Study on Preparation and Photocatalytic Activity of V-Doping Mixed Crystalline Phase TiO$_2$ Powders

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Abstract. The vanadium-doping TiO$_2$ photocatalysts powders with different vanadium contents were prepared by a facile sol-gel method. The TiO$_2$ powders were characterized by PL, XRD, UV-Vis-DRS and Laser particle size analyzer. The photocatalytic performance was evaluated by photo-degradation of methyl blue. The degradation effect of MB was investigated on the influence of heat treatment temperature and vanadium doping amount. The results show that V-doping can promote the TiO$_2$ particles phase transformation from anatase to rutile and restrain the particles size growth. The V-TiO$_2$ sample is a mixture of rutile phase and anatase phase with good crystallinity. The sample of V-TiO$_2$ particle size distribution is relatively uniform and narrow. The absorption spectrum of TiO$_2$ after doping has obvious red shift compared with that before doping. V-doping can inhibit the recombination of photogenerated e$^-$/h$^+$ pairs. The photocatalytic activity of V-TiO$_2$ with n(V): n(Ti) =1: 100 and calcined at 450 $^\circ$C is the best, it is 57% in 100 minutes under the irradiation of fluorescent lamp. It is obviously higher than the activity of undoped TiO$_2$ powders.

1. Introduction
Nowadays global energy shortage and environmental disruption are issue of increasingly concerned. Peoples have done a lot of research work to explore new technology for practical environmental management and developing new energy [1]. The semiconductor photocatalysis technology represented by TiO$_2$ provides a new opportunity to solve these problems. The advantages of TiO$_2$ are high photocatalytic activity, good chemical stability, clean and non-toxic, low cost, no secondary pollution, etc. [2]. So TiO$_2$ is widely used in the field of photocatalysis technology, such as environmental pollution control, hydrogen production by photochemical decomposition of water and photochemical battery [3, 4]. Nevertheless, more widespread application of titanium dioxide photocatalytic have been limited because of its disadvantages in light absorption. It can only absorb ultraviolet light with wavelength less than 387 nm. Thus, less than 5% of the energy from solar radiation which reached the earth’s surface is available. Moreover, the easy recombination of photogenerated e$^-$/h$^+$ pairs results in low photocatalytic efficiency [5]. The effective method to improve TiO$_2$’s photocatalytic performance is to reduce the recombination rate of photogenerated carriers and its band gap width, and improve its quantum efficiency. In recent years, many researches have been made to overcome the inherent weaknesses of TiO$_2$ and improve its photocatalytic properties, such as dye sensitizing [6], formation of semiconductor composites [7], noble metal deposition [8], and ion...
doping [9, 10]. Generally, metal ion doping is a simple and effective modification method [11]. The impurity energy level formed by ion doping in the TiO$_2$'s band gap can make the absorption spectrum red shift and reduce the recombination probability of photogenerated e/h$^+$ pairs in TiO$_2$. A lot of metal ion dopants, such as Fe [12], V [13], Cu [14], Cr and Zn [15], have been tried. The doping of transition metals into TiO$_2$ is an effective way to improve the photocatalytic performance.

However, in existent metal ion doped TiO$_2$ researching files, the utilization of visible light is still not high enough. Meanwhile, it is necessary to further study mechanism of metal ion’s influence on visible light catalytic activity of mixed phase nano-TiO$_2$. So, it is still necessary to study the influence of vanadium ions on the structure and performance of mixed phase TiO$_2$ nanoparticles. In the present study, mixed phase TiO$_2$ samples with different V doping content was prepared by a simple aqueous method. The TiO$_2$ powders were characterized by PL, UV-Vis-DRS, XRD and Laser particle size analyzer. The effects of preparation conditions on photocatalytic performance were studied, and the mechanism of enhancing photocatalytic activity was analyzed.

2. Experiment

2.1. Preparation of TiO$_2$ powders
In the experiment, NH$_4$VO$_3$ (CP, Aldrich) and Ti(OC$_3$H$_7$)$_4$ (CP, Aldrich) are raw materials of vanadium and titanium respectively, HNO$_3$ (CP, Aldrich) is pH regulator. In a 60 $^\circ$C water bath, deionized water and hydrolysis inhibitor are mixed in a certain proportion to obtain solution A. 5 mL Ti(OC$_3$H$_7$)$_4$ was slowly dripped into solution A and mixed to obtain solution B. NH$_4$VO$_3$ with different content was calculated and weighed by the molar ratio (V/Ti). After dissolving in 5 mL deionized water, NH$_4$VO$_3$ was slowly dripped into B. The solution pH was adjusted by 2.5 mol·L$^{-1}$ HNO$_3$ solution. The solution was stirred continuously for 12~14 h to form a uniform yellowish sols. The sols were aged for 48 h and dried at 80$^\circ$C in air, and calcined in air for 3 h at different temperatures. Then V-TiO$_2$ powders were obtained. Undoped TiO$_2$ samples was prepared according to the same experimental steps.

2.2. Characterization of TiO$_2$ powders
The fluorescence spectra (PL) were monitored by FL4500. The X-ray diffraction (XRD) were carried by D8 Advance diffractometer. The sample of particle size distribution were obtained using Mastersizer-2000 Laser particle size analyzer. The UV-Vis diffuse reflectance (UV-Vis) spectra of TiO$_2$ powders were analyzed by UV-2401PC spectrophotometer. Absorption spectrum was measured by 722N visible spectrophotometer.

2.3. Photocatalytic properties of TiO$_2$ powders
0.10 g TiO$_2$ catalyst samples was added into 50 mL methylene blue (MB) solution with mass concentration $p=10$ mg·L$^{-1}$. In order to achieve equilibrium of adsorption and desorption, the suspension was stirred for 30 minutes in dark. The suspension was reacted in a 30 W fluorescent lamp to simulate the visible light source. MB suspension were taken out every 20 minutes for 4 mL. MB was separated after centrifugial with 4000 rpm and 30 minutes per time. The absorbance values of MB solution at maximum absorption wavelength ($\lambda_{max}=664$ nm) were determined. According to Lambert-Beer’s law, the degradation rate of MB solution can be calculated by equation (1).

$$\eta(\%) = \frac{A_0 - A_t}{A_0} \times 100\%$$

In formula (1), $\eta$ is degradation rate of MB, $A_0$ and $A_t$ are the initial and remnant MB absorbance values respectively, $t$ is the reaction time.
3. Results and Discussion

3.1. X-ray Diffraction

The XRD spectrum of V-doped TiO₂ powders sintering at different temperatures are given in figure 1. Figure 1 shows the results that V-TiO₂ sample is composed of anatase phase after calcination at 350 °C, but rutile phase begins to appear. The V-TiO₂ sample is a rutile-anatase phase mixture, and the characteristic peak of TiO₂ is obvious when calcination temperature is 450 °C. However, the characteristic diffraction peak of rutile phase is very sharp, indicating that stable rutile phase has been formed with the temperature rises to 550 °C. The sample has good crystallinity, and the phase is mainly composed of rutile phase. There is no other impurity diffraction peak including vanadium and its oxide in the XRD patterns of samples, indicating that the purity of the sample is high. On the one hand, V-ion is highly dispersed in the crystal boundary of TiO₂ powders in the form of amorphous oxide, on the other hand, the content of vanadium is too low, it exceed the detection limit of the instrument.

![Figure 1. XRD patterns of V-TiO₂ powders with different temperature.](image)

3.2. Particles Size Distribution Curve

The laser particle size distribution curve of V-TiO₂ sample prepared with vanadium doping amount of n (V): n (Ti) = 1:100 and calcination temperature of 450 °C is given in figure 2. It is found that the sample particle size distribution range is 0.182–8.71 μm. More than 90% of the samples with particle size less than 3.5 μm. About 50% of particles with particle size less than 1.0 μm. The average specific surface area of all particles is 5.98 m²·g⁻¹, and the average particle size is 1.7 μm. At the same time, it can be seen that the particle size distribution of V-TiO₂ powders is relatively uniform and normal distribution. The average particle size is small. The specific surface area is large, which is more favorable for improving the photocatalytic reaction performance of the sample.

![Figure 2. Particles size distribution curve of V-TiO₂ samples.](image)
3.3. PL Spectra Analysis

The PL spectra of V-TiO₂ samples before and after doping calcined at 450 °C are shown in figure 4. It can be seen that undoped TiO₂ samples only absorb UV light. The absorption of V-TiO₂ samples in the ultraviolet region is equivalent to that of pure TiO₂, but the absorption in the visible region is enhanced. The absorption spectrum threshold has a significant red shift. This suggests that the incorporation of V doping can improve the absorption ability of TiO₂ powders for light. Furthermore, it can widen the light absorption range to visible light. This is of great significance for the degradation of organic pollutants by solar photocatalysis. When the absorption spectrum threshold is red-shifted from 408 nm to 475 nm, the band gap width of TiO₂ decreases by 0.43 eV (3.04 eV → 2.61 eV) calculated according to equation (2) [18].

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E_g (eV) = \frac{1240}{\lambda(nm)}
\]  

The reason may be the yellow V-TiO₂ samples play a role similar to the photosensitizer, it can absorb a wide range of light radiation and enhance the absorption of visible light. Meanwhile, V-doping can form an impurity level in the middle of TiO₂’s band gap, and electrons in the valence band can absorb photons with lower energy and realize indirect transition [19]. In this way, photons with longer wavelengths are absorbed and utilized. Therefore, the absorption spectrum threshold of TiO₂ is red shifted obviously by vanadium doping.
3.5. Photocatalytic Activity and Reaction Mechanism analysis for MB

Figure 5 shows the degradation activity of V-TiO$_2$ (molar ratio (V/Ti)=0.01) samples prepared under different temperature conditions on MB. The results is obvious that photocatalytic activity increases with the increase of heat treatment. The degradation rate of MB on photocatalyst is the highest after 450 °C. However, the photocatalytic activity decreased with temperature increasing 500 °C. The influence of temperature on the properties of V-TiO$_2$ is mainly attributed to the change of TiO$_2$ structure and the influence of doping elements. In the process of calcination, the partial lattice distortion caused by the substitution of V$^{5+}$ for Ti$^{4+}$ in TiO$_2$ lattice can enhance its photocatalytic activity. The strengthening effect is more obvious with the increasing of temperature. The reaction rate is low, and the precursor reaction is incomplete when the calcination temperature is low. The purity and crystal integrity of the sample are not easy to be guaranteed. This will affect the photocatalytic properties of TiO$_2$ samples. However, the temperature is too high, which promotes the phase transition of TiO$_2$. At the same time, TiO$_2$ particles tend to agglomerate. Thus, the photocatalytic performance is reduced.

Figure 6 shows MB degradation effect on different TiO$_2$ powders calcinated at 450 °C. The performance of vanadium doping samples is higher than that of undoped pure TiO$_2$, which indicates that effective vanadium doping is advantageous to improve TiO$_2$’s photocatalytic properties. With the reaction time increasing, the degradation rate of MB over samples increase gradually. When molar ratio is 0.01, the photocatalytic degradation rate is the highest, it is close to 60% at 100 min. The crystal structure, optical properties and electronic structure of TiO$_2$ were changed by the incorporation
of V doping. Therefore, TiO$_2$’s band gap can be reduced, and the lifetime of the excited carrier be prolonged by V-doping. The recombination rate of photogenerated e$^-$/h$^+$ pairs may be greatly reduced. Nevertheless, the photocatalytic activity of samples is decreased when the doping amount is too large. This is because vanadium may precipitate in the form of oxide and cover the surface of TiO$_2$ during calcination, which reduces the exposure of the effective surface and its absorption of incident light.

Based on the above results, V-TiO$_2$ is a mixed phase with appropriate proportion of anatase and rutile. The possible reaction mechanism of photo-degradation for MB over TiO$_2$ powders could be as follows in figure 7. There is a strong heterojunction at the interface of anatase and rutile. It becomes a fast transmission channel of photogenerated electrons. The photogenerated electrons in rutile with narrow band gap transfer via heterojunction to the CB (conduction band) of anatase phase, which makes the surface electron density of rutile phase decrease correspondingly. On the other hand, the photogenerated holes in anatase migrate to the VB (valence band) of rutile phase with lower potential. Therefore, the photogenerated e$^-$/h$^+$ pairs produced by the photoexcitation in the mixed crystalline TiO$_2$ migrate to the opposite direction respectively. The photogenerated electrons (e$^-$) enriched on the surface of anatase phase. Superoxide radicals (∙O$_2^-$) are formed by the reaction of e$^-$ with O$_2$. Meanwhile, the photogenerated hole (h$^+$) enriched on the surface of rutile phase. Photogenerated hole reacts with H$_2$O or OH$^-$ to produce hydroxyl radicals (∙OH). These strong oxidizing groups, for example ∙O$_2^-$, ∙OH, can oxidize organic dyes MB to pollution-free inorganic molecules of CO$_2$ and H$_2$O [20]. Hence, the appropriate V doping amount and heat treatment temperature contributes to mixed phase with proper composition of anatase and rutile. The Vanadium doping TiO$_2$ nanoparticles shows excellent photocatalytic activity.
4. Conclusions
Mixed crystalline phase TiO₂ powders doped vanadium were successfully prepared by a simple sol-gel method. V-doping can promote the TiO₂ particles phase transformation from anatase to rutile and restrain the particles size growth. The V-TiO₂ sample is a anatase-rutile phase mixture with good crystallinity. The particle size distribution of the sample is uniform, the average particle size is small, and the specific surface area is large. The incorporation of vanadium effectively not only reduced the recombination probability of photogenerated carriers, but also improved the photocatalytic performance. When the calcination temperature is 450 and molar ratio (V/Ti) is 0.01, the photocatalytic properties of samples is the best, it is 57% in 100 minutes in the irradiation of fluorescent lamp. The experimental results are obviously better than those of undoped TiO₂ samples.

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