Synthesis of NaOH-Modified TiOF$_2$ and Its Enhanced Visible Light Photocatalytic Performance on RhB

Chentao Hou *, Wenli Liu and Jiaming Zhu

College of Geology and Environment, Xi’an University of Science and Technology, Xi’an 710054, China;
13572955186@163.com (W.L.); XRD610@126.com (J.Z.)
* Correspondence: houct@xust.edu.cn; Tel.: +86-029-8558-3188
Received: 16 July 2017; Accepted: 16 August 2017; Published: 22 August 2017

Abstract: NaOH-modified TiOF$_2$ was successfully prepared using a modified low-temperature hydrothermal method. Scanning electron microscopy shows that NaOH-modified TiOF$_2$ displayed a complex network shape with network units of about 100 nm. The structures of NaOH-modified TiOF$_2$ have not been reported elsewhere. The network shape permits the NaOH-modified TiOF$_2$ a BET of 36 m$^2$·g$^{-1}$ and a pore diameter around 49 nm. X-ray diffraction characterization shows that TiOF$_2$ and NaOH-modified TiOF$_2$ are crystallized with a pure changed cubic phase which accords with the SEM results. Fourier transform infrared spectroscopy characterization shows that NaOH-modified TiOF$_2$ has more O–H groups to supply more lone electron pairs to transfer from O of O–H to Ti and O of TiOF$_2$. UV–vis diffuse reflectance spectroscopy (DRS) shows that the NaOH-modified TiOF$_2$ sample has an adsorption plateau rising from 400 to 600 nm in comparison with TiOF$_2$, and its band gap is 2.62 eV, lower than that of TiOF$_2$. Due to the lower band gap, more O–H groups adsorption, network morphologies with larger surface area, and sensitization progress, the NaOH-modified TiOF$_2$ exhibited much higher photocatalytic activity for Rhodamine B (RhB) degradation. In addition, considering the sensitization progress, O–H groups on TiOF$_2$ not only accelerated the degradation rate of RhB, but also changed its degradation path. As a result, the NaOH-modified TiOF$_2$ exhibited much higher photocatalytic activity for RhB degradation than the TiOF$_2$ in references under visible light. This finding provides a new idea to enhance the photocatalytic performance by NaOH modification of the surface of TiOF$_2$.

Keywords: TiOF$_2$; NaOH-modified TiOF$_2$; network shape; photocatalysis; RhB

1. Introduction

Nowadays, environmental pollution is affecting human survival and development. Photocatalysis is considered an efficient, stable, and environmentally friendly method for controlling environmental pollution [1]. In the past, TiO$_2$ has been widely used as a photocatalyst in the photo-degradation of organic pollutants. However, it has a wide energy band gap (3.1–3.2 eV) which only permit its UV light response and can easily cause electron–hole recombination [1–4]. Thus, studies on changing morphology [1–3], modification [1,4,5], and other methods were conducted to decrease its band gap or inhibit its electron–hole recombination. The discovery of non-titanium semiconductor photocatalysts with a narrow intrinsic energy band gap, efficiently driven by visible light, may also attract much attention [5–13].

Recently, Li’s research group found that TiOF$_2$ cubes—considered a promising anode material for lithium ion batteries (LIBs) [14–19]—showed visible-light driven property and exhibited excellent performance in photodegradation of Rhodamine B (RhB) and 4-chlorophenol (4-CP) [7]. TiOF$_2$ is also proven to be more active and durable at room temperature due to the covalent bonds of F species with Ti [8,9]. Only a few studies focused on the photocatalytic activity of TiOF$_2$ have been reported [7–9].
As usual, TiOF$_2$ nanoparticles were synthesized via hydrothermal [10,14–18] and solvothermal [7,11,12] methods from titanium (IV) isopropoxide (TIP), and have a cubic shape [7–18]. The size of TiOF$_2$ nanocubes could be affected by alcoholysis time, alcohol kind, solvothermal temperature, different H$_2$O production rate and amount [7,17]. While the photocatalytic activity of TiOF$_2$ is still unsatisfactory, it is necessary to explore novel approaches to improve its photocatalytic performance.

Alkali modification is proven to be an effective method to enhance the catalytic performance for $\alpha$-pinene isomerization, formaldehyde oxidation, and benzene hydroxylation [20–23]. Thus, it stimulated us to modify the TiOF$_2$ catalyst obtained from our earlier studies. In this study, we firstly reported a network-shaped NaOH-modified TiOF$_2$ treated by a hydrothermal process under low temperature. The FTIR measurement showed that more associated O–H exists on the surface of TiOF$_2$, which can remarkably enhance the catalytic activity of TiOF$_2$ toward RhB oxidation under visible light. The NaOH-modified TiOF$_2$ had better photocatalytic performance than TiOF$_2$ in Li’s research [7].

2. Results and Discussion

2.1. Phase Structures and Morphology

The phase and crystallinity of the as-prepared TiOF$_2$ and NaOH-modified TiOF$_2$ samples were tested by XRD analysis. It can be seen from Figure 1, the patterns of as-prepared TiOF$_2$ and NaOH-modified TiOF$_2$ samples all have sharp peaks at $2\theta = 23.6^\circ$, 48.1°, and 54.2°, corresponding to the (100), (200), and (210) planes of the cubic TiOF$_2$ phase (JCPDS no. 08-0060) [7,13] and no peak of any anatase TiO$_2$ (JCPDS no. 21-1272) [24,25] crystal appears, indicating that the as-prepared samples have high crystallinity and pure phase of cubic TiOF$_2$. It also indicates that the height of the (100) crystal planes of the TiOF$_2$ and NaOH-modified TiOF$_2$ are higher, and the (200) and (210) crystal planes are lower than that of the standard cubic TiOF$_2$, indicating a new shape of the as-prepared TiOF$_2$ and NaOH-modified TiOF$_2$. The Scherrer formula was used to calculate the normal distance of certain crystal surfaces of TiOF$_2$ and NaOH-modified TiOF$_2$

$$
\tau = \kappa \lambda / (\beta \cos \theta)
$$

where $\tau$, $\kappa$, $\lambda$, $\beta$, and $\theta$ are the mean normal distance of certain crystal surfaces, the shape constant with a value of 0.89 when $\beta$ is the half width of the diffraction peak (FWHM), the diffracted ray wavelength (0.15418 nm for Cu-Ka), and the diffraction angle in radians, respectively [26].

![Figure 1. XRD pattern with 2θ from 10° to 80° (a) and partial enlarged detail of 2θ from 47° to 56° (b) of as-prepared TiOF$_2$, NaOH-modified TiOF$_2$, commercial P25 and a standard card of TiOF$_2$ and TiO$_2$.](image)

The normal distances of TiOF$_2$ are 7.26, 17.81, 11.67, 10.77, 17.38, and 16.98 nm along the (100), (110), (200), (210), (220), and (215) planes [7,13], respectively, while the distanced of crystal
NaOH-modified TiOF$_2$ change to 15.99, 42.18, 26.26, 30.78, 40.80, and 48.39 nm along the corresponding planes, respectively. It can be seen that the normal distance of the crystalline phase of NaOH-modified TiOF$_2$ shrunk 8.88% and 3.72% along (100) and (110) planes. However, an increase was observed along (200), (210), and (215) planes. This can be explained in that NaOH-modifying induces more O–H adsorbed onto (100) and (110) planes of TiOF$_2$ and, thus, induces the planes’ exposure.

Morphologies and microstructure of original TiOF$_2$ and NaOH-modified TiOF$_2$ were checked by SEM characterization. In Figure 2a,b, TiOF$_2$ crystals displayed a mixture of the cubic image which is accords with the cubic image in [7–18]. Each individual particle crystal is about 50–300 nm and tends to aggregate, forming larger particles while—in Figure 2c,d—the NaOH-modified TiOF$_2$ displayed a more complex network shape with network units in about 100 nm. The NaOH-modified TiOF$_2$ shows phases assembling along certain directions. This accords with the XRD results. The network shape permits much more surface area for photocatalysis. These structures of NaOH-modified TiOF$_2$ have not been reported elsewhere. The Barrett-Joyner-Halenda (BJH) method was used to analyze the pore size distribution and pore volume and the surface area ($S_{BET}$) was calculated using the BET method. The Figure 3a demonstrated that the NaOH-modified TiOF$_2$ showed a typical IV type N$_2$ adsorption–desorption isotherm and mesoporous structure with an average pore diameter of about 49 nm. Thus, its $S_{BET}$ can reach as high as 36 m$^2$·g$^{-1}$, while the average pore diameter and $S_{BET}$ of TiOF$_2$ are only 3 nm and 2.7 m$^2$·g$^{-1}$, which is much lower than that of NaOH-modified TiOF$_2$. The larger surface area permits more O–H and pollutant adsorption and the formation of additional mesopores affects the improvement of mass transfer, enhancing photocatalytic performance accordingly [21,22].

Figure 2. SEM of as-synthesized samples: (a,b) TiOF$_2$; and (c,d) NaOH-modified TiOF$_2$. 
was modified in NaOH solution, thus, more O–H would be chemisorbed onto TiOF$_2$ (4.0 eV) \cite{6}, and other oxides, indicating easier excitation by visible light. This can be explained in that NaOH treatment causes certain facet exposure and network morphologies of TiOF$_2$, changing its light absorption, and further enhanced its visible light photocatalytic properties. NaOH treatment lowered the band gap of TiOF$_2$, enhanced its visible light absorption, and further enhanced its visible light photocatalytic properties.

2.2. FTIR Analysis

Figure 3b shows the FTIR spectra of TiOF$_2$ and NaOH-modified TiOF$_2$. The strong band around 700–500 cm$^{-1}$ could contribute to the Ti–O–Ti stretching vibration \cite{22–24}. The peak around 3379 cm$^{-1}$ and the broad band centered around 3212 cm$^{-1}$ were due to the free and bonding O–H stretching vibration of Ti–OH, respectively \cite{27,28}. The peak at 1620 cm$^{-1}$ was due to the O–H bending vibration of Ti–OH \cite{16,22,29–33}. The broad band centered around 3212 cm$^{-1}$ in NaOH-modified TiOF$_2$ becomes broader than that in TiOF$_2$, meaning that more O–H bonds or associated O–H appeared in NaOH-modified TiOF$_2$. According to previous work, the free O–H stretching vibration used to appear at about 3600 cm$^{-1}$ without bonding O–H \cite{27,28}. It can be seen that the O–H frequency for TiOF$_2$ and NaOH-modified TiOF$_2$ is 221 cm$^{-1}$ and 388 cm$^{-1}$ lower than 3600 cm$^{-1}$, indicating a strong hydrogen bond impact \cite{27,28}. The O–H on the TiO$_2$ surface can enhance the transference of photo-generated electrons and then enhance photocatalytic performance \cite{29}. The peaks around 930 cm$^{-1}$ were due to the Ti–F vibrations in the TiOF$_2$ \cite{16}. The peak intensity decreased from TiOF$_2$ to NaOH-modified TiOF$_2$, indicating F was exchanged by O–H after NaOH modification. All of these show that the NaOH-modified TiOF$_2$ samples contain more O–H groups than TiOF$_2$. It can be explained that TiOF$_2$ was modified in NaOH solution, thus, more O–H would be chemisorbed onto TiOF$_2$, and further exchanged with F. Then, more lone pair electrons in the O–H groups transferring from the O of O–H to Ti and the O of TiOF$_2$, the performance of TiOF$_2$ can be enhanced accordingly \cite{21}. In addition, because RhB is a cationic dye, NaOH brings more O–H onto the surface of TiOF$_2$ to hold more RhB and accelerate its degradation rate \cite{34,35}.

2.3. UV–Vis Analysis

Figure 4 shows that the UV–vis absorption spectroscopy and band gap of as-prepared TiOF$_2$ and NaOH-modified TiOF$_2$ samples. The NaOH-modified TiOF$_2$ has a raised adsorption plateau from 400 to 600 nm, which indicates stronger visible light absorption than that of TiOF$_2$ (Figure 4a). Band gap estimation can be seen in Figure 4b showing that the band gap of NaOH-modified TiOF$_2$ is 2.62 eV, which is lower than that of TiOF$_2$ (2.80 eV) and lower than anatase TiO$_2$ (3.2 eV) \cite{1–4}, NiO (4.0 eV) \cite{6}, and other oxides, indicating easier excitation by visible light. This can be explained in that NaOH treatment causes certain facet exposure and network morphologies of TiOF$_2$, changing its light absorption properties. Thus, the NaOH treatment lowered the band gap of TiOF$_2$, enhanced its visible light absorption, and further enhanced its visible light photocatalytic properties.
where was a photocatalytic process. The concentration of RhB decreased under the same conditions, which means that all samples are visible-light active. It also shows that NaOH-modified TiOF\(_2\) can cause almost complete decomposition of RhB in 3 h, having better photocatalytic performance than all of the TiOF\(_2\) samples. It can be seen in Figure 5a that, in the adsorption test in dark and in light on the process without the catalyst for RhB, the decrease of RhB is very small. It can be concluded that the adsorption and sensitization mechanisms can be negligible in the degradation process. Thus, the degradation of RhB was a photocatalytic process. The concentration of RhB decreased under the same conditions, which means that all samples are visible-light active. It also shows that NaOH-modified TiOF\(_2\) can cause almost complete decomposition of RhB in 3 h, having better photocatalytic performance than all of the TiOF\(_2\) in reference [7,13]. While P25 and TiOF\(_2\) performed poorly compared to NaOH-modified TiOF\(_2\) and TiOF\(_2\)-Ref. The reaction rate of all of the samples are shown in Figure 5b. It can be seen that the data was fitted with the first-order reaction equation as

\[ \ln(C_0/C) = kt \]  

(2)

where \( t \) is the reaction time, \( C_0 \) is concentration of RhB at time 0, \( C \) is the concentration of RhB at time \( t \), and \( k \) is the reaction rate constant.

It can be seen that P25 and TiOF\(_2\) had rate constants of only 0.10 and 0.16 h\(^{-1}\), indicating poor photocatalytic performance. The result is consistent with previous work [8,20]. The calculated rate constants are 1.37, 0.73, and 1.24 h\(^{-1}\) for NaOH-modified TiOF\(_2\), TiOF\(_2\)-Ref, and TiOF\(_2\)-crushed-Ref, respectively. The NaOH-modified TiOF\(_2\) sample shows the best performance among all the photocatalysts, whose degradation rates are much higher than that of P25 and TiOF\(_2\) in our samples.
constants are 1.37, 0.73, and 1.24 h\(^{-1}\) for NaOH-modified TiOF\(_2\), TiOF\(_2\)-Ref, and TiOF\(_2\)-crushed-Ref, respectively. The NaOH-modified TiOF\(_2\) sample shows the best performance among all the photocatalysts, whose degradation rates are much higher than that of P25 and TiOF\(_2\) in our samples and 10.4\% higher than that of TiOF\(_2\)-crushed-Ref The excellent performance could be mainly attributed to its larger S\(_{\text{BET}}\) (32 m\(^2\) g\(^{-1}\) for TiOF\(_2\)-crushed-Ref) and more bonding O–H [7,21].

2.5. Effect of the Sensitization Mechanism

According to previous studies, dyes can be degraded on TiO\(_2\) through a sensitized process under visible light [34,35]. In order to know whether there is a similar path on TiOF\(_2\) and NaOH-modified TiOF\(_2\), UV–vis absorption spectral changes of RhB with visible light irradiation time in the suspension of TiOF\(_2\) and NaOH-modified TiOF\(_2\) were tested. The results are shown in Figure 6. It can be seen in Figure 6 that the spectral change of RhB with the irradiation time on NaOH-modified TiOF\(_2\) is quite different from that on TiOF\(_2\). There is a blue-shift from 558 to 498 nm in the absorption maximum with irradiation time for NaOH-modified TiOF\(_2\), while none in that of TiOF\(_2\). This is attributed to the N-deethylation products of RhB, which confirms the possibility of the sensitization mechanism [34,35]. Thus, NaOH treatment can induce the sensitization process and change the degradation path of TiOF\(_2\).

3. Materials and Methods

Tetrabutyl titanate (TBOT, A.R. grade) was purchased from Fu Chen Chemical Reagent Factory, Tianjin, China. Absolute ethyl alcohol (C\(_2\)H\(_5\)OH, A.R. grade) and sodium hydroxide (NaOH, A.R. grade) was purchased from Fuyu Fine Chemical Co., Ltd., Tianjin, China. Hydrofluoric acid (HF, A.R. grade) was purchased from Xilong Chemical Industry Co., Ltd., Chengdu, China. All reagents are used without further purification. Ultrapure water was used as the experimental water.

NaOH-modified TiOF\(_2\) was synthesized via a modified low-temperature hydrothermal method. In a typical synthesis, 30.4 mL absolute ethyl alcohol was added into 35.2 mL TBOT, which was named solution A. Absolute ethyl alcohol (30.4 mL) and 20.2 mL HF were added into 180 mL ultrapure water, which was named solution B. Solution A was dropped into solution B under medium-speed magnetic stirring at 20 °C for 1.5 h to obtain a faint yellow sol. The sol was aged at room temperature for 2 days to change to a gel. The gel was then transferred into a 50-mL Teflon-lined stainless steel autoclave. When sealed, the autoclave was placed at 100 °C for 2 h in a drying box, then was naturally cooled to room temperature. Ultra-pure water and absolute ethanol were used to wash the obtained white precipitates several times to reach a pH of 7, and then the precipitates were dried at 100 °C. The as-prepared sample was TiOF\(_2\). One gram of the TiOF\(_2\) precursor was dispersed in 100 mL 5 mol L\(^{-1}\) NaOH solution under magnetic stirring with a speed of 4000 r min\(^{-1}\) for 1 h, then the suspension was also washed with ultra-pure water and absolute ethanol to reach a pH

Figure 6. UV–vis absorption spectra of RhB in (a) TiOF\(_2\) and (b) NaOH-modified TiOF\(_2\) suspension under visible light.
of 7. The product was dried at 100 °C for 12 h. The sample was denoted as NaOH-modified TiOF\(_2\). The crystal structure as analyzed by a XD-2 X-ray diffractometer (Beijing Purkinje, Beijing, China) with Cu Kα radiation with a scan rate of 4.0000°·min\(^{-1}\). The morphology was examined by field emission scanning electron microscopy (FESEM, JEOL JSM6700, Tokyo, Japan). Fourier transform infrared (FTIR) spectra were recorded using a Bruker TENSOR27 (Karlsurhe, Germany) using the KBr method. The optical properties were determined by UV–vis diffuse reflectance spectroscopy (UV–vis DRS: Shimadzu 2600, Beijing, China). \(N_2\) adsorption-desorption isotherms were measured at 77 K and the BET method was used to calculate the surface area (\(S_{BET}\)) by a JW-BK122F (Beijing, China).

The degradation of RhB was conducted at room temperature in a 150 mL double-layered quartz reactor containing 50 mg catalyst and 50 mL 5.0 mg·L\(^{-1}\) RhB solution. A 300 W Xe lamp (Jiguang-300, Shanghai, China) was located at a distance of 15 cm from the RhB solution to simulate solar light. A cutoff filter (JB-420, Shanghai, China) was chosen to filter off the light whose wavelength was less than 420 nm to simulate visible light. The solution was magnetically stirred for 30 min to ensure the adsorption–desorption equilibrium, then the xenon lamp was turned on to start the photocatalytic degradation. At 30 min time intervals, about 5.0 mL RhB solution was extracted and centrifuged at high-speed (11,000 r·min\(^{-1}\)) to remove catalysts. Then the concentration of the remaining RhB solutions were analyzed with a Purkinje UV1901 UV–vis spectrophotometer at 554 nm. The photocatalyst was separated from the RhB solution and another run of the reaction was started to investigate the durability of the catalysts.

4. Conclusions

NaOH-modified TiOF\(_2\) was successfully prepared via a modified low-temperature solvothermal method. It exhibited much better photocatalytic performance for RhB degradation. XRD characterization shows that TiOF\(_2\) and NaOH-modified TiOF\(_2\) are crystallized with a pure changed cubic phase which is accord with the SEM results. SEM shows that TiOF\(_2\) crystals displayed a mixture of the cubic images, while the NaOH-modified TiOF\(_2\) displayed a more complex network shape with network units in about 100 nm. These structures of NaOH-modified TiOF\(_2\) have not been reported elsewhere. The network shape permits the NaOH-modified TiOF\(_2\) a surface area of 36 m\(^2\)·g\(^{-1}\) and a pore diameter about 49 nm, which will enhance the adsorption of O–H groups and pollutants. FTIR characterization shows that NaOH-modified TiOF\(_2\) has more O–H groups to supply more lone electron pairs transferring from O of the O–H groups to Ti and O of TiOF\(_2\), in accordance with the BET analysis. UV–vis absorption spectroscopy shows that the NaOH-modified TiOF\(_2\) samples have an adsorption plateau rising from 400 to 600 nm in comparison with TiOF\(_2\) and its band gap is 2.62 eV, lower than that of TiOF\(_2\). Due to the lower band gap, more O–H groups adsorption, network morphologies with larger surface area, and sensitization process, the NaOH-modified TiOF\(_2\) exhibited much higher photocatalytic activity for RhB degradation. In addition, considering the sensitization process, O–H on TiOF\(_2\) not only accelerated the degradation rate of RhB, but also changed its degradation path. This finding provides a new idea to enhance the photocatalytic performance by NaOH modification of the surface of TiOF\(_2\). Considering its synthesizing process, the NaOH-modified TiOF\(_2\) needs much lower temperature and shorter time than TiOF\(_2\)-crushed-Ref, but has much better photocatalytic performance, which provides a more economic choice.

Acknowledgments: Financial support was provided by Shaanxi Key Industrial Projects (2014GY2-07) and the Shaanxi Province Education Department Science and Technology Research Plan (15JK1460).

Author Contributions: In this paper, Chentao Hou and Wenli Liu designed the experiments; Wenli Liu and Jiaming Zhu conducted the experiments; Chentao Hou and Wenli Liu analyzed the data; and Chentao Hou wrote the article.

Conflicts of Interest: There is no conflict of interest existing in the manuscript submission, and it is approved by all of the authors for publication. All the authors listed have approved the manuscript to be enclosed.
References


18. Reddy, M.V.; Madhavi, S.; Rao, G.V.S.; Chowdari, B.V.R. Metal oxyfluorides TiOF₂ and NbO₂F as anodes for Li-ion batteries. *J. Power Sources* 2006, 162, 1312–1321. [CrossRef]

