced visible light absorption,

and slower charge recombination.<sup>141–144</sup> The induced oxygen vacancies, associated with the formation of Ti<sup>3+</sup> species, contribute to improved electronic conductivity and appear at energy levels 0.3 to 0.8 eV below the conduction band minimum of TiO<sub>2</sub>.<sup>141,145</sup> In addition, fluorine has been employed as a structure-directing agent, facilitating the generation of TiO<sub>2</sub> with exposed high-energy (0 0 1) facets, which exhibit superior photocatalytic activity compared to other facets.<sup>23,146,147</sup> Despite the dominance of the (101) facet, efforts have been made to selectively modify TiO<sub>2</sub> during synthesis to favor the growth of the less thermodynamically favored (001) facet.<sup>148</sup> Fluorine ions are particularly notable for their role in controlling the growth of TiO<sub>2</sub> facets.<sup>149,150</sup>

To attain optimal photocatalytic performance, numerous studies on F-doped TiO2 have focused on controlling fluorine doping concentration during synthesis. For instance, in a hydrothermal synthesis of F-doped rutile single crystalline TiO2, the optical band gap of the photocatalyst was effectively adjusted from 3.05 to 2.58 eV by varying the fluorine doping concentration.141 Besides, the concentration of fluorine doping has been identified as a crucial factor in shaping the morphology of TiO2. Using TiCl4 as a precursor, a range of TiO<sub>2</sub> hierarchical nanostructures, including pompon-like and football-like microspheres composed of aligned rutile and anatase nanoparticles, have been synthesized using a hydrothermal method in the presence of NaF. 151 An incremental increase in the concentration of NaF leads to a sequential red shift of the absorption band edge of F-doped TiO2 compared to pure TiO2. Consequently, the band gap of F-doped TiO2 can be tuned from 3.0 eV to 2.2 eV, with the degree of tuning dependent on the fluorine doping concentration.

## 4 Noble metals-supported TiO<sub>2</sub> hybrids

The integration of noble metals onto the surface of TiO2 introduces new functionalities by leveraging the intrinsic properties of metal nanoparticles, significantly enhancing their performance as photocatalysts. Noble metal nanoparticles, such as silver (Ag) and gold (Au), exhibit strong absorption across the UV to near-infrared (NIR) spectrum due to their surface plasmon resonance, which can be tailored by controlling their size, shape, and surrounding medium.<sup>29</sup> Despite Ag's susceptibility to oxidation, it remains a top candidate for plasmonic applications due to its low optical loss in the visible and NIR spectral regions. On the other hand, Au offers superior stability alongside excellent performance in the visible and NIR ranges. While aluminium and copper are alternative plasmonic materials, their poor chemical stability limits their applicability. Palladium (Pd) and platinum (Pt) are catalytically active metals, but both do not support strong plasmonic resonances at visible wavelengths. In hybrid systems formed by depositing noble metals onto TiO2, these metal nanoparticles serve as antennae, efficiently absorbing visible light and generating energetic electrons and holes in the semiconductor. 152,153 This

synergistic effect between  ${\rm TiO_2}$  and noble metals enhances photoreactivity across a broad range of the solar spectrum, overcoming the inherent limitations of wide band gap  ${\rm TiO_2}$  semiconductors.

In contrast to conventional semiconductor photocatalysis, plasmonic photocatalysis exhibits two distinct features: the Schottky junction and localized surface plasmon resonance (LSPR). 154 In semiconductor-noble metal hybrid systems, when illuminated with UV light, the excited electrons of the semiconductor are transferred from the CB to the Fermi level of noble metals, leading to the separation of electron-hole pairs. This metal-semiconductor interface, known as the Schottky junction, promotes charge separation and transfer at the interface. Meanwhile, LSPR plays a crucial role in plasmonic photocatalysis by inducing the collective oscillation of conduction electrons at the interface of metallic structures upon excitation by incident electromagnetic radiation of the same frequency. When noble metals absorb visible light through LSPR, charge carriers in the noble metals are directly injected from excited plasmonic metal nanostructures into the semiconductor, contributing to strong visible light absorption and the generation of active charge carriers. 155 Both the Schottky junction and LSPR significantly enhance the photocatalysis process and the overall photocatalytic efficiency of TiO2 semiconductor (Table 3).

#### 4.1 Ag on TiO<sub>2</sub>

Functionalizing Ag nanoparticles presents challenges related to stability, aggregation, and size control, compounded by their susceptibility to oxidation over time, which can degrade their surface properties. However, the work of Awazu et al. represents a significant advancement in plasmonic photocatalysis by combining TiO<sub>2</sub> with optically active Ag nanoparticles. 156 In this approach, the excitation of surface plasmons on the Ag nanoparticle surface amplifies the near-field amplitude at specific wavelengths in the near UV region, leading to higher concentrations of charge carriers in TiO2 and thereby increasing the efficiency of photocatalysis. The important feature to enable plasmonic photocatalysis in this study is to deposit TiO<sub>2</sub> on Ag nanoparticles coated with thin protective SiO<sub>2</sub> shell to prevent oxidation. This protective shell ensures that the photodegradation rate by the TiO<sub>2</sub> photocatalyst modified with protected Ag nanoparticles is 7 times faster than that of pure TiO2 under UV irradiation. Alternatively, a polymer shell can be used to protect Ag nanoparticles from oxidation, forming a core-shell structure with an Ag core and a polymer shell. For instance, polyacrylic acid is employed for polymer encapsulation on the Ag nanoparticles using Layer-by-Layer synthesis, enabling precise control of the polymer shell thickness at the nanoscale without compromising the plasmon-induced enhancement of the near-field. The TiO2 photocatalyst modified with protected Ag core-shell structures demonstrates a 15% enhancement in their photocatalytic activity in air compared to pure TiO2. Notably, this enhanced activity is retained over time, even upon aging in air, whereas TiO2 modified with bare Ag nanoparticles loses its plasmonic properties gradually.

This phenomenon can be attributed to the progressive oxidation of the unprotected Ag nanoparticles to  $Ag_2O$  at the surface, causing the detrimental loss of their plasmonic properties.

The performance of the plasmonic photocatalyst Ag/TiO<sub>2</sub> is a strong function of the size and shape of Ag nanostructures. Tailoring the size and shape of Ag nanostructures enables the control of the properties of Ag surface plasmons, in turn tuning their impact on the photocatalytic activity of TiO<sub>2</sub>. The enhanced photochemical activity of Ag/TiO<sub>2</sub> composite systems is largely dependent on the plasmon-mediated transfer of energy from Ag nanoparticles to TiO<sub>2</sub> to increase the concentration of electron-hole pairs in the composite. In this case, the Ag nanocubes exhibit superior amplifications in the photochemical reactivity relative to that of the Ag nanospheres and nanowires of similar size for identical Ag mass (volume). The enhancement reactivity of nanocubes can be explained by their large extinction cross-section, more specifically, a higher scattering efficiency.

#### 4.2 Au on TiO<sub>2</sub>

Review

The photocatalytic activity of Au/TiO<sub>2</sub> is influenced by various factors including the Au loading, phase composition, particle size, shape, surface area, and spatial structuring. 24,159-161 Studies have shown that smaller Au nanoparticles tend to favor enhanced photocatalytic performance. 162-165 This size effect is attributed to the shift of the Fermi energy to a more negative potential for smaller nanoparticles, reducing the potential difference between the CB of TiO2 and the Fermi level of the metal nanoparticles. As a result, electron accumulation in the metal nanoparticles increases, leading to an upward shift of the Fermi level to the CB of TiO2, promoting rapid electron transfer from TiO2 to metal nanoparticles for improved photooxidation reactions by photoexcited holes. Conversely, chemically aggregated nanospheres or nanorods may not be as beneficial to the photocatalytic activity of TiO<sub>2</sub> due to differences in their co-catalytic efficiency, influenced by factors such as the percentage of surface-active atoms and Fermi energy shifts resulting from changes in size, shape, and surface-to-volume ratio. Nanorods, for instance, might reduce substrate adsorption and block light penetration on the oxide surface, leading to lower photogeneration of charged species and reduced photoactivity. To control the dispersibility of the co-catalyst nanoparticles, Tatsuma et al. prepared Au/TiO2 composites using the electron trap-mediated deposition method, leveraging the electron traps present in TiO2. 166 This method offered higher dispersibility of the Au co-catalyst compared to the photodeposition method whereby the amount of deposited Au could be controlled and preventing overloading.

Numerous studies have demonstrated that plasmonic metals, when integrated with TiO<sub>2</sub> semiconductor in structurally optimized configurations, can significantly boost light absorption. Li et al. developed spinous TiO<sub>2</sub>-based octahedral nanocages through a template-assisted approach, resulting in enhanced photocatalytic performance compared to spinousless nanocages. La et al. designed an oxygen

vacancy-rich 2D Au/TiO<sub>2</sub> hybrid nanosheet derived from 2D Mxene, achieved *via in situ* growth of Au nanoparticles on preformed TiO<sub>2</sub> nanosheets.<sup>170</sup> The synergistic interplay between Au active species and abundant oxygen vacancies from TiO<sub>2</sub> significantly lowered the reaction barrier and improved catalytic reactions. Guo *et al.* fabricated a hierarchical forest-like plasmonic superstructure consisting of vertically printed macro-sized TiO<sub>2</sub> pillar arrays as tree trunks, dense TiO<sub>2</sub> nanorod arrays as branches, and self-assembled Au nanoparticles as leaves. This plasmonic superstructure effectively absorbs light through surface plasmon resonance effects and multiple scattering, offering high light absorption capacity and interconnect mass transfer channels (Fig. 4).

#### 4.3 Multimetals on TiO<sub>2</sub>

Noble metals like Ag, Au, Pt, and Pd serve as potent co-catalysts in  ${\rm TiO_2}$ , offering numerous benefits to the photocatalytic process. They essentially act as electron traps, assisting in the separation and transfer of charges on the semiconductor surface. This facilitates the creation and movement of electron-hole pairs, thereby improving catalytic reactions.

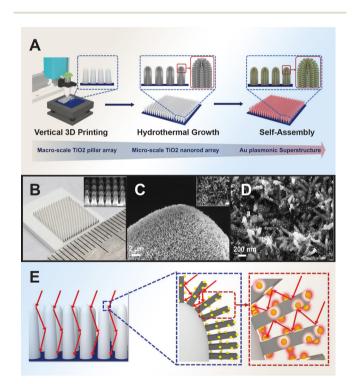


Fig. 4 Fabrication of forest-inspired hierarchical Au plasmonic super-structure. (A) Printing of  ${\rm TiO_2}$  pillar arrays and hydrothermal grown layer of dense  ${\rm TiO_2}$  nanorod arrays, followed by self-assembling Au nano-particles on the hierarchical  ${\rm TiO_2}$  structure. (B) Optical image of a printed  ${\rm TiO_2}$  pillar array. (C) Scanning electron microscopy (SEM) images of the  ${\rm TiO_2}$  nanorods growing on the top surface of a 3D printed  ${\rm TiO_2}$  pillar. (D) SEM image of Au nanoparticles assembled on  ${\rm TiO_2}$  nanorods. (E) Schematic illustration of the light-trapping approaches of Au plasmonic superstructure through the multiple light scattering of the vertically aligned pillars and nanorods in multiscale and LSPR effects of Au nanoparticles. Reproduced with permission from ref. 185. Copyright 2021, Wiley-VCH.

Furthermore, they contribute to modifying the energy levels and band structures of TiO2, broadening its light absorption spectrum to include visible light, and ultimately enhancing its overall photocatalytic performance. 13,171,172 On the other hand, multi-metallic nanoparticles of noble metals represent a novel class of nanomaterials with distinct properties compared to monometallic nanoparticles. 173-176 They offer enhanced versatility and technological utility due to their unique properties and the ability to tune their LSPR properties through configurational and elemental modifications. These multimetallic nanoparticles exhibit multi-functionality, wide tunability, and multiple plasmon bands, making them ideal components for TiO<sub>2</sub> photocatalysts. <sup>179,180</sup> Bimetallic combinations like Au-Ag, 181,182 Au-Pd, 183 and Au-Pt loaded onto TiO<sub>2</sub> have demonstrated efficient photocatalytic activity, due to their ability to efficiently separate electron-hole pairs at the alloy/TiO2 junction. Moreover, controlling the morphology and structure of plasmonic nanoparticles supported on TiO2 can significantly influence product selectivity in photocatalytic reactions.

Studies on visible-light-responsive Au-Ag alloy nanoparticles loaded onto TiO2 have demonstrated successful control over the apparent photocatalytic activity by altering the alloy composition. The photocatalytic reactions were found to be based on plasmon-induced charge separation. 179,186 For instance, colloidal suspensions of Au<sub>x</sub>Ag<sub>1-x</sub> alloys with composition x ranging from 0.2 to 1 exhibit an intense SPR band in the broad visible light range of 420 to 520 nm. When Au<sub>0.3</sub>Ag<sub>0.7</sub> alloy nanoparticles are deposited on TiO<sub>2</sub>, this plasmonic photocatalyst generates SPR at 490 nm, corresponding to the maximum intensity of solar light. 179 The TiO2 photocatalyst containing 1% of each metal (Ag, Au, Pt, Pd) in an alloy structure exhibited a remarkable increase in photoactivity compared to monometallic nanoparticles.

## Defective TiO<sub>2</sub> nanomaterials

Defect engineering in TiO2 involves intentionally introducing imperfections or vacancies into the crystal lattice to tailor its properties for specific applications. The prevalence of these defects has been extensively investigated through theoretical calculations and experimental analyses due to its ability to modify the electronic structure, charge carrier dynamics, and surface reactivity of TiO2. 55,187 Oxygen vacancies and Ti3+ interstitials are two commonly studied defects in TiO2, which are known to influence the electronic properties of TiO2 by generating intermediate bands, hence reducing its band gap. 188,189 Moreover, oxygen vacancies can enhance the donor density and facilitate the separation and mobility of photogenerated electron-hole pairs. 190 By strategically controlling the types and concentrations of defects, defect engineering enables the development of TiO<sub>2</sub>-based materials performance.

Oxygen vacancies are introduced into the TiO2 lattice through various methods, including annealing in an oxygen-

deficient atmosphere or as a byproduct of doping processes involving anions or cations. 125,191 These vacancies can create intermediate energy states within the band gap of TiO2, effectively extending its light absorption into the NIR region. As a result, TiO2 materials with oxygen vacancies exhibit enhanced photoactivity, particularly under visible light irradiation. Black TiO<sub>2</sub>, rich in oxygen vacancies, has been shown to significantly improve the photocatalytic performance compared to white (stoichiometric) TiO2. Additionally, colored TiO2 materials such as blue or gray variants can be obtained through hydrogenation, resulting in sub-stoichiometric oxide. These sub-stoichiometric oxides possess altered chemical compositions and structures, characterized by features like surface disordered shells, oxygen vacancies, Ti3+ centers, and surface hydroxyl groups or Ti-H bonds. 188

In 2011, Chen et al. introduced black TiO2 with a narrowed band gap of 1.5 eV to enhance full spectrum sunlight absorption by subjecting TiO2 nanoparticles to hydrogen thermal treatment.<sup>25</sup> This process induced disorder layers on the TiO<sub>2</sub> surface, resulting in the formation of defective black TiO2-x nanoparticles and giving rise to an increase in photocatalytic activity. Following this, Hu et al. developed black TiO2 hollow spheres with a narrow bandgap using a template-free solvothermal approach. The TiO<sub>2</sub> hollow frameworks, stabilized by encircled protectors like amine molecules, maintained high structural integrity and improved crystallinity of the anatase phase during high-temperature hydrogenation. The thermal hydrogenation process created a disordered shell layer over the crystalline TiO<sub>2</sub> core, with dispersed Ti<sup>3+</sup> within the hollow structure frameworks. The resulting mesoporous black TiO2 hollow spheres exhibited a high photo-response in visible-light absorption and significantly improved photocatalytic activity, attributed to their high crystallinity, hollow structure, Ti<sup>3+</sup> content in the frameworks, and surface disorderliness.

To date, various synthetic techniques beyond hydrogenation have been explored to synthesize black TiO2 with broad spectrum absorption. These methods include metal reduction, plasma-assisted processes, NaBH4 reduction, electrochemical reduction, laser ablation in liquid, and oxidation approaches. 193 In the case of black TiO2 hollow spheres synthesized via aluminum reduction, the formation of oxygen vacancy defects generates mid-gap states, facilitating electron excitation at lower energies. 194 This electron transition from the valence band to the oxygen vacancy mid-levels, or vice versa, enables absorption of visible and infrared light. However, despite these optical enhancements, photogenerated electrons residing at the energy levels of oxygen vacancies are unable to participate in hydrogen production  $(H^+ \rightarrow H_2)$  as their energy levels are situated below the reduction potential of H2O/H2. Consequently, this absence of photocatalytic activity under visible light illumination highlights a limitation in utilizing these oxygen vacancies for hydrogen production.

Sub-stoichiometric titania (TiO<sub>2-x</sub>), also known as colored titania (gray, blue, brown, or black), exhibits efficient light absorption across the UV to the IR region of the solar spectrum. Numerous studies have highlighted its enhanced photo-

activity in various oxidation reactions under visible light compared to ordinary white (stoichiometric)  ${\rm TiO_2}$ .  $^{188,195}$  The synthesis of these materials typically involves thermal treatment of  ${\rm TiO_2}$  in different reducing atmospheres, including vacuum, Ar,  ${\rm H_2/Ar}$ , and pure  ${\rm H_2}$ .  $^{196}$  Generally, increasing the reduction level results in a higher defect density, such as oxygen vacancies and  ${\rm Ti}^{3^+}$  centers, within the  ${\rm TiO_2}$  lattice, leading to darker-colored  ${\rm TiO_2}$  powder.

## 6 Composites of TiO<sub>2</sub> nanomaterials

Composite photocatalysts have emerged as promising materials for overcoming the intrinsic limitations of individual semiconductor photocatalysts. The tailored properties of composite photocatalysts play an essential role in maximizing their photocatalytic performance by improving light absorption, separation, redox capability, charge chemical reactivity. 197,198 For instance, the inclusion of carbon-based materials such as graphene or carbon nanotubes in TiO2based nanocomposites has been particularly effective. When combining TiO<sub>2</sub> with graphene, excited electrons from the conduction band of TiO2 can transfer to graphene through a percolation mechanism. This transfer results in the formation of a heterojunction at the interface which effectively separates the photoinduced electron-hole pairs, thereby suppressing charge recombination. 199 Hybridization with carbon quantum dots results in the formation of new electronic structures and an increase in the photo-response.<sup>200</sup> Combining TiO<sub>2</sub> with various materials such as carbon nitride, metal-organic frameworks, Mxene, and aerogels can lead to the development of advanced composite photocatalysts with enhanced properties and functionalities.

#### 6.1 TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>

Carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) is a 2D polymer composed of carbon and nitrogen atoms arranged in a graphitic structure. Due to its polymeric nature, the surface chemistry of g-C<sub>3</sub>N<sub>4</sub> can be readily modulated through surface engineering at the molecular level.201 In comparison with TiO2, g-C3N4 has a moderate band gap ranging from 2.7 to 2.8 eV, allowing it to absorb visible light with an onset around 450 to 460 nm.<sup>202</sup> Since the metal-free semiconductor was reported to generate hydrogen from water by Wang et al. under visible-light irradiation, 203 g-C<sub>3</sub>N<sub>4</sub> has been widely employed as a guest semiconductor to modify TiO2. The favorable alignment of band positions between g-C<sub>3</sub>N<sub>4</sub> and TiO<sub>2</sub> confers a greater driving force for charge transfer across the heterointerface in constructed  ${
m TiO_2}/$ g-C<sub>3</sub>N<sub>4</sub> heterostructures. This alignment promotes spatial separation of photogenerated electron-hole pairs, consequently enhancing the overall photoconversion efficiency of the system. 204-206

#### 6.2 TiO<sub>2</sub>/MXene

Titanium carbide ( $Ti_3C_2$ , a member of the 'MXene' family) has emerged as a new class of promising 2D materials because of

their unique properties including high conductivity, high chemical stability, and structural, tailored surface chemistry. 207,208 Moreover, Ti<sub>3</sub>C<sub>2</sub> has a large proportion of Ti, which can be readily transformed into TiO2. 209 The Schottky junction formed at the interface between Ti<sub>3</sub>C<sub>2</sub> and TiO<sub>2</sub> could promote the photoinduced charge separation. By a hydrothermal oxidation of layered Ti<sub>3</sub>C<sub>2</sub>, the Ti atoms on Ti<sub>3</sub>C<sub>2</sub> afforded the Ti source and nucleating sites for the in situ growth of highly active (001) facets TiO<sub>2</sub> nanosheets on Ti<sub>3</sub>C<sub>2</sub>, and it also forms an interfacial heterojunction between 2D Ti<sub>3</sub>C<sub>2</sub> and TiO<sub>2</sub> to prevent the defect-induced recombination. This is related to the large gap in work function of the two phases between -OH terminated Ti<sub>3</sub>C<sub>2</sub> (1.8 eV) and TiO<sub>2</sub> (001) surface (4.924 eV), thus hindering the electron transfer from TiO<sub>2</sub> to Ti<sub>3</sub>C<sub>2</sub>, instead allowing the flow of photogenerated holes. As such, the low function -OH terminated Ti<sub>3</sub>C<sub>2</sub> serves as a reservoir of holes through the hole trapping by the Schottky-junction, yielding the spatial separation of photogenerated electrons and holes. 198,210

#### 6.3 TiO<sub>2</sub>/MOF

Metal organic frameworks (MOFs) are a new generation of organic-inorganic hybrid porous materials, making up by metal ions/clusters connected by organic ligands. These structures provide a large surface area and tunable pore sizes, making them excellent candidates for hosting catalytic metal clusters within their frameworks. The metal clusters can function as active sites for catalytic reactions. TiO2 can be synergistically coupled with the catalytic properties of metal clusters within the MOFs structure. This synergy allows for efficient utilization of photoexcited electrons generated by TiO2 in driving catalytic reactions facilitated by the metal clusters. By adjusting parameters such as pore size, surface area, and TiO2 loading, the photocatalytic activity and selectivity of the composite material can be optimized for specific catalytic applications. To give an illustration, combining TiO2 nanosheets with exposed (001) facets and NH2-UiO-66 (MOF) via an in situ growth strategy offers a promising approach for producing bifunctional materials capable of both capturing and photocatalytically reducing cardon dioxide (CO2) under UV-vis light irradiation. This strategy leverages the strengths of TiO2 nanosheets and NH2-UiO-66 MOF while allowing intimate contact between the two components, with the formation of a heterojunction for effective charge transfer.211 Photogenerated electrons from TiO2 can readily transfer to the catalytic sites within MOFs, facilitating gaseous adsorption and subsequent catalytic reactions.

#### 6.4 TiO<sub>2</sub>/COF

Covalent organic frameworks (COFs) are a novel class of crystalline organic polymers constructed from light elements such as carbon, hydrogen, nitrogen, oxygen, and sulfur. These frameworks are linked *via* strong covalent bonds, which bestow them with remarkable stability and robustness. COFs are characterized by unique properties including low density, large surface area, tunable pore size and structure, and easily

customizable functionality. 215-217 Despite these advantages, the photocatalytic performance of pure COFs is limited by high recombination rates of photoinduced electron-hole pairs. To address this limitation, COFs are often integrated with TiO<sub>2</sub> to form composites. TiO2, with its band gap of approximately 3.2 eV, is highly effective in visible light-assisted photocatalysis, making it an ideal candidate for integration with COFs. 218-220 This combination aids in the formation of heterostructures, significantly enhancing the photocatalytic functionality. TiO2/COF composites utilize COFs as efficient photosensors, improving light absorption and overall applicability. The formation of heterojunctions and band gap narrowing in TiO<sub>2</sub>/ COF composites optimizes the interaction between TiO2 and COFs, which have a band gap between 2 and 2.8 eV. This optimization reduces the recombination rate of photoinduced electron-hole pairs, thereby enhancing the production of active species and overall photocatalytic activity. 21,221

#### 6.5 TiO<sub>2</sub>/aerogel

Aerogels are a fascinating class of highly porous materials composed of a network of interconnected nanostructures which exhibit high surface areas, open pores, low densities, and unique physical properties. 222,223 Aerogel can be prepared using sol-gel process followed by supercritical drying, allowing for the production of aerogel in various shapes and sizes that suitable for different applications. Particularly, TiO<sub>2</sub> aerogels consisting of a network of interconnected TiO2 nanoparticles have emerged as a highly favorable architecture, offering ample active sites for photocatalytic reactions and long diffusion pathways for photogenerated electrons. Additionally, TiO2 aerogels have been observed to possess surface trap states where large amounts of photogenerated electrons can be stored upon illumination, which enhances their photocatalytic activity by promoting efficient charge separation and utilization in redox reactions. It was reported that the as-synthesized aerogel can store 1.7 times more electrons relative to commercial anatase nanoparticles. 226

#### 6.6 TiO<sub>2</sub>/other semiconductor composites

Heterojunction photocatalysts are engineered by combining two distinct semiconductor materials. This coupling takes advantage of the unique electronic properties of each semiconductor, creating an interface where efficient charge separation can occur. When these heterojunctions are exposed to light, they generate electron-hole pairs in both semiconductor components. 227-229 The type-II heterojunction, one of the most studied types, features staggered band structures where electrons accumulate in one semiconductor (photocatalyst II) and holes in the other (photocatalyst I), promoting efficient charge separation for photocatalysis. 38,230,231 While the type-II heterojunction configuration enhances charge separation, it also reduces redox ability, which is not ideal for photocatalysis.

Traditional Z-scheme photocatalysts, proposed to address the limitations of type-II heterojunctions, improve charge-separation efficiency while maintaining strong redox abilities.<sup>36</sup> This system consists of two semiconductors with suitable

intermediate couples, such as Fe<sup>3+</sup>/Fe<sup>2+</sup>, IO<sup>3-</sup>/I<sup>-</sup>, and I<sup>3-</sup>/I<sup>-</sup>, arranged in staggered band structures.<sup>232</sup> In operation, photogenerated holes in the VB of photocatalyst I react with electron donors (D), creating electron acceptors (A). Simultaneously, photogenerated electrons in the CB of photocatalyst II react with A, forming D. The retained electrons in the CB of photocatalyst I and holes in the VB of photocatalyst II are then available for reduction and oxidation reactions, respectively.<sup>233</sup> This charge-transfer mode endows the system with strong redox ability and spatially separated redox reaction sites, enhancing photocatalytic performance by facilitating more efficient and selective redox reactions. However, this system is limited to the solution phase, faces side reactions, light shielding issues, and pH sensitivity.234

The all-solid-state Z-scheme was introduced to overcome the limitations of traditional Z-scheme photocatalysts by replacing shuttle redox ion pairs with a solid conductor. In a threecomponent heterojunction (CdS-Au-TiO2), both the holes in CdS and electrons in TiO<sub>2</sub> are injected into Au. 43 This scheme utilizes a solid conductor instead of shuttle redox ion pairs, making it suitable for both liquid and gas applications and significantly shortening the charge-transfer length, thus accelerating charge transfer. 235 In a typical all-solid-state Z-scheme, the CB electrons of photocatalyst II migrate to a solid conductor upon light irradiation and then to the VB of photocatalyst I. This innovation allows for applications in both liquid and gas phases and accelerates charge transfer, significantly enhancing the efficiency of the photocatalytic process. Despite these advancements, it faces challenges such as Schottky barriers, preferential electron transfer leading to neutralization at the conductor, and difficulties in synthesis and assembly.

Direct Z-scheme heterojunctions, evolving from traditional and all-solid-state Z-scheme heterojunctions, refine the concept by eliminating intermediate redox couples or conductors. 236,237 Instead, they couple an oxidative and a reductive photocatalyst based on their VB and CB positions. This setup optimizes charge transfer and enhances photocatalytic activity by ensuring that electrons from the low VB photocatalyst are injected into the VB of the high CB photocatalyst. 47,238 TiO<sub>2</sub>, known for its low VB position, is frequently used as an oxidative photocatalyst and is often coupled with high CB photocatalysts such as CdS, 237 ZnIn<sub>2</sub>S<sub>4</sub>, <sup>239</sup> and Cu<sub>2</sub>O. <sup>240,241</sup> In this scheme, electrons excited to the CB of the low VB photocatalyst are injected into the VB of the high CB photocatalyst, optimizing charge transfer and enhancing photocatalytic activity.

Despite their advantages, Z-scheme heterojunctions face confusion and theoretical challenges. The S-scheme heterojunction, a recent advancement, addresses the limitations of Z-scheme heterojunctions by improving charge separation and maintaining strong redox abilities. 51,234 It comprises an oxidation photocatalyst (OP) and a reduction photocatalyst (RP), where the RP has more negative CB and Fermi levels, and the OP has more positive VB. Electron transfer from the RP to the OP due to Fermi level differences generates an internal electric field and band bending, enhancing photo-induced carrier

transfer. Under illumination, electrons in the OP's CB migrate to the RP's VB and combine with holes, differing from the type-II mechanism. This carrier transfer resembles a "step" at a macroscopic level and an "N" shape at a microscopic level, optimizing photocatalytic performance. A recent study reveals that the TiO<sub>2</sub>/perovskite (CsPbBr<sub>3</sub>) S-scheme heterojunction demonstrates electron transfer from CsPbBr<sub>3</sub> quantum dots to TiO<sub>2</sub>, resulting in an internal electric field directed from CsPbBr<sub>3</sub> to TiO<sub>2</sub> upon hybridization. Upon light irradiation, this internal electric field drives the photoexcited electrons in TiO<sub>2</sub> to CsPbBr<sub>3</sub>, forming an S-scheme heterojunction in the TiO<sub>2</sub>/CsPbBr<sub>3</sub> nanohybrids that significantly

enhances electron-hole pair separation. However, the

S-scheme is still in its early stages and requires further

research to overcome significant conceptual and practical challenges.

### 7 Applications of TiO<sub>2</sub> nanomaterials

The objective of engineering functional TiO<sub>2</sub> materials with tailored electronic properties through morphological control, crystal phase manipulation, doping, and hybridization, is to optimize their performance in photocatalytic applications. Extensive efforts have been dedicated to leveraging TiO<sub>2</sub> for a wide range of photooxidation reactions such as photodegradation of organic pollutants and photocatalytic disinfection (Tables 1–5). Furthermore, TiO<sub>2</sub> has shown promise in photo-

Table 4 Overview of noble metal modified TiO<sub>2</sub> photocatalyst in environmental remediation applications

Photocatalysts	Synthesis methods ( $TiO_2/noble$ metals)	Pollutants	Degradation efficiency	Ref
Ag nanoparticles/ mesoporous TiO <sub>2</sub>	Pyrolysis/photodeposition	(i) Methylene blue, (ii) Phenol	(i) >90% in 300 min, (ii) 85% in 210 min under visible light	260
Ag/TiO <sub>2</sub> particles	Commercial/electrochemical method	2-Chlorophenol	94% in 6 h under UV light	415
Amine-adsorbed Ag/ TiO <sub>2</sub> particles	Sol-gel	Phthalic acid	>90% in 210 min under visible light	416
Ag/TiO <sub>2</sub> nanoparticles	Chemical synthesis	Methylene blue	89.2% in 60 min under solar light	417
Biochar-coupled Ag and TiO <sub>2</sub> particles	Hydrolysis/photodeposition	Methyl orange	85.38% in 60 min under UV light	418
Ag/TiO <sub>2</sub> particles	Laser pyrolysis/wet impregnation and chemical reduction	Methyl orange	90% in 120 min under visible light	419
Ag/β-cyclodextrin TiO <sub>2</sub> membrane	Hydrothermal method/ electrospinning	Dimethyl-hydrazine	96.8% in 80 min under visible light	270
Au/TiO <sub>2</sub> nanotubes	Electro-spinning/deposition- precipitation	Methylene blue	>80% in 140 min under visible light	420
Mesoporous Au/TiO <sub>2</sub>	Sol gel/deposition- precipitation	Safranin-O	97% in 60 min under UV light and 87% in 90 min under solar light	421
One-dimensional Au/	Chemical synthesis/	(i) Rhodamine B,	(i) >90% in 60 min under UV and >80% in	422
TiO <sub>2</sub> nanoforests	photoreduction	(ii) <i>p</i> -Nitrophenol, (iii) Phenol	60 min under visible light, (ii) >40% in 60 min under UV light, (iii) >45% in 60 min under UV light	
Au/TiO <sub>2</sub> nanofibers	Electro-spinning	(i) Methylene blue, (ii) Rhodamine B	(i) 88% in 3 h under solar light, (ii) >90% in 3 h min under solar light	12
Au/TiO <sub>2</sub> film	Commercial/sputtering	Methylene blue	60% in 60 min under 532 nm laser	423
Au/TiO <sub>2</sub> nanostructures	Chemical synthesis	Methylene blue	97% in 150 min under visible LED light	168
Au/TiO <sub>2</sub> nanorod	Hydrothermal/wet impregnation	Bisphenol A	40% in 120 min under visible light $(\lambda_{ m max} = 520 \  m nm)$	164
Pt/TiO <sub>2</sub> particles	Commercial/Photo-deposition	(i) Acetaminophen, (ii) Panadol	(i) 99% and (ii) 83% in 180 min under simulated solar light	424
Pt/TiO <sub>2</sub> @polymeric matrix	Commercial/chemical- reduction	Methylene blue	83% in 130 min under UV and 94% in 400 min under sunlight	262
Pd/TiO <sub>2</sub> particles	Chemical synthesis/photo- deposition	Amoxicillin	97.5% in 5 h under visible light	425
Pd/TiO <sub>2</sub> particles	Chemical synthesis/incipient wetness impregnation	Methyl violet	95% in 20 min under UV light	426
Pd/TiO <sub>2</sub> particles	Sol-gel	<ul><li>(i) Methylene blue,</li><li>(ii) Methylene orange</li></ul>	(i) 99.4% and (ii) 92.6% in 120 min under UV light	263
Pd/TiO <sub>2</sub> films	Sol-gel	Phenol	80% in 5 h under UV light and 23% in 5 h under visible light	427
Au/Pt–TiO <sub>2</sub> nanopillar arrays	Glancing angle deposition/ successive ion layer adsorption and reaction	Methyl orange	40% in 120 min under UV light	184
Ag@Au/TiO <sub>2</sub> nanotubes	Electro-chemical anodization/ displacement reaction	(i) Methyl orange, (ii) Cr(ɪv) ions	(i) 98.1% and (ii) 70.2% in 120 min under solar light	428
Au <sub>0.4</sub> Ag <sub>0.6</sub> /TiO <sub>2</sub>	Chemical synthesis	Methylene blue	99% in 120 min under visible light	261
$Ag_{0.1}Au_{0.1}Pt_{0.1}Pd_{0.1}/TiO_2$	Sol gel/ions reduction	Toluene	86% in 60 min under LED light ( $\lambda_{\text{max}} = 465 \text{ nm}$ )	429

Table 5 Overview of TiO<sub>2</sub> heterojunction photocatalyst in environmental remediation applications

Photocatalysts	Synthesis methods	Pollutants	Degradation efficiency	Ref.
TiO <sub>2</sub> /Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> composite	Hydrothermal	Carbamazepine	98.67% in 240 min under UV light and 55.83% in 8 h under solar light	210
BiOBr/TiO <sub>2</sub>	Solvothermal	Rhodamine B	99.9% in 10 min under visible light	265
$In_2S_3/TiO_2$	Hydrothermal	Rhodamine B	98% in 10 min under simulated solar light	430
rGO/TiO <sub>2</sub> -B/W <sub>18</sub> O <sub>49</sub>	Solvothermal	Rhodamine B	100% in 15 min under full solar-spectrum	264
C-MoS <sub>2</sub> /TiO <sub>2</sub>	Hydrothermal	Methylene blue	99% in 60 min under simulated solar light	266
CdO/TiO <sub>2</sub>	Sol-gel	Imazapyr herbicide	100% in 180 min under visible light	272
Pt/Nb <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	Photodeposition	(i) Diclofenac, (ii) Ketoprofen	(i) 100% in 20 min under UV light, (ii) 100% in 60 min under UV light	431
Bi <sub>2</sub> O <sub>3</sub> /rGO/TiO <sub>2</sub>	Hydrothermal	Tetracycline	94.3% in 90 min under visible light	278
Bi <sub>2</sub> O <sub>3</sub> /Ti <sup>3+</sup> -TiO <sub>2</sub>	Hydrothermal	Tetracycline	100% in 200 min under visible light ( $\lambda > 420 \text{ nm}$ )	432
TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	Hydrothermal	Ciprofloxacin	93.4% in 60 min under simulated solar light	279
$g$ - $C_3N_4$ @ $C$ - $TiO_2$	Hydrothermal	(i) Rhodamine B, (ii) Phenol	(i) 97% in 90 min under visible light, (ii) 92% in 60 min under visible light	433
Cu–Ni/TiO <sub>2</sub>	Chemical method	Gaseous acetaldehyde	88% in 180 min under UV light and 56% in 180 min under visible light	282
TiO <sub>2</sub> -RGO/LDHs	Hydrothermal	Gaseous: (i) toluene, (ii) methanol, (iii) ethyl acetate	(i) 69.9%, (ii) 91.6%, (iii) 99.9% in 60 min under simulated sunlight ( $\lambda \ge 350$ nm)	283

reduction reactions including hydrogen generation through water splitting (Table 6), carbon dioxide reduction (Table 7), nitrogen fixation (Table 8), hydrogen peroxide generation (Table 9), alcohol oxidation (Table 10) and even in photochromic applications. These advancements in TiO<sub>2</sub> photocatalysis aim to unlock the full potential of TiO2 in addressing environmental challenges in water and air pollution as well as advancing sustainable energy solutions.

#### 7.1 Photodegradation for environmental remediation

The rapid growing global populations, urbanization and industrialization have caused severe environmental impact such as global warming, climate change, and pollution. Water pollution is a major global environmental issue with detrimental effects on human health and the ecosystem, resulting from discharge of industrial effluent wastes, pharmaceutical wastes and leaching high content of organic substances such as fertilizers and chemical pesticides aqueous environments. 244-246 According to World Health Organization, an estimated 3.4 million deaths annually are attributable to water-related diseases. Moving forward, half of the world's population will be living in water-stressed areas by 2025. Therefore, re-use of wastewater and to recover water is becoming an important strategy, particularly the world's supply of fresh water is scarce. Over the last decades, Advanced Oxidation Processes (AOPs) have been regarded as effective methods in water purification and wastewater treatment. These processes are light-induced (UV or near-UV) and based on the generation of hydroxyl radicals to oxidize the harmful organic pollutants.<sup>247</sup> Examples of the AOPs processes include ozonation, electrochemical processes, direct decomposition of water and photocatalysis (Fig. 5A). 248,249

Photocatalysis stands out as one of the most successful and thoroughly investigated AOP. Its application offers a sustainable and environmentally friendly solution to address pollution challenges by utilizing light energy to initiate chemical

reactions without producing additional pollutants. This technology finds widespread use in various photodegradation applications, encompassing the elimination of organic pollutants, dyes, and harmful chemicals from both air and water sources. Through photocatalysis, harmful contaminants can be efficiently degraded and transformed into harmless byproducts, contributing to cleaner and healthier environments. The photodegradation of various organic molecules/dyes and photocatalytic disinfection of microbial contaminants in the presence of TiO<sub>2</sub> photocatalyst were reviewed and summarized in Table 1.

7.1.1 Photodegradation of organic dves. The development of TiO2 photocatalysts with enhanced activity has been achieved through facet-engineering strategies. Specifically, (001)-exposed anatase TiO2 nanosheets were prepared to optimize the photodegradation of Rhodamine B molecules. 250 Various anatase TiO2 nanostructures with different sizes and morphologies were synthesized by tuning the hydrolysis rates of reaction precursors under solvothermal conditions. These nanostructures significantly enhanced the photocatalytic degradation of Rhodamine B, with the TiO<sub>2</sub> nanosheet photocatalyst achieving nearly complete degradation 15 minutes of irradiation, approximately twice the efficiency of P-25 TiO2. The enhancement is attributed to the nanosheets' larger specific surface areas and active surfaces, which enable greater dye molecule adsorption and light absorption. Moreover, the nanosized effect of the thin nanosheets contributes to reduced bulk electron-hole recombination, faster interfacial charge carrier transfer, and easier charge carrier trapping

In recent studies on TiO<sub>2</sub> facet engineering, a series of anatase TiO<sub>2</sub> nanoparticles with varying percentages of (001) and (101) facets were synthesized via the hydrothermal method.<sup>251</sup> By adjusting the hydrofluoric acid concentration, the (001) facet percentage was increased to nearly 100%. However, excessive hydrofluoric acid dissolved small crystal

Table 6 Overview of TiO<sub>2</sub>-based photocatalyst in photocatalytic water splitting for hydrogen production

	Synthesis methods	Light source	$ m H_2$ generation rate	Quantum efficiencies	Ref.
TiO <sub>2</sub> hollow spheres	Solvothermal/chemical reduction	300 W Xe lamp	$0.182 \text{ mmol g}^{-1} \text{ h}^{-1}$	ı	292
TiO <sub>2</sub> hollow sphere	Al reduction	300 W Xe lamp	$56.7 \text{ mmol h}^{-1} \text{ g}^{-1}$	90.6% (365 nm)	194
TiO <sub>2</sub> microspheres	Confinement reduction route	Visible light $(\hat{\lambda} > 400~\mathrm{nm})$	$42.6 \mathrm{\mu mol}\mathrm{h}^{-1}$	12.7% (420 nm) and 2.8% (520 nm)	189
$Sr-TiO_{2-x}$ ( $x = 0.3\%$ ) + Pt co-catalyst	Template assisted synthesis	300 W Xe lamp	$19442~\mu mol~g^{-1}~h^{-1}$		400
Rh-loaded TiO,	Impregnation/calcination/hydrogenation	Solar simulator with AM 1.5G filter	$7.27 \text{ mmol g}^{-1} \text{ h}^{-1}$	0.0231% (420 nm)	434
Carbonate-doped phase-junction TiO <sub>2</sub>	Emulsion electrospinning method	Solar simulator with AM 1.5G filter	6108 $\mu$ mol $h^{-1}$ $g^{-1}$	83% (365 nm)	290
Anatase/rutile TiO <sub>2</sub> with hydrogenated heterophase interface structures	Hydrothermal/hydrogenation	UV-vis light, $100~\mathrm{mW~cm^{-2}}$	$136.5~\mu mol~cm^{-2}~h^{-1}$	I	289
Anatase/rutile TiO <sub>2</sub>	MOF-mediated synthesis	UV-vis light, 300 W Xe lamp	$1394  \mu mol  g^{-1}  h^{-1}$	1	294
${ m Ti}_3{ m C}_2/{ m TiO}_2$ nanoflowers	Oxidation and alkalization/ion exchange and calcination	300 W Xe arc lamp	$526  \mu mol  g^{-1}  h^{-1}$	5.86% (350 nm)	208
TiO <sub>2</sub> /Ti-MOF + Pt co-catalyst	Solvothermal	300 W Xe lamp (420–760 nm)	$12.4 \text{ mmol g}^{-1} \text{ h}^{-1}$	19.17% (420 nm)	295
PdAu-TiO <sub>2</sub> -aerogel	Wet chemistry synthesis/supercritical drying	Solar simulator, 100 mW cm <sup>-2</sup>	$22 \mu mol g^{-1} h^{-1}$	` ,	222
Pd-TiO <sub>2</sub> -aerogel	Microwave synthesis/supercritical drying	Visible light (400–800 nm)	$117.5 \text{ mmol g}^{-1} \text{ h}^{-1}$	30.9% (430 nm)	302
N-TiO <sub>2</sub> -aerogel	Plasma-enhanced chemical vapor deposition	Visible-light irradiation	$3.1 \text{ mmol g}^{-1} \text{ h}^{-1}$	5.6% (450 nm)	300
TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub> core–shell fibers	Electrospinning	$300 \text{ W Xe lamp } (\lambda \ge 420 \text{ nm})$	$436  \mu mol  g^{-1}  h^{-1}$	,	435
TiO <sub>2</sub> microflowers/g-C <sub>3</sub> N <sub>4</sub>	Hydrothermal	350 W Xe lamp	$4128  \mu mol  g^{-1}  h^{-1}$	1	436
CdS/TiO <sub>2</sub> nanofibers	Electrospinning	350 W Xe lamp	$2.32 \text{ mmol g}^{-1} \text{ h}^{-1}$	10.14%	437
ZnIn <sub>2</sub> S <sub>4</sub> /TiO <sub>2</sub> heterostructure	Hydrothermal	300 W Xe arc lamp	$6.03 \text{ mmol } \text{g}^{-1} \text{ h}^{-1}$	10.49% (365 nm)	438
TiO <sub>2</sub> /NiCo <sub>2</sub> S <sub>4</sub> core-shell structure	Solvothermal	300 W Xe lamp	$8.55 \text{ mmol g}^{-1} \text{ h}^{-1}$	,	439
Bi <sub>2</sub> WO <sub>6</sub> /TiO <sub>2</sub> heterostructure	Solvothermal	300W Xe lamp	$12.9 \text{ mmol g}^{-1} \text{ h}^{-1}$	1	440
TiO <sub>2</sub> /ZnTe/Au nanocorncob	Hydrothermal	300W Xe lamp	$3344.0  \mu \text{mol}  \text{g}^{-1}  \text{h}^{-1}$	1	441
Multi-edged TiO <sub>2</sub> @Ru atoms	Chemical synthesis	300W Xe lamp	$323.2 \mu mol h^{-1} per 50 mg$	1	53
Ru single atoms-Ru ${\rm O_2/TiO_2}$	Solvothermal/impregnation-adsorption	$300 \mathrm{~W~Xe~lamp,}~200 \mathrm{~mW~cm}^{-2}$	$2.91 \text{ mmol g}^{-1} \hat{h}^{-1}$	2.24% in benzyl-alcohol	297
				(365 nm)	

Table 7 Overview of TiO<sub>2</sub>-based photocatalyst in CO<sub>2</sub> photoreduction

Photocatalysts	Synthesis methods	Light source	Gas generation rate	Quantum efficiencies	Ref.
Eu-TiO <sub>2</sub> nanoparticles	Sol-gel	300 W Xe arc lamp	65.53 $\mu$ mol g <sup>-1</sup> (CH <sub>4</sub> ) and 42.91 $\mu$ mol g <sup>-1</sup> per 9 h (CO)	I	442
Ag/TiO <sub>2</sub> nanoparticles Cu <sub>0.8</sub> Au <sub>0.2</sub> /TiO <sub>2</sub>	Chemical synthesis Photodeposition	300 W Xe lamp with AM 1.5G filter 300 W Xe lamp (500 mW cm <sup>-2</sup> ) with AM 1.5G filter	46 mmol $g^{-1}$ $h^{-1}$ (CH <sub>4</sub> ) 3578.9 µmol $g^{-1}$ $h^{-1}$ (CH <sub>4</sub> ) and 369.8 µmol $g^{-1}$ $h^{-1}$ for C <sub>2</sub> H <sub>4</sub>	1.1	308 312
N-doped carbon dots decorated TiO <sub>2</sub> hollow spheres	Chemical synthesis	300 W Xe arc lamp	$26.8 \mu \text{mol h}^{-1} \text{g}^{-1} (\text{CH}_4)$	0.87% (365 nm)	443
TiO <sub>2</sub> /NH <sub>2</sub> -UiO-66 (MOF) TiO <sub>2</sub> /MIL-101-Cr-NO, (MOF)	Hydrothermal/microwave Chemical synthesis	UV-vis light $(\lambda > 325 \text{ nm}, 300 \text{ W})$ 300 W Xe lamp	1.8 µmol g <sup>-1</sup> h <sup>-1</sup> (CO) 12 mmol g <sup>-1</sup> h <sup>-1</sup> (CO and CH,)	— 11.3% (350 nm)	309
Cu/TiO <sub>2</sub> -aerogel	Hydrothermal/supercritical drying	UV-A/vis light (320–500 nm)	28.2 $\mu$ mol $g^{-1} h^{-1}$ (CO)		314
Pd-porphyrin-based polymers coated hollow TiO <sub>2</sub>	Chemical synthesis	300 W Xe lamp (325–780 nm)	48 $\mu mol~g^{-1}~h^{-1}$ (CH <sub>4</sub> ) and 34.0 $\mu mol~g^{-1}$ h <sup>-1</sup> (CO)	I	311
TiO <sub>2</sub> @polydopamine hollow spheres	Chemical synthesis	350 W Xenon lamp	$1.50  \mathrm{\mu mol}  \mathrm{g}^{-1}  \mathrm{h}^{-1}  (\mathrm{CH_4})$	I	444
(001)TiO <sub>2</sub> -g-C <sub>3</sub> N <sub>4</sub> /BiVO <sub>4</sub> nanosheet	Solvothermal	300 W Xe lamp with 420 nm cut-off filter	65 $\mu$ mol g <sup>-1</sup> per 4 h (CH <sub>4</sub> )	1	320
ZnIn <sub>2</sub> S <sub>4</sub> nanosheets/TiO <sub>2</sub> nanobelts	Solvothermal	300W Xe lamp	1.135 $\mu$ mol $g^{-1} h^{-1} (CH_4)$	I	239
$C-TiO_2/\beta-Bi_2O_3$	Chemical synthesis	300DUV Xe lamp with AM 1.5G filter	$31.07  \mu\text{mol g}^{-1}  h^{-1} \text{ (CO)}$	1	445
TiO <sub>2</sub> /CsPbBr <sub>3</sub> nanofibers	Electrospinning/colloidal synthesis	300 W Xe arc lamp	9.02 $\mu$ mol g <sup>-1</sup> h <sup>-1</sup> (CO)	I	243

Table 8 Overview of TiO<sub>2</sub>-based photocatalyst in N<sub>2</sub> fixation

Photocatalysts	Synthesis methods	Light source	$\mathrm{NH}_3$ generation rate	Quantum efficiencies	Ref.
Defective TiO <sub>2</sub> nanoparticles	Sol-gel	300 W Xe lamp (full spectrum)	$324.86 \text{ mmol g}^{-1} \text{ h}^{-1}$	1.1% (365 nm)	325
Defective TiO <sub>2</sub> particles	Hydrothermal	300 W Xe lamp (full spectrum)	$64.82 \mu mol g^{-1} h^{-1}$		446
Defective TiO <sub>2</sub> nanotubes	Hydrothermal	300 W Xe lamp (full spectrum)	1.2 mmol $L^{-1} h^{-1}$	I	330
Defective Cu-TiO <sub>2</sub> nanosheets	Hydrothermal	300 W Xe lamp (full spectrum)	$78.9 \ \mu mol \ g^{-1} \ h^{-1}$	0.08% (600 nm) and 0.05% (700 nm)	52
Ru atom decorated TiO <sub>2</sub> nanosheets	Hydrothermal	300 W Xe lamp	$56.3  \mu \mathrm{g  g^{-1} h^{-1}}$	,	328
Defective C-TiO <sub>2</sub>	Calcination	300 W Xe lamp (200–800 nm)	$84 \mu mol g^{-1} h^{-1}$	0.04% (400 nm) and 0.01% (420 nm)	326
$Mo_2C/TiO_2$	Sintering	300 W Xe lamp (UV)	$432  \mathrm{\mu g  g^{-1}  h^{-1}}$	0.1% (365 nm)	329
$TiO_2@C/g-C_3N_4$	Calcination	300 W Xe lamp with 420 nm cutoff filter	$250.6 \text{ mmol g}^{-1} \text{ h}^{-1}$	0.14% (420 nm)	327
Ce/S co-doped TiO <sub>2</sub>	Chemical synthesis	300 W Xe lamp with 420 nm cutoff filter	$382.4 \text{ mmol g}^{-1} \text{ h}^{-1}$	3.32% (420 nm)	447
N-TiO <sub>2</sub> hollow microspheres	Hydrothermal	300 W Xe lamp $(\lambda > 400 \text{ nm})$	$80.09  \mu\text{mol } \text{g}^{-1}  \text{h}^{-1}$	0.07% (375 nm)	114
N-TiO,/Ti,C,	Hydrothermal	$500 \text{ W Xe lamp (100 W cm}^{-2})$	$415.6 \text{ umol } ^{\circ} ^{-1} \text{ h}^{-1}$		32

Table 9 Overview of TiO<sub>2</sub>-based photocatalyst in H<sub>2</sub>O<sub>2</sub> generation

Photocatalysts	Synthesis methods	Light source	Quantum $H_2O_2$ generation rate efficiencies	Quantum efficiencies	Ref.
${ m TiO}_{2-x}/{ m G_3N_5}$ ${ m Au/Bi}_2{ m O_3}-{ m TiO}_2$ ${ m TiO}_2/{ m ZnIn}_2{ m S}_4$	Hydrothermal/polymerization and solvent exfoliation 300 W Xe lamp Chemical synthesis/deposition 300 W Xe lamp Chemical synthesis/solvothermal Simulated natural 4100 nm < 3.4.7	300 W Xe lamp 300 W Xe lamp Simulated natural light source (400 mm < ½ < 760 nm, 100 mW cm <sup>-2</sup> )	2.93 µmol L <sup>-1</sup> min <sup>-1</sup> — 339 11.2 mM per 12 h — 448 1530.59 µmol g <sup>-1</sup> h <sup>-1</sup> 10.39% (400 nm) 19	  10.39% (400 nm)	339 448 19
TiO <sub>2</sub> /Au/MXene TiO <sub>2</sub> @BTTA (COF) TiO <sub>2</sub> /Bi <sub>2</sub> O <sub>3</sub> on polystyrene spheres S-doped g-C <sub>3</sub> N <sub>4</sub> /TiO <sub>2</sub>	Hydrothermal, photodeposition Electrospinning/chemical synthesis Hydrothermal/photodeposition Chemical synthesis/electrostatic self-assembly	UV light (360 nm < $\lambda$ < 380 nm, 1 mW cm <sup>-2</sup> ) 300 W Xe lamp ( $\lambda$ = 350-780 nm, 0.64W cm <sup>-2</sup> ) 300 W Xenon arc lamp ( $\lambda$ = 350-780 nm) 300 W Xe lamp	6.80 mg per L per 4 h 740 $\mu$ mol L <sup>-1</sup> h <sup>-1</sup> 1.15 mM h <sup>-1</sup> 2128 $\mu$ mol h <sup>-1</sup> g <sup>-1</sup>		341 342 54 340

**Fable 10** Overview of TiO<sub>2</sub>-based photocatalyst in selective oxidation of alcohol

Photocatalysts	Synthesis methods	Light source	Alcohol	Product	Solvent	Conv. %	Sel.	Ref.
$Gd$ -TiO $_2/poly(o$ -phenylenediamine) nanowires	Hydrothermal/photopolymerization	Simulated solar light	Benzyl alcohol Benzaldehyde Acetonitrile	Benzaldehyde	Acetonitrile	0.96	97.5	346
$TiO_2/Ti_3C_2$	Hydrothermal	300 W Xe lamp (385–740 nm)	Furfuryl alcohol	Furfural	Acetonitrile	66<	66<	22
${\rm TiO_2/Ti_3C_2}$	Chemical synthesis/calcination oxidation	300 W Xe lamp	Benzyl alcohol	Benzaldehyde	<i>n</i> -Hexane	26	86	343
${ m TiO_2}$ (a) COF	Hydrothermal/chemical synthesis	White LED (5 W, $\lambda = 420-780 \text{ nm}$ , 150 mW cm <sup>-2</sup> )	Benzyl alcohol Benzaldehyde Acetonitrile	Benzaldehyde	Acetonitrile	92.5	6.96	21
${ m COF}$ (a) TiO $_2$ core-shell heterojunction	Chemical synthesis	$300 \text{ W Xe lamp}$ $(\lambda \ge 420 \text{ nm})$	Benzyl alcohol	Benzaldehyde Benzotri- fluoride	Benzotri- fluoride	84	93	218

Conv. %: conversion % and Sel %: selectivity %.

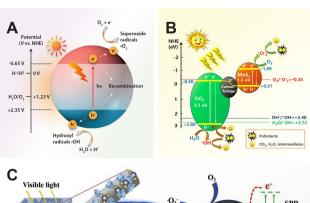
seeds, disrupting crystal growth balance. Optimal photocatalytic efficiency for Rhodamine B decomposition was achieved with 73% exposed (001) facets. Additionally, nanoflower-like rutile  ${\rm TiO_2}$  was synthesized and immobilized on basil seeds for methylene blue photodegradation. This structure, with small particle size and large surface area, enhanced adsorption and degradation, achieving a 98.95% removal efficiency under solar light within 180 minutes.

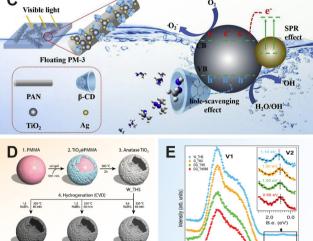
Metal ion doping in TiO2 significantly enhances its photoproperties, particularly for photodegradation catalytic applications. 66,253,254 Li-doped TiO<sub>2</sub> shows up to 2.2 times higher efficiency than undoped TiO<sub>2</sub> 67 and up to 5 times higher efficiency than commercial P25 under visible light.<sup>255</sup> Specifically, doping TiO<sub>2</sub> with 1.0 mol% Li<sup>+</sup> lowers the anataseto-rutile transformation temperature and creates a mixedphase composition of 27.1% rutile and 72.9% anatase at 550 °C, significantly improving the photocatalytic degradation rate of methyl orange.<sup>67</sup> In addition, transition metal ion doping with Al, Cu, Mo, and W also boosts photocatalytic performance for Rhodamine B dye degradation. 256 Al and Cu doping increased activity to 70%, while Mo and W doping achieved 96% under visible light irradiation for 60 minutes. Surface analysis shows that Mo and W doping introduces surface hydroxyl groups essential for photodegradation and increases surface acidity, particularly in W-doped TiO2, which enhances its affinity for chemical particles with unpaired electrons.

The source of dopant and the doping process significantly influence nitrogen incorporation in N-doped TiO<sub>2</sub> nanoparticles. Acidic doping using HNO<sub>3</sub> incorporates nitrogen into substitutional positions, while doping with urea results in interstitial positions, both enhancing photocatalytic activity in the visible range.<sup>257</sup> N-doped TiO<sub>2</sub> from the acidic process demonstrates superior photodegradation of methyl orange due to better UV-visible light absorption. In P-doped TiO<sub>2</sub>, phosphorus doping in the form of P<sup>5+</sup> inhibits crystalline growth, increases surface area, and narrows band gap energies, leading to effective methylene blue degradation.<sup>258</sup> Cationic S-doped TiO<sub>2</sub>, with sulfur atoms as S<sup>4+</sup> substituting lattice Ti atoms, shifts the absorption edge to a lower energy level, enabling visible light photocatalytic degradation of methylene blue and 2-propanol at longer wavelengths.<sup>259</sup>

Incorporating Ag nanoparticles into TiO<sub>2</sub> enhances photocatalytic activity due to plasmonic effects. Ag/TiO<sub>2</sub> composites with 50–100 nm Ag nanoparticles show improved degradation of methyl blue and phenol under simulated sunlight, due to better charge carrier separation and plasmon-enhanced light absorption. However, excessive Ag loading can reduce efficiency by covering active sites and promoting electron-hole recombination. Similarly, TiO<sub>2</sub>/Au nanofiber composites achieve high photocatalytic performance, with 88% degradation of methylene blue and nearly complete degradation of Rhodamine B under solar light. This is attributed to plasmonic hot electrons from Au nanoparticles and efficient charge separation at the Au–TiO<sub>2</sub> interface. Bimetallic Au–Ag/TiO<sub>2</sub> composites further enhance photocatalytic activity. The pres-

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Fig. 5 (A) Schematic illustration of a general photodegradation mechanism of  $TiO_2$  semiconductor. (B) Mechanism of Z-scheme heterojunction C-MoS/ $TiO_2$  photocatalyst for organic pollutant degradation under solar light. Reproduced with permission from ref. 266. Copyright 2022, Elsevier. (C) Photodegradation with Ag/ $\beta$ -cyclodextrin co-doped  $TiO_2$  floating photocatalytic membrane. Reproduced with permission from ref. 270. Copyright 2020, Elsevier. (D) Synthesis of  $TiO_2$  hollow spheres by a hard template-based method, followed by chemical reduction under controlled conditions. (E) X-ray photoelectron spectroscopy characterization showing the valence band spectra and a zoom of the fundamental gap region of the colored  $TiO_2$  hollow spheres, where defect states (V2) are detected. Reproduced with permission from ref. 55. Copyright 2023, Wiley-VCH.

ence of Au–Ag alloy nanoparticles shifts the light absorption from UV to visible spectrum and improves plasmonic effects, resulting in up to 99% degradation of methylene blue under visible light.<sup>261</sup>

Encapsulating TiO<sub>2</sub> within a polymer matrix and coating it with Pt nanoparticles enhances photocatalytic degradation of methylene blue. The Pt/TiO<sub>2</sub> composite achieved 83% degradation under UV light in 130 minutes and 94% under direct sunlight in 400 minutes. Similarly, a Pd/TiO<sub>2</sub> photocatalyst degraded binary dyes, achieving 83.4% mineralization of methylene blue and 75.3% of methyl orange under UV light in 180 minutes, with methylene blue degrading faster due to its thiazine structure compared to the azo bond in methyl

orange.  $^{263}$  Au/Pt-modified  $^{10}$  nanopillar arrays further improved photocatalytic efficiency. Depositing  $\sim$ 4 nm Au/Pt nanoparticles onto the arrays enhanced UV and visible light absorption, leading to 21- and 13-times higher photocatalytic efficiency under UV-vis and visible light, respectively.  $^{184}$  This demonstrates the potential of combining noble metal nanoparticles with  $^{10}$ 2 to harness the entire solar spectrum effectively through plasmonic and electron sink effects.

Constructing heterojunctions by coupling two semi-conductors together is one of the most efficient ways for achieving high pollutant degradation efficiency. For example, a Z-scheme reduced graphene oxide (rGO)/TiO<sub>2</sub>-bronze (TiO<sub>2</sub>-B)/  $W_{18}O_{49}$  photocatalyst, composed of rGO, ultra-thin TiO<sub>2</sub>-B nanosheets, and  $W_{18}O_{49}$  nanofibers, can absorb sunlight from ultraviolet to near-infrared regions. <sup>264</sup> This broad absorption spectrum enables the efficient photocatalytic degradation of Rhodamine B by making full use of available light.

A 1D BiOBr/TiO<sub>2</sub> nanorod heterojunction composite was designed through molecular and interface engineering for efficient removal of organic dye.<sup>265</sup> This composite enhances photocatalytic activity by promoting charge migration and separation of photogenerated electron–hole pairs. The heterojunction acts as a nanochannel, facilitating the rapid transfer of photogenerated holes from the VB of BiOBr to the VB of TiO<sub>2</sub> nanorods, leveraging BiOBr's higher VB (+3.04 eV) compared to TiO<sub>2</sub> nanorods (+2.6 eV). This results in superior photodegradation of Rhodamine B, with an apparent rate constant of 0.49 min<sup>-1</sup> and an 88.5% total organic carbon removal ratio. The efficient separation and extended lifetime of charge carriers allow the holes on the VB of TiO<sub>2</sub> nanorods to oxidize Rhodamine B into CO<sub>2</sub> and H<sub>2</sub>O.

A Z-scheme photocatalyst was constructed using a hydrothermal method, combining carbon-modified MoS<sub>2</sub> (C-MoS<sub>2</sub>) sheets with octahedral anatase TiO2 nanocrystals, achieving 99% methylene blue degradation with a low catalyst loading  $(0.2 \text{ g L}^{-1})$  under simulated solar light in 60 minutes. <sup>266</sup> The C-MoS<sub>2</sub> acts as an electron mediator, facilitating efficient electron-hole separation. The electron-rich (101)-faceted TiO<sub>2</sub> supports the Z-scheme recombination of electrons from TiO2's CB and holes from MoS<sub>2</sub>'s VB. The coupling of (101)-exposed TiO<sub>2</sub> and 2H-MoS2, along with solid-state electron mediators 1T-MoS<sub>2</sub> and carbon, enhances light absorption and accelerates charge transfer at the interface, significantly boosting photocatalytic activity compared to P25, MoS2/TiO2, and C-MoS<sub>2</sub> alone (Fig. 5B). The effective separation of electronhole pairs prolongs their lifetime, facilitating oxidation and reduction reactions in the degradation process.

7.1.2 Photodegradation of organic pollutants. Studies have shown that modifying  $TiO_2$  nanorods enhances the photocatalytic activity compared to unmodified P-25  $TiO_2$ . These modifications, including increased surface area, anatase content, crystallite size, and decreased band gap energy, improve photodegradation efficiency of *p*-cresol by facilitating better light absorption, charge carrier generation, and interfacial interactions. In addition, highly crystalline, phase-pure brookite  $TiO_2$  films with pyramidal features have been fabri-

cated *via* chemical vapor deposition for degrading stearic acid.<sup>268</sup> These brookite films exhibit superior photocatalytic activity under UVA (365 nm) irradiation compared to anatase films. Despite having similar electron–hole recombination dynamics, the enhanced performance of brookite is attributed to its more structured morphology and higher surface area.

Non-metal ion doping with sulfur in TiO<sub>2</sub> photocatalysts enhances visible light absorption and reduces the band gap to 2.78 eV due to sulfur-induced structural defects. The sulfur is primarily present as cationic S<sup>6+</sup>/S<sup>4+</sup> species, which enhance photocatalytic oxidation of acetaldehyde by capturing electrons and improving electrical conductivity. Comparative studies reveal that cationic S-doping (S<sup>6+</sup> substituting Ti<sup>4+</sup>) reduces TiO<sub>2</sub> grain size due to the smaller ionic radius of S<sup>6+</sup>, while anionic S-doping (S<sup>2-</sup> substituting O<sup>2-</sup>) increases grain size. Sdoping (Sabstituting O<sup>2-</sup>) increases grain size. Sdoping cationic S-doping leads to enhanced visible light absorption and photocatalytic activity through chemisorbed hydroxyls and photoinduced holes, while anionic S-doping contributes equally through electrons and holes.

The presence of bimetallic alloy nanoparticles, such as Au-Pd, significantly influences the photocatalytic reaction of phenol decomposition. These nanoparticles act as mediators in undesired redox reactions that would otherwise consume photogenerated radicals inefficiently. As a result, they enhance the photo-oxidation efficiency of toxic aromatic compounds like phenol. Furthermore, the TiO<sub>2</sub> photocatalyst supported by Au-Pd demonstrated superior long-term photoactivity, achieving approximately 90% phenol decomposition under UV irradiation.

A floating photocatalytic membrane composed of Ag and β-cyclodextrin co-doped TiO2 has been developed for the dynamic adsorption and degradation of dimethylhydrazine under visible light.<sup>270</sup> This membrane combines the photocatalytic properties of TiO2 with enhanced adsorption capabilities due to β-cyclodextrin, while Ag doping extends the light absorption into the visible spectrum, resulting in efficient degradation of the contaminant. When placed on the surface of shallow water, the membrane exhibits dual functionality through adsorption and photoactivity under visible light and oxygen. The unique cone-shaped structure of β-cyclodextrin, with its hydrophilic outer surface and lipophilic inner cavity, enhances the adsorptive capacity, making it effective in entrapping target pollutants like unsymmetrical dimethylhydrazine. Besides, Ag nanoparticles enhance light absorption via surface plasmon resonance, while TiO2 nanoparticles improve photoresponse performance across UV and visible light regions. Upon excitation, β-cyclodextrin acts as a hole-scavenger, effectively suppressing electron-hole pair recombination (Fig. 5C).

7.1.3 Photodegradation of herbicides and pesticides. The photocatalytic investigation of B-doped  $\text{TiO}_2$  indicates that a concentration range of 0.5–0.8 wt% of interstitial boron is more effective than pure  $\text{TiO}_2$  for degrading four herbicides and pesticides: diuron, o-phenylphenol, 2-methyl-4-chlorophenoxy-acetic acid, and terbuthylazine under simulated solar irradiation. The B-doped  $\text{TiO}_2$  photocatalyst, synthesized via the sol–gel procedure, exhibits a reduction in the crystal size of

 ${\rm TiO_2}$  particles, along with an increase in pore volume and specific surface area compared to pure  ${\rm TiO_2}$ . Furthermore, the presence of boron in interstitial positions within the  ${\rm TiO_2}$  structure restrains the recombination process, thereby enhancing the photocatalytic activity of  ${\rm TiO_2}$ .

To effectively degrade Imazapyr herbicide, mesoporous  $CdO-TiO_2$  nanocomposites were synthesized using a sol–gel method. These nanocomposites demonstrated photodegradation rates that were 12.2 and 24.5 times higher than those of  $TiO_2$  and P25, respectively.<sup>272</sup> To selectively degrade 2,4-dichlorophenoxyacetic acid herbicide and imidacloprid insecticide from water, the combination of molecular imprinting and photocatalysis was investigated. These common agricultural pesticides were used as templates during synthesis and removed through calcination. The synthesized imprinted  $TiO_2$  material selectively interacted with the herbicide and insecticide, demonstrating significantly enhanced photocatalytic activity compared to bare  $TiO_2$ .<sup>273,274</sup>

7.1.4 Photodegradation of pharmaceutical contaminants. The superior photocatalytic activity of triphasic TiO<sub>2</sub> (76% anatase, 7% rutile, 17% brookite) for metformin degradation highlights the importance of polymorphic diversity in TiO<sub>2</sub>-based materials. The combination of multiple phases enhances performance by suppressing electron–hole recombination and improving charge carrier separation. Interestingly, specific surface area did not correlate with photocatalytic activity, as triphasic TiO<sub>2</sub> outperformed pure anatase and pure rutile despite their larger surface areas. This suggests a complex interplay between crystal structure, phase composition, and surface characteristics in determining TiO<sub>2</sub>'s photocatalytic behavior.

Non-metal ion doping in TiO2 has proven effective for degrading various pharmaceutical compounds in wastewater. A 8 wt% B-doped TiO<sub>2</sub> achieved over 75% degradation efficiency for compounds like 2,4-dichlorophenol, bisphenol-A, ibuprofen, and flurbiprofen under visible light.275 A 5 wt% B-doped TiO<sub>2</sub> showed 70% removal efficiency of metoprolol under simulated sunlight, compared to 48% with pure TiO2. 276 The improved performance is due to increased visible light absorption, smaller crystal and particle sizes, mesoporous anatase-rutile structures, and interstitial boron positions reducing electron-hole recombination. Likewise, P-doped TiO2 with surface oxygen vacancies effectively degrades ciprofloxacin under visible light by narrowing the TiO2 band gap and enhancing charge separation.<sup>277</sup> Surface oxygen vacancies act as charge traps and adsorption sites, facilitating efficient photogenerated charge transfer and additional reaction sites.

The effectiveness of nanostructured photocatalysts, particularly TiO<sub>2</sub> hollow spheres made of self-assembled nanoparticles, is driven by their tailored chemical structure and morphology. These hollow spheres leverage a combination of factors such as high surface area and strong light scattering, which concentrate light within a confined volume, increasing absorption probabilities. Hydrogenated or colored TiO<sub>2</sub> hollow spheres, consisting of hierarchically assembled nanoparticles (Fig. 5D), expand solar spectrum absorption up to 1200 nm.<sup>55</sup>

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This engineered surface boosts charge photogeneration, characteri leading to significant photocatalytic efficacy, achieving 82% designs, 3 degradation of ciprofloxacin after 6 hours under simulated sizes and

leading to significant photocatalytic efficacy, achieving 82% degradation of ciprofloxacin after 6 hours under simulated sunlight. Valence band analysis shows prominent O 2p-related states between 3 and 10 eV (V1) and a less intense Ti 3d-derived state at around 1 eV (V2), as highlighted in the inset (Fig. 5E). The binding energy of V2 shifts from 1.10 to 0.95 eV as the TiO<sub>2</sub> hollow spheres transition from white to dark gray, moving closer to the conduction band minimum. The V2/V1 ratio, increasing from 1.7 to 3.0, indicates a higher concentration of oxygen vacancies in the dark gray samples. This analysis highlights the defect characteristics of TiO<sub>2</sub> hollow spheres and their implications for efficient photocatalysis.

The heterostructural TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> nanosheet-based composite have been studied for the photocatalytic degradation of pharmaceuticals compounds. The TiO2 (0 0 1) facet-decorated Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene was synthesized by a hydrothermal process and demonstrated a photocatalytic degradation of 98.67% of the antiepileptic drug carbamazepine, under irradiation.210 The significant degradation enhancement from 60% for the pristine Ti<sub>3</sub>C<sub>2</sub> MXene could be attributed to the extra holes and electrons generated by (001) facets of TiO2 embedded in Ti<sub>3</sub>C<sub>2</sub> sheets, together with Schottky junctions formed between TiO2-MXene interfaces. Findings has revealed that pH was found to have a noteworthy effect on the carbamazepine degradation kinetics, with lower pH values of 3.0-5.0 are more favourable due to the nanocomposite surface being positively charged from H<sup>+</sup> ions. Combined with a strong oxidation ability of TiO2/Ti3C2 photocatalyst, it would ultimately degrade the carbamazepine into CO2 and H2O by the end of the reaction.

A ternary heterojunction composite of Bi<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and rGO was produced *via* a one-step hydrothermal process.<sup>278</sup> This Bi<sub>2</sub>O<sub>3</sub>/rGO/TiO<sub>2</sub> composite exhibited strong visible-light responsiveness and high separation efficiency of photogenerated carriers due to the Bi–Ti heterojunction, resulting in good photocatalytic activity towards tetracycline under visible-light irradiation. Besides, a Z-scheme nanocomposite of 1D/2D TiO<sub>2</sub> nanorods and g-C<sub>3</sub>N<sub>4</sub> nanosheets was successfully fabricated, achieving 93.4% degradation of ciprofloxacin in 60 minutes.<sup>279</sup> Under simulated sunlight irradiation, the nanocomposite's photodegradation rate was 2.3 times higher than that of commercial TiO<sub>2</sub> powder and 7.5 times higher than that of g-C<sub>3</sub>N<sub>4</sub> nanosheets alone.

Recently, photocatalytic foams are emerging as an effective alternative to traditional slurry and supported catalysts due to their unique structural advantages. Their hierarchical porosity, encompassing both macro and micro levels, provides expansive surface areas akin to slurries. This structure facilitates better interaction between pollutants and the photocatalyst surface, overcoming the diffusion limitations typically associated with supported photocatalysts. The development of photocatalytic foams has been significantly advanced by 3D printing technologies. These technologies offer precise control over the design and fabrication process, allowing for the creation of complex structures with tailored porosity and flow

characteristics. By building objects layer by layer from digital designs, 3D printing can produce foams with optimized pore sizes and shapes, enhancing pollutant flow and contact with the photocatalyst surface. Mattia and co-workers introduced 3D printed  $\text{TiO}_2$  foams that are nanoparticle-free, mechanically robust, and photoactive. These foams offer a promising alternative to slurry photocatalysts for the degradation of pharmaceuticals. In their study, the foams were tested using carbamazepine, a common pharmaceutical pollutant in waterways, within a recirculating flow reactor. The results revealed a quantum yield of  $7.6 \times 10^{-3}$  and an electrical energy per order of 67.6 kW h m<sup>-3</sup>. These figures indicate that the 3D printed  $\text{TiO}_2$  foams outperformed traditional  $\text{TiO}_2$  nanoparticle slurries in terms of efficiency and energy consumption. 57

7.1.5 Photocatalytic disinfection. A recent study explored the use of floating  ${\rm TiO_2}$  photocatalysts to remove microbial contaminants from reclaimed water. Anatase phase  ${\rm TiO_2}$  films were deposited on polystyrene beads via magnetron sputtering. Tests on *Escherichia coli (E. coli)* showed that UVB irradiation alone only disrupted the outer membrane, insufficient for effective inactivation. However, combining  ${\rm TiO_2}$  with UVB light significantly improved the inactivation rate of *E. coli* to over 90% in 45 minutes, destroying both the outer membrane and the peptidoglycan layer. <sup>280</sup>

Transition metal ion doping in TiO2, such as Fe-doped TiO2, significantly enhances antibacterial properties. Under 365 nm UV light, Fe-doped TiO<sub>2</sub> samples (1% to 10%) demonstrated inhibition rates of 67.5% to 99.4% against bacterial growth.87 This improvement is due to the formation of oxygen vacancies and a reduced optical gap in TiO2, leading to better light absorption and reactive oxygen species generation, which damage bacterial cells. Fe doping proves effective even against antibiotic-resistant strains like E. coli by generating reactive oxygen species, causing DNA damage, and peroxidizing membrane phospholipids, thus inhibiting respiration. Co-doping with cerium (Ce) and erbium (Er) also enhances antibacterial efficacy. 281 Ce doping reduces the band gap, allowing absorption of both UV and visible light, while Er doping shifts NIR light into the visible range, increasing light absorption. The combination of Ce and Er co-doping inhibits the recombination of photogenerated charge carriers, resulting in antibacterial efficiencies of 91.23% against Staphylococcus aureus and 92.8% against E. coli.

7.1.6 Photodegradation of air pollutants. The photocatalytic degradation of hydrogen sulfide  $(H_2S)$  was investigated using a series of  $TiO_2$  photocatalysts modified by trivalent metal ions such as Al, gallium (Ga), and indium (In). The study revealed that 4% In doped  $TiO_2$  exhibited the highest photocatalytic  $H_2S$  removal efficiency of 100% over a duration of 120 minutes, nearly 3 times higher than that of commercial P25  $TiO_2$ . The incorporation of Group-IIIA metal ions into  $TiO_2$  resulted in the formation of a shallow acceptor level above the valence band in the energy band structure, leading to a slight redshift at the edge of the visible light absorption band and a decrease in the electron–hole recombination rate. Furthermore,  $In^{3+}$  doping into  $TiO_2$  promoted

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photothermal-catalytic oxidation reactions on the surfaces of In-TiO<sub>2</sub>, thereby significantly enhancing the desulfurization efficiency of H2S.

Acetaldehyde, a common volatile organic compound in the environment, was used to assess the photodegradation efficiency of various TiO<sub>2</sub> nanocomposites. In this study, Cu-Ni bimetallic nanowires were incorporated into a TiO2 matrix via a one-step hydrolysis process to form a new heterostructured photocatalyst. 282 This composite achieved photodegradation efficiencies of 88% under UV light and 56% under visible light for flowing acetaldehyde gas. The enhanced performance is attributed to one-dimensional electron pathways, surface plasmon resonance effects, and an improved bimetallic Schottky barrier. This study provides insights into photon-generated carrier separation and transmission in metal-semiconductor networks and presents an effective method for developing bimetal-based heterostructured photocatalysts.

Combining rGO and layered double hydroxides (LDHs) with TiO<sub>2</sub> synthesizes highly efficient sunlight-driven photocatalysts for degrading volatile organic pollutants such as toluene, methanol, and ethyl acetate.<sup>283</sup> The TiO<sub>2</sub>-rGO/LDHs nanocomposite demonstrates superior photodegradation activity compared to pure TiO2 and TiO2-rGO samples. The enhanced performance is due to graphene's expanded light response range and inhibition of electron-hole pair recombination, while LDHs provide more hydroxide ions to accelerate oxidation reactions, resulting in increased radicals and improved pollutant degradation.

#### 7.2 Photocatalytic water splitting for hydrogen production

Fossil fuel combustion is a primary contributor to greenhouse gas emissions and climate pollutants, causing climate change. The urgent need to transition to zero-emission energy sources drives the quest for alternatives to fossil fuels. Hydrogen emerges as a promising candidate, serving as a versatile and clean energy carrier. Through photocatalytic water splitting, hydrogen production becomes feasible using only water and solar light. This process initiates through photoelectric conversion within a semiconducting material, analogous to photovoltaic power generation. Unlike photovoltaic cells requiring external electrocatalysts, 284 photocatalytic systems integrate both photoelectric conversion and catalytic functions within a single particle or composite. This integration allows for the direct conversion of solar energy into chemical energy, enabling the splitting of water molecules into hydrogen and oxygen without the need for additional components. 14,285

Water splitting is an uphill reaction, requiring an external energy input of at least 1.23 V to overcome the thermodynamic barrier associated with breaking the O-H bonds in water molecules and generating hydrogen and oxygen. Photocatalytic process aiming at water splitting is required to provide this minimum energy input to drive the reaction forward. TiO2 stands as the predominant semiconductor in photocatalytic water splitting. The combination of light absorption, charge separation, and surface redox reactions enables the photocatalytic generation of hydrogen from water using TiO<sub>2</sub> as the

catalyst. When TiO2 photocatalyst is exposed to light, at the catalyst surface, the photo-generated electrons react with water reducing them to hydrogen ions  $(H^+)$ . Simultaneously, the holes react with water molecules, oxidizing them to oxygen gas (O2) or hydroxyl radicals (OH). The accumulated H<sup>+</sup> from the reduction reaction combine with the electrons at the catalyst surface, forming hydrogen gas (H2). Finally, the products of the redox reactions are desorbed from the catalyst surface, completing the catalytic cycle (Fig. 6A). Backus et al. studied the photocatalytic water dissociation at the TiO<sub>2</sub>-water interface with bulk water, revealing that the process begins with hole-assisted deprotonation of nearsurface water molecules and the attachment of hydroxyl groups to the surface.<sup>286</sup> These interfacial processes follow a biexponential model with time constants of 3 and 16 picoseconds. Understanding these timescales is crucial for optimizing the photocatalytic system by enhancing the desired reaction pathway and mitigating competing processes.

All three polymorphs of TiO<sub>2</sub> (anatase, rutile, brookite) have been studied for their photocatalytic activity. Anatase and rutile are often considered for this application while brookite TiO<sub>2</sub> is less common in this context, with their photocatalytic potential less explored compared to other two. The photocatalytic performance of heterophase junction structures combining anatase and rutile TiO2 has garnered attention due to the distinct band gaps and aligned band-edge positions of these two phases. This configuration facilitates improved separation of photogenerated electron-hole pairs when exposed to solar light irradiation. The differing band gaps and matched band-edge positions create favorable conditions for efficient charge transfer across the heterojunction interface, enhancing the overall photocatalytic activity. As a result, these heterophase junction structures hold significant promise for applications in solar-driven photocatalysis, offering enhanced efficiency and performance compared to individual phases of TiO<sub>2</sub>. 287,288

Combining a hydrogenation treatment with heterophase junctions further enhances their performance by introducing a disordered layer with oxygen vacancies and Ti3+ ions. This augmentation improves optical absorption, electrical conductivity, carrier transport, and separation efficiency. For instance, Hu et al. engineered a TiO2 photoelectrode composed of rutile TiO2 nanorods and anatase TiO2 branches with hydrogenated heterophase interfaces through hydrothermal synthesis, hydrogenation, and branching growth processes.<sup>289</sup> The resulting structure exhibited anatase crystallographic planes in the TiO2 branches, along with a disordered layer within the heterophase This optimized photoelectrode significantly enhanced the hydrogen evolution rate for photoelectrochemical water splitting, achieving a rate 20 times higher than that of unhydrogenated TiO2 nanorod arrays. Particularly, the hydrogenated interfaces between anatase branches and rutile nanorods play a crucial role by introducing oxygen vacancies and Ti3+ species. These modifications create new energy levels associated with oxygen vacancies and Ti-OH groups, situated below the band edge positions of the CB and VB of rutile TiO<sub>2</sub>

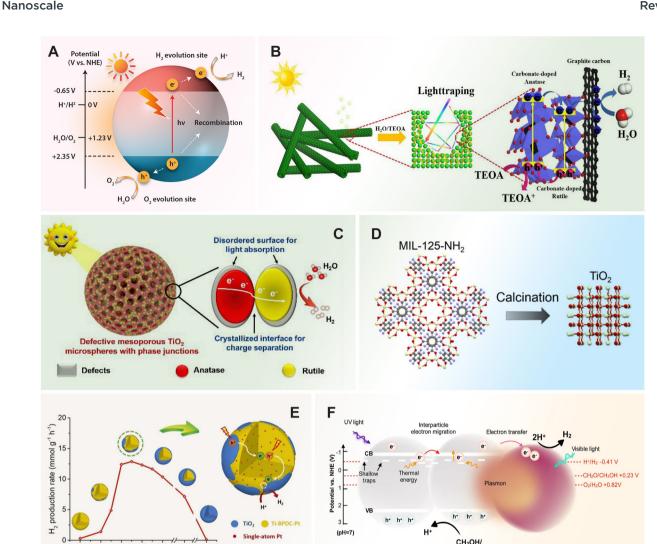


Fig. 6 (A) Schematic illustration of the photocatalytic water splitting mechanism of TiO<sub>2</sub> semiconductor. (B) Photocatalytic hydrogen evolution mechanism of mesoporous carbonate-doped phase-junction TiO<sub>2</sub> nanotubes. Reproduced with permission from ref. 290. Copyright 2018, Elsevier. (C) Defective mesoporous TiO<sub>2</sub> microspheres with phase junctions for visible-light driven water splitting. Reproduced with permission from ref. 189. Copyright 2019, Elsevier. (D) Preparation of MIL-125-NH<sub>2</sub>-derived TiO<sub>2</sub>. Reproduced with permission from ref. 294. Copyright 2018, American Chemical Society. (E) The progress of hydrogen evolution reaction activities with phase composition of TiO<sub>2</sub>/Ti-BPDC-Pt, finely tuned by varying pyrolysis duration. Reproduced with permission from ref. 295. Copyright 2023, Wiley-VCH. (F) Schematic illustration of the electron migration process in metal-containing TiO<sub>2</sub> aerogel monoliths for the photocatalytic hydrogen evolution reaction. Reproduced with permission from ref. 222. Copyright 2020, Elsevier.

nanorods, respectively. The alignment of these energy levels with those of anatase branches and hydrogenated rutile nanorods mitigates the recombination of photogenerated carriers, thereby enhancing the overall photoelectrochemical (PEC) performance. This improved carrier separation and reduced recombination contribute to the enhanced efficiency of the heterophase junction structure in facilitating photocatalytic water splitting.

1.5 2.0 Time (h)

By leveraging morphology, electronic, crystal, and textural structures, electrospun mesoporous carbonate-doped phase-junction  ${\rm TiO_2}$  nanotubes demonstrated exceptional photocatalytic hydrogen evolution activity, achieving 6108  $\mu$ mol h<sup>-1</sup>

g<sup>-1</sup>, which is nearly 6 times higher than that of commercially available P25. The porous nanotube architecture extended the optical path through multiple reflections, enhancing light harvesting efficiency. Carbon doping reduced the bandgap of TiO<sub>2</sub>, significantly enhancing visible light photocatalytic activity. Moreover, the phase junction interface improved charge separation and transfer, resulting in photocurrent densities 2 and 18 times higher than those of pristine anatase and rutile phase samples, respectively (Fig. 6B).<sup>290</sup> These synergistic effects led to the exceptional photocatalytic performance of the electrospun mesoporous carbonate-doped phase-junction TiO<sub>2</sub> nanotubes. Apart from 1D TiO<sub>2</sub> nanostructures with

H<sub>2</sub>O

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phase junctions and porous structures, TiO2 hollow spheres have been widely investigated in the field of photocatalytic water splitting due to their unique structural characteristics and enhanced light harvesting capabilities.<sup>291</sup> The TiO<sub>2</sub> spheres composed of a crystalline core and an amorphous shell structured nanocrystallites, exhibited a hydrogen production rate of 0.182 mmol g<sup>-1</sup> h<sup>-1</sup>, which was twice that of pristine TiO<sub>2</sub>. <sup>292</sup>

Zhang et al. engineered defective mesoporous TiO2 microspheres with phase junctions featuring controllable defect locations using a confinement reduction method. 189 This method exploits on the confinement decomposition effect, which allows for efficient defect production under mild conditions without compromising the mesostructures and phase junctions of the pristine mesoporous microspheres. Furthermore, by adjusting the reduction temperature, defects can be relocated from the nanocrystalline-exposed surfaces to the phase junction interfaces, enabling precise tuning of defect locations (Fig. 6C). The defect formation altered the energy band structure and mediated the visible light adsorption of the TiO2 microspheres. The well-retained phase junction structure facilitated effective photo-induced charge separation. This engineered photocatalyst exhibited a hydrogen production rate of 42.6 µmol h<sup>-1</sup> (based on 50 mg of catalyst) under visible-light irradiation ( $\lambda > 400$  nm). Moreover, the apparent quantum efficiencies were measured at 12.7% and 2.8% at wavelengths of 420 nm and 520 nm, respectively.

In the realm of MOFs, several studies have explored the combination of TiO2 with MOFs to enhance the efficiency of photocatalytic systems for hydrogen evolution reaction under visible light irradiation.<sup>293</sup> The 3D porous structure of Ti<sup>IV</sup>based MOFs provides a structured environment for the controlled growth and arrangement of TiO<sub>2</sub> crystals. Specifically, the templating effect of MIL-125-NH2 enables the formation of well-defined TiO2 nanoparticles with customized size, morphology, and crystallinity, leading to optimized photocatalytic performance. Studies have demonstrated that starting with MIL-125-NH2 as a MOF precursor, TiO2 particles can be synthesized at various temperatures while retaining the welldefined crystal shape of the parent MOF and controlled phase composition (Fig. 6D).<sup>294</sup> For instance, a mixed TiO<sub>2</sub> phase comprising 66% anatase and 34% rutile exhibited a remarkable hydrogen evolution rate of 1394 μmol g<sup>-1</sup> h<sup>-1</sup>, surpassing both commercial Degussa P25 TiO2 and conventionally synthesized TiH<sub>4</sub>O<sub>4</sub>- and MIL-167-derived TiO<sub>2</sub>. This superior performance is credited to the unique templating effect of MIL-125-NH2, which promotes the formation of nanosized anatase and rutile nanoparticles in effective contact, thereby enhancing electron-hole separation and overall photocatalytic efficiency.

A recently developed TiO2/Ti-BPDC-Pt photocatalyst, featuring a TiO2/Ti-MOF heterojunction with high-density Pt singleatomic co-catalysts, has shown promise for photocatalytic hydrogen evolution (Fig. 6E).<sup>295</sup> Single-atom co-catalysts have emerged as an efficient and cost-effective approach in heterogeneous photocatalysis due to their high atomic utilization

efficiency and excellent catalytic activity. These isolated metal heteroatoms can enhance semiconductor band structures, improving light absorption and facilitating electron collection to boost surface charge separation and transfer. 296,297 In this study, a TiO<sub>2</sub>/Ti-BPDC heterojunction is tailored through a surface pyrolytic reconstruction approach, resulting in an intimate interface between TiO2 and the Ti-based MOF, which facilitates efficient charge separation and migration. The strategic placement of Pt within the electron-enriched domain of the heterojunction further enhances the utilization of separated electrons for the reduction of protons, thus promoting hydrogen production. This engineered TiO<sub>2</sub>/Ti-BPDC-Pt catalyst exhibits superior activity, achieving a hydrogen evolution rate of 12.4 mmol g<sup>-1</sup> h<sup>-1</sup>, surpassing other TiO<sub>2</sub>- or MOFbased catalysts.

Among the Pt-group metals, Ru stands out as a competitive alternative to Pt due to its cost-effectiveness and comparable hydrogen evolution performance.<sup>298</sup> The coexistence of two forms of Ru species such as nanoparticles and single atoms, supported on MOF-derived N-doped TiO2/C hybrids exhibits superior photocatalytic hydrogen evolution reaction.<sup>299</sup> This enhanced performance results from the synergistic coupling of Ru nanoparticles and Ru single atoms. Similarly, atomically dispersed Ru atoms on multi-edged TiO2 spheres significantly enhance hydrogen evolution by effectively transferring photogenerated electrons to isolated Ru atoms and facilitating charge separation and transport through the multi-edged TiO2 structure.<sup>53</sup> The in situ X-ray absorption fine structure technique was used to examine the dynamic changes of isolated sites during the catalytic process. Upon light irradiation, the Ru species experience gradual changes in valence and configuration, facilitating the photo-splitting of water into solar fuels.

When Ti<sub>3</sub>C<sub>2</sub> MXene was converted into 3D porous frameworks of Ti<sub>3</sub>C<sub>2</sub>-TiO<sub>2</sub> nanoflowers, the in situ growth of TiO<sub>2</sub> on the surface of Ti<sub>3</sub>C<sub>2</sub> offers intimate interaction between TiO<sub>2</sub> and Ti<sub>3</sub>C<sub>2</sub> for photocatalytic overall water splitting.<sup>208</sup> The photogenerated electrons can transfer from the CB of TiO2 to Ti<sub>3</sub>C<sub>2</sub>, where Ti<sub>3</sub>C<sub>2</sub> serving as an electron sink. The formation of a possible Schottky junction at the interface between Ti<sub>3</sub>C<sub>2</sub> and TiO<sub>2</sub> enhances the separation of photogenerated charge carriers, effectively suppressing recombination. As a result, more electrons participate in the photoreduction process for hydrogen evolution, while more holes engage in the photooxidation process for oxygen evolution. This mechanism contributes to the enhanced efficiency of photocatalytic water splitting facilitated by Ti<sub>3</sub>C<sub>2</sub>-TiO<sub>2</sub> nanoflowers.

TiO<sub>2</sub> aerogel monoliths hold significant promise as efficient and sustainable photocatalysts for hydrogen generation due to the synergetic effect between their building blocks and their 3D macroscopic structure. The porous structure of TiO2 aerogels promotes light trapping and diffusion within the monolith. Upon light entering the aerogel, it undergoes multiple scattering events, resulting to prolonged interaction lengths and increased absorption probabilities. This improves the efficiency of light harvesting by ensuring that a

larger fraction of incident photons is absorbed by the TiO<sub>2</sub> matrix. Likewise, the interconnected pores and tortuous pathways within the aerogel matrix enable light to travel over millimeter length scales through the monolith, hence increasing the probability of photon absorption by TiO<sub>2</sub> nanoparticles.<sup>222</sup> To preserve the fragile structure of the 3D TiO<sub>2</sub> network while enabling it sensitive to visible light, monolithic aerogels composed Pd modified TiO<sub>2</sub> nanoparticle was doped with nitrogen in a gas-phase nitridation process using plasma-enhanced chemical vapor deposition at low temperature. 300 The nitridation-induced nitrogen doping and defect engineering in TiO2 aerogels, coupled with Pd nanoparticle loading achieved the desired enhancement in optical absorption and charge separation efficiency, and hence outperformed the undoped material in visible light-driven photocatalysis for hydrogen production.

Besides doping, the assembly of non-doped TiO2 aerogel composite with noble metal nanoparticles (Au, Pd, PdAu) has been shown to exhibit superior visible light-induced photocatalytic hydrogen production compared to their corresponding powders.<sup>222</sup> By leveraging the plasmonic properties of noble metal nanoparticles and the catalytic activity of TiO2, the formation of inter-particle contacts during nanoparticle assembly lead to the creation of shallow traps within the composite material, resulting to an absorption band around 400-500 nm in the visible range of the electromagnetic spectrum. The combination of shallow traps absorption in the visible range and the LSPR of the metal nanoparticles promoted the hydrogen evolution through the near-field electromagnetic mechanism. Further, thermal energy generated by the LSPR of the plasmonic particles promotes the shallow-trap electron migration process (Fig. 6F). Overall, the observed 3.5 times increase in hydrogen generation underlines the importance of the both the aerogel 3D structure and the type of metal nanoparticle on the photocatalytic activity of the aerogels in enabling light-harvesting and efficient mass transport of reactants to the surface-active sites.

Among the noble metal nanoparticles, Pd has been recognized as a particularly effective photocatalyst under visible light irradiation. One of the key reasons for the high photocatalytic activity of Pd is attributed to the generation of hot electrons from its 4d orbital under visible light irradiation.<sup>301</sup> By using a microwave-assisted non-aqueous sol-gel method, Pd-modified TiO<sub>2</sub> nanoparticles can be synthesized with simultaneous incorporation of Pd ions in the TiO2 lattice and formation of Pd metal nanoparticles on the surface of the TiO2 nanoparticles.302 The subsequent assembly of Pd-modified TiO<sub>2</sub> nanoparticles into macroscopic aerogels results in photocatalyst with a narrow band gap, primarily due to the formation of Pd 4d energy levels, oxygen vacancies, and Ti3+ centers within the TiO2 lattice. While Pd doping and Pd nanoparticle loading can enhance visible-light absorption in TiO2 aerogels, excessive Pd accumulation may hinder charge generation and separation due to shadowing effects and high Schottky barriers.

#### Chemical transformations of CO<sub>2</sub> for sustainable future

Carbon dioxide (CO2) emissions are the primary driver of global warming and climate change. Limiting global warming to 1.5 °C requires rapid and sustained reductions in CO2 emissions and reaching net-zero emissions in the energy sector by 2050. To mitigate this crisis, turning CO<sub>2</sub> into valuable chemicals or fuels has the potential to mitigate global warming by treating hundreds of millions of tons of CO2 annually. Among various CO<sub>2</sub> conversion approaches, photocatalytic CO2 reductions is regarded as one of the most ideal approaches by mimicking natural photosynthesis. Generally, CO2 can be photocatalytically reduced into several carbonaceous molecules including CO, HCOOH, HCHO, CH3OH, and CH<sub>4</sub> (Fig. 7A). In this regard, numerous visible-light-driven photocatalysts for the CO2 conversion have been developed, particularly to optimize the structure and composition of semiconductor photocatalysts to improve their visible light absorption and charge separation efficiency, e.g., creating heterojunctions, forming surface defects, incorporating metal co-catalysts, and engineering exposed crystal facets etc. 16,48,216,304-307

Recently, a TiO2 catalyst was engineered by anchoring single Ag atoms onto the surface of the anatase TiO2 nanoparticles for photocatalytic CO2 to CH4 conversion. The Ag/ TiO2 catalyst exhibited photochromism which was attributed to the trapping of photogenerated electrons.308 The resulting active state of the photochromic catalyst effectively facilitates the separation and migration of photogenerated charge carriers. In addition, the isolated Ag atoms and adjacent Ti sites play complementary roles in catalyzing the conversion of CO<sub>2</sub> to CH4. The isolated Ag atoms serve to stabilize two key intermediates (\*CO and \*CHO) formed during the reaction process, while the adjacent Ti sites are responsible for activating water molecules to generate more protons, hence both simultaneously affording active sites to increase the production of CH<sub>4</sub> rather than CO (Fig. 7B). Ultimately, the Ag/TiO<sub>2</sub> catalyst achieved high activity and selectivity of 46.0 mmol g<sup>-1</sup> h<sup>-1</sup> and 91% respectively, for photocatalytic CO<sub>2</sub> methanation.

Besides Ag atoms, Cu single atoms and Au-Cu alloy nanoparticles were co-loaded on TiO2 by photodeposition for the photocatalytic production of solar fuels from CO<sub>2</sub> and H<sub>2</sub>O.<sup>312</sup> The optimized photocatalyst achieved high formation rates of 3578.9  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> for CH<sub>4</sub> and 369.8  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> for C<sub>2</sub>H<sub>4</sub>. The synergy between Cu single atoms and Au-Cu alloy nanoparticles enhanced the adsorption and activation of CO2 and H<sub>2</sub>O and lowered the activation energy barrier for CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> formation, enabling highly efficient and stable production of these solar fuels.

Typically, the scope of CO<sub>2</sub> conversion work is often limited to the low adsorption of CO2 on the surface of photocatalysts owing to the low specific surface area and the lack of matched pores. The efficiency of CO2 conversion heavily relies on the availability of CO<sub>2</sub> molecules near the active sites of the photocatalyst, where they can interact with photoexcited electrons and participate in catalytic reactions. Facing this challenge, combining a CO<sub>2</sub> capture material with semiconductor photoReview Nanoscale

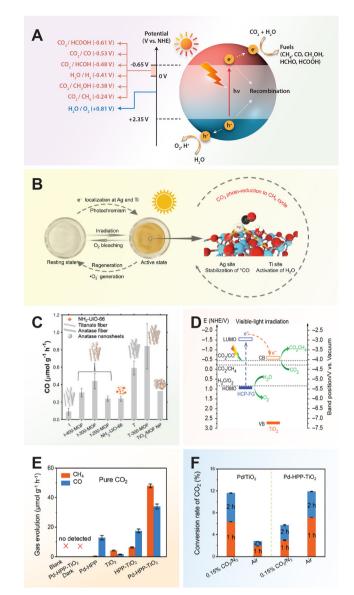


Fig. 7 (A) Schematic illustration of the CO<sub>2</sub> photoreduction mechanism of TiO<sub>2</sub> semiconductor. (B) Photochromic cycle of Ag/TiO<sub>2</sub> (left) and the photocatalytic CO<sub>2</sub> to CH<sub>4</sub> conversion cycle over the Ag-Ti active site on Ag/TiO<sub>2</sub> (right). Reproduced with permission from ref. 308. Copyright 2024, Royal Society of Chemistry. (C) Photocatalytic CO evolution rates of TiO<sub>2</sub>/NH<sub>2</sub>-UiO-66 nanocomposite compared to titanate fiber. Reproduced with permission from ref. 309. Copyright 2019, Wiley-VCH. (D) Proposed mechanism of charge separation and transfer within the TiO<sub>2</sub>/graphene composite under visible-light ( $\lambda \geq$  420 nm) irradiation. Reproduced with permission from ref. 310. Copyright 2019, Springer Nature Group. (E) The evolution rates of CH<sub>4</sub> and CO in photocatalytic CO<sub>2</sub> reduction and (F) comparison of the conversion yield of CO<sub>2</sub> in Pd/TiO<sub>2</sub> and Pd-HPP-TiO<sub>2</sub>. Reproduced with permission from ref. 311. Copyright 2022, Springer Nature Group.

catalysts has been proposed to provide an attractive means for increasing  $\mathrm{CO}_2$  conversion efficiency. Xu *et al.* designed photocathode comprised of a layered hybrid heterojunction of  $\mathrm{TiO}_2$  on 2D  $\mathrm{Ti}_3\mathrm{C}_2$  MXene nanosheets, functionalized with imine ligands and Pd nanoparticles (Pd/N-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>) for  $\mathrm{CO}_2$  con-

version.313 The photocathode of Pd/N-TiO2/Ti3C2 exhibited an evolution rate of total hydrocarbon (formate, methanol, ethanol) 5-fold higher than that of Pd-Ti<sub>3</sub>C<sub>2</sub> photocathode. The electrode was stable for 16 hours without a change in its efficiency. The high efficiency of Pd/N-TiO2/Ti3C2 is ascribed to the high surface area and narrow band gap (2.1 eV) TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterojunction materials which provide abundant active sites in favor of the adsorption of CO2 molecules and promote strong visible light absorption, respectively as well as the plasmonic resonance effect of Pd nanoparticles. Kreft et al. synthesized Cu/TiO<sub>2</sub>-aerogel composite featuring Cu(II)-nanoparticles on the surface of a highly porous TiO<sub>2</sub> aerogel for aqueous CO2 reduction to CO without the need for external sacrificial reagents. 314 Notably, the presence of O2 in the reaction environment enhances CO productivity while suppressing H<sub>2</sub> generation.

Combining TiO<sub>2</sub> photocatalyst with MOFs allows for the synergy between the light-absorption and electron-generation capabilities of TiO2 with a high concentration of open active sites in the framework of MOFs for CO2 capture and conversion processes. 315,316 In addition, optimizing the morphology of the heterojunction components and engineering the interface between the two materials are critical for achieving a close interaction and maximizing photocatalytic performance. This can involve controlling the size, shape, and distribution of TiO2 nanoparticles on the MOF surface. Studies have shown that improved CO2 photoreduction was achieved through synthesizing TiO2 nanoparticles onto various preformed MOFs, producing TiO<sub>2</sub>/HKUST-1, 317 TiO<sub>2</sub>/Co-ZIF-9, 318 and TiO<sub>2</sub>/NH<sub>2</sub>-UiO-66 composites.<sup>211</sup> The superior photocatalytic activity is ascribed to the development of an intimate interaction between TiO2 and MOFs forming a heterojunction, while retaining the high CO<sub>2</sub> uptake and porosity of MOFs. The TiO<sub>2</sub>/MOF composites exhibited better durability and significantly more efficient in reducing CO<sub>2</sub> to CO compared to their individual components. Crake et al. synthesized TiO<sub>2</sub>/ NH2-UiO-66 nanocomposites with superior photocatalytic activity in CO2 photoreduction, specifically focusing on the role of heterojunctions, highlights the importance of both crystalline phase and morphology control in enhancing charge transfer and overall photocatalytic performance. 309 Forming anatase phase nanofibers and growing MOF particles on their surface allows for precise control of composite morphology, which in turn maximizes charge transfer efficiency. Accordingly, the electrons transfer from TiO2 into the MOF and holes from the MOF into TiO2, accompanied by strong band bending in TiO2 induced by the MOF, leading to an improved charge separation and facilitating efficient charge transfer in the heterojunction structure. Therefore, the TiO<sub>2</sub>/ NH<sub>2</sub>-UiO-66 nanocomposite produced 9 times more CO when compared to titanate under UV-vis light irradiation, confirming the synergistic effect of forming a composite (Fig. 7C).

Wang *et al.* incorporated  $TiO_2$  units within the pores of a chromium terephthalate-based MOF (MIL-101) and its derivatives, forming "molecular compartments" where photocatalytic reactions can occur in a confined environment.<sup>319</sup> These com-

partments facilitate the close proximity of TiO2 units and catalytic metal clusters, promoting efficient charge transfer and catalytic activity for CO2 reduction. The observed apparent quantum efficiency for CO2 photoreduction of 11.3% at 350 nm in the composite consisting of 42% TiO2 in a MIL-101 derivative (42%-TiO2-in-MIL-101-Cr-NO2) demonstrates the effectiveness of this composite for photocatalytic CO2 conversion. Furthermore, TiO<sub>2</sub> units in one type of compartment in this composite are 44-fold more active than those in the other type, emphasizing the importance of precise positioning of TiO<sub>2</sub> within the composite. Simultaneously, the photocatalytic process generates molecular oxygen as a byproduct, contributing to the overall sustainability of the CO<sub>2</sub> conversion process.

Wang et al. developed a porous composite structure by integrating anatase TiO2 crystals with reactive (001) facets on graphene surface and subsequently encapsulated in hypercrosslinked polymer layers by in situ knitting strategy.310 Given abundant adsorptive sites of the porous capture materials for efficient CO<sub>2</sub> uptake, the photoreduction of CO<sub>2</sub> of modified TiO<sub>2</sub> photocatalyst proceeded under modest conditions without sacrificial reagents and co-catalysts, yielding 27.62 μmol g<sup>-1</sup> h<sup>-1</sup> for CH<sub>4</sub> production under visible-light irradiation. In comparison, the CO2 conversion products were hardly identified over commercial TiO2 (P25), and pristine TiO<sub>2</sub> with reactive (001) facets because of their weak visible light-responsive ability.

With the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels lying more negative than the VB and CB levels of TiO2, respectively, the hypercrosslinked polymer-graphene can act both as CO2 adsorbent and photosensitizer, in which their photoinduced electron-hole pairs are migrated and separated at the interface with TiO<sub>2</sub> via their interfacial interaction. Therefore, the CO<sub>2</sub> reduction is prone to happen at the catalytic sites on TiO<sub>2</sub> instead on hypercrosslinked polymer-graphene, giving rise to better CO<sub>2</sub> conversion efficiency (Fig. 7D). Moreover, a selectivity of 83.7% for CH<sub>4</sub> production is achieved during the photocatalytic reaction, suggesting negligible side reaction of hydrogen evolution under visible-light irradiation.

Recently, Ma et al. reported a novel approach for the preparation of a composite photocatalyst by hyper-crosslinking porphyrin-based polymers (HPP) on the surface of hollow TiO<sub>2</sub>, followed by coordination with Pd(II). 311 In a pure CO<sub>2</sub> environment, this composite photocatalyst, Pd-HPP TiO2 exhibited remarkable CO2 reduction efficiency, achieving high evolution rates of 48.0 and 34.0 µmol g<sup>-1</sup> h<sup>-1</sup> for CH<sub>4</sub> and CO, respectively (Fig. 7E). In the presence of 5 vol% O2, the CO2 reduction over a catalyst without hyper-crosslinked porphyrin-based polymer (Pd/TiO2) drastically decreases to only 6% of that observed in pure CO<sub>2</sub>. On the other hand, the inhibition from O<sub>2</sub> is significantly mitigated over composite photocatalyst (Pd-HPP TiO<sub>2</sub>), which maintains 46% of the CH<sub>4</sub> evolution rate observed in pure CO<sub>2</sub> conditions. The composite photocatalyst, Pd-HPP-TiO<sub>2</sub> demonstrated notable photocatalytic activity even in the presence of air, with a CO2 conversion yield of 12% and CH<sub>4</sub> production of 24.3 µmol g<sup>-1</sup> after 2 hours of UV-visible

light irradiation (Fig. 6F). This performance is 4.5 times higher than that observed over Pd/TiO2. The hyper-crosslinked porphyrin-based polymer layer effectively enriches CO<sub>2</sub> at Pd(II) sites, thereby mitigating the reduction of O2. Moreover, water adsorbed on TiO2 undergoes oxidation by the holes present in the valence band of TiO<sub>2</sub>. This process serves to reduce charge recombination, thereby enhancing CO<sub>2</sub> conversion efficiency.

Bian et al. developed a cascade Z-Scheme photocatalytic system using 2D g-C<sub>3</sub>N<sub>4</sub> for the reduction half-reaction and 2D BiVO<sub>4</sub> nanosheets for the oxidation half-reaction, combined with an energy platform of (001)TiO2.320 This (001)TiO2-g-C<sub>3</sub>N<sub>4</sub>/BiVO<sub>4</sub> nanosheet heterojunction exhibited exceptional photocatalytic activity for CO<sub>2</sub> photoreduction and water splitting without cocatalysts, achieving a 19-fold improvement in photoactivity for CO2 reduction to CO under visible-light irradiation compared to BiVO<sub>4</sub>. This performance surpasses other reported Z-Scheme systems, even those using noble metals as mediators.

#### 7.4. Nitrogen fixation for ammonia production

Since the initial discovery in 1977 that nitrogen (N2) could be reduced to ammonia (NH<sub>3</sub>) on the surface of TiO<sub>2</sub>, <sup>321</sup> the pursuit of achieving N2 fixation using sunlight has become a significant research focus. N2 fixation is the conversion of atmospheric N2 into NH3 or other N2-containing compounds, which is an essential process for the production of fertilizers and various industrial applications. 322 As is known, N2 is a highly stable compound with a bond dissociation energy of N≡N of approximately 941 kJ mol<sup>-1</sup>, making it thermodynamically challenging to convert it into NH3 or other N-containing compounds. The Haber-Bosch process, which is the most widely used method for industrial NH3 production, achieves the industrial-scale NH3 synthesis through high temperatures (300-500 °C) and pressures (200-300 atm), which leads to huge energy consumption and high CO<sub>2</sub> emission.<sup>323</sup> Therefore, a less energy consuming alternative would be highly desirable.

Photocatalytic conversion of N<sub>2</sub> to NH<sub>3</sub> is a green alternative for the Haber-Bosch process. It typically involves using light energy to generate electrons and holes within a semiconductor and combine with water protons to reduce N2 to NH3 (Fig. 8A). 17,324 The current strategies for developing efficient TiO<sub>2</sub> photocatalysts for N<sub>2</sub> fixation prioritize the creation of active sites through the introduction of defects in TiO2. These defects, such as oxygen vacancies, aim to weaken the N≡N triple bond of adsorbed N2 molecules by facilitating the transfer of electrons into the antibonding orbital of N2. This activation process enables their subsequent reaction with photogenerated electrons for N2 reduction reactions. In addition, defects in the TiO2 structure enable efficient charge separation and accelerate charge carrier transfer from photocatalysts to the adsorbed reactants. 18 It was demonstrated that by finetuning the concentration of oxygen vacancies, TiO2 can achieve a 3-fold increase in charge separation efficiency compared to pristine TiO2. 325 The oxygen vacancy defect structures coordinate both the charge separation efficiency and the disso-

NH<sub>3</sub>

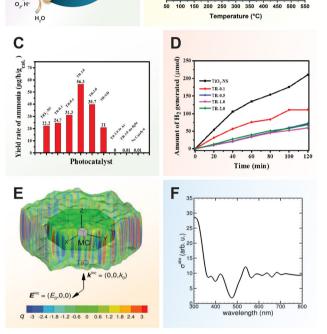


Fig. 8 (A) Schematic illustration of the N<sub>2</sub> photoreduction mechanism of TiO<sub>2</sub> semiconductor. (B) N<sub>2</sub>-temperature programmed desorption profiles of the commercial anatase TiO<sub>2</sub> and oxygen vacancy-rich C-TiO<sub>2</sub>. Reproduced with permission from ref. 326. Copyright 2022, Wiley-VCH. (C) The yield rate of photocatalytic fixation of N<sub>2</sub> to NH<sub>3</sub> and (D) the quantity of H<sub>2</sub> generated in water by single Ru atom decorated TiO<sub>2</sub> nanosheet photocatalysts. Reproduced with permission from ref. 328. Copyright 2019, American Chemical Society. (E) Surface charge distribution of a carbon coated hexagonal Mo<sub>2</sub>C and TiO<sub>2</sub> particle with core–shell structure under the illumination of sunlight and (F) corresponding absorption cross sections across the spectrum of sunlight. Reproduced with permission from ref. 329. Copyright 2023, Elsevier.

ciative adsorption capacity of  $N_2$ , leading to a normalized  $N_2$  photofixation rates of 324.86 mmol  $g^{-1}$   $h^{-1}$  (under full spectrum illumination), with corresponding apparent quantum yields of 1.1% under 365 nm illumination.

The oxygen-rich  $TiO_2$ , prepared by calcination of  $Ti_3C_2$  MXene, exhibited superior photocatalytic  $N_2$  fixation performance compared to both P25 and commercial anatase  $TiO_2$ . Specifically, it achieved a  $N_2$  fixation rate of 84  $\mu$ mol  $g^{-1}$   $h^{-1}$ , utilizing  $CH_3OH$  as the proton source. Typically, chemisorption of  $N_2$  on carbon occurs at around 280 °C, while on  $TiO_2$ , it occurs at approximately 360 °C. In contrast, physical adsorption of  $N_2$  takes place at a lower temperature of about 120 °C.  $^{327}$  The significantly higher temperature programmed desorption signal observed for oxygen vacancy-rich C-TiO $_2$ 

compared to commercial anatase  $TiO_2$  indicates stronger chemisorption of  $N_2$  on the former (Fig. 8B). This enhanced chemisorption capability of oxygen vacancy-rich C-TiO<sub>2</sub> is crucial for the activation of  $N_2$ , highlighting its potential for efficient  $N_2$  reduction in photocatalytic processes.

Controlling defects in TiO2 nanotubes can be achieved through an amine-assisted remedying strategy using urea, dicyandiamide, and cyanamide as precursors. 330 This approach involves the preparation of hydrogen-treated TiO2 nanotubes, which are engineered to possess oxygen vacancies. By using urea, dicyandiamide, or cyanamide as precursors, the process can be optimized to introduce and regulate the concentration of oxygen vacancies in the TiO2 nanotubes. The resulting defect-rich nanotubes extended the visible light absorption and suppressed the recombination of photogenerated electron-hole pairs, which led to improved photocatalytic performance in N2 fixation reactions. The NH3 production rate, reaching 1.2 mmol L<sup>-1</sup> h<sup>-1</sup> under full spectrum light irradiation, represents a significant enhancement compared to pristine TiO2, with an approximate 8.6-fold increase in efficiency.

While another effective way of increasing NH3 production yield in photocatalytic N2 fixation is through doping TiO2 with metal heteroatoms.<sup>52</sup> Copper, as a dopant, can effectively regulate the concentration of oxygen vacancies and introduce substantial compressive strain in ultrathin TiO2 nanosheets. Particularly, defect-rich TiO<sub>2</sub> nanosheets containing 6 mol% copper demonstrated stable performance for the photocatalytic reduction of N2 to NH3 in water, showcasing superior photoactivity even up to 700 nm. Modifications with oxygen vacancies and strain effects in TiO2 nanosheets enable strong chemisorption and activation of molecular N2 and water, leading to high rates of NH3 evolution under visible-light irradiation. Analysis using diffuse reflectance infrared Fourier transformation spectroscopy provides compelling evidence that N≡N triple bonds can be activated on the defect-rich TiO<sub>2</sub> nanosheets containing 6 mol\% copper, forming NH4+ species under light irradiation. The observed rates of O2 (59.1 µmol  $g^{-1} h^{-1}$ ) and NH<sub>3</sub> (78.9 µmol  $g^{-1} h^{-1}$ ) evolution during the tests closely match the theoretical ratio of 3:4 for the reaction  $N_2 + 3H_2O \rightarrow 2NH_3 + 1.5 O_2$ , with no detectable  $N_2H_4$  byproduct observed. This suggests high selectivity and efficiency of the photocatalytic N<sub>2</sub> fixation process on the defect-rich TiO<sub>2</sub> nanosheets.

The recent development of single atom decorated  $TiO_2$  semiconductor with engineered oxygen vacancies has demonstrated remarkable catalytic activity in photocatalytic  $N_2$  fixation. Single atom metals dispersed on supports offer homogeneous catalytically active sites, a low-coordination environment for metal atoms, and maximum metal utilization efficiency, resulting in enhanced catalytic activity, stability, and selectivity across various processes.  $^{53,328,331}$  The composite catalyst containing 1 wt% of Ru exhibited a significantly improved ammonia generation rate of 56.3  $\mu g g^{-1} h^{-1}$ , more than doubling that of pure  $TiO_2$  nanosheets (Fig. 8C).  $^{328}$  Upon decoration with Ru, the photocatalytic activity of  $TiO_2$ 

nanosheets for the competing reaction, such as the hydrogen evolution reaction decreased. The hydrogen evolution activity was suppressed, reaching an almost saturated value of 30  $\mu mol\ h^{-1}$  at 0.5 wt% Ru, compared to 105.3  $\mu mol\ h^{-1}$  in pure  $TiO_2$  nanosheets (Fig. 8D). This decrease in hydrogen evolution reaction activity with the introduction of Ru species is attributed to the interference with the transportation of photoelectrons from  $TiO_2$  to  $H^+$  by combining with the oxygen vacancies, thus inhibiting hydrogen evolution reaction.

In addition to metal doping, non-metal introduction into the TiO<sub>2</sub> lattice has been investigated as a strategy in modifying the electronic structure of TiO2 and facilitating the separation of photogenerated charge carriers. Specifically, N-doping in Ti<sub>3</sub>C<sub>2</sub>-TiO<sub>2</sub> was found to enhance the carrier separation and improve the ammonia production yield to 415.6  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>, which represents an 8-fold increase compared to pure TiO2.32 Likewise, N-doping TiO<sub>2</sub> hollow microspheres along with the creation of oxygen vacancies displayed an ammonia yield of 80.09 μmol g<sup>-1</sup> h<sup>-1</sup>.114 This enhancement is associated with the synergistic effect between the N-doping, oxygen vacancies, and hollow microsphere structure that collectively contributes to the boosted efficiency of photocatalytic N<sub>2</sub> fixation. Firstly, the incorporation of nitrogen dopants narrows the bandgap of TiO<sub>2</sub> from 3.18 eV to 2.83 eV, leading to improved absorption of visible light. Further, the creation of oxygen vacancies assists to impede the recombination of photo-generated carriers, hence increasing the efficiency of charge separation. Besides, the hollow microspheres structure of the catalysts provides a large surface area and promotes light absorption and utilization. These findings highlight the potential of tailored nanostructures and dopants for enhancing the performance of photocatalysts in nitrogen fixation applications.

Recently, a composite material consisting of carbon coated hexagonal Mo<sub>2</sub>C and TiO<sub>2</sub> was developed for photocatalytic N<sub>2</sub> fixation.<sup>329</sup> In contrast to pure TiO<sub>2</sub>, this composite photocatalyst effectively separates the photogenerated electrons and holes, facilitating the efficient conversion of atmospheric N2 into NH3 directly from air. The carbon-coated hexagonal photocatalyst demonstrated a remarkable enhancement in photocatalytic N2 fixation performance, achieving a 16-fold increase compared to pure TiO2 under room temperature and ambient pressure conditions. In the proposed heterojunction formed by TiO<sub>2</sub> and Mo<sub>2</sub>C, an important aspect is the alignment of their conduction band potentials. Specifically, the conduction band potential of Mo<sub>2</sub>C is strategically positioned to facilitate the conversion of N2 to NH3. Relative to TiO2, the conduction band potential of Mo<sub>2</sub>C is lower, thereby creating a favorable energy gradient that facilitates the transfer of photoelectrons from TiO2 to Mo2C. Moreover, the graphitized carbon layer structure enhances the concentration of photoelectrons on Mo<sub>2</sub>C, owing to the highly conductive carbon layer. N2 molecules readily adsorb onto the carbon vacancies of the molybdenum atoms, where they receive photoelectrons. Subsequently, the activated nitrogen species combine with protons in water, ultimately undergoing reduction to form ammonia. The hydroxyl radicals generated by photocatalytic

water splitting of the catalyst, undergo oxidation by TiO<sub>2</sub> holes, leading to the formation of O<sub>2</sub>. The validation from numerical simulations further supports the consistency between the trend of absorption cross-sections of the core–shell structured carbon-coated hexagonal Mo<sub>2</sub>C/TiO<sub>2</sub> across the sunlight spectrum in simulations and the absorption measured in experiments (Fig. 8E and F). This agreement between simulation and experimental results provides confidence in the accuracy of the proposed model and supports further exploration of the material's photocatalytic properties and potential applications.<sup>332</sup>

#### 7.5. Photocatalytic hydrogen peroxide production

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is a potent oxidising agent that decomposes into water and oxygen. It is widely used in chemical manufacturing, paper making, textile bleaching and water treatment industries. Currently, H2O2 is primarily produced industrially through the anthraquinone oxidation, which is energy intensive process that generates large amounts of hazardous by-products. 333,334 One alternative method is via the direct synthesis from hydrogen gas and oxygen gas in the presence of noble metal or alloy catalysts but the inherent risk of explosions from the combustible hydrogen-oxygen mixture severely limits its use on a larger industrial scale.335-337 A safer and greener method of H2O2 production is to utilise TiO2 as a photocatalyst for reducing water and oxygen into H2O2. However, pristine TiO<sub>2</sub> has significant limitations, such as poor light absorption and low H2O2 yield, due to the combination of synthesized H<sub>2</sub>O<sub>2</sub> with hydroxyl groups forming peroxide complexes that decompose H<sub>2</sub>O<sub>2</sub>. 337,338 To address these issues, various modification strategies have been employed in TiO2-based photocatalytic systems to enhance H<sub>2</sub>O<sub>2</sub> production.

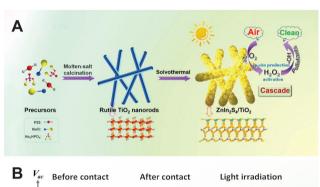
For example, Gan *et al.* synthesized ultrathin  $C_3N_5$  nanosheets and assembled them on oxygen-deficient  $TiO_2$  arrays. This coupling created a type-II heterojunction with an internal electric field to drive carrier separation and charge transfer, leading to efficient photocatalytic  $H_2O_2$  production. The optimal heterojunction achieved the highest  $H_2O_2$  formation rate of 2.93  $\mu$ mol  $L^{-1}$  min $^{-1}$  in a 90% water/10% ethanol mixture, which is about 4.1 times higher than that of the  $TiO_{2-x}$  arrays. Similarly, a S-scheme heterojunction photocatalyst was created by coupling  $TiO_2$  with three-dimensionally ordered macroporous sulfur-doped graphitic carbon nitride using electrostatic self-assembly. This photocatalyst achieved high photocatalytic  $H_2O_2$  production activity, yielding 2128  $\mu$ mol  $h^{-1}$   $g^{-1}$  without the need for hole scavengers.

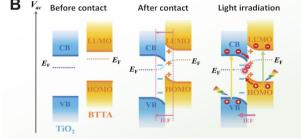
Another composite material uses Au and MXene as co-catalysts to explore the relationship between the photocatalytic activity of the brookite TiO<sub>2</sub>/Au/MXene composite under UV light for the formation of hydrogen peroxide.<sup>341</sup> This combination effectively improved the electron–hole pair separation and charge transfer rate of brookite TiO<sub>2</sub>. Under UV light exposure, brookite TiO<sub>2</sub> forms electron–hole pairs, with electrons transferring to the conduction bands of Au and MXene. Concurrently, holes oxidize 2-propanol to create protons, while electrons react with O<sub>2</sub> to form superoxide anion radicals, ultimately producing H<sub>2</sub>O<sub>2</sub>. The composite with 0.4% gold and

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15% MXene content was optimal, generating 6.80 mg  $L^{-1}$   $H_2O_2$  at pH 3 after 4 hours of UV photo-irradiation. This  $H_2O_2$  production was 10 times greater than that of brookite  $TiO_2$  alone.

Hu *et al.* synthesized a 2D/1D hierarchical layered  $ZnIn_2S_4$  modified  $TiO_2$  photocatalyst for  $H_2O_2$  production, which was rapidly activated into hydroxyl radicals for wastewater purification in a Fenton-like cascade reaction. This process is driven by a Z-scheme heterojunction mechanism, where photoexcited electrons from  $TiO_2$  recombine with holes from  $ZnIn_2S_4$ , leading to the reduction of  $O_2$  to  $H_2O_2$ . The  $ZnIn_2S_4$   $TiO_2$  catalyst achieved an  $H_2O_2$  evolution rate of 1530.59  $\mu$ mol  $g^{-1}$   $h^{-1}$  with a 10.39% external quantum efficiency under 400 nm irradiation. The produced  $H_2O_2$  was activated by unsaturated sulfur atoms in  $ZnIn_2S_4$ , degrading 90% of tetracycline antibiotics (50 ppm) in wastewater within 1 hour (Fig. 9A).





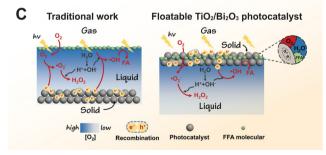


Fig. 9 (A) Schematic illustration of the preparation of the  $ZnIn2S_4/TiO_2$  heterojunction for *in situ*  $H_2O_2$  production and its activation for water remediation under visible light irradiation. Reproduced with permission from ref. 19. Copyright 2022, Elsevier. (B) Charge carrier transfer mechanism of S-scheme  $TiO_2$ @BTTA photocatalysts. Reproduced with permission from ref. 342. Copyright 2023, Elsevier. (C) Schematic illustration comparing traditional solid photocatalyst with floatable  $TiO_2/Bi_2O_3$  photocatalyst, highlighting redox reactions occur at the distinct gas-liquid-solid tri-phase interface. Reproduced with permission from ref. 54. Copyright 2022, Wiley-VCH.

Yang et al. developed a composite system comprising  $TiO_2$  nanofibers hybridized with porous 4,4,4-(benzene-1,3,5-triyltris(ethyne-2,1-diyl))tribenzaldehyde (BTTA) COF, serving as a dual-function photocatalyst for simultaneous hydrogen peroxide production and selective furfuryl alcohol oxidation. This composite system offers several advantages, including a large surface area, superior light absorption, efficient carrier separation, and enhanced redox power through the S-scheme heterojunction (Fig. 9B). Specifically, the  $TiO_2$ -BTTA composite with a 6:1 weight ratio exhibited the highest  $H_2O_2$  production activity at 740  $\mu$ mol  $L^{-1}$  h<sup>-1</sup> and achieved approximately 92% oxidation of furfuryl alcohol.

Going beyond traditional powder photocatalysts, which suffer from severe agglomeration, limited light absorption, poor gas reactant accessibility, and difficulties in reuse, the development of floatable composite photocatalysts presents a promising alternative. These novel floatable composite photocatalysts were synthesized by immobilizing hydrophobic TiO2 and Bi<sub>2</sub>O<sub>3</sub> on lightweight polystyrene spheres using hydrothermal and photodeposition methods.<sup>54</sup> The photocatalysts are solar transparent and improve contact between reactants and the photocatalyst. Floatable photocatalysts offer significant advantages, such as the rapid diffusion of oxygen to the solid-water interface, which enhances H<sub>2</sub>O<sub>2</sub> evolution (Fig. 9C). This rapid oxygen delivery facilitates electron consumption, thereby minimizing electron-hole recombination. By combining the benefits of floatable and S-scheme photocatalysts, the TiO<sub>2</sub>/Bi<sub>2</sub>O<sub>3</sub> composite achieves a significantly enhanced H<sub>2</sub>O<sub>2</sub> yield of 1.15 mM h<sup>-1</sup> and an furoic acid formation rate of 0.45 mM h<sup>-1</sup>. The innovative design maximizes photocatalytic reaction kinetics and provides a new route for efficient heterogeneous catalysis.

#### 7.6. Photocatalytic selective oxidation of alcohol

The selective oxidation of alcohols to produce aldehydes, carboxylic acids, or ketones is an important chemical process in industry. However, the industrial alcohol oxidation processes use strong oxidants which are toxic with hazardous by-products and require energy intensive conditions such as high temperature and pressure. Hence, there is a pressing need to develop environmentally friendly and sustainable processes for alcohol oxidation under ambient conditions. One promising strategy for oxidation of alcohols is through photocatalysis which can be performed under room temperature and atmospheric pressure and taps on renewable solar energy. TiO<sub>2</sub> has garnered significant attention as a photocatalyst for alcohol oxidation due to its abundance, low cost, and non-toxicity. However, its large bandgap limits its activity to the UV region, resulting in lower solar energy utilization.

Courtois *et al.* investigated the photoreforming of tertiary alcohols on Pt-loaded rutile  ${\rm TiO_2(110)}.^{345}$  The process involves hole-mediated disproportionation, which results in the formation of an alkane and the corresponding ketone. Wolde and co-workers synthesized gadolinium-doped  ${\rm TiO_2}$  nanorods decorated with poly(*o*-phenylenediamine) nanowires to enhance photocatalytic performance.<sup>346</sup> Gadolinium doping

increases adsorption capacity, introduces half-filled f-orbitals, and causes an optical redshift. Poly(o-phenylenediamine), a conducting polymer, improves photocatalytic activity in the visible region by acting as an electron donor and hole transporter. The composite was tested for photocatalytic benzyl alcohol oxidation coupled with p-dinitrobenzene reduction under simulated solar light. The best performance was achieved with 10% gadolinium doping, resulting in a 90.6% yield of benzaldehyde from benzyl alcohol and an 89.1% yield of p-nitroaniline from p-dinitrobenzene in acetonitrile, while in water, the yields were 70.5% for benzaldehyde and 85.0% for p-phenylenediamine.

When Ti<sub>3</sub>C<sub>2</sub> MXene is combined with TiO<sub>2</sub>, it significantly enhances the photocatalytic selective oxidation of alcohols, such as benzyl alcohol. Accordingly, the selective oxidation of benzyl alcohol to benzaldehyde over TiO2 relies on the synergy between electrons and holes. Ti3+ species in TiO2 are crucial for generating alcohol cation radicals and activating molecular O2, which enhances the conversion efficiency of benzyl alcohol.347,348 However, the VB potential of TiO2 (2.9 V vs. RHE) is more positive than the benzaldehyde/oxidized benzaldehyde redox potential (2.5 V vs. RHE), leading to further oxidation of benzaldehyde to byproducts like benzoic acid and CO<sub>2</sub>, reducing selectivity. Therefore, creating TiO<sub>2</sub> with a high concentration of Ti3+ species and a less positive VB could improve both conversion efficiency and selectivity for benzaldehyde during the photocatalytic oxidation of benzyl alcohol. The TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> composite enhances the photocatalytic selective oxidation of alcohols by stabilizing oxygen vacancies and Ti3+ species. This stabilization boosts the production of active intermediates for the conversion of benzyl alcohol to benzaldehyde. The up-shifted valence band of TiO2 in the composite prevents further oxidation of benzaldehyde, increasing selectivity and efficiency.<sup>343</sup>

Recently, Ti<sub>3</sub>C<sub>2</sub>/TiO<sub>2</sub> nanocomposite was used for photocatalytic oxidation of biomass-derived alcohols, and other aromatic alcohols to corresponding aldehydes. 22 The enhanced photocatalytic activity is attributed to the abundant functional groups on the Ti<sub>3</sub>C<sub>2</sub> MXene and the in situ formation of TiO<sub>2</sub> nanoparticles on the MXene sheets. The proposed reaction mechanism involves TiO2 nanoparticles forming a close interface with MXene nanosheets. Under full-spectrum illumination, electrons are excited from the valence band to the conduction band of TiO2, then quickly transferred to the Ti3C2 nanosheets, aiding the separation and prolonging the lifespan of photogenerated carriers. The system facilitates oxidation through photogenerated holes and tert-butoxy radicals, driven by the reduction of adsorbed oxygen. The Ti<sub>3</sub>C<sub>2</sub>/TiO<sub>2</sub> composite shows higher photocatalytic conversion efficiency and selectivity for furfuryl alcohol oxidation than pristine TiO<sub>2</sub>, with the optimized photocatalyst achieving a 99% yield of furfural.

Besides MXene, Lu et al. developed core-shell composites composed of TiO<sub>2</sub> nanobelts as the core and COFs of varying thicknesses as the shell, which enhanced the reactivity, selectivity, and stability for benzyl alcohol oxidation.<sup>21</sup> The COFs,

with their narrow bandgap, absorbed visible light and generated electrons and holes in their conduction and valence bands, respectively. Electrons migrated from the COF's conduction band to TiO2's conduction band, while holes facilitated the oxidation of benzyl alcohol to form carbon-centered radicals. These radicals reacted with superoxide radicals, produced by the accumulated electrons activating O2, to form benzaldehyde. The TiO2@COF composite with a 15 nm COF shell demonstrated the highest benzyl alcohol conversion (92.5%) with a maximum rate constant of  $6.73 \times 10^{-2} \text{ h}^{-1}$ under visible light (>420 nm), performing 10.1 times better than TiO2 alone and 12.9 times better than COF alone.

#### 7.7. Photochromic systems for electronic devices

A TiO2-based color switching system typically involves the reversible color displaying capability of TiO2, which allow the material to change its color in response to an external stimulus, such as an applied voltage or light irradiation. 349-351 A 2D TiO2 layer has been used as the electrochromic layer combining with a MXene layer (e.g., Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>) for flexible transparent electrodes in electrochromic devices.352 To attain the desired TiO<sub>2</sub> phase, the anatase TiO<sub>2</sub> phase was derived from Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> through annealing in air, which demonstrated with good electrochromic properties. The Ti<sub>3</sub>C<sub>2</sub>Tx and TiO<sub>2</sub> 2D nanosheets were self-assemble into Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and TiO<sub>2</sub> films through liquid/ liquid interfacial self-assembly to give a uniform and high coverage layer and transferred consecutively onto a polyethylene terephthalate substrate to form TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> heterostructures. The heterostructures demonstrated outstanding electrochromic performance (e.g., fast coloration speed and high coloration efficiency) because of the 2D nature of the TiO2 flakes as well as the well-balanced porosity and loosely networked structures that promote efficient ion diffusion and electron transport. In addition, the 2D network structure also assists in redistributing the induced strain uniformly, enhancing both the mechanical strength and the flexibility of the film, which is important for the application in flexible electrochromic devices.

Several reports have demonstrated the photoreversible color-switching systems based on photocatalytic TiO2 nanocrystals to induce a reversible redox reaction of chromic dyes, resulting in changes in color. 353,354 Later developments in TiO2-based photoreversible color switching systems focused on improving cyclability and coloring duration through doping and surface engineering.355-357 For instance, binding organic sacrificial electron donors to the surface of TiO2 is beneficial for the stabilization of nanocrystals and removal of photogenerated holes, thereby enabling cycling of the color-switching system until the surface-bound sacrificial donors are exhausted or depleted. On the other hand, the doping-induced lattice distortion in anatase TiO2 nanocrystals promotes efficient charge separation and migration, altering the kinetics of redox reactions, and tuning the material's optical properties. These enhancements enable TiO2 nanocrystals to undergo rapid and reversible changes in color upon exposure to light. 355,358

By leveraging on the photocatalytic property and color changing capability of TiO<sub>2</sub> nanocrystals under redox reaction (Ti<sup>3+</sup> and Ti<sup>4+</sup>), a photoreversible color-switching paper based on these TiO2 nanocrystals can repeatedly write and erase content in response to UV irradiation and oxygen exposure (Fig. 10A). To promote good coloration response in atmospheric conditions, N-doping was introduced in creating large quantity of defects (oxygen vacancies) on the TiO2 surface to improve the chemisorption of polyol groups for scavenging photo-generated holes. In addition, N-doping also induces substantial physisorption of polyol molecules that acts as a protective layer on the surface of TiO2 nanocrystals by limiting the diffusion of ambient oxygen molecules, thereby reducing the rate of oxidation of Ti<sup>3+</sup> species back to Ti<sup>4+</sup> (Fig. 10B). When exposed to UV irradiation, the TiO2 nanocrystals undergo photoexcitation, generating electrons that induce reduction of Ti4+ to Ti3+ ions in the nanocrystal lattice. This

led to a color change from white to black or dark blue at the

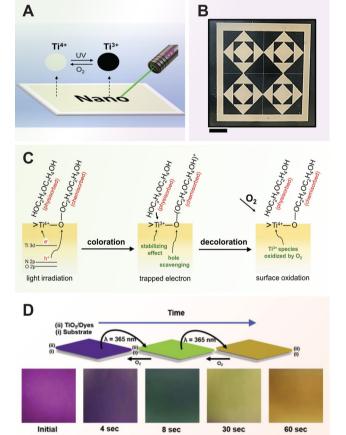


Fig. 10 Photochromic function of  ${\rm TiO_2}$  semiconductor. (A) Schematic illustration of the writing process on the rewritable paper using a laser pen and (B) light-printed pattern on rewritable film using a UV lamp. (C) Photoreversible color-switching mechanism of N-doped  ${\rm TiO_2}$  nanocrystals. Reproduced with permission from ref. 359. Copyright 2022, Wiley-VCH. (D) Color-switching process and the corresponding color change of the film under continuous UV irradiation. Reproduced with permission from ref. 356. Copyright 2019, Elsevier.

irradiated regions, allowing for visible writing or marking on the paper surface (Fig. 10C). To erase the writing or markings, the rewritable paper is exposed to oxygen or air, which serves as an oxidizing agent. Oxygen molecules react with the reduced Ti<sup>3+</sup> ions in the TiO<sub>2</sub> nanocrystals, oxidizing them back to Ti<sup>4+</sup> ions and restoring the original white color of the paper. This color-switching systems process is typically rapid, enabling multiple cycles of writing and erasing without degradation of the paper substrate.

Combining oxygen vacant TiO2 and reduced graphene oxide enables the realization of four distinct types of photochromic devices, each exhibiting unique properties and functionalities (i.e., multi-wavelength photochromism, intensity-dependent photochromism, time-dependent photochromism, dualresponse hydro-/photochromism).356 All of the mentioned photochromic devices can exhibit rapid and reversible color changes through precise control of applied stimuli and demonstrate distinct multi-color states. By carefully engineering the composition and structure of the composite material, the multi-wavelength photochromic device can selectively respond to specific regions of the electromagnetic spectrum. The intensity-dependent photochromic device responds sensitively to variations in the intensity of incident light. In the time-dependent photochromic device, color changes evolve gradually over time in response to continuous light illumination (Fig. 10D). The dual-response hydro-/photochromic device exhibits reversible color changes in response to both light irradiation and variations in humidity. The success of these designs hinge on the development of a highly reductive catalyst as well as the manipulation of the film structure and the dye reduction kinetics to exhibit distinctive and customizable responses to various stimuli, such as light, humidity, or temperature changes. This approach enables the development of versatile and functional photochromic materials with applications across diverse fields, including optoelectronics, advanced sensors, displays, and rewritable media.

## 7.8. Photocatalytic reactions for plastics: polymerization, degradation and conversion

The ability of semiconductors to generate free radicals upon photoexcitation, allows them to be employed for initiating heterogenous free radical polymerization, which is a commonly used method for synthesizing polymers from vinyl monomers. The radicals are generated via the photodegradation of surrounding organic compounds<sup>360</sup> or water when they react with the holes in the VB of TiO2 (refer to section 1). These compounds containing radicals would then serve as the initiators for free radical polymerization to take place. The first photocatalytic surface-Initiated polymerization TiO2 photoinitiated polymerization were reported by Kraeutler et al., for the bulk polymerization methyl methacrylate (MMA).361 Other semiconductors, such as ZnO and CdS, shows similar photoinitiation ability for free radical polymerization.362-364 Apart from PMMA, 365-368 polymerization of other vinyl monomers have also been reported including homopolymers such as poly (styrene), 362,364 and co-polymers consisting of different repeat

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units.<sup>369</sup> Interestingly, such heterogeneous surface-initiated polymerization technique opens the pathway to fabricate coreshell structures that have a polymer shell encapsulating the inorganic semiconducting particles. For instance, Kong *et al.* synthesized TiO<sub>2</sub> particles embedded within antibacterial poly [2-(*tert*-butylamino)ethyl methacrylateco-ethylene glycol dimethacrylate] shell.<sup>369</sup> Wang *et al.* synthesized core–shell nanospheres with TiO<sub>2</sub> core embedded within PMMA, poly (styrene) or Poly(*N*-isopropylacrylamide) (PNIPAM) shell, along with tunable spherical structures that can be manipulated through the compatibility between the polymers and TiO<sub>2</sub> par-

ticles. 370 For other non-photoactive particles (e.g., SiO<sub>2</sub>), a thin

layer of TiO2 coating would allow them to achieve similar

photocatalytic polymerization ability. 370,371 On the other hand, the generation of radical by TiO2 can also lead to depolymerization, which reduces the molecular weight of polymers, and hence, resulting in degradation to the physical properties of plastic materials. Polyolefins, the largest class of polymers produced, can be subjected to accelerated degradation by radicals generated by TiO2, despite being amongst the most chemically resistant among plastics. 372,373 For instance, the hydroxyl radicals generated by TiO2 can lead to hydrogen abstraction of polyolefins, forming alkyl radicals that causes a series of reaction including chain scissions. Zapata et al. reported about 57-60% reduction in molecular weight of polypropylene with TiO2 nanotubes embedded within as compared to 37% reduction for pure polypropylene, after subjecting to 0.55 W m<sup>-2</sup> of 340 nm irradiation for 10 days.<sup>374</sup> Similarly, Day reported significant reduction in embrittlement times (defined as 50% reduction in elongation as break) of 100 µm thick polyethylene films embedded with different forms (e.g. polymorphs, coated/uncoated) of TiO<sub>2</sub>.<sup>375</sup> Uncoated anatase appears to the most active, with 20 000 mg kg<sup>-1</sup> incorporated embedded in polyethylene, a ten times reduction in embrittlement time is observed as compared to the pristine polyethylene. Zhao et al. also reported on enhanced photocatalytic degradation of polyethylene using copper phthalocyanine modified TiO2, leading to faster photodegradation rates.449 On the other hand, TiO2 particles have commonly been incorporated into polyvinyl chloride to prevent UV degradation.<sup>16</sup> Their ability for UV absorption can compete with direct UV-induced degradation associated with vinyl polymers, given the bonds energy of C-C (375 kJ mol<sup>-1</sup>) and C-H (420 kJ mol<sup>-1</sup>) falls within the range of UV light energies.<sup>372</sup> However, they will also induce photocatalytic oxidative degradation with radical generation, leading to the loss of gloss on the polyvinyl chloride surface and the degradation of mechanical properties. Nevertheless, it has been reported that the penetration of UV light reduces by 90% at a depth of  $20 \mu m$ ,  $^{376,377}$  thereby limiting the degradation to a shallow surface, while the bulk of polyvinyl chloride remains largely protected.

Photocatalytic depolymerization also opens up a pathway for plastic recycling, as monomeric building blocks can be recovered for re-polymerization. Such chemical recycling techniques are often less energy-intensive than conventional mechanical method.  $^{378-380}$  In comparison, mechanical recycling methods causes material degradation leading to lower quality and reduced properties of the recycled materials, thereby often being labelled as a "downcycling" process. This is unlike chemical recycling that deconstructs the material at a molecular level, allowing a renewed production of the pristine material. For example, Daraboina and Madras employed  ${\rm TiO}_2$  synthesized by combustion synthesis to perform photocatalytic degradation of PMMA, poly(butyl methacrylate) (PBMA) and their co-polymers, yielding their respective monomers.  $^{381}$  These recovered monomers can serve as the feedstock for the repolymerization of these poly (alkyl methacrylates).  $^{382}$ 

Similarly, photocatalysis can also be an effective tool to convert plastic materials to other chemical species beyond their monomeric/oligomeric form, allowing them to be repurposed upon reaching their end of life. 383-386 Recently, Nguyen and Edalati employed TiO2 for the photoconversion of poly (ethylene terephthalate) (PET) to terephthalate and acetic acid, and the latter is widely used in chemical, plastic and food production.<sup>387</sup> They also found brookite polymorph of TiO<sub>2</sub> to be most active in this photocoversion process, followed by rutile, and finally anatase. Other than such direct photoconversion of plastics, the polymers also can undergo an initial step of degradation/depolymerization to smaller chemical compound prior to photocatalytic conversion into other useful molecules. For example, Han et al. reported photocatalytic conversion of ethylene glycol derived from alkaline hydrolyzed PET, into glycolic acid, glycolaldehyde, and ethanol, using photocatalytic carbonized polymer dots graphitic carbon nitride. 388 Similarly, for TiO2, Bhattacharjee et al. performed enzymatic pretreatments on polyesters plastic prior to photo conversion of PET and polycaprolactone using Pt-loaded TiO2, resulting in the formation of pentanal and formic acid products.<sup>56</sup> In cases where the chemical products obtained are of higher value than the initial plastic, such processes would be referred to as an "upcycling" process. For example, using TiO2 modified with potassium stearate or N,N-diethyl-3-(trimethoxysilyl)propan-1amine, Peng et al. reported the successful photoconversion of poly(styrene) wastes into benzoic acid with 18-44.2 mol% yields under mild conditions.<sup>389</sup> Such aromatic compounds would find applications food, cosmetic and pharmaceutical products.

In addition, many of the photoconversion process of plastic materials described above can be conducted with a simultaneous production of hydrogen fuel. This process commonly known as photoreforming first described by Kawai and Sakata in 1981, using Xe-lamp irradiation on platinized TiO<sub>2</sub> photocatalyst in the presence of water and chlorine or nitrogen containing organic molecules.<sup>37</sup> The difference between photoforming and typical photocatalytic water splitting is the participation of the organics (*i.e.*, polymer or plastic-derived chemicals) as a feedstock for hydrogen production. In photoreforming, the oxidation of the organic compound replaces oxygen evolution reaction for hole consumption, thereby acting as a hole scavenger that supresses the electron–hole recombination, resulting in the increase rate of H<sup>+</sup>/H<sub>2</sub>O reduction boost-

ing H<sub>2</sub>O production as compared to typical photocatalytic water splitting. 384,390,391 More importantly, the additional production of clean H2 fuel further adds value to the photocatalytic conversion of plastic materials.

## Conclusions and perspectives

Photocatalysis is recognized as a promising sustainable technology for solving environmental and energy problems by harnessing solar light. Numerous research attempts in the field of photocatalysis have clearly shown that TiO2 is one of the most extensively studied photocatalysts due to its excellent photocatalytic properties. The continuous progress in TiO2 photocatalyst research is driven by the material's inherent advantages such as chemical stability, non-toxicity, cost-effectiveness, and strong oxidative power under UV light. However, the challenges of narrow light absorption and fast charge recombination have prompted extensive research into TiO<sub>2</sub> material engineering. In view of these developments, the emergence of TiO2 photocatalysis and the modification methods of TiO2-based photocatalysts were comprehensively reviewed in this paper.

Advancements in engineering TiO2 through doping have extended its activity into the visible light range. However, metal doping faces challenges such as thermal instability, high fabrication costs, and increased charge-carrier recombination, which reduce efficiency. Conversely, non-metal doping is generally more cost-effective and stable but requires careful control to avoid disrupting the lattice structure. By integrating techniques like morphological control, crystal phase manipulation, doping, and hybridization, researchers have improved charge carrier separation and extended the applicability of TiO<sub>2</sub> in a wide range of photooxidation and photoreduction reactions. These applications include organic pollutant degradation, photocatalytic disinfection, hydrogen generation, CO2 reduction, nitrogen fixation, hydrogen peroxide generation, alcohol oxidation, plastic polymerization and degradation, and photochromic applications.

Future research in TiO<sub>2</sub> photocatalysis is poised to focus on several key areas, particularly the modification of TiO<sub>2</sub> materials to enhance their performance. Advances in 3D printing technologies have significantly impacted the development of these materials. 3D printing allows for precise control over the design and fabrication process, enabling the creation of complex structures with tailored porosity and flow characteristics. By building objects layer by layer from digital designs, 3D printing can produce photocatalytic materials with optimized pore sizes and shapes, enhancing the flow of pollutants and improving contact with the photocatalyst surface. This precision in design is expected to lead to significant improvements in the efficiency and effectiveness of photocatalytic

Another promising area of future research is the development of single-atom catalysts. These catalysts represent the ultimate small-size limit for metal particles, containing iso-

lated metal atoms singly dispersed on supports. Single-atom catalysts maximize the efficiency of metal atom use, which is particularly important for supported noble metal catalysts. The well-defined and uniform dispersion of single atoms offers great potential for achieving high catalytic activity and selectivity. By utilizing each metal atom to its fullest potential, single-atom catalysts can provide exceptional performvarious catalytic applications, including photocatalysis.

Photocatalytic upcycling and depolymerization of polymers have emerged as promising strategies to address plastic pollution and advance a circular economy. Recycling polymers with backbone structures primarily composed of C-C bonds is particularly challenging due to the lack of functional groups, making these materials difficult to break down and reuse. Consequently, the valorization of common commodity plastics such as polyethylene (PE) and polypropylene (PP), which are major contributors to the plastic pollution problem, is a crucial next step.

Traditional studies of TiO2 photocatalysis have used static ensemble-averaged methods, providing valuable but limited insights into fundamental processes. Future research will utilize advanced in situ and time-resolved techniques to capture real-time dynamic processes, such as ultrafast electron dynamics and charge carrier lifetimes, revealing key mechanisms like charge separation and transfer. For example, in situ extended X-ray absorption fine structure has been used to study the dynamic changes in chemical valence and coordination environment of isolated metal centers in a multi-edged TiO<sub>2</sub>-supported single-atom Ru photocatalyst. Additionally, femtosecond time-resolved, surface-specific vibrational sum frequency generation spectroscopy has investigated the photoinduced reaction at the TiO2-water interface, observing the interfacial water molecule reactions with high temporal precision. In situ mass spectrometry will further aid in analyzing gaseous products and intermediates, elucidating reaction pathways and mechanisms.

Future research in TiO<sub>2</sub> photocatalysis will increasingly rely on theoretical calculations, such as density functional theory, molecular dynamics simulations, and kinetic modeling, to complement experimental techniques. These computational methods will model electronic structures, predict reactivity, and develop comprehensive reaction models, providing a holistic understanding of photocatalytic mechanisms. This integration will enable the optimization and development of more efficient and tailored photocatalysts for various applications. Currently, research on TiO2 photocatalysts largely depends on experimental work, which can be complex and costly. Moving forward, the incorporation of machine learning, big data, and artificial intelligence holds significant potential to generate high-performance models that predict material properties and elucidate property-structure relationships. These advanced computational tools can streamline the research process through high-throughput screening, reduce experimental complexity, and lower costs. This approach will not only enhance our understanding of TiO2-based photocatalysts but also drive

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the development of more effective and efficient materials, advancing their practical applications on an industrial scale.

### **Author contributions**

Conceptualization and writing – original draft: S. Y. Tee, J. Kong, J. J. Koh, C. P. Teng, X. Wang, X. Wang, S. L. Teo. Conceptualization, supervision and writing – review & editing: W. Thitsartarn, M-Y Han, and Z. W. Seh. All authors have read and agreed to the published version of the manuscript.

## Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

### Conflicts of interest

There are no conflicts to declare.

# Acknowledgements

This research is supported by the National Research Foundation, Singapore, and Agency for Science, Technology and Research (A\*STAR), under its low carbon energy research (LCER) phase 2 HETFI Directed Hydrogen programme (Grant No.: U2307D4001), the A\*STAR SERC MTC YIRG (Grant No.: M21K3c0125), and the A\*STAR IMRE–SCG Chemicals Advanced Composite Joint Lab (IAF-ICP Project No.: I1801E0024).

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