Communication

Grey Rutile TiO$_2$ with Long-Term Photocatalytic Activity Synthesized Via Two-Step Calcination

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Abstract: Colored titanium oxides are usually unstable in the atmosphere. Herein, a gray rutile titanium dioxide is synthesized by two-step calcination successively in a high-temperature reduction atmosphere and in a lower-temperature air atmosphere. The as-synthesized gray rutile TiO$_2$ exhibits higher photocatalytic activity than that of white rutile TiO$_2$ and shows high chemical stability. This is attributed to interior oxygen vacancies, which can improve the separation and transmission efficiency of the photogenerated carriers. Most notably, a formed surface passivation layer will protect the interior oxygen vacancies and provide long-term photocatalytic activity.

Keywords: gray color; rutile titanium dioxide; oxygen vacancy; photodecomposition; surface passivation

1. Introduction

Among titanium oxides, TiO$_2$ is well investigated in the photocatalysis research field because of its high chemical stability, low cost, and nontoxicity [1]. However, it can only absorb ultraviolet light, resulting in low photocatalytic efficiency. To expand its light absorbance range and enhance the separation efficiency of the photogenerated carriers, many efforts, such as doping with other elements, sensitizing with dyes, and coupling with metal or nonmetal nanoparticles or different semiconductor materials, have been made to solve the aforementioned problems [2–7]. Very recently, TiO$_2$ nanotubes synthesized via the electrochemical anodization of titanium foil exhibited visible light response characteristics for the photodecomposition of formaldehyde [8].

It has been reported that when TiO$_2$ is partially reduced by H$_2$ or CO, or bombarded by high-energy particles (laser, electron, or Ar$^+$), the obtained colored TiO$_2$ powers show visible light photocatalytic activity. In 2010, a blue titanium dioxide with a mixture of anatase and rutile phase was synthesized via hydrolysis and the reduction of isopropyl titanium, showing a higher photocatalytic activity than that of commercial anatase TiO$_2$. The higher photocatalytic activity was attributed to the presence of Ti$^{3+}$ in the interior of the titanium dioxide crystal [9]. In 2011, Giamello et al. used an isotope labeling method to study the existence of Ti$^{3+}$ in rutile titanium dioxide in detail [10]. In the same year, a black TiO$_2$ with a strong absorption of visible light was synthesized via a high-temperature hydrogenation reduction of P25 TiO$_2$ by Chen et al. The obtained higher photocactivity of the black TiO$_2$ was attributed to the reduced band gap of titanium dioxide caused by the generation of the surface disordered structure [11]. Another kind of simple method to produce colored TiO$_2$ is the addition of fluorine species during TiO$_2$ preparation [12,13]. In 2014, Xu et al. synthesized stable blue TiO$_2$ nanoparticles with a non-stoichiometric TiO$_2$-x core and stoichiometric TiO$_2$ shell structure for the photodecomposition of methylene blue (MB) dyes under visible light irradiation [12]. In addition to...
the black- or blue-color TiO$_2$, Ye et al. found that TiO$_2$ nanocrystal assemblies show a yellow color, caused by the interfacial Ti–Ti electronic bonding. Until now, many outstanding works on colored TiO$_2$ have been reported [14–28]. They usually showed a broader light absorbance range and higher photocatalytic activity than that of white TiO$_2$. However, the mechanisms for the higher photocatalytic activity still remain a controversy. Some studies have suggested that it is ascribed to a surface disorder; other reports suggest that it is caused by the “oxygen vacancy” states associated with the Ti$^{3+}$ within the band gap of the TiO$_2$ [16,29,30]. Most notably, the reported colored titanium oxides are usually unstable in the atmosphere because of a large number of oxygen vacancies and the presence of Ti$^{3+}$ with poor stability [24]. It is still a challenge to synthesize a stable colored TiO$_2$ photocatalyst.

In contrast to anatase TiO$_2$, rutile TiO$_2$ has attracted less attention in the photocatalytic research field because of its low photocatalytic activity [31,32]. Herein, gray rutile (GR) titanium dioxide particles (marked as TiO$_2$-GR), which are composed of microcrystals with oxygen vacancies on the surface, are synthesized by two-step calcination successively performed in a high-temperature reduction atmosphere and in a lower-temperature air atmosphere. The as-synthesized gray rutile TiO$_2$ exhibits a higher photocatalytic activity than that of white rutile (WR) TiO$_2$ (marked as TiO$_2$-WR). This is attributed to the presence of oxygen vacancies, which can improve the photogenerated carrier separation and transmission efficiency. Most notably, the formed surface passivation layer will protect the interior oxygen vacancies and provide long-term photocatalytic activity.

2. Materials and Methods

2.1. Materials

Hexanoic acid (HA), tetrabutyl titanate (TBOT), methylene blue (MB) dye, and glucose were purchased from Sinopharm Chemical Reagent Company. All chemicals were of AR grade. The ultrapure water used in the experiment was obtained from a Mill-Q (electric resistivity 18.2 MΩ·cm) water purification system.

2.2. Synthesis of TiO$_2$-GR and TiO$_2$-WR

First, uniform spherical anatase TiO$_2$ particles (Figure 1a and Figure S1a) with a diameter of 200–300 nm were synthesized via a previous reported method [33]. In a typical process, hexanoic acid (0.46 g) dissolved in ethanol (230.0 mL), and TBOT (1.70 g, 10% ethanol solution) was mixed by stirring at room temperature. Then, 35.0 mL H$_2$O was dropped into the mixture with vigorous stirring for 12 h at room temperature. The products were obtained after centrifugal separation and were then ready for use for the next two-step calcination procedure.

Second, the as-prepared TiO$_2$ nanosphere was firstly calcinated in a tubular high-temperature furnace with continuous argon flow at 900 °C for 3 h. Then, it was further calcined at 500 °C in air atmosphere for 10 h, and gray rutile TiO$_2$ particles with polyhedron morphology were obtained (TiO$_2$-GR, Figure 1b and Figure S1b). A white rutile TiO$_2$ used as a reference sample (TiO$_2$-WR, Figure 1c and Figure S1c) was prepared by the calcination of the as-prepared TiO$_2$ nanosphere at 900 °C for 3 h in an air atmosphere.

The as-prepared photocatalysts were stored in an air atmosphere at room temperature.

2.3. Photocurrent Measurements

The photocurrent measurements were carried out on an electrochemical analyzer (CHI660D Instruments, Shanghai Chenhua Instrument Co., Ltd., Shanghai, China) using a standard three-electrode system. The as-prepared samples, a commercial Pt gauze electrode (Gaoss Union Technology Co., Ltd., Wuhan, China, 2 cm × 2 cm, 60 mesh), and saturated calomel electrode were used as working electrodes, counter electrode, and reference electrode, respectively. The working electrode was prepared as follows: 0.05 g of the sample was ground with 0.10 g terpinol for 10 min to make uniform slurry. Then, the slurry was evenly dripped onto a 4.0 cm × 1.0 cm indium tin oxide-coated
glass (ITO glass) electrode masked by an adhesive tape with thickness of 0.5 mm and smoothed by a 
doctor’s blade. Therefore, the formed film about had a thickness of 0.5 mm. Next, these electrodes 
were dried in an oven and were calcined at 350 °C for 30 min in an air atmosphere. The electrode was 
immersed in a 0.10 M NaClO4 aqueous solution to measure the transient photocurrent under a 300 W 
Xe arc lamp irradiation with an incident light power density of 130 mW/cm² at 0.4 V vs. the saturated 
calomel electrode.

![Figure 1](image-url)

**Figure 1.** Morphology of spherical anatase TiO₂ (a), TiO₂-gray rutile (TiO₂-GR) (b), and TiO₂-white 
rutile (TiO₂-WR) (c).

### 2.4. Photoactivity Measurements

The photocatalytic discoloration of MB dyes was performed on a reformative XPA-7 photocatalytic 
reaction instrument (Xujiang Electromechanical Plant, Nanjing, China). The incident light power 
was 162 mW/cm², which was measured by a handheld Optical Power Meter (Newport 1916-R, 
Newport Corporation, California, CA, USA). The light exposure area of the quartz bottle was about 
19.1 cm². The discoloration effect was measured using the absorption spectroscopic technique. In the 
typical process, an aqueous solution of the MB dyes (10.0 mg/L and 30.0 mL) and 20.0 mg of the 
as-prepared photocatalysts were mixed in a 50 mL cylindrical quartz tube and left overnight in darkness 
to reach the adsorption equilibrium for the MB dyes. Then, the mixture was exposed to 1000 W Xe lamp 
irradiation with or without the light cutoff filters (λ > 420 nm), under ambient conditions and magnetic 
stirring. At given time intervals, the reaction solution was sampled and analyzed by a UV-visible 
spectrophotometer (UV 2250, Shimadzu, SHIMADZU (CHINA) Co., Ltd., Shanghai, China).

### 3. Results and Discussion

A spherical anatase TiO₂ (Figure 1a and Figure S1a) in a white color was fabricated as the raw 
material for the gray TiO₂-GR via the hydrolysis of TBOT in the presence of alkyl chain carboxylic 
acids [33]. It was determined that alkylchain carboxylic acids remained on the surface of the TiO₂ 
nanospheres, which were used as a reductant for the subsequent high-temperature reduction of titanium 
dioxide [4]. Both the gray rutile TiO₂ and the reference sample (TiO₂-WR) exhibited polyhedron 
morphology (TiO₂-GR, Figure 1b and Figure S1b).

After calcination at 900 °C in an Ar atmosphere, it can be seen from the High Resolution 
Transmission Electron Microscope (HRTEM) pattern that a surface layer composed of a large number 
of microcrystals surrounded by a disordered structure formed on the obtained gray TiO₂ (Figure S2a). 
The disordered structure is believed to be mainly caused by the presence of oxygen vacancies, which are 
response for the black color of TiO₂ [14,30]. Then, after further calcination at 500 °C in an air atmosphere,
a dense layer with ordered lattice was formed by the refilling of oxygen atoms into the oxygen vacancies
on the outmost layer of TiO₂ particles (Figure S2b). The formed dense layer with the size of 2–5 nm is
on the outermost layer of the TiO₂-GR particle, which would act as a surface passivation layer to hinder
the further diffusion and infiltration of oxygen molecules into the interior oxygen vacancies. As a result,
the interior lattice disordered structure would be retained. The lattice width of the surface passivation
layer is 0.21 nm, which is ascribed to the (210) crystal faces of the rutile TiO₂ (JCPDS 21-1276; Figure S2b).
However, no such surface layer structures were observed on the surface of the TiO₂-WR particles
(Figure S2c). The lattice widths are 0.32 nm and 0.25 nm, which belong to the (110) and (001) crystal faces
of the rutile TiO₂, respectively (JCPDS 21-1276; Figure 2a). The X-ray diffraction (XRD) peaks of the
gray TiO₂ centered at 2θ = 27.75°, 36.4°, 39.45°, 41.55°, 44.35°, 54.6°, 56.9°, 63.05°, 64.35°, 69.25°, 70.05°,
and 82.6° are ascribed to the (110), (101), (111), (210), (211), (220), (002), (310), (301), (112), and (321)
crystal planes of the rutile TiO₂, respectively (Figure 2b), which is consistent with the referenced white
rutile TiO₂. Both of the XRD peaks of TiO₂-GR and TiO₂-WR are similar to that of the standard rutile
TiO₂ (PDF# 87-0710). The Rietveld analysis (TOPAS V 6.0) of the XRD patterns shows that TiO₂-GR
has an average particle size of 48.5 nm. This result is different from that intuitively observed from the
HRTEM patterns, which is attributed to the different detection areas between XRD and HRTEM.
Herein, the HRTEM patterns are mainly afforded the surface layer crystal structure of TiO₂ particles.
Therefore, it can be inferred that the as-synthesized TiO₂-GR nanoparticles are mainly composed of
microcrystals with an average size of about 48.5 nm, while their surface layers are composed of smaller
microcrystals. Additionally, the analysis results indicate that the broadening of the diffraction peak is
mainly due to grain refinement, and there is no existing microstrain. However, compared with the
cell parameters of the standard rutile TiO₂ (PDF# 87-0710), both TiO₂-GR and TiO₂-WR show a lattice
expansion, with average lattice distortions of 0.11% and 0.13%, respectively. It is proposed that this is
mainly caused by the different treatments during the high-temperature calcination process. No peaks
centered at 2θ = 25.9°, ascribed to carbon (JCPDS 26-1079), were observed in the XRD patterns of
gray TiO₂ [34].

![Figure 2. HRTEM (a) and XRD patterns (b) of gray rutile TiO₂.](image)

The chemical state of the surface species of TiO₂-GR and TiO₂-WR was determined by X-ray
photoelectron spectroscopy (XPS), which was further analyzed by an XPS peak-fitting program
(version 4.0, Hong Kong, China). The C1s XPS peaks of TiO₂-GR centered at 284.6 eV (FWHM = 4.55 eV)
and 282.9 eV (FWHM = 1.96 eV), which is similar to that of TiO₂-WR, were ascribed to the *C and
(*CO)Ti species caused by the carbon contaminant (Figure 3a,b) [35,36]. It was reported that if a
carbon atom was doped in the crystal lattice of TiO₂, a bonding energy peak ascribed to C* or Ti*–C
emerged at 281.6 eV or 454.90 eV, respectively [37,38]. However, no such carbon bonding energy peaks
were observed for either TiO₂-GR or TiO₂-WR. This indicates that there were no carbon atoms doped
in the crystal lattice of the prepared gray TiO$_2$, which means that the gray color did not originate from the carbon residues. As shown in Figure 3c,d, the Ti2p XPS peaks of TiO$_2$-GR were centered at 464.53 eV (FWHM = 2.84 eV) and 458.20 eV (FWHM = 3.82 eV), which are ascribed to Ti$^{4+}$ 2p$_{1/2}$ and Ti$^{4+}$ 2p$_{3/2}$ of TiO$_2$, respectively [39], which is similar to that of TiO$_2$-WR. Two reduced titanium ion XPS peaks centered at 462.43 eV (FWHM = 3.91 eV) and 455.92 eV (FWHM = 2.63 eV) were observed for TiO$_2$-GR, which could be ascribed to the low valence state titanium of nonstoichiometric TiO$_2$$_x$ (0 < X < 2), mainly including Ti$^{3+}$ 2p$_{1/2}$ of Ti$_2$O$_3$ and Ti$^{2+}$ 2p$_{3/2}$ of TiO$_2$ [40,41], which is consistent with the O 1s XPS peak results. However, the TiO$_2$-WR showed no reduced titanium ion XPS peaks. The O 1s XPS peaks mainly consisted of three components (Figure 3e,f). The two peaks centered at 529.47 eV (FWHM = 3.30 eV) and 531.58 eV (FWHM = 4.48 eV) were ascribed to the lattice oxygen of the stoichiometric TiO$_2$ [42] and nonstoichiometric TiO$_2$$_x$ (0 < X < 2) [43,44], respectively, and the latter may also include some hydroxyl oxygen species [45]. The small O 1s peak centered at 527.51 eV (FWHM = 2.21 eV) could be attributed to the attached ionic oxygen of CO or O$_2$ [46].

![Figure 3](image_url)

**Figure 3.** C 1s XPS spectra of TiO$_2$-GR (a) and TiO$_2$-WR (b); Ti 2p XPS spectra of TiO$_2$-GR (c) and TiO$_2$-WR (d); O 1s XPS spectra of TiO$_2$-GR (e) and TiO$_2$-WR (f).

It has been reported that the produced Ti$^{3+}$ originated from the oxygen vacancies on the surface of the gray TiO$_2$. The removed oxygen atoms left behind two excess electrons per oxygen vacancy, which could be harvested by the neighboring Ti atoms, and induce the formation of Ti$^{3+}$ ions showing EPR signals [47]. Therefore, Electron Paramagnetic Resonance (EPR) is one powerful method for identifying the presence of oxygen vacancies in solid materials. A low-field signal with a g-value close to the free-electron value (g = 2.0023) is generally attributed to an unpaired electron trapped on an oxygen vacancy site [11]. Herein, as shown in Figure 4, an EPR signal with a g-value of 1.997 is attributed to the Ti$^{3+}$ centers in the rutile phase environment. As a comparison, there were no EPR peaks at the same position observed from the TiO$_2$-WR EPR signals. It is believed that the surface Ti$^{3+}$ would tend to adsorb atmospheric O$_2$, which would be reduced to O$_2^-$, and shows an EPR signal at g = 2.02 [11]. The absence of such a peak in the TiO$_2$-GR EPR signals indicates that after long calcination in an air atmosphere, the surface oxygen vacancies are refilled by oxygen atoms and the Ti$^{3+}$ is mainly present under the formed surface passivation layer, which is proposed as a key factor for the observed excellent stability of TiO$_2$-GR.
weight increase is ascribed to the refilled interior oxygen vacancies, indicating that the surface weight loss from 380°C with negligible weight variation. The slight weight gain and loss wave before 125°C (TGA) in open air, as shown in Figure S3. The sample was thermally stable up to 650°C in open air, with negligible weight variation. The slight weight gain and loss wave before 125°C are ascribed to the adsorption and desorption of O2, CO2, or H2O on the surface of TiO2-GR in the air. A distinguishable weight loss from 380°C is ascribed to the dissociation of the surface –OH. Above 650°C, the obvious weight increase is ascribed to the refilled interior oxygen vacancies, indicating that the surface passivation layer would be destroyed at this temperature. This shows that the as-prepared TiO2-GR has high thermal stability.

A higher photocatalytic activity is attributed to the presence of oxygen vacancies that can create a higher light absorbance and improve the separation and transmission efficiency of photogenerated carriers, which is preliminarily confirmed by the UV-vis spectra, photocurrent, and photoluminescence spectra. The suggested photocatalysis mechanism is shown in Figure 6a. It is proposed that the photocatalysis of TiO2-GR may undergo two different photogenerated carrier transfer pathways when pumped by UV light and visible light separately. It can be seen, in both pathways, that the oxygen vacancies all play a vital role. Compared with TiO2-WR, the as-prepared TiO2-GR exhibits a broad spectral absorption in the visible light region (Figure 6b). This can be attributed to the transitions from the TiO2 valence band to the oxygen vacancy levels, or from the oxygen vacancies to the TiO2 conduction band pumped by visible light [30], which is responsible for the distinguishable higher photoactivity of TiO2-GR than that of TiO2-WR. These results are consistent with the photocurrent density results under visible light irradiation (Figure 6c). This indicates that, in this case, the visible light absorption of TiO2-GR does lead to charge carrier generation and contributes directly to the photocurrent. However, as shown in Figure 6c,d, the photocurrent density under a full-spectrum light condition is about 100 times that under a visible light condition, which indicates that the contribution of visible light to the improvement of the photocatalytic activity is very limited. This is consistent
with previously reported results [48]. Therefore, it is proposed that the main factor for the higher photocatalytic activity of TiO\textsubscript{2}-GR is the photogenerated carrier transfer path pumped by UV light. [49] In this process, the Vo is still proposed to be a key factor for the improvement of the separation efficiency of the photogenerated carriers. First, the Vo can act as a trap site for the temporary storage of electrons, which can be further pumped to the conduction band to react with the substrates, resulting in suppressed recombination of photogenerated carriers. [50]. Herein, the suppressed recombination of photogenerated carriers is preliminarily confirmed by the photoluminescence spectra. If the recombination of carriers was suppressed, the photoluminescence of semiconductor materials would be quenched to some degree [51, 52]. As shown in Figure 6e, compared with the reference TiO\textsubscript{2}-WR sample, the TiO\textsubscript{2}-GR samples show a much lower photoluminescence intensity. This indicates that the as-prepared gray TiO\textsubscript{2}-GR has a much higher photoinduced charge separation efficiency than that of the white TiO\textsubscript{2}-GR materials. In addition, because of the presence of free electrons bound loosely to the titanium atom in the oxygen vacancies [47], the surface electric conductivity of TiO\textsubscript{2}-GR will be improved, as a result of improving the carriers’ transmission efficiency [26], which is also helpful for improving the photocatalytic activity.

**Figure 5.** (a) Methylene blue (MB) dye photocatalytic discoloration plots of TiO\textsubscript{2}-GR and TiO\textsubscript{2}-WR samples under full-spectrum light irradiation; (b) MB dye photocatalytic discoloration plots of TiO\textsubscript{2}-GR and TiO\textsubscript{2}-WR samples under visible light irradiation; (c) photocatalytic activity tests of TiO\textsubscript{2}-GR samples stored for different times via the photocatalytic discoloration of MB dyes under full-spectrum light irradiation; (d) photocatalytic activity cycle tests of TiO\textsubscript{2}-GR samples under full-spectrum light irradiation. The aqueous solution of the MB dyes (10.0 mg/L, 30.0 mL) without photocatalysts was used as the control sample marked as a blank in Figure 5a,b. $C/C_0$ is the ratio of the real-time concentration to the initial concentration of MB dyes.
which provides long-term photocatalytic activity. This study provides a considerable reference for the design and synthesis of other semiconductor photocatalysts rich in oxygen vacancies, with high activity and high stability.

**Author Contributions:** Conceptualization, G.C. and B.T.; methodology, G.C. and Y.L.; validation, Y.F. (Yanfei Fan), and X.S.; investigation, Y.L., P.C., and Y.F. (Yaqi Fan); writing (original draft preparation), Y.L.; writing (review and editing), G.C. and B.T.; supervision, B.T.; project administration, B.T.; funding acquisition, B.T. All of the authors have read and agreed to the published version of the manuscript.

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**Supplementary Materials:** The following are available online at http://www.mdpi.com/2079-4991/10/5/920/s1: Figure S1: Morphology of spherical anatase TiO$_2$ (a), TiO$_2$-GR (b), and TiO$_2$-WR (c). Figure S2: HRTEM of TiO$_2$-only calcination at 900 °C in Ar atmosphere (a), TiO$_2$-GR (b), and TiO$_2$-WR (c). Figure S3: TGA curve in open air for the TiO$_2$-GR sample.

**4. Conclusions**

In summary, gray rutile titanium dioxide was synthesized via two-step calcination, performed successively in a high-temperature reduction atmosphere and in a lower-temperature air atmosphere. The results indicate that, compared with the white rutile titanium dioxide, the as-prepared gray titanium dioxide exhibits the typical characteristics of black- or blue-color TiO$_2$, such as the presence of Ti ions in a low valence state, surface disorder structure, and oxygen vacancies, which are caused by the loss of oxygen atoms under reduction reaction conditions. According to previous reports [14], it is proposed that the presence of Ti$^{3+}$ or a surface disorder structure is mainly induced by oxygen vacancies. The as-synthesized gray titanium dioxide exhibits a higher photocatalytic activity than does white rutile TiO$_2$. This is attributed to the interior vacancies, which can create a higher light absorbance and improve the separation and transmission efficiency of photogenerated carriers. Most notably, it is proposed that the two-step calcination can produce a surface passivation layer on the surface of gray titanium dioxide particles, as a result of protecting the interior oxygen vacancies, which provides long-term photocatalytic activity. This study provides a considerable reference for the design and synthesis of other semiconductor photocatalysts rich in oxygen vacancies, with high activity and high stability.

**Figure 6.** (a) Schematic illustration of the photocatalysis mechanism of TiO$_2$-GR; (b) UV-vis diffuse reflectance spectra of TiO$_2$-GR and TiO$_2$-WR; (c) photocurrent density of TiO$_2$-GR and TiO$_2$-WR under visible light irradiation; (d) photocurrent density of TiO$_2$-GR and TiO$_2$-WR under full-spectrum light irradiation; (e) photoluminescence spectra of TiO$_2$-GR and TiO$_2$-WR with an excitation wavelength of 380 nm.
Conflicts of Interest: The authors declare no conflict of interest.

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