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Functions of boric acid in fabricating TiO_2 for photocatalytic degradation of organic contaminants and hydrogen evolution



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A R T I C L E I N F O A B S T R A C T Keywords: Photocatalysis Degradation Hydrogen evolution Organic contaminants Boric acid-induced hydrolysis for fabricating TiO₂ photocatalyst for photodegradation of organic contaminants (such as phenol, methyl orange and methylene blue) and hydrogen evolution is developed. The water dehydrated from boric acid in absolute ethanol promote the slow hydrolysis of tetrabutyl titanate during the hydrothermal process so that the crystalline size of TiO₂ is smaller. Boric acid not only function as hydrolytic reagent for tetrabutyl titanate, but also as support for TiO₂ nanoparticles during the annealing procedure. Moderate dosage of boric acid and calcinating temperature during the synthesis of TiO₂ promote the exposure of active (001) facets and large surface area, resulting to the excellent photocatalytic activity in the degradation of

organic contaminants and hydrogen evolution.

Introduction

With the rapid development of modern industry, environmental pollution and energy crisis are becoming two major issues besetting us, which urge scientists to find effective measures to ameliorate the situation [1,2]. Photocatalytic pollutant degradation and hydrogen production, which can improve environment quality and provide clean fuel respectively just under solar irradiation, are effective and promising way to solve these two problems [3–6]. In the past decades, TiO_2 has been thoroughly studied for the photocatalysis because of its nontoxicity, low cost, high stability and excellent photocatalytic activity [7-9]. The photogenerated hydroxyl radicals OH• resulting from the interaction between photoholes with water and/or oxygen on the surface of TiO₂, owing strong oxidizing ability (standard redox potential +2.8 V), can oxidized most of organic compounds to mineral endproduct, such as carbon dioxide and water [10]. On the other side, the photogenerated electrons can reduce hydrogen ions in water to hydrogen in the present of sacrifice agent [11]. Therefore, TiO₂ was usually used to photodegrade organic pollutants or photocatalytic hydrogen generation [12–16]. However, its wider band gap (about 3.2 eV) illustrates that the light absorption of TiO₂ is in UV-light region, extensively hampering the utilization of solar irradiance [12]. To extend the absorption region of TiO₂ to visible region and improve the photocatalytic activity, three strategies as following are often adopted: i) hybridizing TiO2 with other semiconductive materials, which can effectively decrease recombination of photo-hole and photo electron

[17–20]; ii) hydrogenating TiO₂ to produce colorful TiO₂ so that visible-light can be effectively absorbed [8,12,21]; iii) doping metal or non-metal into TiO₂, which dopes hetero-orbit into band gap of TiO₂, decreasing actual band gap of TiO₂ [22–25].

Among the three measures to enhance the photocatalytic performance of TiO₂, introducing doping non-metal dopants into TiO₂ is relatively simple and promising method because it is conducive the electron-hole separation and improves the visible-light absorption property [22]. Boron-doped TiO₂ has been researched in photodegradation of various organic pollutants in recent years [26-29]. The relationship between the content of boron dopants with photocatalytic performance was also investigated [30]. With boric acid (H₃BO₃) as boron resource and tetrabutyl titanate as precursor, a tiny amount of water was usually introduced to hydrolyze tetrabutyl titanate to TiO₂ [28,29], which makes the process of hydrolysis quick and size of TiO₂ large that impacts photocatalytic performance. In this article, the functions of H₃BO₃ in fabricating TiO₂ with excellent photocatalytic activity in the degradation of organic contaminants and the hydrogen generation are extensively investigated. The excessive boric acid not only induces the slow hydrolysis of tetrabutyl titanate, but also be expected to serve as hard template and boron resource during the hydrothermal process and annealing procedure, so that the products possess high surface area and porous structure. It was found that the amount of H₃BO₃ and annealing temperature is relative to the factors impacting photocatalytic activity such as crystallinity, surface area and pore size. Therefore, this research is important to develop outstanding

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photocatalyst TiO_2 and demystify the function of boric acid in synthesizing TiO_2 with excellent photocatalytic activity.

Experimental

Materials

Butyl titanate (Kermel, 99.0%), ethanol absolute (Fangzheng, analytical reagent grade), boric acid (Fuchen, 99.5%), methanol (Concord, 99.90%), phenol (Fuchen, analytical reagent grade), Methyl Orange (Beijing, analytical reagent grade), Methylene Blue (Beijing, analytical reagent grade), Ethylene glycol (Fangzheng, analytical reagent grade), Glycerol(Huadong, analytical reagent grade), P25 (Macklin,99.8%) are all used as received.

Characterizations

Transmission electronic microscopy (TEM, Tecnai G2 F20 S-TWIN) and scanning electronic microscopy (SEM, JSM-7500) are used to observe morphology of all samples. X-ray diffractometer (Bruker D8 ADVANCE, CuK_{α} (1.5418 Å), 40 kV, 40 mA) records the powder X-ray diffraction (XRD) patterns. The scanning speed is 4 degrees per minutes from $2\theta = 4^{\circ}$ to 80° . Laser Confocal Micro-Raman Spectroscopy (LabRAM HR800, Horiba Jobin Yvon, France) with 532 nm laser presents Raman spectra for all samples. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI) is utilized to analyze the elemental components. The nitrogen adsorption-desorption experiments are performed on an automatic specific surface and porosity analyzer (V-sorb-2800, Gold APP Instruments, Beijing). The sample was firstly degassed in vacuum at 120 °C for 4 h before analysis. The surface area is calculated based on the adsorption data with a relative pressure (P/P_0) ranging from 0.05 to 0.35 according to Brunauer-Emmett-Teller (BET) theory. The total pore volume of each sample is calculated by using single point adsorption data at P / $P_0 = 0.9970$. Diffuse reflectance UV-vis spectroscopy was conducted on a spectrophotometer (Shimadzu UV-3600) equipped with an integrating sphere. Optical band gaps are determined from Tauc plots for an indirect band gap material, F(R) = $\left(\frac{(1-R)^2}{2R} \times hv\right)^{1/2}$ using the Kubelka-Munk formalism, where R corresponds to the reflectivity (%R / 100) and the band gap is obtained from the intersection of the tangent to the energy axis of the function. The surface acidity of the TiO2-xB-600 samples were determined by NH3-TPD experiments, using chemisorption instrument (VDSorb-91i, Vodo instrument, Quzhou, China). The detailed procedure for NH₃-TPD is as follow: 0.05 g of TiO₂-xB-600 was placed inside the U-type quartz qube and pretreated in helium atmosphere at 150 °C for 1 h. Subsequently the sample was cooled down to room temperature and titrated with pure NH₃. Afterwards, the physically-absorbed NH₃ was removed by helium gas for 0.5 h. The desorption process was performed from 30 to 500 $^\circ \rm C$ with a ramp of 10 °C /min and recorded by a thermal conductivity detector (TCD).

Catalyst preparation

In general, tetrabutyl titanate (10 mL), ethanol absolute (10 mL) and boric acid were added into a Teflon-lined stainless steel autoclave in turn. The mixture was stirred with a glass rod before seal up and then hydrothermal treated at 180 °C in oven for 24 h. The product was named as $O-TiO_2$ (original TiO₂). After filtration, the product was dried in oven at 80 °C overnight and annealed at high temperature (400–800 °C) in muffle furnace for two hours. Then the annealed powder was boiled up in a large amount of water for one hour and thermally filtered so that boric acid or boron oxide in sample can be removed. The product was dried in oven at 100 °C for two hours and named as TiO_2 -xB-y, in which x represents the gram number of boric acid used in hydrothermal process and y indicates the annealing temperature. For example, TiO₂-5B-600 means that 5 g boric acid was used and the annealing temperature is 600 °C. As control experiment, sample was not annealed at high temperature, just washed with boiled water, it was termed as TiO_2 -xB, x still represents the gram number of boric acid.

Photodegradation of phenol and dyes

The photodegradation of phenol is carried out on a photochemical reactor (YM-GHX-V II, Yuming Instrument, Shanghai, China). The Xenon lamp is used as the light source, and its power is 1000 W, the luminous intensity is 170 mW cm⁻². Typically, photocatalyst (50 mg) and phenol aqueous solution (50 mL, 10 mg L^{-1}) are charged into a quartz tube reactor in turn. Then, the tubes containing reactants are placed around a Xenon lamp and magnetically stirred in dark for 0.5 h before irradiation in order to achieve an adsorption and desorption equilibrium between the photocatalyst and the phenol solution. The Xenon lamp is placed in a quartz cold well cooled down by circulating water at 10 °C so that the impact of infrared radiation on reaction can be eliminated. The picture of photochemical reactor can be seen in Fig. S1. During the irradiation, samples are taken at constant time intervals (once an hour), sampling 1 mL each time, and then analyze the contents of residual phenol and intermediates by high performance liquid chromatograph (HPLC, LC-20A, Shimadzu) equipped with a C-18 column (4.6*250 mm, 5um). The UV detector (SPD-20A) is set to a wavelength of 270 nm, and the mobile phase is water/acetonitrile (1:1 (v/v)) with flow rate of 0.8 mL/min.

In photocatalytic degradation methyl orange (MO) and methylene blue (MB), the whole experimental procedure is essentially the same as the photocatalytic degradation of phenol except that the initial concentration of MO and MB solution is controlled at 5 mg L^{-1} . The residual concentration of MO is detected by HPLC, the wavelength of UV detector is 460 nm, the mobile phase is water/acetonitrile (3:7 (v / v)) with a flow rate of 1 mL / min. The residual concentration of MB is measured by a UV/Vis spectrophotometer at 660 nm (Beijing P&S General T6 New Century).

Photocatalytic hydrogen production

Photocatalytic hydrogen production is carried out in a custom topirradiation quartz reactor with gas sampling hole. The photocatalyst is dispersed in a methanol solution (50 mL, 20 vol %), and bubbled with N₂ under stirring for 30 min so that the air in the reactor can be sufficiently discharged. Then the quartz reactor is sealed and irradiated under Xenon lamp. Its power is 300 W and the wavelength distribution is 350–780 nm. The output light intensity was controlled at 200 mW cm⁻². The reactor is cooled by running water at room temperature. The picture of instrument for photocatalytic hydrogen generation is shown in Fig. S2. The evolved gas is analyzed by gas chromatography (CHU-ANHAO GC-7890, Shanghai, China) equipped with a thermal conductive detector (TCD) and a 5A molecular sieve column. Nitrogen gas is used as carrier gas. The temperature of column oven, inlet and TCD is set to 50, 50 and 150 degrees, respectively.

Results and discussions

Photodegradation of phenol and dyes

Phenol is one of the most common organic pollutants in surface water sources and is widely found in industrial waste water, which is harmful to all living organisms [31,32]. Photocatalytic degradation of phenol in wastewater is an effective measure to improve the quality of water [32]. To evaluate the photocatalytic activity of TiO_2 samples hydrolyzed by boric acid and calcinated at different temperature, we firstly conduct photodegradation of phenol with these samples as catalyst in water.



Fig. 1. Photocatalytic performance of TiO_2 samples in photodegradation of phenol.

Table 1
Structure characteristics and photoactivity of TiO ₂ -xB-y samples.

sample	Relative crystallinity	crystallite size(nm)	XRD(001/101)	Raman(514/144)	Apparent rate constants for photodegradation of phenol Ka($\times 10^{-2},h^{-1})$
TiO ₂ -5B-500	0.642	103	0.185	0.069	19.55
TiO ₂ -5B-600	1	168	0.204	0.106	35.64
TiO ₂ -5B-700	2.653	521	0.188	0.059	19.49
TiO ₂ -5B-800	3.413	> 1000	0.197	0.060	5.45
TiO ₂ -1B-600	1.052	184	0.169	0.070	14.52
TiO ₂ -10B-600	1.480	279	0.206	0.088	65.18
110 ₂ -10B-000	1.400	2/9	0.200	0.000	05.16

As shown in Fig. 1a, phenol shows a stable existence under Xe lamp irradiation in the absence of catalyst, whereas degradation occurs if TiO₂ catalysts exist in the system. TiO₂-5B and commercial P25 exhibit similar photocatalytic performance, which cannot effectively photodegrade phenol even in nine hours. When TiO₂-5B is calcinated at higher temperature, the photocatalytic activity increased. Compered to TiO₂-5B-500, TiO₂-5B-700 and TiO₂-5B-800, TiO₂-5B-600 shows excellent photocatalytic performance, which is even higher than the performance of commercial P25. If the calcination temperature is higher than 600, the photocatalytic performance decrease, maybe resulting from the increase of crystallite size and the decrease of surface area. The linear transforms of $\ln(C_0/C) \sim t$ shown in Fig. 1b illustrate that the photocatalytic degradation of phenol is first-order reaction. The apparent rate constant of TiO₂-5B-600 is larger than TiO₂-5B-500, TiO₂-5B-700 and TiO₂-5B-800 according the slope values of lines (Table 1). As control experiment, TiO₂-600, produced through waterinduced hydrolysis of tetrabutyl titanate, show poor photocatalytic activity (Fig. 1c). This result illustrates that boric acid play positive function to improve the photocatalytic activity of TiO₂-5B-600. To further investigate the function of boric acid, TiO2 catalysts with different dosages of boric acid during the hydrothermal step are prepared under same conditions, that is, TiO₂-1B-600 and Ti-10B-600. As was expected, TiO₂-10B-600 exhibits the highest photocatalytic performance than other all samples because almost 100% degradation of phenol in only five hours. Linear transforms of $\ln(C_0/C) \sim t$ indicates that TiO₂-10B-600 possess the largest apparent rate constant (Fig. 1d). Furthermore, we also investigate the degradation of phenol and intermediates distribution along with the reaction time with TiO₂-10B-600 as photocatalyst (Fig. 1e). During this photodegradation, small amount of intermediates such as hydroquinone, catechol and benzoquinone are also detected and finally degraded, which is similar to the other report [33]. More importantly, the photocatalytic performance of TiO₂-10B-600 for phenol degradation still highly remains even after four experimental cycles, suggesting it possesses a stable degradation ability (Fig. 1f). TiO₂-10B-600 exhibits different photocatalytic activities under different pH conditions (Fig. 1g and h). The results indicate that the photodegradation of phenol is more favorable in near-neutral solution or acid solution than in alkaline solution, suggesting that TiO₂-10B-600 has broad applicability in practical application for photodegradation of phenol.

The photocatalytic degradation of MO and MB by TiO₂-10B-600 is also investigated (Fig. 2). The results suggest that TiO₂-10B-600 has photodegradation ability to both anionic dye MO and cationic dye MB. When the irradiation time is 7 h, 80% of MO and almost 100% of MB were degraded (Fig. 2a). The linear transforms of $\ln(C_0/C) \sim t$ in Fig. 2b indicate that the photodegradation of MO and MB is also first-order reaction. It is proved that TiO₂-10B-600 has general applicability in photocatalytic degradation of organic contaminations.

Characterizations of TiO₂-xB-y

To explore the specific functions of boric acid in fabricating TiO₂ samples with different photocatalytic performance, series of characterizations are conducted to probe the microstructure of all samples. In the hydrothermal process for synthesizing TiO₂ in absolute alcohol containing boric acid, no extra water was introduced into the system and tetrabutyl titanate yet was hydrolyzed to TiO2. In control experiment, TiO₂ powder cannot be achieved if boric acid is absent in the system under same hydrothermal conditions. XRD pattern of the solid product achieved after hydrothermal process presents obvious characteristic diffraction of anatase TiO₂ and boron oxide (Fig. 3a), confirming that the water promoting the hydrolysis of tetrabutyl titanate generated from the dehydration of boric acid at hydrothermal condition and boric acid became into boron oxide. Furthermore, due to the poor solubility of boric acid or boron oxide in absolute ethanol, the solid boric acid or boron oxide can serve as support to load the generated TiO₂. From the SEM image of O-TiO₂, it can be clearly observed that small TiO2 nanoparticles load on the surface of laminated boric acid/ boron oxide (Fig. 3b). In the following annealing process, boron oxide can also function as hard template to generate TiO₂ with large surface area and pore structure. After boron oxide is washed in boiling water, TiO₂-xB-y can be achieved. The SEM image of TiO₂-5B-600 shown in Fig. 3c indicates that TiO₂-5B-600 is composed of assembled TiO₂ nanoparticles. The TEM image of TiO₂-5B-600 further points out that the size TiO₂ nanoparticles in TiO₂-5B-600 are about $25 \sim 50$ nm (Fig. 3d). Its microstructure illustrates that the sample are not completely crystalline and a layer of amorphous state around TiO₂ nanoparticles showing lattice fringe can be clearly observed (Fig. 3d). We also use XRD characterizations to research the impact of the calcination temperature and the dosage of boric acid on the microstructure of TiO₂-xBy (Fig. 4a and b). In order to study the crystallinity of TiO₂-xB-y, TiO₂-5B-600 is selected as the reference sample so that its relative crystallinity is set as 1. The relative crystallinity of the remaining samples can be estimated according to the ratio of (101) diffraction intensity of TiO₂-xB-y to that of TiO₂-5B-600 (Table 1). It can be clearly observed that the crystallinity of the sample is better as the annealing temperature is increased. At the same time, the dosage of boric acid used during the synthesis is also considered to be a factor affecting the crystallinity. The larger dosage of boric acid leads to the higher crystallinity of the sample. In addition, according to the line width analysis of anatase (101) diffraction peak based on Scherrer formula calculation, the crystallite size of TiO₂ increase along with the raise of calcination temperature (Table 1). In the pattern of TiO₂-5B-800, the characteristic diffraction peaks of rutile can be obvious observed. Moreover, it is well established that (001) face of anatase phase is more active in photocatalysis because photogenerated electrons favor to assemble on lowenergy (101) face while photogenerated holes migrate to high-energy (001) faces, making for the separation between electrons with holes [34]. The more exposure of (001) faces in anatase TiO_2 is, the higher photocatalytic activity of TiO2 possesses. After careful analysis of XRD



Fig. 2. Photocatalytic performance of TiO₂-10B-600 in photodegradation of MO and MB.



Fig. 3. a) XRD patterns of O-TiO₂ and standard diffractions of anatase and boric acid; b) SEM image of $O-TiO_2$; c) SEM image of TiO_2 -5B-600; d) TEM image of TiO_2 -5B-600.



Fig. 4. a) XRD patterns of TiO₂-5B-y; b) XRD patterns of TiO₂-xB-600; c) Raman spectra of TiO₂-5B-y; d) Raman spectra of TiO₂-xB-600.



Fig. 5. a) Nitrogen isotherms of TiO₂-5B-y; b) porous width distribution of TiO₂-5b-y samples; c) The plots of transformed KM function $[\alpha h\nu]^{1/2}$ vs. $h\nu$ based on diffuse reflectance spectra of TiO₂-5B-y; d) The plots of transformed KM function $[\alpha h\nu]^{1/2}$ vs. $h\nu$ based on diffuse reflectance spectra of TiO₂-xB-600.

patterns, it is found that the (001)/(101) ratios of TiO₂-5B-600 and TiO₂-10B-600 are higher than other samples (Table 1). Because active photogenerated hydroxyl radicals OH• possess standard redox potential of +2.8 V, which can decompose organic to end-products [10], TiO₂-5B-600 and TiO₂-10B-600 exhibit excellent photocatalytic activity in photodegrade phenol. If only 1 g of boric acid is used in the hydro-thermal process, the (001)/(101) ratio is only 0.17, which is significantly lower than TiO₂-5B-600 (0.204) and TiO₂-10B-600 (0.206). So, we conclude that boric acid is favor to fabricate TiO₂ with high (001)/(101) ratio, resulting to the final TiO₂ product possess excellent photodegradation activity.

We also use Raman spectra to investigate the impact of annealing temperature on microstructure of TiO₂. As shown in Fig. 4c and d, the characteristic Raman bands of anatase locating at 144 cm^{-1} (Eg), 197 cm^{-1} (Eg), 399 cm^{-1} (B1 g), 513 cm^{-1} (A1 g), 519 cm^{-1} (B1 g) and 639 cm^{-1} (Eg) can be observed for all samples [35,36]. For TiO₂-5B-800, even though the rutile crystal phase was observed in XRD, no rutile signal was detected in the Raman spectrum because the amount of the rutile crystal phase was very small. It has been established that the full width at half maximum (FWHM) and frequency of Raman peaks of TiO₂ are related to crystallite size of TiO₂. If the particle size of TiO₂

decreases, the Raman peaks become broad and systematic frequency shifts [37]. Compared to the sample TiO₂-5B-700 and TiO₂-5B-800, the peaks of Eg mode (144 cm⁻¹) in the spectra of TiO₂-5B-500 and TiO₂-5B-600 are broad and exhibit a slightly red shift, suggesting that the particle sizes of anatase in TiO2-5B-500 and TiO2-5B-600 are smaller [34]. In addition, the intensity ratio of A_{1g} (514 cm⁻¹) / E_g (144 cm⁻¹) represents the percentage of exposed [001] facets of TiO2. After careful analysis, it is found that the intensity ratio of A_{1g} (514 $\mbox{cm}^{-1})$ / E_g (144 cm⁻¹) for TiO₂-5B-500, TiO₂-5B-600, TiO₂-5B-700 and TiO₂-5B-800 are 0.07, 0.11, 0.06, and 0.06, respectively, illustrating that TiO₂-5B-600 possess more photocatalytic active sites. In comparison, the intensity ratio of A_{1g} (514 cm⁻¹) / E_g (144 cm⁻¹) for TiO₂-1B-600 is only 0.07, which is lower than the corresponding values of TiO₂-5B-600 and TiO₂-10B-600. (0.11 and 0.09 respectively) further indicating boric acid is make for active TiO₂ photocatalyst. This result is in accordance with the XRD analysis.

Nitrogen adsorption-desorption experiments point out that all the samples are mesoporous properties (Fig. 5a). As the calcination temperature increases, the BET specific surface area and pore diameter gradually decrease (Fig. 5b). Large surface area and mesoporous structure make the sample own more active sites and can easily interact



Fig. 6. a) XPS full spectra of TiO₂-5B-y samples; b) XPS full spectra of TiO₂-xB-600 samples; c) XPS Ti2p spectra of TiO₂-xB-y samples; d) XPS O1s spectra of TiO₂-xB-y samples.



Fig. 7. a) Photocatalytic performance of TiO₂-5B-y in hydrogen evolution; b) Photocatalytic performance of TiO₂-xB-500 in hydrogen evolution.



Fig. 8. Photocatalytic hydrogen evolution properties of TiO_2 -10B-500 with different sacrificial agents.

with substrates so that TiO_2 -5B-500 may exhibit excellent photocatalytic performance.

The UV–vis diffuse reflection shows that as the calcination temperature increases (from 500 to 800), the optical band gap of the sample gradually decreases (3.08-2.96) so that the absorption wavelength shifts to the visible region. However, the photocatalytic activity of TiO₂-5B-y is not correlated to the change of band gap. In addition, there is also no obvious relationship between the dosage of boric acid with band gap for these TiO₂-xB-y samples, which is same to the previous reports that boron dopant cannot impact the band. These results illustrate that the photodegradation of organic contaminants is not sensitive to visible light but ultraviolet light. The key factor for the photocatalytic degradation of organic contaminants is crystallite size and surface area.

Although a large amount of boric acid is used during the synthesis of TiO_2 -xB-y samples, boron element is not detected according to XPS analysis, suggesting boron atom is not doped into the samples. So, we conclude that the boric acid just impacts the crystallite size and crystallinity so that promote the photocatalytic activity in the photogradation of organic contaminants. The XPS Ti2p spectra and O1s spectra point out the existence of Ti(IV), illustrating the generation of

TiO₂ during the synthesis. (Fig. 6). Although there are slight shifts in Ti2p spectra and O1s spectra between different samples, there is not obvious correlation between the photocatalytic activities and the shift of bonding energy. So, we attribute the slight shift of bonding energy to the measurement error for different samples. We also use NH₃-TPD experiment to determine the surface acidity of as prepared TiO₂ samples and hope to find out the relationship between the catalytic performance and surface acidity. Unfortunately, the experiment results indicate that there is almost no difference between TiO₂-xB-600 samples and the surface acid sites on these catalysts are negligible (Fig. S3). So, we conclude that the surface acid of as-prepared TiO₂ do not affect the photocatalytic performance in the photodegradation of organic contaminants. This result further illustrates that boron element is not doped into TiO₂-xB-600 samples and the dosage of boric acid during the preparation of TiO₂-xB-600 samples do not determine the surface acidity of final products.

Photocatalytic H_2 evolution

We also evaluate the photocatalytic activity of TiO₂ catalysts for photocatalytic hydrogen evolution (Fig. 7). Firstly, commercial P25 almost has no photocatalytic activity for the hydrogenation evolution, which is same to the performance of TiO₂-5B-700 and TiO₂-5B-800. TiO₂-5B-600 shows a poor photoactivity for this reaction, which is different form the photodegradation of organic contaminants. Compared with TiO₂-5B-y samples, TiO₂-5B-500 exhibits the best hydrogen evolution performance (Fig. 7a) with the photoactivity of 133.6 umol/ h/g cat. The photocatalytic performance of TiO2-5B-400 for hydrogen evolution is even higher than TiO2-5B-600. Combined the photocatalytic performance with the characterizations above, we conclude that the surface area plays a key function in the photocatalytic hydrogen evolution except the exposure of active (001) facets. Furthermore, the dosage of boric acid utilized during the hydrothermal hydrolysis and calcination can also impact the photocatalytic performance in the hydrogen evolution. The hydrogen evolution rate of TiO₂-10B-500 is 168.4 umol/h/ g $_{\rm cat}$ which is higher than the one of TiO_2-5B-500 (Fig. 7b). So, it can be concluded that the dosage of boric acid indeed impacts the photocatalytic performance of TiO₂-5B-y.

With TiO₂-10B-500 as photocatalyst, the importance of sacrificial agents for photocatalytic hydrogen evolution is further investigated. No hydrogen is detected in the system when any sacrificial agent is absent. With the same content of sacrificial agents in the system, the rate of hydrogen evolution is as follow: triethanolamine > methanol > ethylene glycol > glycerol (Fig. 8). As we all known, only when the redox potential of sacrificial agent is more negative than the valence band potential of catalyst, it is easy to capture the photogenerated holes on the valence band of catalyst, which is beneficial to the conduction band electrons to realize the H⁺ to hydrogen reduction process, and the catalyst is not inactivated by oxidation itself [38]. The excellent performance of triethanolamine (344.6 umol/h/g_{cat}) as a sacrificial agent with TiO₂-10B-500 as photocatalyst proves that triethanolamine is more easily oxidized during the hydrogen evolution process of the system than alcohol sacrificial agents.

Conclusions

Through boric acid-induced hydrolysis of butyl titanate in hydrothermal conditions, a series of TiO_2 catalysts possessing excellent photocatalytic activity for the degradation of organic contaminants and hydrogen evolution are synthesized. Boric acid not only promote the hydrolysis of butyl titanate to TiO_2 by dehydration under hydrothermal process, but also function as solid template to support TiO_2 during the hydrolysis and annealing process. More importantly, moderate amount of boric acid is favor to fabricate TiO_2 with high (001)/(101) ratio, resulting to the final TiO_2 product owns excellent photocatalytic activity. In addition, annealing temperature is important to the catalytic performance of TiO_2 samples because higher annealing temperature obviously influences the surface area of sample Moderate annealing temperature and dosage of boric acid contribute to the anatase owning more active sites for photocatalysis.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.110614.

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