**Black TiO\textsubscript{2}: What are exact functions of disorder layer**

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**Abstract**
Among the substantial amount of photocatalyst materials, TiO\textsubscript{2} has been enthusiastically studied for a few decades due to its outstanding photocatalytic activity and stability. Recently, black TiO\textsubscript{2} consisting of approximately 2 nm of thin disorder layer around the surface showed surprisingly high solar hydrogen generation ability. The disorder layer of TiO\textsubscript{2} can enhance its light absorption, charge separation, and surface reaction abilities, however exact fundamentals of photocatalytic water-splitting pathways are still ambiguous. Herein, recent progress and investigations on exact functions of disorder layer and its application in photocatalytic CO\textsubscript{2} reduction will be discussed. Throughout the comprehensive studies on disorder layer of TiO\textsubscript{2}, disorder engineering on photocatalyst materials will suggest the further extension of developing solar-fuel production technologies.

**KEYWORDS**
black TiO\textsubscript{2}, disorder layer, photocatalysis

1 | INTRODUCTION

Since Fujishima and Honda’s photoelectrochemical water splitting from TiO\textsubscript{2}, various kinds of metal oxides with p-type or n-type semiconductors have been focused for high solar-to-hydrogen conversion efficiency.\textsuperscript{1} TiO\textsubscript{2} is the most popular photocatalyst in terms of not only outstanding photocatalytic activities including water splitting for hydrogen and removal of organic pollutants for environmental applications but also excellent photocorrosion stability.\textsuperscript{2–4} However, the photoconversion efficiency of TiO\textsubscript{2} has been hampered by its large bandgap energy around 3.2 eV, which means that only ~4% of solar light can be harvested.\textsuperscript{4,5} To solve this drawback, doping strategies with transition metal ions (eg, Fe, Mn, Cr, V, and Cu) or nonmetal atoms (eg, N, C, and S) have been employed to extend light absorption to visible light.\textsuperscript{4,6} More recently, disorder engineering of the TiO\textsubscript{2} surface was reported by Chen et al\textsuperscript{7} in 2011. Since then, many follow-up research proved that very thin, approximately 2 nm, disorder layer (DL) on crystalline TiO\textsubscript{2} surface can induce strong visible light absorption and their absorption tail is approaching to near-infrared region.\textsuperscript{7} The TiO\textsubscript{2} with DL surface absolutely looks very dark, sometimes black, and their photocatalytic activity for H\textsubscript{2} production is much higher than that of pure TiO\textsubscript{2}. The defective crystal, named DL, with high visible light absorption, has been described as the main reason for high solar hydrogen conversion, but visible light harvesting from the DL could not contribute to hydrogen production seriously so far. Nevertheless, metal oxide photoanodes or photocatalyst powders with various DLs not only from hydrogenated TiO\textsubscript{2} but also reduced by chemicals (eg, Li-ethylenediamine) or metals (eg, Mg) have shown superior hydrogen evolution from solar
light. Various methodologies of preparing black TiO$_2$ and its applications are summarized in Table 1.

In general, solar water splitting or CO$_2$ conversion from photocatalyst or photoelectrochemical cell consists of three consecutive steps: (a) solar light absorption, (b) hole-electron separation and transport, (c) surface reaction. Because visible light harvesting by DL could not contribute to hydrogen evolution, the main positive effects of DL might be from enhanced hole-electron separation and transport and/or enhanced surface oxidation or reduction reaction. Herein, we will discuss current progress and investigations on functionalities of black TiO$_2$ and its applications in photocatalytic CO$_2$ reduction to give thorough understanding and insights on the DL and further extend beyond the intrinsic properties.

### Table 1 Phase, treatment strategy, and its applications of black TiO$_2$

| Year | Phase          | Treatment strategy                          | Application | Ref   |
|------|----------------|---------------------------------------------|-------------|-------|
| 2011 | Rutile         | Low-pressure H$_2$ gas treatment            | PEC         | Wang et al$^{11}$ |
| 2012 | Anatase        | H$_2$ gas treatment                         | PCH         | Zheng et al$^{12}$ |
| 2013 | Anatase        | Hydrogen plasma                             | PCH         | Wang et al$^{13}$ |
| 2013 | Anatase, rutile| Molten Al and H$_2$S treatment              | PCH         | Yang et al$^{14}$ |
| 2014 | Anatase        | H$_2$-Ar gas treatment                       | PCH         | Liu et al$^{15}$ |
| 2014 | Mixed (anatase + rutile) | NaBH$_4$ solution treatment | PCH         | Tan et al$^{16}$ |
| 2014 | Mixed (anatase + rutile) | Pulsed UV laser irradiation | PEC         | Nakajima et al$^{17}$ |
| 2015 | Anatase        | High energy proton implantation             | PCH         | Liu et al$^{18}$ |
| 2015 | Mixed (anatase + rutile) | Hydrothermal method | PCR         | Qingli et al$^{19}$ |
| 2016 | TiO$_2$-B      | Hydrogen plasma-assisted reduction          | PEC         | Tian et al$^{20}$ |
| 2016 | Mixed (anatase + rutile) | Li-EDA treatment | PCH         | Zhang et al$^{8}$ |
| 2016 | Anatase        | Cu treatment-H$_2$ flow                      | PCR         | Zhao et al$^{21}$ |
| 2016 | Brookite       | Hydrothermal method combined with postannealing under N$_2$ flow | PCR | Xin et al$^{22}$ |
| 2017 | Anatase + rutile | Hydrothermal method with chemical reduction | PCH | Liu et al$^{23}$ |
| 2017 | Pure or mixed anatase and rutile | Magnesium reduction of P25 | PEC | Xu et al$^{24}$ |
| 2017 | P25            | Al reduction                                | PCH         | Song et al$^{25}$ |
| 2018 | Mixed (anatase + rutile) | Li-EDA treatment and thermal annealing | PCH | Cho et al$^{26}$ |
| 2018 | Anatase        | Annealing at H$_2$-Ar gas                   | PCR         | Billo et al$^{27}$ |
| 2018 | Rutile         | Annealing at H$_2$-Ar gas                   | PEC         | Wang et al$^{28}$ |
| 2019 | Mixed (anatase + rutile) | Annealing at H$_2$ gas | PCR | Ye et al$^{29}$ |
| 2019 | Rutile         | Atomic layer deposition                     | PEC         | Ali-Löytty et al$^{30}$ |
| 2019 | Anatase        | Magnesiothermal reduction                   | PCH         | Li et al$^{31}$ |

Abbreviations: Li-EDA, lithium-ethylenediamine; PCR, photocatalytic CO$_2$ reduction; PCH, photocatalytic H$_2$ generation; PEC, photoelectrochemical water splitting.

### 2. Charge Separations in Black TiO$_2$

Within the limited range and amount of light absorption, the separated charge utilization is a critical factor in the solar water-splitting process. Efficient charge separation is promoted by an internal electromagnetic field formed within the electronic structure of a material. Typically, well-matched band alignment between unitidical semiconductors such as metal oxides or chalcogenides, so-called heterojunction, provides an energetically favorable structure for charge separation. Black TiO$_2$ has been reported to possess significantly altered electronic structure and surface properties, even it originates from crystalline polymorph of itself. Liu et al$^{37}$ suggested that Ti and O sublattice distortions
could largely blueshift the valence band maximum (VBM), leading to bandgap reduction of black TiO$_2$. As illustrated in Figure 1A,B, Ti and O sublattice distortion of anatase TiO$_2$ supercell showed blueshifted VBM, accompanied by redshift or no change in conduction band minimum (CBM) level. Along with the VBM shift, additionally created intermediate mid-gap energy levels serve as trapping or sinking sites for photogenerated charge carriers.$^{8,37}$ Zhang et al also reported significantly blueshifted valence band energy state (Figure 1C) along with additionally generated intermediate defect states by Perdew-Burke-Ernzerhof calculation (Figure 1D,E). In this regard, when black TiO$_2$ or DL is formed on the surface of pristine TiO$_2$ by disorder engineering (core-shell structure or linear-junctioned), the well-matched heterojunction can drive the efficient separation of electron-hole pairs through type-II band alignment.$^{8,40}$ In other words, the photogenerated holes will be more favorably driven to the surface DL due to higher VBM energy to participate in the photocatalytic surface reaction.

Cho et al$^9$ have successfully localized DL within a commercial P25 (composed of both anatase and rutile TiO$_2$) and formed order/disorder multiple heterojunctions within a single TiO$_2$ nanoparticle. As shown in Figure 2A-D, THE potential and charge distribution across the order/disorder multiple heterojunctions exhibited interfacial polarization across the region, where it can form energy band cascade (Figure 2E), exceeding H$_2$ production rate of commercial Pt/TiO$_2$ system without novel metal cocatalyst.$^9$ Also, Xia et al$^{41}$ proposed that due to collective movements of interfacial dipoles present at the crystalline/disordered interfaces of TiO$_2$, the built-up charge at the boundary induces interfacial polarization.

Furthermore, since charge recombination is also influenced by surface adsorption (between absorbate and associated derivate), oxygen vacancy can serve as carrier

**FIGURE 1** A, 2 × 2 × 1 Anatase supercell, where the sky blue and red balls represent Ti and O atoms, respectively. Reproduced with permission from Reference,$^{37}$ Copyright 2013, American Physical Society. B, The variations of VBM (represented by squares), CBM (circles), and total energy (triangles) calculated by PBE (colored in black) and by the hybrid functional (red) as a function of the distortion of (B) the O sublattice and the Ti sublattice. Reproduced with permission from Reference,$^8$ Copyright 2016, The Royal Society of Chemistry. C, Valence band XPS spectra of A-TiO$_2$ and R-TiO$_2$, and the Li-EDA treated materials. Reproduced with permission from Reference,$^8$ Copyright 2016, The Royal Society of Chemistry. D, Calculated bandgap diagrams; left: A-TiO$_2$/R-TiO$_2$, right: Li-EDA-treated A-TiO$_2$/black R-TiO$_2$. Reproduced with permission from Reference,$^8$ Copyright 2016, The Royal Society of Chemistry. E, Comparison of the electronic structure in pristine (blue) and reduced (red) TiO$_2$ surfaces calculated using the PBE + $U$ approach ($U = 3.2$ eV for the 3d orbitals of Ti). A magnified image for close inspection of the band alignment and defect states is shown on the right. The shaded regions indicate the conduction band and the valence band in each polymorph. The energy values in each structure are aligned by comparing the deep-lying Ti 3p orbital levels and are shown with reference to the vacuum energy level. Reproduced with permission from Reference,$^8$ Copyright 2016, The Royal Society of Chemistry. CBM, conduction band minimum; DOS, density of state; Li-EDA, lithium-ethylenediamine; XPS, X-ray photoelectron spectroscopy; PBE, Perdew-Burke-Ernzerhof [Color figure can be viewed at wileyonlinelibrary.com]
scavenger. At the disordered surface, adsorbed molecular oxygens (O$_2^-$ or O$^-$) to the defect sites can induce hole trapping at the surface.

In addition, the DL provides a lower energy barrier for both adsorption and dissociation required under photocatalytic reaction, allowing efficient charge transport at the TiO$_2$ surface.

Apart from TiO$_2$-based photocatalyst materials, some metal oxide semiconductors such as WO$_3$ and BiVO$_4$ are also reported to form similar DL and exhibit enhancements in charge separation performance. The disordered crystal of WO$_3$, which can be expressed as W$_{1-x}$O$_{3-y}$, was confirmed to have altered local electronic structure at the atomic scale, dramatically enhancing charge transfer efficiency of DL/WO$_3$.

Also, a thin (2 nm thick) surface DL formed on monoclinic bismuth vanadate (BiVO$_4$) could improve charge separation and transfer efficiencies, leading to 2.1 times higher photocurrent than bare BiVO$_4$ photoelectrode.

Meanwhile, Yan et al. announced that the improved photoactivity of disordered rutile TiO$_2$ is not only owing to its increased charge separation efficiency but also due to the enhanced charge injection efficiency. The defects in DL provides the shallow states energy level at the surface, which results in facilitating transfer of minority charge carrier from TiO$_2$ to water. On the other hand, the previous investigation of Park's group regarding the electrochemical water splitting ability of TiO$_2$ with DL is shown in Figure 3A,B. In the case of disordered TiO$_2$, the over-potential of both oxygen and hydrogen evolution reaction is improved, which implies that the enhanced water-splitting reactivity certainly contributes to higher photocatalytic H$_2$ production performance.

Although there have been many reports that present enhanced reactivity of TiO$_2$ by the formation of a defect in DL, the role of a defect in hydrogen or oxygen evolution reaction mechanism is still ambiguous. In fact, atomic defects in TiO$_2$ are divided into oxygen and titanium vacancies and these vacancies are randomly distributed along DL of TiO$_2$. Moreover, TiO$_2$ has various crystal phases with many facets, each of which has different surface energy state, adsorption energy, and reactivity. Thus, the relationship among the defect, crystal phase, and exposed facet makes a complex understanding on reaction mechanism and the uncertainty of defect cannot suggest a clear answer of why disordered TiO$_2$ has higher reactivity. Nevertheless, the defect of TiO$_2$ obviously plays an important role in water-splitting reaction, following that there have been many efforts to discover how defect influences photocatalytic and photoelectrochemical reaction.

**FIGURE 2** A, Potential map of disorder-engineered P25 (DE-P25) at rutile/disorder layer/anatase multiple heterojunctions. Reproduced with permission from Reference, Copyright 2018, American Chemical Society. B, Corresponding averaged potential vs distance plot of DE-P25 within a selected region. Reproduced with permission from Reference, Copyright 2018, American Chemical Society. C, Charge density map of DE-P25 derived from the potential map. Reproduced with permission from Reference, Copyright 2018, American Chemical Society. D, Charge density graph vs distance in the same region. Reproduced with permission from Reference, Copyright 2018, American Chemical Society. E, Proposed interfacial polarization across the multiple heterojunctions and their relative positions of the electronic band structure. Reproduced with permission from Reference, Copyright 2018, American Chemical Society. CBE, conduction band edge, VBE, valence band edge [Color figure can be viewed at wileyonlinelibrary.com]
Valdés et al.\textsuperscript{48} investigated the water oxidation and photo-oxidation reaction mechanism on the rutile TiO\textsubscript{2} (110) surface by using the density functional theory calculation (Figure 3C). The result showed that the rate-limiting step during the water oxidation reaction was step A, which is the formation of the adsorbed hydroxyl group at coordinatively unsaturated site. Adsorption of the hydroxyl group on the clean rutile (110) surface is difficult because water molecules rarely dissociate without any point defect. On the other hands, Li et al.\textsuperscript{49} investigated photocatalytic oxygen evolution on anatase TiO\textsubscript{2} surface (Figure 3D). In the case of anatase (101), (001), and (102) surfaces, the first proton removal step to form an adsorbed hydroxyl group requires high overpotential, same as (110) surface of rutile TiO\textsubscript{2}. Although the result from Valdés and Li could not suggest the direct correlation of defects on the reactivity of anatase and rutile TiO\textsubscript{2} by using a clean surface model, the rate-limiting step of either water oxidation or photo-oxidation reaction was confirmed to be the formation of the adsorbed hydroxyl group at the active site.

Step A: $\text{2H}_2\text{O} + * \rightarrow \text{H}_2\text{O} + \text{HO}^* + \text{H}^+ + e^-$.

Step B: $\text{H}_2\text{O} + \text{HO}^* + \text{H}^+ + e^- \rightarrow \text{H}_2\text{O} + \text{O}^* + 2(\text{H}^+ + e^-)$.

Step C: $\text{H}_2\text{O} + \text{O}^* + 2(\text{H}^+ + e^-) \rightarrow \text{HOO}^* + 3(\text{H}^+ + e^-)$.

Step D: $\text{HOO}^* + 3(\text{H}^+ + e^-) \rightarrow \text{O}_2 + * + 4(\text{H}^+ + e^-)$.

Apart from the mechanistic study on the water oxidation reaction of TiO\textsubscript{2}, the behavior of water molecules nearby the defect on the TiO\textsubscript{2} surface has been widely studied. Interestingly, many reports announced that oxygen vacancy at the bridging oxygen site on both anatase (101) and rutile (110) surface can strongly induce the hydroxyl group adsorption with much smaller free-energy change of water dissociation than the clean surface (Figure 3E).\textsuperscript{50,52,53} In other words, the absence of oxygen atom at the bridging oxygen site is energetically very unstable, so the oxygen vacancy prefers to be filled with hydroxyl group from the dissociation of the nearby water. Considering that the rate-limiting step of water-splitting reaction on rutile TiO\textsubscript{2} is the formation of adsorbed hydroxyl group, as reported by Valdés et al.,\textsuperscript{48} the water dissociation ability of defect may help to provide hydroxyl group, which in turn reducing overpotential for the water oxidation reaction. However, the significant deviation arises that the water oxidation reaction starts
with the adsorption of the hydroxyl group at five-coordinated titanium ion, while the hydroxyl group adsorption induced by defect occurs at the bridging oxygen site.\textsuperscript{48,49} Moreover, defect in TiO\textsubscript{2} is not only located at the surface but also able to exist at the subsurface, resulting in increasing huge complexity of expecting the role of defect.\textsuperscript{54–56} Thus, intensive and extensive mechanism studies on defects in DL of TiO\textsubscript{2} are necessary to elucidate how defects improve photocatalytic or photoelectrochemical water-splitting reaction.

\section*{APPLICATIONS IN PHOTOCATALYTIC CO\textsubscript{2} REDUCTION}

The utilization of carbon dioxide into valuable products has been recently spotlighted due to the worldwide environmental crisis. It is notable that one of the fascinating strategies to remove carbon dioxide is the photocatalytic reduction of CO\textsubscript{2} into \textit{C\textsubscript{1}} products, such as methane, methanol, carbon monoxide, and so forth.\textsuperscript{57–59} However, photocatalytic CO\textsubscript{2} reduction is not energetically favorable because it is generally operated in aqueous media containing carbonate ions. In detail, hydrogen production reaction and CO\textsubscript{2} conversion reaction compete together at the same catalyst surface because the standard reduction potential of CO\textsubscript{2} into \textit{C\textsubscript{1}} products is closely located at the reduction potential of water (Figure 4A).\textsuperscript{60} Moreover, the negative energy level of the standard reduction potentials of CO\textsubscript{2} makes it harder to chose appropriate photocatalyst materials. Among the limited candidates for photocatalytic CO\textsubscript{2} reduction, TiO\textsubscript{2} is known as the best photocatalyst for CO\textsubscript{2} reduction because of its large bandgap energy with highly negative energy levels of CBM, long charge carrier lifetime, and fast water oxidation kinetics.\textsuperscript{57,61} Interestingly, it is reported several times that DL of black TiO\textsubscript{2} can improve photocatalytic CO\textsubscript{2} reduction.\textsuperscript{62,63} As mentioned above, fast charge separation and good surface reactivity of DL may utilize photoexcited electron-hole pairs, which results in a higher photocatalytic CO\textsubscript{2} conversion rate. In this chapter, recent reports in photocatalytic CO\textsubscript{2} reduction by disordered TiO\textsubscript{2} are introduced in detail.

\begin{figure}[h]
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\caption{A, Schematic illustration of photocatalytic CO\textsubscript{2} reduction mechanism and the standard reduction potentials of CO\textsubscript{2} reduction reactions. Reproduced with permission from Reference,\textsuperscript{60} Copyright 2017, American Chemical Society. B, Correlation curve between space-time yield of CH\textsubscript{4} and CO\textsubscript{2} band from diffuse reflectance infrared Fourier transform spectroscopy results. Reproduced with permission from Reference,\textsuperscript{64} Copyright 2018, American Chemical Society. C, Comparison graph of CO gas production rate of black TiO\textsubscript{2} nanotube arrays with different thermal treatments. Reproduced with permission from Reference,\textsuperscript{65} Copyright 2020, Elsevier. D, Schematic illustration of photocatalytic CO\textsubscript{2} reduction mechanism in Ni-loaded inverse opal structured TiO\textsubscript{2}. Reproduced with permission from Reference,\textsuperscript{28} Copyright 2019, Elsevier. E, Comparison graph of selectivity between CH\textsubscript{4} and CO production from reduced TiO\textsubscript{2} with different facet exposure. Reproduced with permission from Reference,\textsuperscript{66} Copyright 2017, The Royal Society of Chemistry. F, Schematic illustration of electron-hole separation in facet engineered reduced TiO\textsubscript{2}. Reproduced with permission from Reference,\textsuperscript{66} Copyright 2017, The Royal Society of Chemistry [Color figure can be viewed at wileyonlinelibrary.com].}
\end{figure}
Energetic study of photocatalytic CO2 reduction on defective TiO2 was reported by Ji et al.67 They found that oxygen vacancy at the anatase TiO2 (101) surface has much higher activity on CO2 reduction than Ti atom in the perfect surface. Also, Liu et al68 found that oxygen vacancy can either improve the binding of CO2, activation, and dissociation or stabilize the reaction intermediates. In line with the theoretical investigations, Yin et al64 announced that disordered hydrogenated blue TiO2 prepared by low-temperature lithium-ethylenediamine solvothermal reaction outperforms pristine TiO2 in CH4 formation rate and the selectivity. In Figure 4B, in situ diffuse reflectance infrared Fourier transform spectroscopy results of blue TiO2 during photocatalytic CO2 reduction showed a proportional relationship between the amount of CO2 band and the space-time yield of CH4. These results demonstrated that improved photocatalytic performance of hydrogenated blue TiO2 is originated from the existence of key intermediate CO2 species, which is produced from oxygen vacancy of the disordered surface. On the other hand, Gao et al65 reported that black TiO2 nanotube prepared via aluminothermic reduction showed the remarkable ability of photocatalytic CO2 reduction into CO compare to pristine TiO2 nanotube (Figure 4C). Even though the results from Yin et al64 and Gao et al65 showed different C1 products from each TiO2, it is notable that black TiO2 greatly increased its photocatalytic reduction performance from its oxygen vacancy around the surface.

The photocatalytic performance of black TiO2 can be further enhanced by introducing cocatalyst or active facet exposure. Ye et al28 synthesized inverse opal structured Ni-loaded black TiO2 and applied in photocatalytic CO2 reduction and the introduction of nickel on black titania improved twice of its photocatalytic performance (Figure 4D). Moreover, Fang et al66 prepared a high Ti3+ concentration of reduced TiO2 with active (001) facet exposure. Interestingly, reduced TiO2 with (001) facet exposure showed higher CH4 and CO production rate than normally reduced TiO2, while the selectivity of methane production, reached 83.4% (Figure 4E). The author suggested that the pristine anatase (101) facet cannot overcome electron-hole recombination at the adjacent trapping sites while the exposure of (001) and (101) facets can separate electron-hole pairs into each facet thereby enhancing photocatalytic performance (Figure 4F).

5 CONCLUSION

Although the true functionalities of black TiO2 still have somewhat counterintuitive explanations, it is clear that black TiO2 outperforms its crystalline polymorph with significantly modified photoelectrochemical properties beyond their intrinsic states. However, regardless of disorder-engineering methods, the position of DL must be selectively localized on the surface or within the heterogeneous interface, since recombination process in black TiO2 is dominantly governed by trap-assisted nonradiative charge recombination. As mentioned throughout the text; (a) the suggested VBM blueshift of black TiO2 reinforcing charge transfer and transport at the order/disorder interface cannot fully attribute for overall enhancements in separation efficiencies and its recombination pathways, (b) the kinetic properties of DL during water-splitting pathways is still unclear whether the actual redox reaction takes places on the very surface or the subsurface between the DL and the core. More advanced theoretical studies and experiments to define the nature of black TiO2 will further complete the overall comprehension of designing semiconductor materials to a selective and optimal state. Such thorough investigations will boost photocatalytic and photoelectrochemical efficiencies without the employment of novel metal cocatalysts, thereby contributing practical applications in overall energy and environmental technologies.

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