Controllable Synthesis and Tunable Photocatalytic Properties of Ti$^{3+}$-doped TiO$_2$

Ren Ren, Zhenhai Wen, Shumao Cui, Yang Hou, Xiaoru Guo & Junhong Chen

Photocatalysts show great potential in environmental remediation and water splitting using either artificial or natural light. Titanium dioxide (TiO$_2$)-based photocatalysts are studied most frequently because they are stable, non-toxic, readily available, and highly efficient. However, the relatively wide band gap of TiO$_2$ significantly limits its use under visible light or solar light. We herein report a facile route for controllable synthesis of Ti$^{3+}$-doped TiO$_2$ with tunable photocatalytic properties using a hydrothermal method with varying amounts of reductant, i.e., sodium borohydride (NaBH$_4$). The resulting TiO$_2$ showed color changes from light yellow, light grey, to dark grey with the increasing amount of NaBH$_4$. The present method can controllably and effectively reduce Ti$^{4+}$ on the surface of TiO$_2$ and induce partial transformation of anatase TiO$_2$ to rutile TiO$_2$, with the evolution of nanoparticles into hierarchical structures attributable to a high pressure and strong alkali environment in the synthesis atmosphere; in this way, the photocatalytic activity of Ti$^{3+}$-doped TiO$_2$ under visible-light can be tuned. The as-developed strategy may open up a new avenue for designing and functionalizing TiO$_2$ materials for enhancing visible light absorption, narrowing band gap, and improving photocatalytic activity.

Since Fujishima discovered the photocatalytic splitting of water by using titanium dioxide (TiO$_2$) electrodes, TiO$_2$ has become the most attractive photocatalyst because of its multiple advantages, such as structural stability, abundance, environmentally-friendliness, and low-cost$^{1,2}$. However, the relatively wide band gap in TiO$_2$ greatly hinders efficiently harvesting solar energy for applications in photocatalysis, solar cells, and photoelectrochemical cells. Accordingly, significant research has been devoted to understanding the fundamental processes and exploring routes to enhance the photocatalytic activity and efficiency of TiO$_2$$^{3,4}$. Fortunately, continuous breakthroughs have been made in the preparation, functionalization, and modification of TiO$_2$-based photocatalysts to improve the absorption of visible light (~50% of solar light) for photocatalytic applications$^{5-7}$. In general, modifying TiO$_2$ with a suitable dopant not only changes the mechanism and kinetics under UV irradiation but also introduces more visible-light activity that is absent with pure TiO$_2$$^{8}$. Three strategies have been proposed to advance properties and corresponding photocatalytic applications of TiO$_2$: 1) impurity-doping or dye-anchoring on TiO$_2$ catalysts, which can extend its absorption range to visible light region$^{9-11}$; 2) synthesizing TiO$_2$ nanocrystals with specific crystal surface orientations because some specific crystalline planes, e.g., (001) plane, tend to show a higher catalytic activity than others and mixed crystallographic facets$^{12,13}$; 3) Fabricating TiO$_2$-based nanohybrids with other functional materials, such as carbon nanotubes (CNTs) and graphene, to attain a synergistic effect between them$^{14-16}$.

Recently, Chen et al. reported a conceptually different method to improve solar absorption ability by introducing disorders in the surface layers of nanophase TiO$_2$, i.e., Ti$^{3+}$-doped TiO$_2$.$^{17}$ The study showed that disorder-engineered TiO$_2$ nanocrystals exhibit substantially improved solar-driven photocatalytic activities for photo-oxidation of organic molecules and water splitting. Unfortunately, the preparation

Department of Mechanical Engineering, University of Wisconsin-Milwaukee, 3200 North Cramer Street, Milwaukee, WI 53211, USA. Correspondence and requests for materials should be addressed to Z.W. (email: wenzhenhai@yahoo.com) or J.C. (email: jhchen@uwm.edu)
processes had to be conducted in a high-pressure hydrogen system for a reaction period of as long as five
days, which leads to disadvantages of long reaction time, low yield, and more waste residues. Therefore,
it is highly desirable to develop improved methods for fabrication of such Ti$^{3+}$-doped TiO$_2$. Many inves-
tigations have demonstrated that Ti$^{3+}$-containing (blue) TiO$_2$ that contains oxygen vacancies exhibit
significant photocatalytic activity in the visible light region; however, the catalyst could not maintain
such activity for a sufficiently long period of time. In addition, hierarchically structured TiO$_2$-based
materials were reported to improve the performance of the materials because their highly porous struc-
tures were beneficial for enhancing the utilization efficiency of light. TiO$_2$-based photocatalysts synthesized by hydrothermal
treatment have drawn great attention since hydrothermal methods possess advantages of convenience,
relatively low processing temperature, and high yield. Although NaBH$_4$ was previously reported for
reducing TiO$_2$ through a hydrothermal method, the resulting photocatalytic performance was inade-
quate because only a small amount of NaBH$_4$ was used. Fang et al. added amount of NaBH$_4$ during the
synthesize process but no more than $0.4 \text{ g}$, which is may insufficient to enable the formation of defective
or partially reduced TiO$_2$. In summary, there is still lack of comprehensive and systematic investigation
and discussion to study how NaBH$_4$ affect the morphology, structure, and photocatalytic activity of the
reducing TiO$_2$.

In the present research, a systematic research was reported by preparing of a series of Ti$^{3+}$-doped TiO$_2$
by tuning the amount of NaBH$_4$, yielding color changes of the TiO$_2$ products from white, light yellow,
light grey, to dark grey with the increasing amount of NaBH$_4$. More importantly, we firstly reported an
increased concentration of NaBH$_4$ applied in the hydrothermal reaction would facilitate the conversion
of anatase TiO$_2$ into rutile TiO$_2$ with the evolution of nanoparticles into hierarchical structures thanks
to a high pressure and strong alkali environment in this system. Moreover, it is demonstrated that the
as-developed Ti$^{3+}$-doped TiO$_2$ with a mixed phase and nanostructure can potentially lower the recombi-
nation rate of electron-hole pairs due to the presence of Ti$^{3+}$ and oxygen vacancies that are able to trap
photo-excited electrons on the surface.

**Results**

Reduced TiO$_2$ samples were synthesized by adding different amounts of sodium borohydride (NaBH$_4$)
in the hydrothermal reaction at $180^\circ \text{C}$ for 16 hours. Specifically, 0, 2, 7, 10 and $12 \text{ g} \text{ NaBH}_4$ were used
in separate experiments; and the as-obtained products were denoted as pristine TiO$_2$, TiO$_2$-1, TiO$_2$-2,
TiO$_2$-3 and TiO$_2$-4, respectively. Figure 1 shows the digital photographs of the series of TiO$_2$ samples.
With the increasing amount of NaBH$_4$, the color of the resulting powders changes from light yellow for
TiO$_2$-1, light grey for TiO$_2$-2, dark grey for TiO$_2$-3, to light grey for TiO$_2$-4, and all of these samples show
a striking contrast to the white color of the pristine TiO$_2$. These results indicate that the hydrothermal
treatment, which occurs at a mild reaction temperature, high-pressure, and a reduced atmosphere, did
affect the surface properties of TiO$_2$.  

![Figure 1. Photographs of pristine TiO$_2$ (a) and doped TiO$_2$ samples, (b) TiO$_2$-1, (c) TiO$_2$-2, (d) TiO$_2$-3 and (e) TiO$_2$-4.](image-url)
To determine the crystal structure and possible phase changes during the hydrothermal synthesis, X-ray diffraction (XRD) was carried out to study the series of samples during the evolution process (Fig. 2a). All of the samples show diffraction peaks matching well with the crystal structure of the anatase phase TiO$_2$ (71–1169, JCPDS). No new XRD peaks are observed for samples with 2, 7, and 10 g of NaBH$_4$, i.e., TiO$_2$–1, TiO$_2$–2, and TiO$_2$–3. However, a set of diffraction peaks appear at 27.4°, 36.1°, 44.1° and 56.6° for TiO$_2$–4; these four peaks can be well indexed to the characteristic peaks of (110), (101), (210), and (220) crystal planes of rutile phase TiO$_2$ (75–1751, JCPDS), suggesting that TiO$_2$–4 contained both anatase phase and rutile phase TiO$_2$. The average crystallite size of TiO$_2$ was estimated according to the Scherrer’s equation (1)

$$D = K \cdot \lambda / \beta \cos \theta$$

where $K$ is the Scherrer constant, $\lambda$, the X-ray wavelength, $\beta$, the peak width of half maximum, and $\theta$ is the Bragg diffraction angle. The particle sizes for pristine TiO$_2$, TiO$_2$–1, TiO$_2$–2, TiO$_2$–3 and TiO$_2$–4 are 15.20 nm, 16.36 nm, 16.55 nm, 16.84 nm, and 19.76 nm, respectively. The intensities of the diffraction peaks became weaker with the increase of the amount of NaBH$_4$ from 2 g to 10 g, suggesting a decreased crystallinity for TiO$_2$ samples after the hydrothermal treatment possibly due to the formation of defects under a relative higher pressure in a reducing environment. The crystalline degree in turn grew stronger with further increasing the amount of NaBH$_4$ to 14 g, which can be attributed to the increased pressure promoting the reorganization or restructuring of crystallites, thereby leading to the enhancement of the product crystallinity$^{31,32}$. Raman spectroscopy was also used to characterize the series of TiO$_2$ samples (Fig. 2b). Raman peaks appear at 147, 397, 515, and 637 cm$^{-1}$ corresponding to Eg, B$_1g$, A$_1g$, and Eg lattice vibration modes, respectively, which indicates that all samples are majorly dominated by anatase type titanium dioxide. The Raman bands shift toward a lower wavenumber possibly due to the increase in particle size from pristine sample to reduced sample$^{33,34}$.

The morphology and structure of the as-prepared TiO$_2$ were further characterized by scanning electron microscopy (SEM). Figure 3a–e present typical SEM images of the pristine TiO$_2$, TiO$_2$–1, TiO$_2$–2, TiO$_2$–3, and TiO$_2$–4, respectively. The size of TiO$_2$ particles increased with increasing the amount of NaBH$_4$ in the synthesis process, which is most likely due to the agglomeration of nanoparticles induced by a higher concentration of NaBH$_4$. The results are basically in agreement with the particle size calculation by using Scherrer’s equation from XRD results. It should be noted that, for TiO$_2$–4, there also appeared some hierarchical microstructures with an average size of 2 to 4 μm that were constructed by a large number of nanofibers about 20–30 nm in diameter, as shown in Fig. 3f,g (ESI, Figs. S1c and S1d). Actually, a small fraction of hierarchical microstructures were also found in the sample TiO$_2$–3 (ESI, Fig. S1a and S1b), suggesting gradual evolution of nanostructures from nanoparticles to nanofiber upon tuning the amount of NaBH$_4$. Hierarchical structures were previously proven to be beneficial for improving photocatalytic activity because of their special hierarchical porous structure, good permeability, and a large surface area compared with other low dimensional structures$^{29,35,36}$. Furthermore, the TiO$_2$ hierarchical structure can absorb more light through multiple reflections and lead to more photogenerated electrons to participate in the photocatalytic degradation process$^{37,38}$. Therefore, TiO$_2$–4 is expected to offer enhanced light-harvesting capability and a higher specific surface area than other TiO$_2$ samples.

The morphology and structure of as-prepared TiO$_2$ were further elucidated by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images shown in Fig. 4. Figure 4a shows the TEM image of nanoparticles from sample TiO$_2$–4 with discernible TiO$_2$ nanofibers, which is in agreement with the SEM observation. The TiO$_2$ nanofibers were formed possibly due to the high pressure during the phase transition process$^{39,40}$. Figure 4b,c display the HRTEM images of an individual particle.
and nanofiber from sample TiO$_2$-4, respectively. In addition, a set of well-defined diffraction rings are observed in selected area electron diffraction (SAED) patterns (Fig. 4d), which is in good agreement with the anatase phase of synthesized TiO$_2$ nanocrystals$^{41}$. Pristine TiO$_2$ nanocrystals show a lattice spacing=$\approx 0.350$ nm that is close to that of anatase TiO$_2$ (101) (0.351 nm). After the hydrothermal treatment by adding different amounts of NaBH$_4$, the characteristic TiO$_2$-3 (ESI, Fig. S2) and TiO$_2$-4 nanocrystal lattice spacing of 0.351 nm corresponds to the (101) lattice plane of anatase TiO$_2$, which is consistent with previous results$^{42}$. There is no noticeable change in the nanocrystal lattice spacing value corresponding to the anatase (101) plane, which indicates that the Ti$^{3+}$ has been introduced into the lattice without modifying the dimension of the unit cell$^{43}$.

Figure 5 shows the nitrogen gas adsorption and desorption isotherms of the series of TiO$_2$ samples; all of these curves can be classified as type IV isotherm characteristic of mesoporous materials with the presence of a hysteresis loop in the relative-pressure range of 0.6–1.0$^{44,45}$. The specific surface areas and average pore diameters of the synthesized TiO$_2$ were analyzed based on nitrogen adsorption and

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**Figure 3.** SEM images of pristine TiO$_2$ (a) and as-obtained TiO$_2$ nanostructures: (b) TiO$_2$-1, (c) TiO$_2$-2, (d) TiO$_2$-3 and (e) TiO$_2$-4; (f) and (g) hierarchical structures TiO$_2$-4.
desorption measurements (Table 1). There is no remarkable change between pristine TiO\(_2\) and TiO\(_2\)-1, both of which have a BET surface area of around 78.8 m\(^2\) g\(^{-1}\), while TiO\(_2\)-2 shows a remarkable decrease in surface area and only has a BET surface area of 44.6 m\(^2\) g\(^{-1}\). Notably, TiO\(_2\)-3 shows a BET surface area of 87.9 m\(^2\) g\(^{-1}\) that is substantially higher than that of the pristine TiO\(_2\). However sample TiO\(_2\)-4 again shows a significantly decreased surface area of 49.4 m\(^2\) g\(^{-1}\). The pore size distribution was estimated by employing the BJH (Barret-Joyner-Halenda) method. TiO\(_2\)-4 shows an average pore size of 97.8 Å that is significantly lower than those of other samples. It should be noted that the hierarchical structure could be beneficial for enhancing the surface area of a material, while the particle size and the pore volume are

Figure 4. TEM micrographs of sample TiO\(_2\)-4: (a) overview image of TiO\(_2\)-4, HRTEM images of TiO\(_2\)-4 nanoparticles (b) and nanotube (c). (d) SAED pattern of synthesized TiO\(_2\)-4.

Figure 5. N\(_2\) adsorption-desorption isotherms for pristine TiO\(_2\) and as-obtained TiO\(_2\).
also key factors affecting the surface area. Both SEM images and calculations using Scherrer’s equation based on XRD patterns suggest the TiO2-4 sample possesses the largest particle size compared with other samples, which might offset the effect from the hierarchical structure.

X-ray photoelectron spectroscopy (XPS) measurements were carried out to investigate the chemical states and electronic structure of Ti4+ in pristine TiO2, TiO2-3 and TiO2-4. As presented in Fig. 6, the XPS signal of Ti 2p was recorded ranging from 454 to 465 eV for the pristine TiO2 and TiO2-4. The Ti 2p3/2 peak shifts from 457.2 eV of pristine TiO2 to 456.8 eV for TiO2-4 accompanying with the negative shift of Ti 2p1/2 peak from 463.2 eV to 462.4 eV, suggesting the partial reduction of TiO2 with the formation of Ti3+ on the surface of the as-prepared TiO2-4. The existence of Ti3+ in the sample TiO2-4 was also confirmed by the X-band Electron Paramagnetic Resonance (EPR) spectra, as shown in Fig. S5.46–48. Based on the EPR results, it is found that TiO2-4 shows a peak intensity of ca. 561, which is three times higher than that of the pristine TiO2 (160.4). Because the intensity signal of EPR evidences the amount of unpaired electrons, it is reasonable to conclude that the amount of Ti3+ ions in the TiO2-4 sample is much higher than that in the pristine TiO2.49 Also signals with g values in the range of 2.0 to 2.08 are belong to photogenerated holes that are trapped by the subsurface lattice oxygen. It is generally agreed that the holes are located at oxygen vacancies which react with the O2− and OH− to form O− and OH− radicals on the surface of catalysts for oxidative decomposition of organic materials. Based on the integrated area of the signals, a larger amount of O− radicals present on the surface of Ti3+-doped materials resulted in more effective photocatalysis.49 It should be noted that the energy difference between XPS Ti2p 3/2 and Ti2p 1/2 peaks for the sample TiO2-4 is ca. 5.55 eV; this value is slightly lower than that of the pristine TiO2 (ca. 6.0 eV).50–52 The slight change in energy difference of the Ti2p peaks can be attributed to the formation of a mixed phase of rutile and anatase in the sample TiO2-4.53 In addition to Ti3+, oxygen vacancies can also be possibly produced during the hydrothermal process.54,55 Figure 6b exhibits the O 1s XPS spectra of the pristine TiO2 and TiO2-4. The Ti-O peak shifts from 528.6 eV for the pristine TiO2 to 528 eV for the TiO2-4; in addition, a new peak located at 530 eV is attributed to Ti-OH, confirming the formation of hydroxyl group on the TiO2 surface after the hydrogen treatment.22,56 We also observed the similar O 1s peak broadening and identical Ti 2p peaks in the as-prepared sample TiO2-3 (ESI, Fig. S3).

UV-visible diffuse reflectance spectra were obtained to investigate the light absorption characteristics of the series of TiO2 samples (ESI, Fig. S4). The absorption edges are measured to be 397.1 nm, 406.0 nm, 394.7 nm, 411.9 nm and 438.2 nm for pristine TiO2, TiO2-1, TiO2-2, TiO2-3 and TiO2-4 respectively. As is well known, the positive shift of the absorption spectra of the photocatalyst is in favor of enhancing photocatalytic performance. It should be noted the variation in the intensity of the spectra background

| Sample  | BET Surface Area (m²/g) | Adsorption average pore width (Å) | Total pore volume (cm³/g) |
|---------|-------------------------|-----------------------------------|--------------------------|
| Pristine TiO2 | 78.9                   | 171.8                             | 0.339                    |
| TiO2–1   | 78.8                   | 197.5                             | 0.389                    |
| TiO2–2   | 44.6                   | 171.2                             | 0.191                    |
| TiO2–3   | 87.9                   | 145.2                             | 0.319                    |
| TiO2–4   | 49.4                   | 97.8                              | 0.121                    |

Table 1. Surface properties of pristine TiO2 and as-synthesized TiO2.

Figure 6. X-ray photoelectron spectra (XPS) of (a) Ti2p and (b) O1s of pristine TiO2 and TiO2-4.
could be attributed to the amount of TiO$_2$ samples used for testing or the particle size of the samples. Figure 7a shows diffuse reflectance spectra of pristine TiO$_2$ and TiO$_2$-4. It can be seen the absorption onset is around 397.1 nm for pristine TiO$_2$, but this absorption extends into the visible region (438.2 nm) for TiO$_2$-4, which can be attributed to the Ti$^{3+}$ doping, the crystallite size, and the phase structure of the samples. The red shift of absorption edge indicates a decrease in the band gap. The corresponding band gap energy value was obtained by plotting the Kubelka-Munk function against the photon energy, as shown in Fig. 7b. The band gap energy value of TiO$_2$-4 is 3.1 eV, which is smaller than that of pristine TiO$_2$ (3.28 eV).

Photocatalytic reactions for the degradation of methylene blue (MB) aqueous solution were performed to investigate the photocatalytic activity of the series of TiO$_2$ samples, as shown in Fig. 8. All of the TiO$_2$ samples after the hydrothermal treatment showed an enhanced photodegradation rate for MB compared with the pristine TiO$_2$ under simulated sunlight irradiation (AM 1.5G and 100 mW cm$^{-2}$). The evolution of methylene blue solution, under 10 minutes dark environment and 50 minutes visible light irradiation, are shown in Fig. 8b. Among the samples after hydrothermal reactions, the TiO$_2$-4 catalyst showed the highest photocatalytic activity. After irradiation for 20 min, nearly 97.2% of MB was degraded by the sample TiO$_2$-4. The TiO$_2$-4 sample was far more efficient than any other samples TiO$_2$-3, TiO$_2$-2, TiO$_2$-1, and pristine TiO$_2$ that present a degradation percentage of about 84.3%, 76.1%, 47.4%, and 23.5%, respectively. It should be noted that, in the dark environment, the TiO$_2$-4, despite of a relatively lower BET surface area, shows a significantly improved adsorption capability compared with pristine TiO$_2$, indicating the Ti$^{3+}$ on the surface of TiO$_2$-4 may also play a key role in promoting the capability to adsorb the organic dye, thereby leading to an outstanding photocatalytic activity.

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**Figure 7.** (a) UV-visible diffuse reflectance spectra of pristine TiO$_2$ and TiO$_2$-4. (b) Curve-fitting by using the Kubelka-Munk function method for the calculated absorbance against the photon energy for the pristine TiO$_2$ and TiO$_2$-4.

**Figure 8.** (a) Photocatalytic degradation rate of methylene blue vs. irradiation time using pristine TiO$_2$ and as-synthesized TiO$_2$ samples. (b) The evolution of photodegradation of methylene blue solution under visible-light irradiation. (O: Original methylene blue aqueous solution; D: Dark environment; 10~50: 10~50 minutes visible light irradiation)
Discussion

Our work has demonstrated an improved approach to realize controllable synthesis of Ti$^{3+}$-doped TiO$_2$ by hydrothermal method using sodium borohydride (NaBH$_4$) as a reductant. In comparison with the method reported previously, the as-prepared Ti$^{3+}$-doped TiO$_2$ could be synthesized using a facile and convenient hydrothermal method. During the hydrothermal process, NaBH$_4$ can act as a reductant directly or hydrolyze to release the reductive H$_2$ (Reaction 2). In such a reducing atmosphere, the reduction of Ti$^{4+}$ is facilitated by atomic hydrogen with the generation of Ti$^{3+}$ on the TiO$_2$ surface (Eq. 3).

$$\text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4\text{H}_2$$

(2)

$$8\text{Ti}^{4+} + \text{NaBH}_4 + 8\text{OH}^- \rightarrow 8\text{Ti}^{3+} + \text{NaBO}_2 + 8\text{H}_2\text{O}$$

(3)

$$\text{NaBO}_2 + 2\text{H}_2\text{O} \rightarrow \text{NaOH} + \text{H}_2\text{BO}_3$$

(4)

With the increasing amount of NaBH$_4$ applied in the hydrothermal treatment, more hydrogen was released from the NaBH$_4$ hydrolytic process to generate a higher pressure at a mild temperature. Therefore, the TiO$_2$-4 sample could have the highest defect concentration. In addition, the high concentration of NaBH$_4$ not only induces a higher pressure due to the generation of H$_2$, but also results in a stronger alkali environment that originates from further hydrolysis of NaBO$_2$ (Reaction 4). Under such a condition, part of anatase TiO$_2$ transformed into rutile TiO$_2$ with the evolution of nanoparticles into hierarchical structures. According to the XPS results, Ti 2p peaks of TiO$_2$ shift to a lower binding energy, confirming the presence of Ti$^{3+}$ decorating on the surface of as-obtained TiO$_2$-4. In addition, oxygen vacancies are also produced during the hydrothermal process which can trap photo-excited electrons together with additional formation of Ti$^{3+}$. Thus, it is reasonable that the TiO$_2$-4 sample possesses the highest photocatalytic activity since the hierarchical structure can multiply UV light absorption which results in a high efficiency of light-harvesting. Moreover, given the fact that P25 TiO$_2$ with mixed phases of rutile and anatase possess a higher catalytic activity than pure phase rutile and anatase TiO$_2$ and TiO$_2$-4 exhibited the highest photocatalytic degradation efficiency of methylene blue despite the fact that the BET surface area of TiO$_2$-4 is smaller than those of the pristine TiO$_2$ and TiO$_2$-3, it is reasonable to deduce that the hierarchical structure, the mixed phase (rutile and anatase), and the Ti$^{3+}$ defects in the TiO$_2$-4 may synergistically contribute to enhancing the catalytic activity. It should be noted that the band gap of TiO$_2$-4 based on the Kubelka-Munk function is 3.1 eV, which is slightly smaller than that of pristine TiO$_2$ (3.28 eV), confirming that adding NaBH$_4$ as a reductant causes the absorption edge of TiO$_2$ to shift to a lower energy region. Therefore, this study may offer a simple and low-cost route to functionalize the TiO$_2$ and enhance its visible light absorption ability with a narrowed band gap, thereby leading to an improved photocatalytic activity.

In summary, a set of Ti$^{3+}$-doped TiO$_2$ samples with controllable photocatalytic properties were designed and prepared using a hydrothermal method via tuning the amount of NaBH$_4$. The as-developed method showed a well-controlled manner in tuning the surface properties of TiO$_2$, as evidenced by color changes from white, light yellow, light grey, to dark grey upon adjusting the amount of NaBH$_4$. In addition, we firstly reported that, with a high concentration of NaBH$_4$ applied in the hydrothermal reaction, a high pressure and strong alkali environment were introduced to facilitate the conversion of anatase TiO$_2$ into rutile TiO$_2$ with the evolution of nanoparticles into hierarchical structures. More importantly, it is demonstrated that the as-developed Ti$^{3+}$-doped TiO$_2$ with a mixed phase and nanostructure can potentially lower the recombination rate of electron-hole pairs due to the presence of Ti$^{3+}$ and oxygen vacancies that are able to trap photo-excited electrons on the surface. Furthermore, with the absorption edge of TiO$_2$ shifting to the visible-light region by adding NaBH$_4$ as a reductant, the synthesized TiO$_2$ is expected to exhibit a higher photocatalytic activity and efficiency.

Methods

Preparation of Ti$^{3+}$-doped titanium dioxide. To fabricate the Ti$^{3+}$-doped TiO$_2$, a two-step hydrothermal synthesis procedure was implemented. First, 5 ml of 50 wt. % titanium (IV) bis (ammonium lactato) dihydroxide (purchased from Sigma-Aldrich) solution was dispersed in 60 ml 0.08 g/L glucose with stirring for 0.5 hour. 65 ml of the above solution was then transferred into an autoclave for hydrothermal reactions at 170°C for 8 hours. Then the products were washed by deionized water and ethanol for 4 times each and filtered. After the calcination treatment at 500°C for 3 hours, dried TiO$_2$ powders were obtained. Different amounts of sodium borohydride (purchased from Alfa Aesar) caplets were directly added into 60 ml water and mixed with 0.50 g TiO$_2$ powder for hydrothermal reactions in an autoclave at 180°C for 16 hours. Finally, the Ti$^{3+}$-doped titanium dioxide powders were collected by filtration, washed alternately 3 times with deionized water and ethanol, and then dried at 60°C in air for 10 hours.

Material Characterizations. The X-ray powder diffraction (XRD) analyses were conducted on a Scintag XDS 2000 diffractometer equipped with a scintillation counter and Cu K-alpha radiation (0.154056 nm) reflection mode. The microscopic morphology and structures of the samples are obtained using a Hitachi (S-4800) scanning electron microscope (SEM) and Hitachi H-9000NAR transmission electron microscope (TEM). The XPS spectra were acquired using a K-alpha spectrometer and the samples were typically rotated 180° to ensure a uniform thin film on the sample surface. The surface elemental composition and binding energy of Ti$^{3+}$ and Ti$^{4+}$ were determined. The UV-Vis diffuse reflectance spectra were collected using a Perkin-Elmer Lambda 950 spectrophotometer equipped with a deuterium lamp and a halogen lamp. The optical band gaps of the samples were calculated using the von-Kolmogoroff equation. The Zeta-potentials of the samples were measured using a Malvern Zetasizer Nano-ZS instrument. The BET surface areas and pore structures were measured using a Micrometrics ASAP 2020 analyzer. The photocatalytic activities were determined using a commercial methylene blue solution as a probe under simulated sunlight illumination.
electron microscope (TEM). X-ray photoelectron spectroscopy (XPS) was conducted by using VG ESCA 2000 with an Mg Kα source and the Cls peak at 284.5 eV as an internal standard. The specific surface area was obtained using ASAP2020 (Micromeritics, U.S.A) Brunauer-Emmett-Teller (BET) nitrogen adsorption-desorption. The N2 adsorption-desorption measurements were carried out at 77 K using a Quantachrome Autosorb gas-sorption system. The samples were degassed at 180 °C for 2 hours before the measurements. The Raman spectra of the Ti3+-doped TiO2 powders were measured using a Raman microscope (Bruker RFS 100/S spectrometer) with an excitation wavelength of 1,064 nm at an input power of 1 mW. The optical absorption spectroscopy measurements were obtained using an Ocean Optics SD2000 UV-visible spectrophotometer with a closed quartz cell (optical path length: 1 cm).

**Photocatalytic reaction.** 30 mg of the powder samples were ultrasonically dispersed in 50 mL deionized water followed by the addition of 0.01 g / L methylene blue (MB) aqueous solution. The mixture was then stirred under darkness for 10 minutes to achieve adsorption-desorption equilibrium. Subsequently, the suspension with continuous stirring was exposed under a Xe lamp (AM 1.5 G and 100 mW cm−2) with an incident direction normal to the surface of the solution. At given irradiation intervals, 3 mL aliquots of the suspension were collected and separated by centrifugation. The absorption spectrum of the supernatant was measured using a UV-Vis spectrometer (Ocean Optics SD2000). The concentration of MB was determined by monitoring the changes in the absorbance maximum at 662.6 nm.

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Author Contributions
J.H.C., Z.H.W. and R.R. designed the experiment. S.M.C. did the SEM and TEM measurements. R.R. and X.R.G. planned the experiments. R.R. and Z.H.W co-wrote the manuscript. Z.H.W., Y.H. and J.H.C. were involved in interpretation of the result and commented on the manuscript. All authors reviewed the manuscript.

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