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Tailoring Photocatalytic Materials Through Defect Engineering: Control, Mechanism, and Experimental Protocols

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1.1 Introduction

Photocatalysis process inspired by natural photosynthesis and dating back more than 100 years is considered a distinct class of chemical transformations [1, 2]. It employs the light energy to activate and drive several reactions that are challenging, sometimes even impossible [1–3]. In this process, electron–hole pairs (e^-/h^+) were formed when catalytic feedstocks were irradiated by UV lamps, xenon lamps, or even sunlight. Then, these generated electrons–hole pairs can migrate to generate oxidizing species, including hydroxyl radical (•OH) or superoxide radical ($\bullet O_2^-$) that display strong oxidation of inorganic and organic matters, converting them into unharmful products and sometimes into high-added chemicals and fuels [4–6]. Most recently, several classes of photocatalytic materials including traditional semiconducting photocatalysts, 2D photocatalysts, molecular photocatalysts, photovoltaic-assisted catalysts, plasmonic metal photocatalysts, and novel emerging photocatalytic feedstocks such as quantum dot-based materials have shown tremendous benefits in several photocatalytic applications (Figure 1.1) [1].

Even though the great progress has been made in the photocatalysis process in many applications including biological sector, organic reactions, energy storage, green fuels production, and environmental implementations, highly reactive photocatalytic feedstocks are still much needed at the present and in the future [7–14]. In order to address this issue, defects can significantly influence the properties of photocatalytic feedstocks, especially their photocatalytic performance

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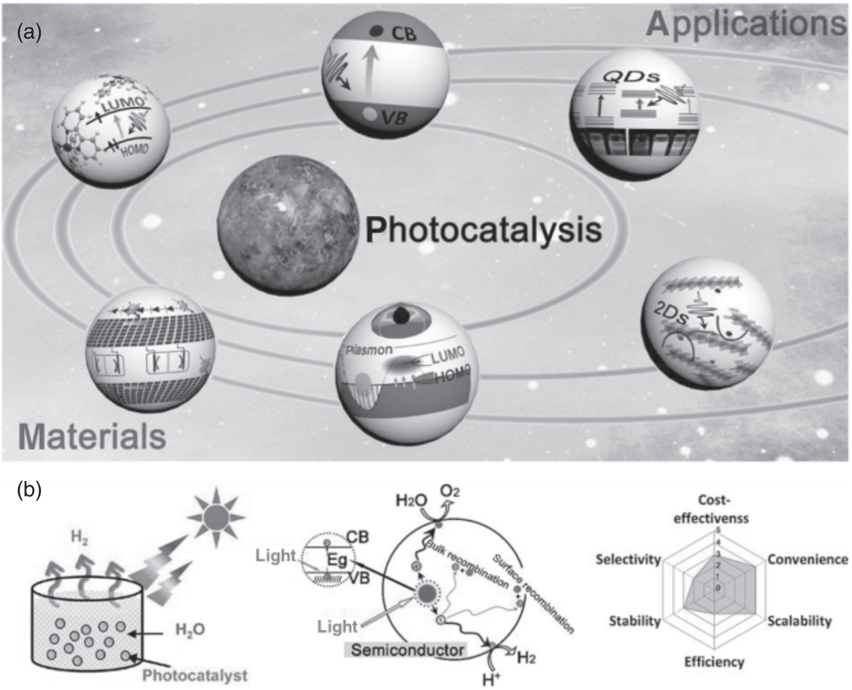

Figure 1.1 (a) Examples of photocatalytic feedstocks. (b) Particles dispersion in single reactor, two side reactions at single particle, benefits of photocatalysis. *Source:* Reproduced from Yang and Wang [1] / with permission of American Chemical Society.

(i.e., light absorption, charge separation, surface reactivity, energy levels, and stability) (Figure 1.2) [15, 16]. Besides, by carefully introducing specific types and concentrations of defects, researchers and industrialists can enhance the desired characteristics of photocatalytic materials for a wide range of photocatalytic applications [17–23]. Moreover, it allows the fine-tuning of material properties by adjusting defect concentrations and types. By strategically introducing and manipulating defects, materials can be optimized to achieve specific performance requirements, such as improved charge separation and light absorption in photocatalytic materials, which enhance their photocatalytic activities [24, 25]. It is important to note that certain defects can exhibit unique functionalities that are not present in perfect photocatalytic materials. For example, defects like point defects or surface defects can serve as active sites for chemical reactions, resulting in enhanced photocatalytic activity of some target feedstocks [15]. Defects can also alter the electronic band structure, which is beneficial in the photocatalysis process. In this account, defect engineering is an integral part of design and synthesis of photocatalytic materials. Additionally, understanding the relationship between defect characteristics (size, distribution, and type) and the resulting photocatalytic material properties helps guide the development of new photocatalysts with desired attributes [15]. While defect engineering offers exciting opportunities, it also presents some challenges [26, 27]. Interestingly, careful control of defect introduction and optimization is

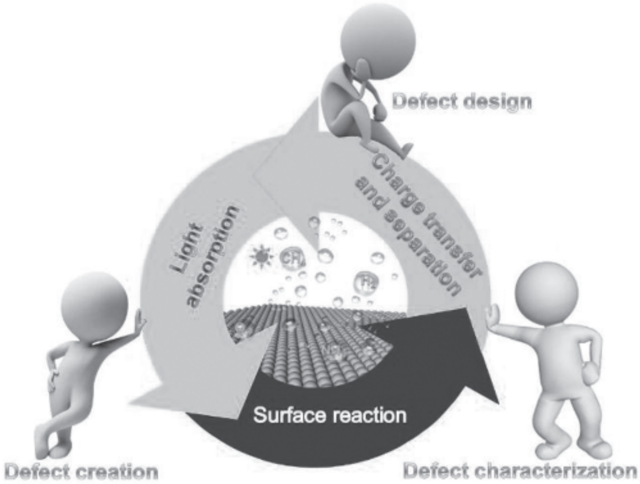

Figure 1.2 Benefits of defects design, creation, and characterization in photocatalytic materials. *Source:* Reproduced from Bai et al. [15] / with permission of Elsevier.

necessary to ensure reliability, stability, and reproducibility of photocatalytic materials [28]. Then, the reliability of defect-engineered photocatalytic feedstocks must be evaluated under various conditions to understand their long-term behavior and efficiency [29]. This chapter provides an overview of the design of defect engineering in organic and inorganic feedstocks with a focus on their structures and electronic and photoelectronic properties. In addition, it summarizes the preparation methods of these feedstocks and provides information about the characterization techniques and theoretical modeling utilized to confirm the successful preparation of defective engineered materials. Finally, benefits and drawbacks of defective photoactive feedstocks usages are presented. To sum up, this chapter provides an excellent platform for the fabrication of defect-engineered materials and their applications in fields such as organic chemistry, phototherapy, and environmental and energy implementations at present and in the future.

1.2 Defects Creation and Applications

In the recent decades, several works have been reported on the defect engineering in photocatalytic feedstocks and excellent results have been discovered so far in many photocatalytic applications (Figure 1.3a) [30, 31]. As a matter of interest, the preparation of defective engineered materials has been regarded as a desired option for highly efficient photocatalytic feedstock synthesis [30, 31]. It is worth mentioning that the control of defect formation in photocatalytic materials is essential for optimizing their efficiency in several applications. Strictly speaking, defect formation or creation (i.e., point defects, volume defects, line defects, surface defects, planar defects, and volume defects) in photocatalytic materials involves the usages of sophisticated strategies (Figure 1.3b) [30, 31].

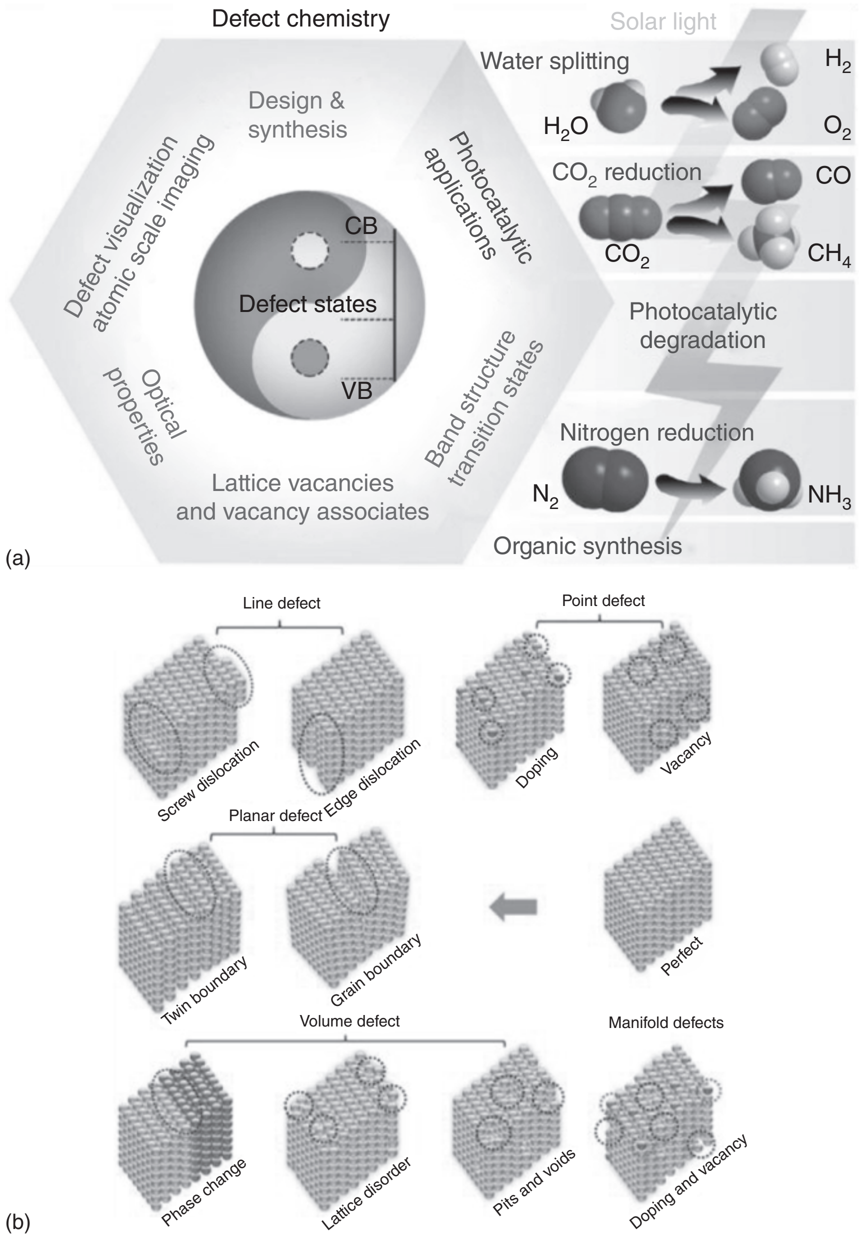

Figure 1.3 Defect chemistry of photocatalytic materials from design to visualization and photocatalytic implementations (a), and different defects creation with local atomic structures in the photocatalytic materials (b). *Source:* Reproduced from Zafar et al. [30] / with permission of John Wiley & Sons.

It should be noted that the creation/formation of defects in photocatalytic feedstocks is the stringent requirement for the defect creation and formation in photocatalysis. The strategies of creating or forming defects in photoactive materials are extremely dependent on the types of defects. Till now, several synthetic strategies have been reported to prepare photocatalytic materials containing defects, which can usually be divided into two classes: introduction of defects into prefabricated photocatalytic feedstocks and creation of defective sites during the preparation of photocatalytic materials [15]. Generally speaking, dopants, vacancies, voids, and lattice disorder in the surface or bulk of photocatalysts have been widely utilized in the preparation of highly efficient photoactive materials.

1.2.1 Dopants

To date, the controlled introduction of specific impurities (dopants), including cationic dopants, anionic dopants, and dual dopants, into the structure of photocatalytic material to modify its photocatalytic features has emerged as one of the excellent options in the synthesis of highly photoactive feedstocks [15]. Doping can be considered a kind of interior alterations or surface modification to rebuild the site configuration of photocatalytic materials, which can be realized at elevated temperature with liquid, gas, or solid precursors [15, 32, 33]. For example, in 2021, Helmy et al. developed S-doped TiO_2 (GST) nanoparticles (NPs) utilizing the sol–gel method, and an aqueous solution of *Malva parviflora* plant is employed as the green and adaptable medium with good reducing and capping features to promote the S-doping and crystal growth of TiO_2 [34]. The authors utilized X-ray powder diffraction (XRD), ATR–Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), electrochemical impedance spectra, energy dispersive X-ray analysis (EDX), X-ray photoelectron spectroscopy (XPS), etc., to confirm the successful doping of sulfur into TiO_2. Using the FTIR technique, they observed absorption peaks at 1139 and 1311 cm^{-1}, which can be attributed to symmetric and asymmetric stretching of S=O bond, respectively; meanwhile, the peak appearing at 1056 cm^{-1} can be attributed to the symmetric S=O bond (Figure 1.4a).

Based on XPS results, the S2p XPS peaks at the binding energy of 168.3 eV for CST and GST materials can be attributed to the higher oxidation state of S^{2-} ions usually present in binding energy over 168 eV (Figure 1.4b–d). They found that S^{2-} ions very likely substituted the O^{2-} ions in TiO_2. Besides, some sulfate entities ($SO_4{}^{2-}$) could be produced on the TiO_2 surface. They concluded that the obtained S-doped TiO_2 nanoparticles display excellent antimicrobial activity against *Streptococcus pyogenes, Candida albicans*, *and Salmonella typhimurium*, and high antioxidant features that reach more than 90% inhibitions (Figure 1.4e).

In 2016, Dai et al. reported Ce-doped Bi_2MoO_6 (Ce-BMO) with distinct Ce/Mo molar ratios (5%, 10%, 20%, and 40%) via a facile one-step hydrothermal strategy with greatly enhanced visible-light-driven photocatalytic efficiency for the degradation of highly dangerous nerve agent simulants and dyes, as well as bacterial photodestruction [35]. They utilized XRD to reveal the composition and crystallinity of the fabricated photocatalysts and inductively coupled plasma mass spectrometry

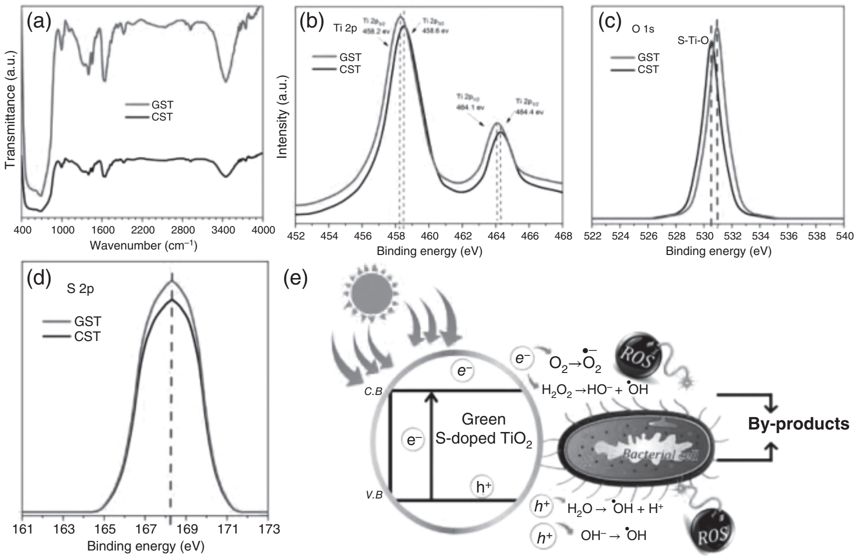

Figure 1.4 (a) ATR–FTIR spectra of S-doped TiO_2 NPs employing ethanol as the solvent (labeled as CST) and S-doped TiO_2 NPs (denoted as GST) employing $TiCl_4$ and thiourea as Ti and S sources; (b–d) XPS spectra for Ti 2p, O 1s, and S 2p core levels for CST and GST NPs; and (e) photodestruction mechanism of bacteria over S-doped TiO_2 NPs. FTIR: Fourier transform infrared spectroscopy, XPS: X-ray photoelectron spectroscopy. *Source:* Reproduced from Helmy et al. [34] / with permission of Elsevier.

(ICP-MS) to assess the relative content of cerium atoms in Ce-doped Bi_2MoO_6. Then, they applied SEM, transmission electron microscopy (TEM), UV-vis diffuse reflectance spectra (UV–Vis-DRS), Brunauer–Emmett–Teller (BET), XPS, photoluminescence (PL), time-resolved photoluminescence spectra (TR-PL), and Raman spectra to get an insight about morphology, chemical structure, and optical features of the as-prepared photocatalysts. Through the aforementioned techniques, Dai's group noticed that Ce-doped BMO displays different distortion and symmetry breaking of the MoO_6 octahedron, especially for the material Ce-BMO (40%). Referring to ICP-MS measurements, they revealed that the replacement of a Mo atom by a Ce element only occurred in Ce-BMO materials with high doping amount, which is different from the doping step of Ce-BMO with insufficient doping amount (Figure 1.5). They also observed that when cerium ions were included into Bi_2MoO_6, the doping step undergoes two stages: in the first step, the substitution of Ce^{3+} cation (ionic radius equal to 0.102 nm) for Bi^{3+} cation (ionic radius = 0.103 nm); in the second step, the substitution of Ce^{4+} cation (ionic radius equal to 0.087 nm) for Mo^{4+} cation (ionic radius = 0.065 nm). More importantly, they evidenced that the cerium doping process can lead to distinct types of crystal defects (i.e., symmetry disturbance, redox couple, and oxygen vacancy).

Interestingly, they concluded that the redox couples formed in the Ce-doping step such as Ce^{3+}/Ce^{4+} and Mo^{4+}/Mo^{6+} could obviously boost the ROS generation by one-electron and two-electron reactions, separately, which is conductive for efficient

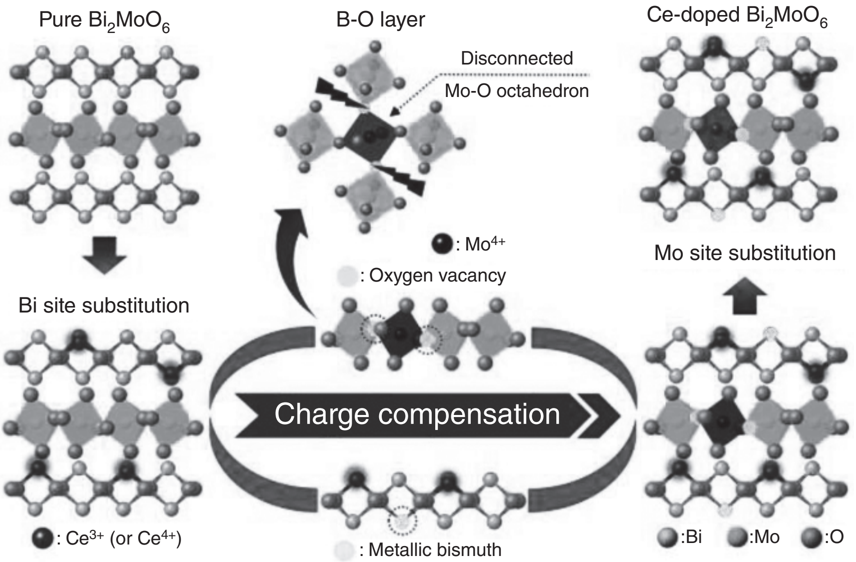

Figure 1.5 Formation pathway of crystal defects in a Ce-doped Bi_2MoO_6 structure. *Source:* Reproduced from Dai et al. [35] / with permission of American Chemical Society.

bacterial inactivation and other applications. The formation of crystal defects by Ce-doping not only brings new advantages for improving the photocatalytic efficiency of Bi_2MoO_6-based feedstocks, but also brings an excellent route to synthesize high-efficient photocatalysts by controlling the type and amount of crystal defects.

In summary, in addition to the above-mentioned photocatalysts, various doped photoactive feedstocks have been reported in the literature, highlighting their photocatalytic features enhancement, including bandgap engineering, charge carrier separation, surface and optical properties, resulting in an improvement of their stability and interaction with reactants. Additionally, doped photocatalysts have shown great promises in various applications such as green energy production, valuable chemical synthesis, and environmental implementations [36–40]. In the future, advanced methods should be applied in the synthesis of doped photocatalysts such as finding new and more efficient dopants and understanding the mechanisms behind doping effects to predict and manipulate photocatalytic features more effectively for large-scale applications of the photocatalysis processes.

1.2.2 Vacancies

Vacancies including cation/anion vacancies and interstitial sites in photocatalytic materials are critical to improve their photocatalytic performance. Besides, by fabricating photocatalysts with a controlled number of vacancies, researchers and industrialists can control their properties for specific applications such as environmental remediation, energy conversion, and other areas requiring photocatalytic processes. For example, in 2021, Kang et al. developed $Mo_{1-x}S_2$ ($Mo_{1-x}S_2/TiO_2$)

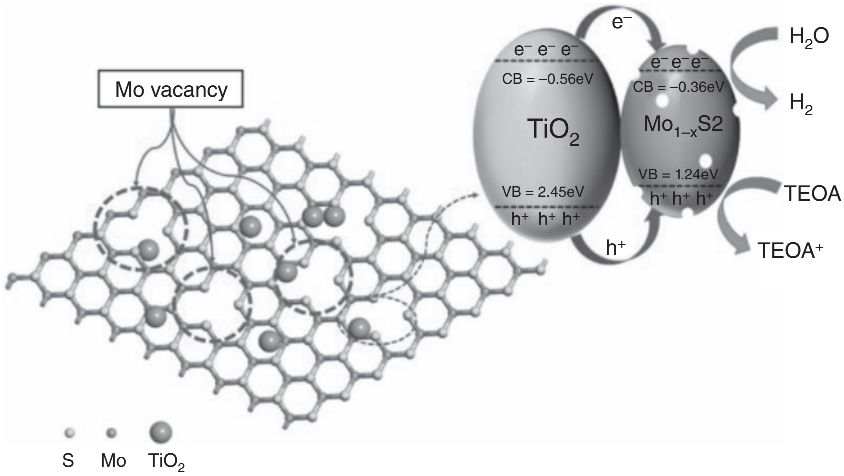

Figure 1.6 Photocatalytic hydrogen production mechanism over the $Mo_{1-x}S_2/TiO_2$ photocatalyst. *Source:* Adapted from Dai et al. [35].

with controllable Mo vacancies using the hydrothermal strategy for the hydrogen evolution reaction (HER) (Figure 1.6) [41].

They utilized XRD, SEM, TEM, high-resolution transmission electron microscopy (HRTEM), UV–Vis-DRS, XPS, Raman spectrometer, PL, and photoelectrochemical measurements in order to confirm the chemical composition, crystalline structure, morphology, and photoelectric properties of the obtained photocatalyst. Besides, the content of the Mo and S elements in the as-prepared photocatalyst was measured employing ICP-OES. They demonstrated that the 2.5:1 ratio of $Mo_{1-x}S_2$ material displays the highest content of Mo vacancies. On the other hand, when the amount of $NaBH_4$ raises to a 6:1 ratio, the reduced amount of Mo vacancies can be explained by the fact that excessive $NaBH_4$ damages the structure of MoS_2, leading to the release of S atoms. More importantly, they proved that the rapid electron transfer hindered the recombination of photogenerated charge carriers. The $Mo_{1-x}S_2$ nanosheets acted as co-catalysts, which exposed more active sites in the presence of Mo vacancies, resulting in enhanced HER activity. They revealed that the rapid charge separation and transportation resulted in good HER activity. As an achievement of their work, they indicated that at an optimal molar ratio of 2.5:1 $Mo_{1-x}S_2/TiO_2$, the H_2 production rate was 1561 $\mu mol\,g^{-1}\,h^{-1}$ in triethanolamine medium, which is nearly 5.3 and 2.7 times higher than that of pure TiO_2 and MoS_2/TiO_2, respectively.

In another report, Liu et al. (2021) successfully prepared Bi atom and oxygen vacancy (OV)-rich $Bi_{12}TiO_{20}$ nanofiber (Bi/BTO) materials using the electrospinning method and subsequent chemical reduction strategy for NO removal [42]. During this study, they employed XRD, SEM, TEM, PL, surface photovoltage (SPV) spectra, and photoelectrochemical properties to get an insight about the composition, structure, and photocatalytic features of the as-fabricated photocatalyst. They concluded that the Bi/BTO photocatalytic feedstock displays significantly improved photocatalytic NO removal efficiency compared to pristine BTO under visible light exposure. The enhancement of photocatalytic efficiency is attributed to the integrative effect of OVs and surface plasmon resonance effect of Bi atoms. The presence of OVs is evidenced by XPS and electron paramagnetic resonance (EPR) spectroscopy. Besides, the density functional theory (DFT) studies indicate that the OVs in BTO lead to the generation of a defect level, which is conductive to increase light absorption. In addition, based on EPR measurements, they discovered that Bi could act as an electron sink, improving the separation and transfer of photoinduced electron–hole pairs (Figure 1.7).

Generally speaking, the introduction or creation of vacancies in defective photocatalytic materials is a desired option for optimizing their photostability and enhancing their photocatalytic performance. In the recent years, vacancies (i.e., anion and cation vacancies) have shown several benefits such as improved charge carrier dynamics, increased surface reactivity, tuned electronic properties of photocatalytic feedstocks, and also enhanced production of reactive oxygen species, which are responsible for the improvement of defective photoactive materials' performance in wide range of implementations such as environmental remediation, valuable products synthesis, and energy conversion technologies [43–47]. Even though great advancements have been made in defective photocatalytic materials with several vacancies, some issues still limit their applications [48, 49]. Among them, careful consideration is much needed regarding the control over defect concentration, reduced structural stability of defective photocatalysts, influence on their electrical properties, and recombination and aggregation issues. More importantly, the existence and distribution of vacancies in defective photocatalytic materials can be complicated to characterize accurately. Thus, advanced techniques are needed urgently to probe their existence and further understanding of how these vacancies influence photocatalytic mechanisms of photoactive feedstocks.

1.2.3 Lattice Disorder

Like element doping and vacancy creation, lattice disorder plays a critical role in improving the photocatalytic features of photocatalytic materials, but it can have both beneficial and negative effects [50, 51]. More precisely, it can enhance the surface reactivity of photocatalytic feedstocks by creating defect sites that can serve as active sites for photocatalytic reactions, trap charge carriers (electrons and holes), and facilitate the absorption of light. However, lattice disorder in defective photoactive materials often contributes to a loss of their crystallinity, and the excess of disorder can introduce recombination centers that trap charge carriers in the defective photocatalytic materials, thereby impacting their stability and efficiency in several applications. Even though there are aforementioned benefits and limitations of lattice disorder in photocatalytic materials, several photoactive feedstocks have been developed, recently, and further utilized in numerous implementations. For example, in 2019, Yang et al. reported a polyol process to form anatase TiO_2 NCs employing distinct surface ligands, suggesting that the proper choice of polyol as a solvent can be utilized to control both the surface disorder and crystalline structure of NCs. In order to evidence the lattice disorder in the obtained photocatalyst,

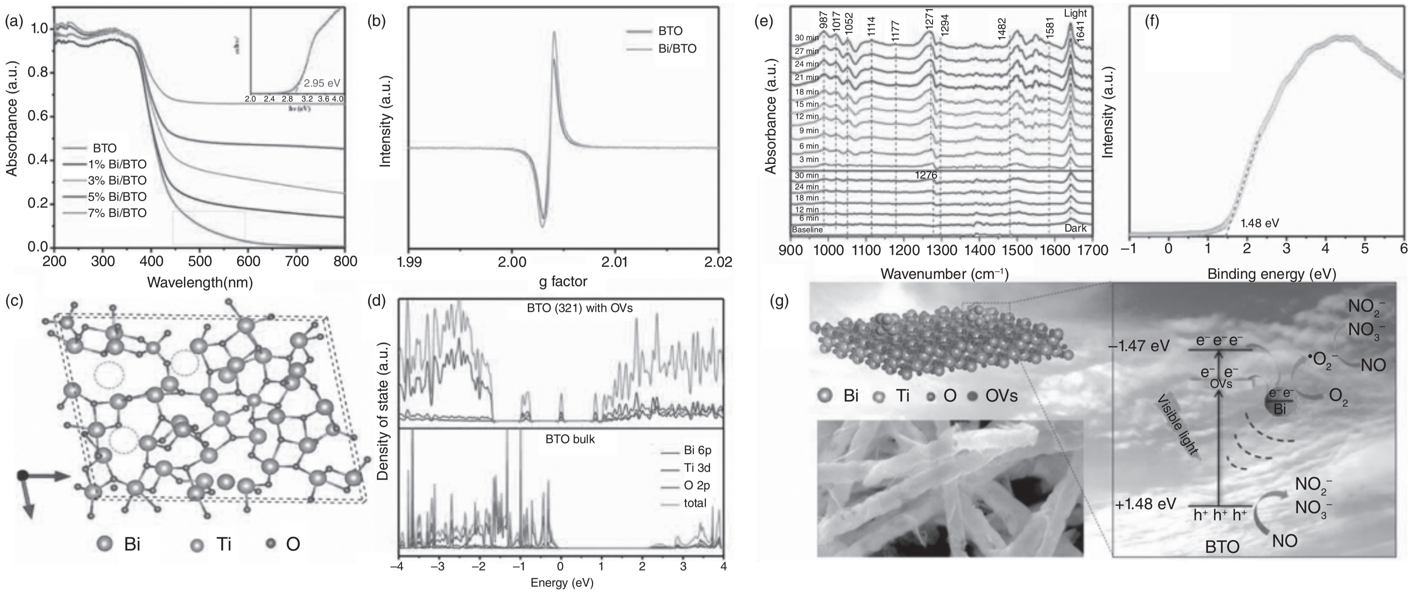

Figure 1.7 (a) UV–vis absorption spectra of the raw BTO and modified X% Bi/BTO (X = 1, 3, 5, and 7); (b) EPR spectra of raw BTO and modified 3% Bi/BTO; (c) crystal structure of BTO (321) plane along with OV formation (red circles denote OVs); (d) the density of states of bulk BTO and BTO (321)-rich OVs; (e) in-situ FTIR spectra of photocatalytic removal of NO gas over modified 3% Bi-BTO catalyst under dark and visible light irradiation; (f) VB-XPS spectra of raw BTO; and (g) plausible photocatalysis mechanism for NO removal over Bi/BTO catalyst. EPR: electron paramagnetic resonance, FTIR: Fourier transform infrared spectroscopy, VB: valence band, XPS: X-ray photoelectron spectroscopy. *Source:* Reproduced from Liu et al. [42] / with permission of Elsevier.

they employed XRD, Raman spectra, TEM, FTIR, UV-visible absorption, XPS, fluorescence spectra, ζ-Potential, electrochemical measurements, etc.; they indicated that Sn^{2+} cation is kinetically stable compared to Ti^{4+} and can occupy only the interstitial sites in $[TiO_4]$ and $[TiO_6]$, leading to a decrease in the lattice distortion energy. Besides, they demonstrated that the decrease in NC size appears with lattice expansion rising, with rising Sn^{2+} cation doping concentration with a rise in bulk defects, involving an optimal balance between them for simultaneous retention of the photoreduction efficiency and visible light absorption behavior of the TiO_2 NCs. Regardless of the as-fabricated photocatalyst application, they observed that under UV exposure, Sn^{2+}-doped TiO_2 NCs displayed higher photoreduction activity compared to undoped TiO_2, suggesting the existence of advantageous carrier trapping in Sn^{2+}-doped TiO_2 NCs. Besides, Sn^{2+} ions doping forms oxygen vacancies into TiO_2 NCs and the oxygen vacancies possess a pivotal role in the color switching of methylene blue [52].

In another research study, Li et al. reported an excellent example for this approach; they investigated structural disorder and its impacts on the optical features, electronic state, and photocatalytic efficiency of $ZnFe_2O_4$ (abbreviated as ZFO) obtained via the conventional solid-state reaction under different annealing temperatures (Figure 1.8).

In this study, Li's group utilized XRD, X-ray absorption spectroscopy (XAS), XPS, EPR, UV–Vis DRS, PL, and also DFT in order to get a deep insight about the impact of structural disordering and OV in the ZFO material on its band structure and oxygen reactive production for enhancing its photocatalytic behavior. They observed that a greater annealing temperature condition heavily leads to Fe^{III} transfers to the

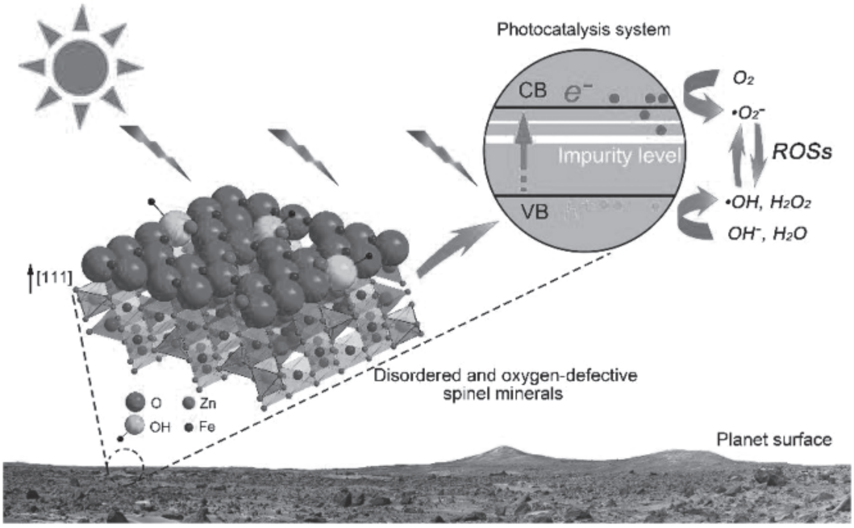

Figure 1.8 Disordered and oxygen-defective spinel minerals for ROSs photocatalytic production on the surface of a sunlit planet. ROSs: reactive oxygen species.
Source: Reproduced from Li et al. [53] / with permission of Elsevier.

tetrahedral site step by step and ZFO turns disordered [53]. They concluded that disordered and OV in $ZnFe_2O_4$ produces more hydroxyl radicals after irradiation compared to ordinary and defect-free ones, resulting in its narrower bandgap, accursed impurity levels, higher trapping e^- centers (VO^+), and a higher adsorption site of hydroxyl species. Besides, they mentioned that $ZnFe_2O_4$ is a model case to examine the effect of cation distribution on the semiconducting feature and photocatalytic efficiency and, therefore, pin down the important role of complicated spinel minerals in taking part in some vital redox chemical reactions in practical geological environment on the solid planet. In conclusion, lattice disorder in photocatalytic feedstocks can enhance their photocatalytic features like reactivity, charge carrier separation, and light absorption. However, it can lead to structural instability, increased charge recombination, and reduced selectivity of the modified photocatalysts. It should be noted that understanding and controlling lattice disorder is essential for optimizing photocatalyst structure for efficient applications, especially in environmental remediation, chemical production, and energy conversion [54–56]. Thus, more efforts in photocatalytic materials with lattice disorder, including computational modeling and comprehensive characterization techniques, should be applied to get insights into how lattice disorder affects photocatalytic efficiency, thereby facilitating the design of more effective photocatalytic feedstocks. Table 1.1

Table 1.1 Examples of photocatalysts along with their applications and type of defects.

Photocatalysts	Defect types	Applications	References
Ag-BiOI	Oxygen vacancies (OVs)	Trimethoprim degradation	[57]
$Bi_2O_2CO_3$	OVs	NO removal	[58]
Bi_2MoO_6	OVs	NO removal	[59]
$Bi_4Ti_3O_{12}$	OVs	NO removal	[43]
Bi@$SrTiO_3$	OVs	Photocatalytic Cr (VI) reduction	[60]
TiO_{2-x}@S-A500	OVs	Phenolic pollutants degradation	[37]
$CoMoO_4$/Carbon Nitride S-scheme	OVs	Photocatalytic H_2 production	[38]
TiO_2/CdS	Ti^{3+} defects	CO_2 reduction	[61]
In_2O_3@CN	N defects	Atrazine degradation	[45]
WO_3	Line defects	Photocatalytic CO_2-to-CH_4 conversion	[62]
$ZnIn_2S_4/TiO_2/$MS-SiO_2	Zn defects	Methyl orange and hexavalent chromium reduction	[63]
Au/ZnO	OVs	Rhodamine B and levofloxacin	[64]
N-deficient g-C_3N_4	N defects	Microcystin-LR degradation	[65]

defines examples of the last reported defective photocatalytic feedstocks, especially with oxygen vacancies, and demonstrates the increase of interest in these defective materials for various photocatalytic applications [37, 43, 57–65].

1.3 Characterization of Defects

It should be noted that defect characterization is important for understanding the relationship between defect formation and photocatalytic material properties. Besides, through the combination of experimental techniques and computational methods, researchers and industrialists can gain comprehensive insights about the types of defects, concentrations, and distributions and their pivotal role in photocatalytic efficiency, stability, and reactivity of photocatalytic feedstocks. In addition to the above-discussed techniques (i.e., XRD, SEM, FTIR, TEM, HRTEM, PL, SPV, EPR, TR-PL, ICP-MS, and Raman spectra) that have been widely utilized in defect characterization, other advanced techniques are also employed for the same purpose. Among them, microscopic characterization including atomic force microscope (AFM), scanning transmission electron microscopy (STEM), aberration corrected transmission electron microscope, scanning tunneling microscopy (STM), and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) has been recently utilized in defect understanding [15]. Besides, spectroscopic characterizations such as X-ray absorption fine structure (XAFS), positron annihilation spectroscopy (PAS), and X-ray spectroscopy (EDX) are employed in defect characterization [15]. Overall, despite the substantial efforts made in characterization techniques of defects, more sophisticated experimental techniques and computational methods are still much needed in order to enhance our ability to engineer photocatalytic materials with tailored defect structures for interesting applications.

1.4 Benefits and Limitations

It was proven that defects can provide a wide range of beneficial effects in photocatalytic materials, further enhancing their performance in photocatalytic applications [56, 57, 66–71]; their benefits are presented as follows:

a) Bulk or surface defects in photocatalytic materials can create new active sites for several chemical reactions, which can enhance their photocatalytic activity. Besides, types of defects such as element doping, vacancies, and lattice disorder can serve as reactive sites for adsorbing liquid and gaseous reactants, enhancing the performance of photocatalytic materials.
b) Some defects can act as traps for photogenerated charge carriers (electrons/holes). Then, by stabilizing these carriers, defects can also reduce their recombination rates and extend their lifetime, thus improving the photocatalytic efficiency of photoactive feedstocks.

c) It is noteworthy that defects could facilitate the separation and transfer of photogenerated charge carriers through providing pathways for charge transfer and their transportation, resulting in improved photocatalytic efficiency of photocatalytic materials.
d) The introduction of various defects can also modify the electronic band structure of photocatalytic materials, leading to the engineering of new bandgaps, enhancing light absorption, and further improving efficiency of the photocatalytic materials under visible light exposure.
e) The existence of defects can alter the surface energy of photocatalytic materials, thereby increasing their reactivity. This is particularly beneficial in specific applications, where surface interactions play an important role, especially in photocatalysis processes.
f) Specifically, defects including oxygen vacancies in different feedstocks can facilitate the formation of reactive oxygen species under light irradiation, which are crucial for the oxidative degradation of organic and inorganic contaminants employing the photocatalytic processes.
g) Some defects can enhance the structural integrity of photocatalytic materials by preventing the movement of dislocations and other defects under thermal stress, thereby improving their thermal and mechanical stabilities.

Even though defect engineering in photocatalytic materials provides a powerful option for optimizing their photocatalytic properties for a large range of applications, it presents some drawbacks which are stated as follows:

a) Unfortunately, certain defects can trap charge carriers (electrons/holes), resulting in increased recombination rates and low photocatalytic efficiency.
b) Defects may result in instability in photocatalysts, especially under prolonged irradiation or harsh environmental conditions. Thus, photocatalytic materials with excessive or uncontrolled defects can lose their photocatalytic activity within the time.
c) The introduction of defects might create new active sites that can improve unwanted side reactions, resulting in reduced selectivity of photocatalysts for the production of desired products.
d) On the one hand, surface defects may result in the accumulation of reaction by-products, especially blocking active sites and thus hindering the photocatalytic activity. Besides, bulk defects can also negatively impact the electronic features of the photocatalytic materials.
e) On the other hand, defects that alter photocatalytic features can make the photocatalytic materials more susceptible to chemical attack, influencing their lifetime and operational viability.
f) Defects can create electric fields that influence the movement of charge carriers. While this can be beneficial, it can also result in unfavorable drift mechanisms that decrease charge transfer and photocatalytic performance of the reported photocatalysts.
g) In some cases, while defects can improve photocatalytic performance, a high density of defects can overwhelm the advantageous effects, potentially

impairing electron transfer and the photocatalytic performance of photocatalytic feedstocks.

h) Some defects can generate new electronic states within the bandgap, which may negatively impact the band structure of the utilized photocatalytic material. This modification can shift the energy levels required for efficient charge separation.
i) If defects in photocatalytic feedstocks are not uniformly distributed, it can result in heterogeneous photocatalytic performance within the photocatalytic material. This nonuniformity can convolute the reaction dynamics, leading to inconsistent performance of photocatalysts.
j) Characterizing defects in photocatalytic feedstocks can be complex. Misunderstanding of defect types or concentrations in defective photocatalysts can lead to inappropriate photocatalytic material selections or processing conditions, hampering the development of desired photocatalysts.
k) The existence of defects might make photocatalytic materials more sensitive to changes in environmental conditions, including temperature or pH, thereby influencing their performance.
l) Developing photocatalytic materials with controlled defects often involves complex synthesis methods, eventually leading to the high cost of producing these classes of photocatalytic materials, further limiting their scalability for practical industrial applications.

1.5 Conclusion

In recent years, several efforts have been devoted to examine the surface-defect-engineered photocatalysts for numerous applications (i.e., environmental applications, biology, and organic synthesis), with substantial progress being made. It should be noted that, in the recent years, the use of defective photocatalytic feedstocks has increased significantly, thanks to their unique features including high reactivity and versatility. This chapter aims to offer a comprehensive overview of recent progress achieved in the usage of defective photocatalytic materials in numerous implementations. Even though defects in photocatalytic materials cannot be easily detected and characterized, several techniques have shown some efficiency to characterize defects including AFM, STEM, STM, HAADF-STEM, XAFS, PAS, EDX, etc. However, studies have shown that certain defects cannot be easily characterized. In the future, newer approaches utilizing advanced research and modern technology should be applied in the synthesis and characterization of defective photocatalysts for highly effective photocatalyst preparation. Besides, photocatalysis processes are limited to academic laboratory settings with existing challenges because of their limited conversion performance, and the creation of practical applications that takes advantage of the unique properties of defective photocatalytic feedstocks will lead to a bright future in a fruitful field of research work, especially for materials science, chemistry, and physics Consequently, theoretical, experimental, and mechanistic challenges in the usage of defective photocatalytic materials should be dealt with urgently, thanks to their substantial features (i.e., effective light absorption, charge separation/transfer, and synergetic effects) for several applications at present and in the future.

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Declarations

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Conflict of Interest

The authors declare that they have no conflict of interest.

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