Acid-assisted synthesis of TiO₂ nanoparticles for enhancement of visible light photocatalytic efficiency

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Abstract. Compared with pure phase TiO₂, the mixed-phase TiO₂ nanoparticles with oxygen vacancies can help to reduce the carrier recombination rate and band gap, which is contribute to the visible light photocatalysis performance. In this study, three kinds of acid were separately used to prepare TiO₂ nanoparticles by hydrothermal method without any post-heat treatment for enhancement of visible light photocatalytic efficiency. When utilized to assist photocatalysis degradation of methyl orange in water under visible light irradiation, the TiO₂ nanoparticles obtained from HCl (H-TiO₂) and CH₃COOH (A-TiO₂) showed stable photocatalysis performance for increasing the cycles up to ten times while only five cycles for TiO₂ nanoparticles obtained by HNO₃-assisted (N-TiO₂). The photocatalysis performance of H-TiO₂ powder and A-TiO₂ powder are both better than that of the N-TiO₂ powder. Therefore, the TiO₂ samples prepared by HCl- and CH₃COOH-assisted method in this work are regarded as excellent photocatalysts for water cleaning.

1. Introduction
Titanium dioxide (TiO₂) has been a kind of widely investigated wide-bandgap semiconductor materials because of its environmentally friendly, good chemical stability, good cycling performance and cheap [1–4]. Nowadays, TiO₂ has known as an effective photocatalyst under UV light illumination [1,5]. The photocatalytic activity of TiO₂ is produced from the electron transition under light illumination. The producing electrons and holes are with reducing ability and holes with oxidizing ability, respectively. The photocatalysis performance of semiconductor material is decided by the relative position of its conduction and valence band. The low efficiency of TiO₂ under visible-light illumination limits its wide application in degradation of pollutants, which is because of the rapid carriers’ recombination inside of the TiO₂ of electrons from conduction band and holes from valence band [6,7].

Over the past decade, numerous methods have been proposed to enhance the visible light photocatalytic efficiency of TiO₂ powders [8–10]. The photocatalysis performance of amorphous TiO₂ is always worse than crystallized TiO₂. The amorphous TiO₂ is long-range disorder. Therefore, they are with more bulk defects. The characteristic of amorphous TiO₂ leads to higher recombination rate of carriers than that of crystallized TiO₂ [5]. According to previous works, the crystallized TiO₂ formed by both anatase phase and rutile phase shows much higher photocatalytic efficiency than pure phase TiO₂. The mixed phase TiO₂ with the appropriate band gap exhibits enhancement of charge separation [8,11]. An internal electric field is formed between the phase cross sections [12]. The mixed phase junction
plays a decisive role in the effective separation of carriers, thus prolonging charge lifetimes, resulting in greater photocatalytic reactivity [13]. The crystallized TiO$_2$ need high temperature to construct the phase junction. However, the post-heat calcination treatment will cause the growth of grain, loss of hydroxyl groups and repugnant agglomerations of TiO$_2$ powders, which is resulting in deteriorating the photocatalytic activity. In addition, defects have been demonstrated to regulate the band gap [14,15]. The defect level and the shallow donor level can help to reduce the band gap inside of the crystalline TiO$_2$ thus expanded the range of photocatalysis performance [16,17]. Oxygen vacancies are one kinds of defects in crystalline TiO$_2$. In addition, the density of states below the Femi energy level could be produced by the oxygen vacancy defects [18]. Thus, the carriers are significantly promoted efficient separation [19]. Therefore, introducing oxygen vacancies in crystalline TiO$_2$ is another useful route to promote the visible light photocatalytic efficiency.

In this paper, highly crystallized mixed-phase TiO$_2$ with oxygen vacancies were synthesized by acid-assisted hydrothermal method without any high temperature calcination. Titanium butoxide (TBT) was used as titanium source, while HCl, CH$_3$COOH or HNO$_3$ played an assistant role to promote the formation of the mixed-phase and introduce the oxygen vacancies. The methyl orange (MO) in water was photodegraded under visible light illumination with the existence of TiO$_2$ powders. The TiO$_2$ obtained from HCl (H-TiO$_2$) or CH$_3$COOH (A-TiO$_2$) exhibited a visible light photocatalytic efficiency higher than that of TiO$_2$ obtained from HNO$_3$ (N-TiO$_2$). The visible light photocatalysis performance of the mixed-phase TiO$_2$ nanoparticles respectively from HCl, CH$_3$COOH and HNO$_3$ were indeed investigated, which are given more choice for commercial production of TiO$_2$ in the future.

2. Experiments

2.1. Preparation of TiO$_2$ nanoparticles

In a beaker, 7.5 mL titanium butoxide (TBT) was slowly added in sequence to 120 mL ethanol under constant stirring, and then continue stirring for 30 minutes to form a homogeneous solution A. In order to prevent the hydrolysis of TBT due to high air humidity, the beaker was wrapped with plastic wrap. Solution B is either 4 mL 36 wt% hydrochloric acid (HCl) aqueous solution or 12 mL 99.5 wt% acetic acid (CH$_3$COOH) aqueous solution or 4 mL 98 wt% nitric acid (HNO$_3$). Dropwise solution B into solution A under constant stirring. After completing dropwise, the solution C is formed by continue stirring for 30 minutes. Afterwards, transfer the mixed solution C to a Teflon-lined autoclave for further hydrothermal reaction at the temperature of 140 °C for time of 4 h to complete the precipitation procedure. The powders were collected by centrifugation at 9000 r/min for 5 min. Then, the samples washed with distilled water for two times and followed ethanol for two times. Finally, the three TiO$_2$ samples are dried at 80 °C in air for 24 hours for further characterizations and photocatalytic experiments.

2.2. Characterization

The morphology information was obtained by using a field emission scanning electron microscopy (FESEM, Apreo S HiVac). The X-ray diffraction patterns were conducted on Rigaku SmartLab XRD diffractometer with the 0.15406 nm $\lambda$ value of Cu K$_\alpha$ radiation. Fourier infrared spectroscopy experiments were conducted with an IR Prestige-21 spectrometer (Shimadzu). The UV-1900i near-infrared spectrometer (Shimadzu) is used to collect the UV-vis absorption spectra. An Autosorb-IQ2- MP Quantachrome Instruments is using to analysis the specific surface area (SSA) and pore size distribution (PSD). The low-temperature N$_2$ adsorption/desorption was performed. The Brunauer-Emmette-Teller method was used to calcinate the SSA. On the other side, the Barrett-Joyner-Halenda method was used to recorded the PSD.

2.3. Photocatalytic activity evaluations

Both the visible light photocatalytic experiments and the cycling photodegradations were performed in water by photodegraging the original concentration of 0.01 mM methyl orange (MO) under the visible light illumination. The wavelength of light is all more than 420 nm. The visible light source was offered.
by a 250 W Xenon lamp with a filter. In a typical procedure, 20 mg catalyst powders were disperse in 100 mL MO solution. Firstly, the samples were stirred without any light for several hours. The aim of this process is reaching an adsorption–desorption equilibrium before photodegradation. The dye concentration was collected at the wavelength of around 465 nm, which was determined by a UV-1900i equipment.

3. Results and Discussion

Figure 1 show the morphologies of samples discerned from the FESEM images. TiO$_2$ nanoparticles respectively obtained by HCl-assisted (H-TiO$_2$, Fig. 1a), CH$_3$COOH-assisted (A-TiO$_2$, Fig. 1b) and HNO$_3$-assisted (N-TiO$_2$, Fig. 1c) hydrothermal approach show different morphologies. Compared with the N-TiO$_2$ nanoparticles, H-TiO$_2$ and A-TiO$_2$ show much higher homogeneity. The H-TiO$_2$ shows the best dispersibility of the three samples. For the other two TiO$_2$ samples, A-TiO$_2$ shows less agglomeration than N-TiO$_2$ powders. In fact, N-TiO$_2$ nanoparticles show obvious harden in the same magnification. Generally, the more agglomeration and serious harden of the catalyst shows the worse photocatalytic performance [20].

![Figure 1. FESEM images of the (a) H-TiO$_2$, (b) A-TiO$_2$ and (c) N-TiO$_2$ nanoparticles.](image)

Fig. 2a illustrates the XRD patterns of three samples: the H-TiO$_2$, A-TiO$_2$ and N-TiO$_2$ nanoparticles. The peaks of the A-TiO$_2$ can be only indexed to two well crystallized phases without brookite phase: rutile phase (JCPDS No. 21–1276) and anatase phase (JCPDS No. 21–1272). The H-TiO$_2$ and N-TiO$_2$ nanoparticles synthesised by the HCl-assisted and HNO$_3$-assisted hydrothermal method respectively, show the three-phase mixture of anatase, rutile and brookite phase (JCPDS No. 29–1360).

Fig. 2b shows the FTIR spectra. Obviously, the peaks of –OH stretching bands of the H-TiO$_2$ and A-TiO$_2$ nanoparticles are higher than that of N-TiO$_2$. According to reported works, oxygen vacancies prefer to bond with the dissociative water [21,22]. More hydroxyl groups thus are produced on the surface of catalyst nanoparticles by oxygen vacancies. The hydroxyl groups are helping to improve the photocatalytic efficiency. The hydroxyl groups act as capture centres for photoinduced electrons leading to effectively separation of the electrons and the holes [23,24].

![Figure 2. Characterizations of H-TiO$_2$, A-TiO$_2$ and N-TiO$_2$ nanoparticles: (a) XRD patterns, (b) FTIR spectra.](image)
The photocatalytic stability of the H-TiO$_2$ (Fig. 3a), A-TiO$_2$ (Fig. 3b) and N-TiO$_2$ (Fig. 3c) nanoparticles were confirmed by repetitively degrading methyl orange (MO) in water under the illumination of visible light. The H-TiO$_2$ and A-TiO$_2$ nanoparticles were confirmed ten cycles while only five cycles for N-TiO$_2$ nanoparticles. The H-TiO$_2$ and A-TiO$_2$ nanoparticles show more stable and better photocatalytic ability than N-TiO$_2$ nanoparticles. This implied that more oxygen vacancies leading to higher photocatalytic activity. Compared with the A-TiO$_2$ nanoparticles, H-TiO$_2$ powder shows higher photocatalytic efficiency. This implied that the special mixed-phase of H-TiO$_2$ contribute to its high photocatalytic activity. This heterojunction structure of TiO$_2$ with anatase, rutile and brookite phase could further reduce the recombination rate of photogenerated carriers [21,25].

Under the identical condition, the H-TiO$_2$ exhibited much higher activity than the A-TiO$_2$ and N-TiO$_2$ nanoparticles. The dye molecules were degraded 95% of initial amount with the assistance of H-TiO$_2$ within 5 hours whilst it took same time for A-TiO$_2$ to degrade 80% and N-TiO$_2$ with almost all initial MO molecules, respectively. Compared with efficiencies of N-TiO$_2$ nanoparticles, the present H-TiO$_2$ and A-TiO$_2$ showed superior efficiencies. This is attribute to the abundant surface hydroxyl groups played the capture centers role of photoinduced electrons [25] and the light harvesting increased by the reduced band gap [26,27].

![Figure 3](image.png)

Figure 3. The cycling photodegradations of methyl orange in the presence of the (a) H-TiO$_2$, (b) A-TiO$_2$ and (c) N-TiO$_2$ nanoparticles under visible-light illumination.

4. Conclusions
Mix-phase TiO$_2$ nanoparticles with oxygen vacancies were synthesized through facile acid-assisted hydrothermal synthesis without any post-calcination. By using HCl or CH$_3$COOH, the synthesized TiO$_2$ sample H-TiO$_2$ or A-TiO$_2$ nanoparticles shows uniform nanoparticles morphology with well dispersion. The oxygen vacancies leading to the abundant surface hydroxyl groups and the mixed-phase TiO$_2$ leading to the reduced band gap both guaranteed the excellent photocatalytic performance. The H-TiO$_2$ and A-TiO$_2$ nanoparticles compared with N-TiO$_2$ nanoparticles show better photocatalytic performance when employed to assist the degradation of methyl orange in water under the illumination of the visible light. The stable high photocatalytic performance and the facile method of the H-TiO$_2$ and A-TiO$_2$ nanoparticles will drive the industrial application.

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