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Experimental Study on Nitrogen-Doped Nano-Scale TiO_2 Prepared by Microwave-Assisted Process at Low Temperature

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Abstract

Nitrogen-doped nano-scale TiO_2 was prepared by microwave-assisted process at low temperature with $Ti(SO_4)_2$ as raw material, and ammonia water as precipitant and nitrogen source. The obtained powder was characterized by XRD, XPS, UV-Vis diffuse reflection spectroscopy, TEM and etc. Its photocatalytic activity under UV light was evaluated with methyl orange solution as target contaminant. The results from XRD analysis showed that the titled TiO_2 existed in an anatase phase. The particle size read from XRD was 5~10 nm, in general accordance with that from TEM. XPS analysis exhibited an N1s peak around 399 eV, which indicated an N-Ti-O structure in TiO_2. UV-Vis diffuse reflection spectroscopy exhibited a red shift of the absorption edge, which indicated that the sample had a certain absorption of visible light at 400~500 nm. The results of photocatalysis experiment proved that the titled TiO_2 has a higher photocatalytic activity.

Keywords: Microwave-assisted process, Titanium dioxide, Nitrogen-doped, Visible light

Preface

Photocatalysis is in line for a new environmentally friendly technology of processing toxic pollutants directly by the solar light irradiation. TiO_2, non-toxic and odorless, has a high photocatalytic activity, stable chemical property and low cost, and therefore is the most potential and the most studied photocatalyst. However, the band gap of anatase TiO_2 is 3.2 eV, which corresponds to the absorption wavelength of 387.5 nm in UV region. It indicates that anatase TiO_2 only absorbs UV light, 3%~5% of solar energy. This weakness limits the indoor application of TiO_2 photocatalysis technology. Therefore, to develop a modified visible-light sensitive TiO_2 photocatalyst plays an important role in increasing the utilization rate of solar energy and promoting the application of photocatalysis technology, and is the most important and challenging research subject in the photocatalysis field.

Asahi et al's theory and corresponding application (2001, p. 269-271) proved that the nitrogen-doped process is a feasible approach to obtain a visible-light sensitive TiO_2. This achievement causes a research and development rush toward nitrogen-doped TiO_2 photocatalyst in the world. The previous reports showed that the preparation methods of nitrogen-doped TiO_2 photocatalyst can be classified into process treatment and after-process treatment. The process treatment is that nitrogen is doped in the formation process of TiO_2, while the after-process treatment is that nitrogen is doped in the product TiO_2. Asahi et al (2001, p. 269-271) investigated the after-process treatment, and reported that the precursor (anatase TiO_2), having been calcined at high temperature in the production of TiO_2, was calcined at high temperature again in the nitrogen-doped process. Two times of calcinations caused the powder sintering, in turn affected its light absorption characteristics. However, in the process treatment reported by Z Wang et al (2005, p. 366-368), ammonia water was dropped into tetrabutyl titanate solution, and the obtained hydrolyzed product was calcined to get nitrogen-doped TiO_2. In the above-mentioned methods, calcinations at high temperature not only increased the energy consumption, but also caused TiO_2 powder sintering, in turn lowered their catalysis efficiencies. Therefore, the more efficient nitrogen-doped process of TiO_2 at low temperature is an important research trend.

With ammonia water as precipitant and nitrogen source, and by microwave-assisted process instead of traditional heating process, the titled method not only avoids the high-temperature calcinations, but also is easy to handle. The obtained modified TiO_2 photocatalyst has a high photocatalytic activity.

1. Experiment

1.1 Materials and equipments

Main equipments: ML08S-1 experimental microwave oven from Nanjing Huiyan Microwave Co., Ltd.; DGG-103 electrothermal blowing dry box from Tianjin Tianyu Test Instrument Co., Ltd.; Z93-1B electric stirrer from Tianjin Lihua Instrument Co., Ltd.

Main reagents: ammonia water, titanium sulfate, sulfuric acid, barium chloride, methyl orange solution and etc. All of them are analytical reagents.

1.2 Preparation of nitrogen-doped nano-scale TiO_2

Formulate a 100 g/L^{-1} $Ti(SO_4)_2$/ H_2SO_4 solution (pH=2), and regulate pH to 10 by adding concentrated ammonia drop-by-drop into the solution under the condition of stirring. Irradiate the obtained solution for 10 min in an experimental microwave oven, centrifugally separate the sample, and irradiate it again. Wash the obtained sample to neutrality (detect SO_4^{2-} by barium chloride test), dry up, and grind to get nitrogen-doped TiO_2. Use NaOH instead of concentrated ammonia to prepare nitrogen-free TiO_2 for comparison. This paper studies and compares the effects of different radiation time of the second time. The following discussed "radiation time" refers to that of the second time.

1.3 Characterization of catalyst

The crystal structure of TiO_2 powder is determined with X'pert PRO X-Ray Diffractormeter (Co target, Kα radiation) from PANalytical of Holland. The average diameter of particles is calculated on the basis of Scherrer equation. The structure of N in TiO_2 powder is determined with PHI-1600 X-ray Photoelectron Spectroscopy (XPS) from PE Corporation of USA. The microdefects and structure of TiO_2 powder are analyzed with Philips T20ST TEM/HRTEM, wherein the scattering and interference of electron can be imaged with TEM (Transmission Electron Microscope); the resolution of HRTEM (High Resolution Transmission Electron Microscope) reaches 0.1 nm or lower, therefore, the microdefects and structure of TiO_2 powder can be directly observed on the atomic scales with HRTEM. The light absorption of TiO_2 powder is analyzed in the range of 200~800 nm with UV-3600 UV-Vis Spectrophotometer.

1.4 Characterization of photocatalytic activity

Use 60 W UV lamp as light source. Add 800 mL 25 mg/L methyl orange solution into 1,000 mL beaker, and introduce 0.8 g nitrogen-doped TiO_2 powder to form a suspension of dye and photocatalyst. Thoroughly disperse the powder in the suspension by ultrasonic vibration in a dark condition for 30 min. Fix a sleeve-type UV lamp vertically in the center of the beaker, and blow from the bottom of the beaker to keep the catalyst suspended. Turn on the light source and begin timing after 5 minutes of preheating. Take sample every 30 min, centrifugally separate them, and analyze the obtained supernatant in the range of 200~800 nm with UV-3600 UV-Vis Spectrophotometer.

The degradation rate of methyl orange solution by nano-scale TiO_2 is defined as: $(M_0-M_t)/M_0$. Here, M_0 represents the absorbance of solution at the beginning of the reaction, and M_t represents the absorbance of solution after a period of reaction.

2. Results and discussions

2.1 Phase analysis

Figure 1 exhibits XRD spectrum of TiO_2 obtained after different time of radiation. It indicates that TiO_2 prepared by microwave-assisted process exists in an anatase phase. Meanwhile, the diffraction peak becomes sharper and sharper with the increase of radiation time. It indicates that the crystallization degree of anatase TiO_2 becomes better and better with the increase of radiation time. The average diameter calculated from the Scherrer equation is 5~10 nm.

2.2 UV-Vis spectrum analysis

Figure 2 exhibits UV-Vis spectrum of TiO_2 obtained after different time of radiation. From figure 2, we can see that the visible light absorption of nitrogen-doped TiO_2 is better than that of nitrogen-free TiO_2, while the UV light absorption of nitrogen-doped TiO_2 is a little bit lower than that of nitrogen-free TiO_2. It indicates that the doped nitrogen widens the absorption range of TiO_2. This is because that a few nitrogen atoms from ammonia water are inserted into TiO_2 lattice, which causes the hybrid of orbital N2p and orbital O2p and the formation of a new valence band. The new valence band shifts to the conduction band, and the band gap between them, namely, the electron transition energy from the valence band to the conduction band, becomes smaller. Therefore, the absorption of nitrogen-doped TiO_2 exhibits a red shift, that is to say, the doped nitrogen widens the light absorption range of TiO_2. In addition, figure 2 also indicates that the number of nitrogen atoms inserted into TiO_2 increases with the rise of the radiation time, which leads to the increase of the visible light absorption of catalyst.

2.3 XPS analysis

Figure 3 exhibits XPS spectrum of TiO_2 obtained after different time of radiation. From figure 3, we can see an N1s characteristic peak around 399 eV instead of 396 eV reported by Asahi et al (2001, p. 269-271). Gyorgy et al (2003, p. 265-270) studied the nitrogenization on the surface of titanium, and reported that TiN can exist in very different phases. Therefore, the different positions of N1s characteristic peaks may result from the different processes and different conditions. The peak of TiN is generally at 396.9 eV (Saha et al, 1992, p. 3072-3079), and the peaks of chemical absorption, NO, NO_2 and etc. are at 400 eV or above (Wu et al, 1990, p. 55-67; Di Li et al, 2005, p. 3293-3302). These investigations indicate that the peak around 399 eV probably corresponds to the structure of Ti-O-N or N-Ti-O, instead of the structure of Ti-N, N-O or N-N. Meanwhile, Gole et al (2004, p. 1230-1240) reported that N1s characteristic peak of Ti-O-N or Ti-N-O is above 400 eV. Therefore, it is concluded that the peak at 399 eV is responsible for N-Ti-O structure in TiO_2 lattice. This conclusion is similar to the report from Sathish et al (2005, p. 6349-6353). In addition, figure 3 also indicates that N1s peak of sample after exposure to microwave radiation for 60 min is stronger than that for 30 min.

2.4 Microtopography analysis

The samples exposed to microwave radiation for different time are studied by TEM for further investigation of their shape and size (Figure 4). The result indicates that the sample has an obvious, rod-shaped or knob-shaped crystal structure with smooth surface and high crystallinity. The average diameter is 5 nm, which is in accordance with the result from XRD. An obvious agglomeration of catalyst is observed on TEM picture, this is because that the dehydration procedure in preparing nano powder by wet process leads to the formation of hard-to-disperse agglomeration.

The results of elemental analysis by TEM are shown in table 1. It proves that there is nitrogen in the obtained sample, and its content increases with the prolonging of radiation time. This result is in accordance with that from XPS. Therefore, it further verifies that nitrogen, in certain pattern, exists in TiO_2 lattice.

2.5 Characterization of Photocatalysis

Under the same reaction conditions, the self-made nitrogen-doped TiO_2 shows excellent degradation effects on methyl orange solution. The degradation rate of methyl orange solution is over 70% after 2 hours. Figure 5 exhibits that the degradation rate of methyl orange solution increases with the prolonging of radiation time. Under the condition of exposure to microwave radiation for 60 min, the degradation rate of methyl orange solution is up to 92.3% after 2 hours of reaction. It indicates that the self-made nitrogen-doped TiO_2 shows better degradation effects on methyl orange solution than nitrogen-free TiO_2 does.

3. Conclusion

(1) Nitrogen-doped nano-scale TiO_2 was prepared by microwave-assisted process at low temperature with $Ti(SO_4)_2$ as raw material, and ammonia water as precipitant and nitrogen source.

(2) The obtained nitrogen-doped nano-scale TiO_2 exists in an anatase phase, has a certain absorption of visible light at 400~500 nm, and shows a higher degradation rate of methyl orange solution. Its average diameter is 5~10 nm.

(3) The point in the future study is to optimize the reaction conditions to solve the issue of aggregation, and to systematically investigate the photocatalytic activity of nitrogen-doped TiO_2 under UV and visible light.

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Table 1. The results of elemental analysis by TEM

	T=30 min		T=60 min	
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
N	7.928	15.538	12.928	23.712
O	27.740	47.595	27.672	44.431
Ti	64.330	36.866	59.398	31.856

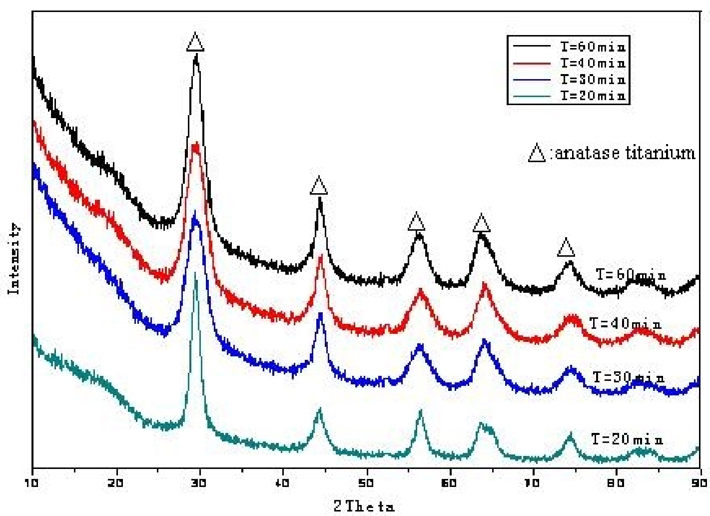


Figure 1. XRD spectrum of the obtained TiO_2 after different time of radiation

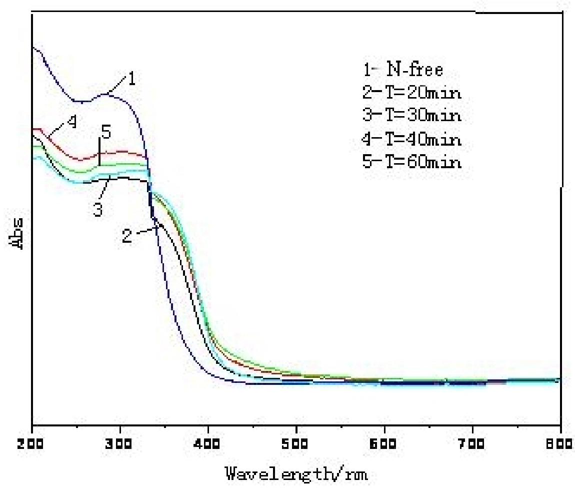
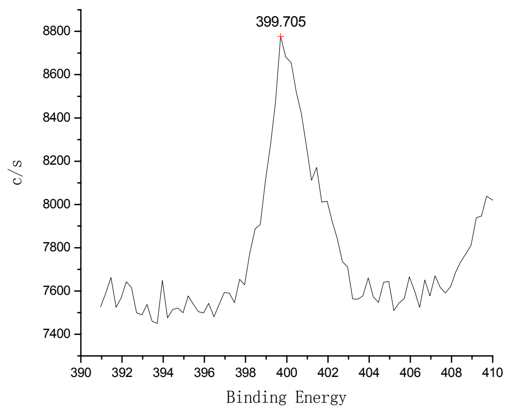
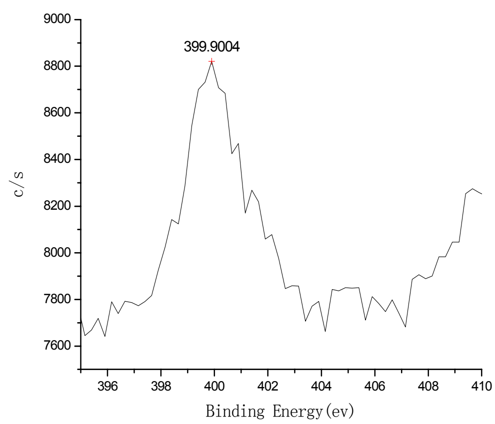


Figure 2. UV-Vis spectrum of the obtained TiO_2 after different time of radiation

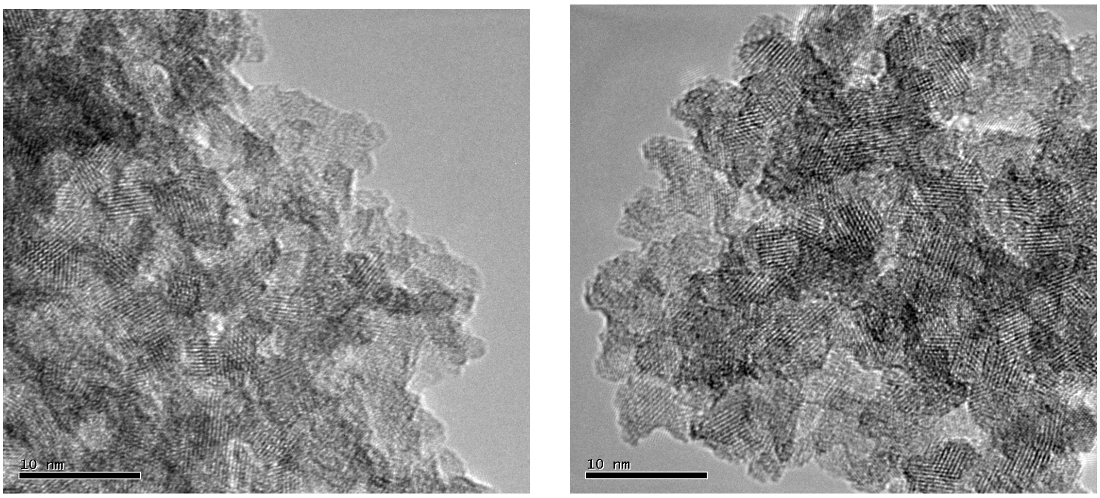


(a) T=30 min



(b) T=60 min

Figure 3. XPS spectrum of the obtained TiO_2 after different time of radiation.



(a) T=30 min (b) T=60 min

Figure 4. TEM images of the obtained TiO_2 after different time of radiation

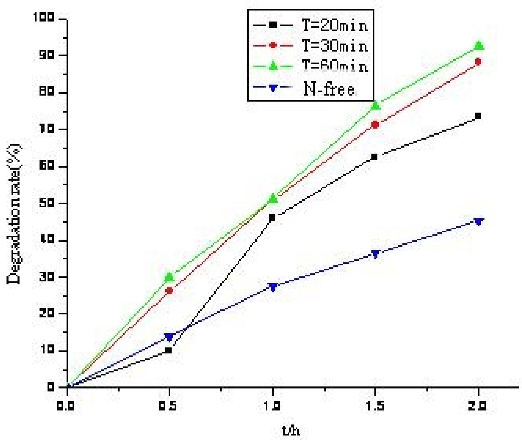


Figure 5. The degradation rate of methyl orange solution