Facile Vacuum Annealing-Induced Modification of TiO₂ with an Enhanced Photocatalytic Performance

Zhenpeng Cui, Min Zhao, Xueyan Que, Jingjing Wang, Yang Xu, Mohamed Nawfal Ghazzal, Christophe Colbeau-Justin, Duoqiang Pan,* and Wangsuo Wu

ABSTRACT: In this work, the photocatalytic performance enhancement of hydrothermally prepared TiO₂ was achieved by facile vacuum annealing treatment. Calcination of TiO₂ powder in air (CA-TiO₂) maintained its white color, while gray powder was obtained when the annealing was performed under vacuum (CV-TiO₂). Fourier transform infrared, total organic carbon, X-ray photoelectron spectroscopy, and electron paramagnetic resonance analyses proved that vacuum annealing transformed ethanol adsorbed on the surface of TiO₂ into carbon-related species accompanied by the formation of surface oxygen vacancies (Vo). The residual carbon-related species on the surface of CV-TiO₂ favored its adsorption of organic dyes. Compared with TiO₂ and CA-TiO₂, CV-TiO₂ exhibited an improved charge carrier separation with surface Vo as trapping sites for electrons. Vacuum annealing-induced improvement of crystallinity, enhancement of adsorption capacity, and formation of surface Vo contributed to the excellent photocatalytic activity of CV-TiO₂, which was superior to that of commercial TiO₂ (P25, Degussa). Obviously, vacuum annealing-triggered decomposition of ethanol played an important role in the modification of TiO₂. In the presence of ethanol, vacuum annealing was also suitable for the introduction of Vo into P25. Therefore, the current work offers an easy approach for the modification of TiO₂ to enhance its photocatalytic performance by facile vacuum annealing in the presence of ethanol.

INTRODUCTION

Since the discovery of the Fujishima–Honda effect in 1972,1 tremendous efforts have been devoted in investigating the potential applications of photocatalytic oxidation and reduction reactions.2,3 Due to its excellent stability, nontoxicity, and cost effectiveness, titanium dioxide (TiO₂) has become one of the most studied photocatalysts.4–6 However, the photocatalytic performance of TiO₂ is limited by its intrinsic wide band gap and fast recombination of photogenerated charge carriers.7,8 Thus, the enhancement of photocatalytic performance of TiO₂ by modification is of great interest.5,6,9 The photocatalytic activity of TiO₂ can be improved either by reducing its band gap to expand its photoresponse range from the UV to the visible range, which takes up the main proportion of solar light, or by preventing the recombination of photogenerated charge carriers by trapping or transfer.6,10,11 To promote its charge carrier separation ability, TiO₂ is commonly coupled to other semiconductors with a smaller band gap or to metallic nanoparticles.12–15 The commercially available TiO₂ (P25, Degussa) possesses high photocatalytic activity due to the mixed anatase and rutile phase, allowing efficient charge carrier transfer.16,17 In order to reduce its band gap, TiO₂ is usually doped with metallic or nonmetallic elements to form an intermediate band state into its band gap, which extends the absorption properties of TiO₂ to visible light.9,18,19 Asahi et al.20 reported the incorporation of nitrogen (N) into TiO₂ for photocatalytic degradation of organic pollutants under visible light. Carbon (C)-doped TiO₂ for efficient water splitting under visible light has been reported.21,22 C-doped TiO₂ showed high crystallinity and a unique microstructure, contributing to its remarkable photocatalytic degradation ability.23 Self-doped TiO₂ with titanium (Ti⁴⁺) was proposed and enabled an increase in the activity under visible light for efficient photocatalytic degradation of methylene blue (MB) and rhodamine B (RhB).24 Co-doped TiO₂ with Ti⁴⁺ and N exhibited synergistic effects for photocatalytic water oxidation.25

Besides, the introduction of surface oxygen vacancy (Vo) into TiO₂ was proposed as a credible alternative to improve the photocatalytic activity of TiO₂.8,26–31 This straightforward method has been widely achieved by annealing treatment under a reducing atmosphere, and it can realize not only doping TiO₂ but also creating defects, which improves the surface adsorption of the molecule and prolong the charge carrier lifetime.32 The resultant TiO₂ photocatalyst, so-called “black titania”, was obtained upon a thermal treatment under high pressure of H₂ and exhibited obvious visible light
absorption. Due to the H doping of TiO₂, the optical band gap energy (E_g) value of black titania was reduced to 1.54 eV by introducing electronic states forming between the valence band and conduction band. Other emerging methods, such as the annealing of TiO₂ in anaerobic medium (without oxygen) or under vacuum, led to the formation of Ti³⁺ and Vo, the amounts of which determined the color of TiO₂ (from gray to black). Since vacuum annealing avoids the use of highly flammable H₂ gas, it offers safer working conditions and needs more investigations.

In this work, we performed vacuum annealing by sealing hydrothermally prepared TiO₂ in a vacuumed glass tube. Meanwhile, calcination of TiO₂ in air was also conducted for comparison. The variations of TiO₂ before and after heat treatment were characterized in detail. Photocatalytic activities of TiO₂ photocatalysts were checked by decomposing organic pollutants, and the differences of their photocatalytic activities were discussed.

■ RESULTS AND DISCUSSION

Characterizations of TiO₂ Photocatalysts. X-ray diffraction (XRD) and diffuse reflectance spectroscopy (DRS) measurements were performed to investigate the influences of heat treatment on the crystalline structure and optical band gap of TiO₂, CA-TiO₂, and CV-TiO₂. All TiO₂ photocatalysts show similar diffraction patterns (Figure 1a), attributed to the anatase phase of TiO₂ (JCPDS-21-1272). Therefore, hydrothermally prepared TiO₂ maintains the anatase phase after calcination in air and annealing under vacuum. The broad peak (indicated by the arrow, Figure 1a) in the diffraction pattern of CV-TiO₂ is due to the formation of amorphous carbon. The sharper and narrower (101) peak of CA-TiO₂ and CV-TiO₂ indicates the enhancement of crystallization of TiO₂ after heat treatment. Based on the full width at half maximum of (101) plan and Debye–Scherrer formula (eq S1), the average crystallite sizes of TiO₂, CA-TiO₂, and CV-TiO₂ are estimated to be 9.9, 16.0, and 21.7 nm, respectively. DRS spectra (Figure 1b) show that all TiO₂ photocatalysts absorb in the UV range (200−400 nm), and no visible light absorption can be observed. Compared with TiO₂ and CA-TiO₂, CV-TiO₂ shows decreased absorbance, which is also observed in Chen and co-workers’ work. It is clear that both TiO₂ and CA-TiO₂ appear to be white (the common color of TiO₂, Figure 1b, inset), while CV-TiO₂ turns out to be gray, similar to carbon-doped TiO₂. This obvious color difference indicates that annealing of TiO₂ under vacuum produces gray calcinate. Vacuum annealing-induced formation of gray calcinate darkens the color of CV-TiO₂. The resultant gray calcinate is composed of carbon-related species resulting from ethanol decomposition on the surface of TiO₂, which will be proved by Fourier transform infrared (FT-IR), total organic carbon (TOC), and X-ray photoelectron spectroscopy (XPS) analyses later. The gray calcinate cannot be washed away. It is reported that C-doped TiO₂ showed obvious absorption of visible light due to the C doping into the crystal structure of TiO₂. Since CV-TiO₂ shows no absorption of visible light, there is no doubt that vacuum annealing of TiO₂ results in the formation of gray calcinate without C doping of CV-TiO₂. When existing on the surface of CV-TiO₂, the gray calcinate may impair the absorption of UV absorption.
light by CV-TiO$_2$. The $E_g$ values were estimated from the intercepts of their corresponding Kubelka–Munk (K–M) plots (Figure 1c) to be 3.17, 3.18, and 3.20 eV for TiO$_2$, CA-TiO$_2$, and CV-TiO$_2$, respectively. All $E_g$ values are around 3.2 eV, which is in agreement with the intrinsic $E_g$ of anatase. All TiO$_2$ photocatalysts only absorb UV light due to the wide band gap, as they are composed of TiO$_2$ with a crystal phase of anatase, which agrees with the XRD analysis (Figure 1a).

Therefore, XRD and DRS analyses proved that calcination has no influence on the crystal phase and $E_g$ values of all TiO$_2$ photocatalysts but increases the crystallinity and sizes of CA-TiO$_2$ and CV-TiO$_2$. The microscopic structures were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), and the images are shown in Figure 2. SEM images (Figure 2a–c) show that TiO$_2$, CA-TiO$_2$, and CV-TiO$_2$ exhibit granular structures constructed by compactly aggregated nanoparticles. According to TEM images (Figure 2d–f), the average sizes of all TiO$_2$ photocatalysts are in the order of TiO$_2$ < CA-TiO$_2$ < CV-TiO$_2$ and estimated to be around 10, 15, and 20 nm, respectively. This result is in agreement with the estimated crystallite sizes by XRD analysis. The dimensions of CA-TiO$_2$ and CV-TiO$_2$ increase because heat treatment enables TiO$_2$ nanoparticles to merge into bigger ones. Compared with CA-TiO$_2$, CV-TiO$_2$ shows larger particles in size, which indicates that vacuum annealing favors further fusion of TiO$_2$ nanoparticles. Thus, it is obvious that heat treatment enlarges the average crystallite sizes of TiO$_2$, especially vacuum annealing.

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The N$_2$ adsorption–desorption isotherms and Barrett–Joyner–Halenda (BJH) pore size distribution curves are employed to investigate the surface area and pore diameter of TiO$_2$, CA-TiO$_2$, and CV-TiO$_2$. Figure 3 shows that the isotherms of all samples are of type II according to the IUPAC classification. Absorption of N$_2$ by TiO$_2$, CA-TiO$_2$, and CV-TiO$_2$ can be ascribed to the interaggregated pores, which are structured by the neighboring nanoparticles, as shown in the SEM images (Figure 2a–c). The surface areas and average pore diameters of TiO$_2$, CA-TiO$_2$, and CV-TiO$_2$ are determined to be 128.30, 58.80, and 34.30 m$^2$/g and 133.41, 272.35, and 478.60 Å, respectively. It is reasonable that the surface areas of all TiO$_2$ photocatalysts decrease successively as their average crystallite sizes increase, which is verified by XRD (Figure 1a) and TEM (Figure 2d–f). The average pore diameters of all TiO$_2$ photocatalysts gradually enlarge as heat treatment induces the fusion of TiO$_2$ nanoparticles. Among all
TiO₂ photocatalysts, CV-TiO₂ shows the smallest surface area and biggest pore diameter, corresponding to its largest average crystallite size, implying that vacuum annealing favors the fusion of TiO₂ nanoparticles. Energy dispersive X-ray spectroscopy (EDS) was conducted to determine the elemental composition of all TiO₂ photocatalysts. As the EDS analysis was performed by depositing all TiO₂ photocatalysts on aluminum foil, the influence of conductive paste, which contained C, was excluded. EDS spectra (Figure S2) of all samples clearly show the presence of O and Ti, further confirming that they are all composed of TiO₂. FT-IR analysis was conducted to further analyze the chemical composition of all samples. FT-IR spectra (Figure 4a) of TiO₂, CA-TiO₂, and CV-TiO₂ show bands at 3423 and 1635 cm⁻¹, which are assigned to the stretching and bending vibrations of the O–H bond from adsorbed water or ethanol.⁴¹,⁴³ The vibration of the O–Ti–O bond is observed in the range of 500–900 nm.⁴² The bands at 2972, 1430, and 1505 cm⁻¹ in the FT-IR spectrum of TiO₂ are attributed to C–H and C–O vibrations, which may originate from the residual ethanol.⁴¹,⁴² Ethanol can be stabilized on the surface TiO₂ through hydrogen bonding interactions between the O–H and Ti–O bonds.⁴³ The absence of C–H and C–O vibration bands in the FT-IR spectra of CA-TiO₂ and CV-TiO₂ is due to the evaporation and decomposition of ethanol during heat treatment. The total amount of organic carbon in each sample was detected by TOC. The TOC values of TiO₂, CA-TiO₂, and CV-TiO₂ are measured to be 0.68, 0.00, and 0.26% (wt %), respectively. The presence of organic carbon (0.68%) undoubtedly demonstrates the adsorption of ethanol by TiO₂. The absence of organic carbon (0.00%) in CA-TiO₂ indicates the complete disappearance of ethanol. It is reported that the decomposition of ethanol occurs on the surface of TiO₂ in the presence of oxygen (O₂) forming carbon dioxide (CO₂) and H₂O.⁴⁴,⁴⁵ As a result, CA-TiO₂ maintains the white color of TiO₂ due to the complete removal of ethanol. The amount of organic carbon in CV-TiO₂ (0.26%) decreases compared with that of TiO₂ (0.68%). Under anaerobic conditions, the formation of gray calcinate (Figure 1b, inset) may result from the carbonization of ethanol by dehydration, which extracts lattice O from TiO₂, leaving carbon-related species on its surface.⁴⁴ Hence, heat treatment of TiO₂ with adsorbed ethanol on its surface results in quite different appearances of CA-TiO₂ and CV-TiO₂.

To characterize the chemical structure and binding energy of all samples, XPS analysis was performed. XPS spectra (Figure 4b) of all TiO₂ photocatalysts show characteristic peaks of C (1s), Ti (2s, 2p), and O (1s). The C 1s XPS spectra (Figures 4c and S3) show that the peaks of C–C (284.6 eV) and C–O (286.1 eV) decrease after heat treatment. As mentioned above, there is no carbon in CA-TiO₂, and thus, its C (1s) peak must come from the adventitious carbon species.²³ The decrease in the C–C peak (284.6 eV) proves that heat treatment induces evaporation and decomposition of ethanol adsorbed on the surface of TiO₂ in air but leads to the carbonation of ethanol under vacuum, producing carbon-related species, as the C 1s peak height of CV-TiO₂ is higher than that of CA-TiO₂.²³,⁴⁶ There is no C–Ti peak (280.4 eV) in C 1s spectra (Figure S3), which suggests that no C is doped into the lattice of TiO₂, which is in accordance with DRS analysis.²²,²³ Ti 2p XPS spectra (Figure 4d) exhibit almost the same Ti 2p½ (458.9 eV) and Ti 2p½ (464.6 eV), implying the uncharged binding state of Ti⁴⁺ after heat treatment.⁴³ According to the O 1s XPS spectra (Figure 4e), the Ti–O–Ti peak (530.1 eV) is almost the same for TiO₂, CA-TiO₂, and CV-TiO₂, while CV-TiO₂ presents a new peak (532.1 eV) (Figure S3), indicating the formation of oxygen vacancy (Vo).²³,⁴⁷,⁴⁸ Electron paramagnetic resonance (EPR) spectra (Figure 4f) show that CV-TiO₂ exhibits a clear signal characterized by the magnetic field strength centering at 3366 G and the electron’s so-called g-factor of 2.004 originating from the presence of unpaired electrons trapped on Vo.²³,⁴⁹–⁵¹ There is no Ti³⁺ signal since its detection at room temperature is not possible.⁵² As TiO₂ and CA-TiO₂ have no signal, EPR analysis further proves that vacuum annealing induces the formation of Vo in CV-TiO₂. This easy approach for the creation of Vo is also suitable for P25. In the presence of ethanol, vacuum annealing induced the formation of Vo in P25, while no Vo is identified for vacuum annealing of P25 without ethanol (Figure S4). Consequently, vacuum annealing results in the evaporation and decomposition of ethanol, forming carbon-related species on the surface of TiO₂ and the formation of Vo on its surface by the extraction of O from the Ti–O–Ti bond.⁵²,⁵³

**Photocatalytic Activity.** The photocatalytic activities of all TiO₂ photocatalysts were evaluated by the photocatalytic degradation of organic dyes under UV light. In the absence of TiO₂ photocatalysts, the photolysis of RhB, methyl orange (MO), and MB is negligible (Figure 5a–c). The photocatalytic activities of TiO₂, CA-TiO₂, and CV-TiO₂ are compared to the photocatalytic performance of P25 (as a reference photocatalyst). As shown in Figure 5a, compared with TiO₂ and CA-TiO₂ photocatalysts (~10%), increased adsorption of RhB by CV-TiO₂ (~30%) was observed, although it possesses the smallest surface area (Figure 3). This high adsorption capacity...
of RhB may result from the presence of carbon-related species on the surface of CV-TiO₂, which favors the adsorption of organic dyes. Under UV light irradiation, CA-TiO₂ and CV-TiO₂ show enhanced photocatalytic activity relative to TiO₂. The photocatalytic performance of CV-TiO₂ is drastically improved, and it is even higher than that of P25. Cycling tests are performed to check the stabilities of TiO₂, CA-TiO₂, and CV-TiO₂. Figure 5b shows the repeated four cycling tests of photocatalytic degradation of RhB by recovering all TiO₂ photocatalysts after each run. It is obvious that CV-TiO₂ shows the best photocatalytic activity, and the photocatalytic degradation rate becomes slow as the adsorption of RhB gradually decreases. The photocatalytic activity of CV-TiO₂ is also investigated by decomposing MO and MB. Figure 5c shows that CV-TiO₂ can efficiently decompose MO and MB, which is similar to the degradation of RhB. The excellent photocatalytic performance of CV-TiO₂ may originate from its high adsorption capacity and the presence of Vo, which contributes to the separation of photogenerated electrons and holes.

**Proposed Photocatalytic Mechanism.** Figure 6a shows the transient photocurrent response of TiO₂, CA-TiO₂, and CV-TiO₂.

![Figure 6. Transient photocurrent curves (a) and PL spectra (b) of TiO₂, CA-TiO₂, and CV-TiO₂.](image)

CV-TiO₂. Compared with TiO₂, CA-TiO₂ and CV-TiO₂ present clear enhancement of transient photocurrent, indicating the improved charge carrier separation properties, which originate from their improved crystallinity. The relative lower photocurrent of CV-TiO₂ than that of CA-TiO₂ may be caused by the trapping of electrons by Vo. Trapping electrons by Vo on the surface of CV-TiO₂ can prevent the recombination of electrons and holes, further elongating the lifetime of holes. Thus, more holes contribute to the formation of more hydroxyl radicals (OH·), which play a key role in the photocatalytic degradation of RhB by oxidation. Photoluminescence (PL) spectra further support this assumption. Figure 6b shows that the fluorescence intensity of CV-TiO₂ is lower than that of TiO₂ and CA-TiO₂. The emission signals in the PL spectrum are from the recombination of photogenerated electrons and holes. The lower fluorescence intensity implies less recombination of electrons and holes as a result of the trapping of electrons by Vo. The reduced recombination of electrons and holes favors the formation of more OH· for photocatalytic oxidation. Therefore, the enhanced photocatalytic activity of CV-TiO₂ is due to the improved crystallinity, increased adsorption capacity, and formation of Vo.

**CONCLUSIONS**

In summary, the effects of heat treatment on the crystal phase and structure, band gap, morphology, composition, and photocatalytic properties of TiO₂ photocatalysts were investigated in detail. It is proved that all TiO₂ photocatalysts are composed of the anatase phase, and calcination improves the crystallinity and increases the average crystallite size and pore diameter but decreases the surface area of CA-TiO₂ and CV-TiO₂ with quite different appearances. CA-TiO₂ maintains the white color of TiO₂ because calcination in air can completely evaporate and decompose the ethanol adsorbed by as-synthesized TiO₂. However, vacuum annealing leads to the carbonization of ethanol by dehydration and the extraction of lattice O from TiO₂, leaving gray calcinite and Vo on the surface of CV-TiO₂. The gray calcinate is composed of carbon-related species, which darken the color of CV-TiO₂ and favor the adsorption of organic dyes. Meanwhile, the formation of Vo on the surface of CV-TiO₂ traps photogenerated electrons, which promotes the charge carrier separation and enables more holes to participate in the formation of oxidizing species involved in the photocatalytic degradation. The improved crystallinity, enhanced adsorption capacity, and formation of Vo contribute to the improved photocatalytic performance of CV-TiO₂ relative to P25 in the degradation of organic pollutants. Thus, the decomposition of ethanol plays a vital role in vacuum annealing-induced modification of TiO₂. This work offers an easy approach for the modification of TiO₂ to enhance its photocatalytic performance by facile vacuum annealing in the presence of ethanol. Vacuum annealing with ethanol-induced formation of Vo is also suitable for commercial TiO₂ (P25). Therefore, this easy method may be universal for the modification of semiconductor photocatalysts to improve the photocatalytic activity. The quantitative creation of Vo is of great importance, as too much Vo is detrimental to the photocatalytic performance. Further work concerning the controllable formation of Vo via vacuum annealing by controlling the amount of adsorbed ethanol is underway.

**EXPERIMENTAL SECTION**

**Materials.** Titanium tetraisopropoxide (TTIP, 95%, Macklin) was used as the precursor for the hydrothermal synthesis of TiO₂. Deionized water (DI, 18.2 MΩ-cm, Millipore system), ethanol, isopropanol, and acetone (AR grade, Rionlon) were used as solvents. A custom-built high-borosilicate glass tube was applied for vacuum annealing.

Nafion D-521 dispersion (5% w/w in water and 1-propanol, Alfa Aesar) and fluorine-doped tin oxide substrates (FTO, Youxuan Tech) were used to prepare the working electrode for transient photocurrent measurements. RhB (AR grade, Shanghai Zhongqin), MO, and MB (AR grade, Beijing Chemical Reagent) were selected as model organic pollutants for the evaluation of the photocatalytic activity.

**Synthesis of TiO₂ Photocatalysts.** The synthesis of TiO₂ was conducted according to a reported hydrothermal method. In a typical synthesis, TTIP (10 mL) was placed in a Teflon liner, and DI water (3 mL) was added dropwise while stirring at room temperature. Then, the mixture was stirred for 30 min, transferred to a Teflon-lined autoclave, and kept at 180 °C for 24 h in a high-temperature furnace. After cooling down to room temperature, white precipitates appeared at the bottom of the Teflon liner and were separated.
by centrifugation. The as-synthesized TiO₂ powders were washed three times with ethanol and dried by lyophilization overnight. The white TiO₂ powders were placed in a porcelain crucible or sealed in a high-borosilicate glass tube for calcination in air or annealing under vacuum at 500 °C for 2 h at a heating rate of 2 °C/min. The treated TiO₂ powders in air and under vacuum were labeled as CA-TiO₂ and CV-TiO₂, respectively. All the as-prepared and sintered TiO₂ powders were collected for further characterizations and tests.

Characterizations. The diffraction patterns of TiO₂, CA-TiO₂, and CV-TiO₂ were recorded using XRD (X'Pert PRO) with a Cu Ka radiation source (λ = 1.5406 Å), and their corresponding crystallite sizes were estimated using the Debye–Scherrer formula (eq S1). The absorption properties of all TiO₂ photocatalysts were studied by UV–vis DRS (UV–2600), and their E₀ values were estimated from the intercepts of their corresponding K–M plots (eqs S2–S4). The morphologies of all samples were observed by SEM (Apreo S) and TEM (JEM-2100F). Brunauer–Emmett–Teller surface areas and the nitrogen adsorption and desorption isotherms of all TiO₂ photocatalysts were measured using an accelerated surface area and porosity analyzer (ASAP 2460). The pore size distribution was collected by the BJH method. The elemental composition was determined by EDS (X1 Analyzer, AMETEK). To do so, the powders of each TiO₂ photocatalyst were dispersed in DI water, deposited on aluminum foil, and dried naturally in air. Further chemical structure analyses were performed by FT-IR spectra (Bruker Alpha) and XPS (Escalab Xi+) with Al Ka radiation. The binding energy of the C 1s peak (adventitious carbon species) was fixed at 284.6 eV to set the binding energy scale. The contents of organic carbon in all TiO₂ photocatalysts were analyzed on a TOC analyzer (TOC-PH). To do so, the powders of each TiO₂ photocatalyst were combusted in an oxygen atmosphere and the amount of CO₂ produced was measured. The concentrations of organic carbon species in all TiO₂ photocatalysts were determined by EDS (X1 Analyzer, AMETEK). To do so, the powders of each TiO₂ photocatalyst were deposited on aluminum foil, and the E₀ values were estimated from the intercepts of their corresponding K–M plots (eqs S2–S4).

Photocatalytic Degradation Tests. Photocatalytic degradation tests of organic pollutants were carried out under UV light irradiation (mercury lamp, 500 W) in a photochemical reaction apparatus (Beijing Princess Technology) equipped with short-wavelength pass filters (<400 nm) to filter the visible light. TiO₂, CA-TiO₂, and CV-TiO₂ (1 mg/mL) were added into aqueous solutions of RhB (10 ppm, 25 mL) and stirred in the dark for 120 min before photocatalytic tests. For comparison, the photocatalytic performance of commercial TiO₂ (P25, Degussa) was also evaluated. The photocatalytic activity of CV-TiO₂ was further assessed through the degradation of MO (25 ppm) and MB (10 ppm) organic dyes under the same conditions. The photolysis of organic dyes under the same conditions without TiO₂ photocatalysts was performed as the control. The concentrations of organic dyes were monitored by following the maximum absorbance of RhB at 554 nm, MO at 464 nm, and MB at 664 nm. The ratios of residual organic dyes versus irradiation time were calculated by the expression C/C₀, where C and C₀ were the recorded concentration at different time intervals of irradiation and the initial concentration, respectively. The stability and reusability of all TiO₂ photocatalysts were checked by performing cycling tests of photocatalytic degradation of RhB four times.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c03762.

Digital photograph of vacuum annealing of TiO₂; vacuum annealing of P25; EDS and XPS of TiO₂ photocatalysts; EPR spectra of P25; UV–vis spectra of organic dyes; and corresponding digital photographs during the photocatalytic degradation (PDF)

AUTHOR INFORMATION

Corresponding Author

Duoqiang Pan – Frontiers Science Center for Rare Isotopes and School of Nuclear Science and Technology, Lanzhou University, Lanzhou 730000, China; orcid.org/0000-0002-0875-0274; Email: panduoqiang@lzu.edu.cn

Authors

Zhenpeng Cui – Frontiers Science Center for Rare Isotopes and School of Nuclear Science and Technology, Lanzhou University, Lanzhou 730000, China

Min Zhao – School of Nuclear Science and Technology, Lanzhou University, Lanzhou 730000, China

Xueyan Que – College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Jingjing Wang – School of Nuclear Science and Technology, Lanzhou University, Lanzhou 730000, China

Yang Xu – School of Nuclear Science and Technology, Lanzhou University, Lanzhou 730000, China

Mohamed Nawfal Ghazal – Institut de Chimie Physique, UMR 8000 CNRS, Université Paris-Saclay, Orsay 91405, France; orcid.org/0000-0002-2040-995X

Christophe Colbeau-Justin – Institut de Chimie Physique, UMR 8000 CNRS, Université Paris-Saclay, Orsay 91405, France

Wangsuo Wu – Frontiers Science Center for Rare Isotopes and School of Nuclear Science and Technology, Lanzhou University, Lanzhou 730000, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c03762

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. Nature 1972, 238, 37–38.

(2) Ravelli, D.; Dondi, D.; Fagnoni, M.; Albini, A. Photocatalysis. A multi-faceted concept for green chemistry. Chem. Soc. Rev. 2008, 37, 409–428.

(3) Li, R.; Weng, Y.; Zhou, X.; Wang, X.; Mi, Y.; Chong, R.; Han, H.; Li, C. Achieving overall water splitting using titanium dioxide-
based photocatalysts of different phases. *Energy Environ. Sci.* 2015, 8, 2377–2382.
(14) Linsebigler, A. L.; Lu, G.; Yates, J. T. Photocatalysis on TiO₂ Surfaces: Principles, Mechanisms, and Selected Results. *Chem. Rev.* 1998, 95, 735–758.
(15) Ma, Y.; Wang, X.; Jia, Y.; Chen, X.; Han, H.; Li, C. Titanium Dioxide-Based Nanomaterials for Photocatalytic Fuel Generations. *Chem. Rev.* 2014, 114, 9987–10043.
(16) Schneider, J.; Matsuoka, M.; Takeuchi, M.; Zhang, J.; Horiiuchi, Y.; Anpo, M.; Bahnemann, D. W. Understanding TiO₂ photocatalysis: mechanisms and materials. *Chem. Rev.* 2014, 114, 9919–9986.
(17) Yamakata, A.; Vequizon, J. J. M.; Matsuhashi, H. Distinctive Behavior of Photogenerated Electrons and Holes in Anatase and Rutile TiO₂ Powders. *J. Phys. Chem. C* 2015, 119, 24538–24545.
(18) Yu, X.; Jeon, B.; Kim, Y. K. Dominant Influence of the Surface on the Photoactivity of Shape-Controlled Anatase TiO₂ Nanocrystals. *ACS Catal.* 2015, 5, 3316–3322.
(19) Chen, X.; Liu, H.; Huang, F. Black titanium dioxide (TiO₂) nanomaterials. *Chem. Soc. Rev.* 2015, 44, 1861–1885.
(20) Levinson, R.; Berdahl, P.; Akbari, H. Solar spectral optical properties of pigments-Part I: model for deriving scattering and absorption coefficients from transmittance and reflectance measurements. *Sol. Energy Mater. Sol. Cells* 2007, 91, 319–349.
(21) Jia, T.; Wu, J.; Song, J.; Liu, Q.; Wang, J.; Qi, Y.; He, P.; Qi, X.; Yang, L.; Zhao, P. In situ self-growing 3D hierarchical BiOBr/BiOBrO Z-scheme heterojunction with rich oxygen vacancies and iodine ions as carriers transfer dual-channels for enhanced photocatalytic activity. *Chem. Eng. J.* 2020, 396, 125258.
(22) Scanlon, D. O.; Dunnill, C. W.; Buckeridge, J.; Shevlin, S. A.; Logsdail, A. J.; Woodley, S. M.; Catlow, C. R. A.; Powell, M. J.; Palgrave, R. G.; Parkin, P. J.; Watson, G. W.; Keal, T. W.; Sherrwood, P.; Walsh, A.; Sokol, A. A. Band alignment of rutile and anatase TiO₂. *Nat. Mater.* 2013, 12, 798.
(23) Li, X.; Lin, H.; Chen, X.; Niu, H.; Liu, J.; Zhang, T.; Qiu, F. Dendritic α-Fe₂O₃/TiO₂ nanocomposites with improved visible light photocatalytic activity. *Phys. Chem. Chem. Phys.* 2016, 18, 9176–9185.
(24) Naldoni, A.; Altmare, M.; Zoppellaro, G.; Liu, N.; Kment, S.; Zboril, R.; Schmuki, P. Photocatalysis with Reduced TiO₂: From Black TiO₂ to Cocatalyst-Free Hydrogen Production. *ACS Catal.* 2019, 9, 345–364.
(25) Gesesse, G. D.; Le Neel, T.; Cui, Z.; Bachelier, G.; Remita, H.; Colbeau-Justin, C.; Ghazali, M. N. Plasmonic core–shell nanostucture as an optical photocative nanolens for enhanced light harvesting and hydrogen production. *Nanoscale* 2018, 10, 20140–20146.
(26) Ohtani, B.; Prieto-Mahaney, O. O.; Li, D.; Abe, R. O.; Ohtani, B.; Prieto-Mahaney, O. O.; Li, D.; Abe, R. What is the electronic origin of the visible-light absorption for photocatalysis with black hydrogenated titanium dioxide? *J. Chem. Phys.* 2014, 140, 221701.
(27) Hu, J.; Li, J.; Cui, W.; Liu, L.; Liang, Y.; Cui, W. Surface oxygen vacancies enriched FeO(OH)/Bi₂O₃ nanoparticiles: fenton synergy degradation of organic pollutants. *J. Hazard. Mater.* 2020, 384, 121399.
(28) Zhou, Y.; Liu, Y.; Liu, P.; Zhang, W.; Xing, M.; Zhang, J. A facile approach to further improve the substitution of nitrogen into reduced TiO₂−x with an enhanced photocatalytic activity. *Appl. Catal., B* 2015, 170–171, 66–73.
(29) Chen, X.; Liu, L.; Yu, P. Y.; Mao, S. S. Increasing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystals. *Science* 2011, 331, 746–750.
(30) Wang, J.-O.; Zhang, W.; Li, S.; Meng, S.; Guo, H. Distribution and concentration of surface oxygen vacancy of TiO₂ and its photocatalytic activity. *J. Phys. Chem. A* 2020, 53, 424001.
(31) Jia, Y.; Li, S.; Ma, H.; Gao, J.; Zhu, G.; Zhang, F.; Park, J. Y.; Cha, S.; Bae, J.-S.; Liu, C. Oxygen vacancy rich BiOBr₂-BiOBrO₂−x composites for UV-vis NIR activated high efficient photocatalytic degradation of bisphenol A. *J. Hazard. Mater.* 2020, 382, 121131.
(32) Han, L.; Su, B.; Liu, G.; Ma, Z.; An, X. Synthesis of oxygen vacancy-rich black TiO₂ nanoparticles and the visible light photocatalytic performance. *Mol. Catal., A* 2018, 456, 96–101.
(33) Park, G. C.; Seo, T. Y.; Park, C. H.; Lim, J. H.; Joo, J. Effects of Calcination Temperature on Morphology, Microstructure, and Photocatalytic Performance of TiO₂ Mesocrystals. *Ind. Eng. Chem. Res.* 2017, 56, 8235–8240.
(34) Suganuma, S.; Nakajima, K.; Kitano, M.; Yamaguchi, D.; Kato, H.; Hayashi, S.; Hara, M. Hydrolysis of Cellulose by Amorphous Carbon Bearing SO-H, COOH, and OH Groups. *J. Am. Chem. Soc.* 2008, 130, 12787–12793.
(35) Chen, X.; Zhao, D.; Liu, K.; Wang, C.; Liu, L.; Li, B.; Zhang, Z.; Shen, D. Laser-Modified Black Titanium Oxide Nanospheres and Their Photocatalytic Activities under Visible Light. *ACS Appl. Mater. Interfaces* 2015, 7, 16070–16077.
(40) Zang, Y.; Li, L.; Xu, Y.; Zuo, Y.; Li, G. Hybridization of brookite TiO2 with g-C3N4: a visible-light-driven photocatalyst for As5+ oxidation, MO degradation and water splitting for hydrogen evolution. J. Mater. Chem. A 2014, 2, 15774–15780.

(41) Wang, J.; Zhang, F.; Li, X.; Zhu, J.; Li, H. Synchronical pollutant degradation and H2 production on a Ti3+-doped TiO2 visible photocatalyst with dominant (001) facets. Appl. Catal., B 2013, 134–135, 198–204.

(42) Ruan, L.; Wang, X.; Wang, T.; Ren, Z.; Chen, Y.; Zhao, R.; Zhou, D.; Fu, G.; Li, S.; Gao, L.; Lu, Y.; Wang, Z.; Tian, H.; Kong, X.; Han, G. Surface Defect-Controlled Growth and High Photocatalytic H2 Production Efficiency of Anatase TiO2 Nanosheets. ACS Appl. Mater. Interfaces 2019, 11, 37256–37262.

(43) Li, N.; Wang, B.; Si, Y.; Xue, F.; Zhou, J.; Lu, Y.; Liu, M. Toward High-Value Hydrocarbon Generation by Photocatalytic Reduction of CO2 in Water Vapor. ACS Catal. 2019, 9, 5590–5602.

(44) Lettieri, S.; Gargiulo, V.; Allè, M.; Amati, M.; Zeller, P.; Maraloini, V.-A.; Borbone, F.; Pavone, M.; Muñoz-García, A. B.; Maddalena, P. Simple Ethanol Refluxing Method for Production of Blue-Colored Titanium Dioxide with Oxygen Vacancies and Visible Light-Driven Photocatalytic Properties. J. Phys. Chem. C 2020, 124, 3564–3576.

(45) Muggli, D. S.; Mccue, J. T.; Falconer, J. L. Mechanism of the Photocatalytic Oxidation of Ethanol on TiO2. J. Catal. 1998, 173, 470–483.

(46) Saktihivel, S.; Kisch, H. Daylight Photocatalysis by Carbon-Modified Titanium Dioxide. Angew. Chem., Int. Ed. 2003, 42, 4908–4911.

(47) Wan, J.; Chen, W.; Jia, C.; Zheng, L.; Dong, J.; Zheng, X.; Wang, Y.; Yan, W.; Chen, C.; Peng, Q.; Wang, D.; Li, Y. Defect Effects on TiO2 Nanosheets: Stabilizing Single Atomic Site Au and Promoting Catalytic Properties. Adv. Mater. 2018, 30, 1705369.

(48) Tan, H.; Zhao, Z.; Zhu, W.-B.; Coker, E. N.; Li, B.; Zheng, M.; Yu, W.; Fan, H.; Sun, Z. Oxygen Vacancy Enhanced Photocatalytic Activity of Pervoskite SrTiO3. ACS Appl. Mater. Interfaces 2014, 6, 19184–19190.

(49) Ye, K.; Li, K.; Lu, Y.; Guo, Z.; Ni, N.; Liu, H.; Huang, Y.; Ji, H.; Wang, P. An overview of advanced methods for the characterization of oxygen vacancies in materials. Trends Anal. Chem. 2019, 116, 102–108.

(50) Qu, J.; Ge, Y.; Zu, B.; Li, Y.; Dou, X. Transition-Metal-Doped p-Type ZnO Nanoparticle-Based Sensory Array for Instant Discrimination of Explosive Vapors. Small 2016, 12, 1369–1377.

(51) Liang, X.; Wang, P.; Gao, Y.; Huang, H.; Tong, F.; Zhang, Q.; Wang, Z.; Liu, Y.; Zheng, Z.; Dai, Y.; Huang, B. Design and synthesis of porous M-ZnO/ CeO2 microspheres as efficient plasmonic photocatalysts for nonpolar gaseous molecules oxidation: Insight into the role of oxygen vacancy defects and M=Ag, Au nanoparticles. Appl. Catal., B 2020, 260, 118151.

(52) Zhu, Q.; Peng, Y.; Lin, L.; Fan, C.-M.; Gao, G.-Q.; Wang, R.-X.; Xu, A.-W. Stable blue TiO2-x nanoparticles for efficient visible light photocatalysts. J. Mater. Chem. A 2014, 2, 4429–4437.

(53) Vequizo, J. J. M.; Matsuura, H.; Ishiku, T.; Kamimura, S.; Ohno, T.; Yamakata, A. Trapping-Induced Enhancement of Photocatalytic Activity on Brookite TiO2 Powders: Comparison with Anatase and Rutile TiO2 Powders. ACS Catal. 2017, 7, 2644–2651.

(54) Asahi, R.; Morikawa, T.; Irie, H.; Ohwaki, T. Nitrogen-Doped Titanium Dioxide as Visible-Light-Sensitive Photocatalyst: Designs, Developments, and Prospects. Chem. Rev. 2014, 114, 9824–9852.

(55) Ahmed, A. Y.; Kandiel, T. A.; Ivanova, I.; Bahnemann, D. Photocatalytic and photoelectrochemical oxidation mechanisms of methanol on TiO2 in aqueous solution. Appl. Surf. Sci. 2014, 319, 44–49.

(56) Han, X.; Kuang, Q.; Jin, M.; Xie, Z.; Zheng, L. Synthesis of Titania Nanosheets with a High Percentage of Exposed (001) Facets and Related Photocatalytic Properties. J. Am. Chem. Soc. 2009, 131, 3152–3153.

(57) Yuan, X.; Kobylanski, M. P.; Cui, Z.; Li, J.; Beaunier, P.; Drago, D.; Colbeau-Justin, C.; Zaleska-Medynska, A.; Remita, H.