Photocatalytic Degradation of Methyl Orange over Nitrogen-doped TiO2 Prepared by Ultrasonic Method

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Abstract. Nitrogen-doped nano-sized titania（N-TiO_2）photocatalysts were prepared by sol-gel process followed by ultrasonication.The photocatalytic decomposition of methyl orange in aqueous solution was used as a probe reaction to estimate their photocatalytic activities.Applying means of XRD,TEM and UV-Vis DRS and XPS,we analyzed the crystallite sizes,the cystal pattern,the optical property of TiO_2 samples. The synthesized N-TiO_2 nanocrystals are catalytically active and absorb well into the visible region up to 600 nm.N-TiO_2 showed high degradation of methyl orange under ultraviolet as well as visible light irradiation since it has small grain,wide dispersion and strong visible-light absorption.

INTRODUCTION

Given its high chemical stability,special photocatalytic properties,and environmentally friendly nature,nano-sized titania（TiO2）has been extensively used to deal with water purification, wastewater treatment, hazardous waste control, and air purification[Chen, 2009] [Gao,2002]. However, TiO2 has a wide band gap (3.2 eV) and can only be excited by ultraviolet light less than 387 nm. It is great interest to develop the visible light photocatalysts to extend the absorption wavelength range into visible light region [Yang,2012] [Zhou,2006]. Previous study found that the nitrogen-doped titania has a higher visible photocatalytic activity because of its better absorption of visible light.[Asahi,2001][Bangkedphol S,2010].But it is difficult to prepared nonmetal doped photocatalysts by simple wet chemical methods such as co-precipitation, sol-gel method, because it is time-consuming, requires specific pH control and high temperature [Burda C,2003].[Wang Hui-Lei,2014].

At present, research on modification of preparation methods and improving the photocatalytic efficiency by ultrasound technology are becoming hot-pots in this field [Deliang Lin,2012] [Senthilkumaar,2005]. Sonochemistry arises from acoustic cavitations,the collapse of bubbles generates localized hot spots with transient temperatures of about 5000 K, pressure of about 20 MPa, and heating and cooling rates greater than 109K s−1. These special physical and chemical conditions accelerate the hydrolysis reaction, decrease the size of TiO2 grain and particle, improve its dispersion and increases surface area. The chemical and physical effects arising from acoustic cavitation also promote the effective doping component into the TiO2 [Liu,2004] [Deliang Lin,2012]. However, to the best of our knowledge, there is no comprehensive report addressing the ultrasound frequency effects for the synthesis of Nitrogen-doped titania nanocomposites.

Herein, we present an ultrasonic-assisted sol–gel method to prepare nitrogen-doped nano-sized TiO2 photocatalysts. The as-prepared samples were characterized with various techniques, such as powder X-ray diffraction (XRD), transmission electron microscopy (TEM), diffuse reflectance spectra (DRS),and X-ray Photoelectron Spectroscopy（XPS）.

METHODS

Synthesis

Nitrogen-doped nano-sized TiO2 was synthesized by Tetrabutyl titanate (Ti(OC4H9)4 ,TBOT)

in the presence of water and ethyl alcohol absolute under ultrasound irradiation. Certian amount of TBOT, mixed with ethanol ,with vigorous mechanical stirring was added dropwise to a mixture of Acetic Acid, deionized water and ethyl alcohol absolute under irradiation with a high intensity ultrasonic of 28 kHz. in a sonication cell，then，as a nitrogen source, Triethylamine was added into it dropwise. The samples were then irradiated with an ultrasonic cleaning tank(28 kHz) for 1 h, followed by aging in a closed beaker at room temperature for 4 d .After aging, these wet gel were dried at 80◦C (353 K) for about 10 h to vaporize water and then ground to fine powders to obtain dry gel samples. The dried power were calcined at 500◦C (773 K) in muffle furnace for 2h,named as N-TiO2. As reference experiments, pure samples named as O-TiO2 was also prepared without ultrasonic irradiation or nitrogen doping, and all other conditions keep the same.

Characterization

Glancing-angle X-ray diffraction pattern was obtained using D/Max-Ⅲ diffractometer. The accelerating voltage and the applied current were 40 kV and 30 mA, respectively.The average grain size of the TiO2 was calculated using the Scherrer formula.The transmission electron microscopy (TEM) patterns obtained on a electron m –icroscopy were used to determine the morphology of aggregated particles and crystallite size.The scan accelerating voltage and magnification were 100 kV and 135,000times, respectively.X-ray photoelec-tron spectroscopy (XPS) measurements were obtained with a XPS system (ESCALAB250) with AlKαX radiation.All the binding energies were referenced to C1s peak at 284.6 eV of the sur-face adventitious carbon..The diffuse reflec- tance spectrum from 200 to700 nm of as-prepared TiO2 obtained on an UV –VIS spectrophotometer were used to determine the absorption edge and band gap energy of the product.

Photocatalytic decomposition of methyl orange

The photocatalytic experiments were performed in a glass photocatalytic reactor.The irradiation was carried out using 300 W (311 nm) high pressure Hg arc lamp and 250 W xenon lamp. 250 ml of methyl orange solution containing an appropriate amount of O-TiO2 or N-TiO2 samples was magnetically stirred and ultrasonic irradiated, and O2 was continuously pumped into the reaction solution before and during illumination. 10ml of methyl orange solution was withdrawn and centrifuged every five or ten minutes.Then，its characteristic absorption at 464nm was obtained with a UV–vis spectrophotometer in order to measure the changes concentration of methyl orange.

RESULTS AND DISCUSSION

XRD analysis

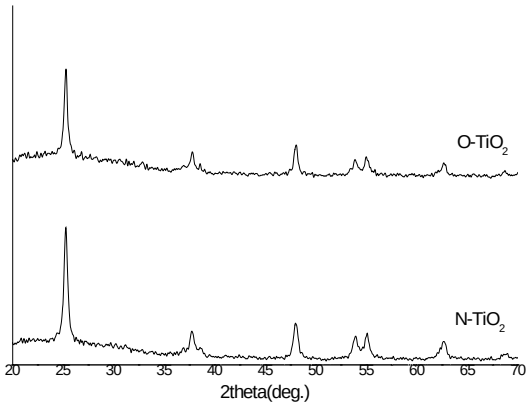

Figure 1. XRD patterns of O-TiO2 and N- TiO2

Fig.1 presents the XRD patterns of collected dry O-TiO2 and N-TiO2 powders. The two samples show clear anatase TiO2 peak corresponding to the planes (101) at $2\theta = 25.3°$,and no peaks of rutile phase were observed.The apparent intensity of the (101) peak of N-TiO2 increase compared to O-TiO2.The N-TiO2 powers obtained by ultrasound-assisted sol-gel technique does not show any Ti-N diffraction patterns with characteristics of crystalline phases mainly because of low content of nitrogen. The crystallite size of O-TiO2 and N- TiO2 from Scherrer formula was 21.18nm and

20.85nm respectively.

TEM images

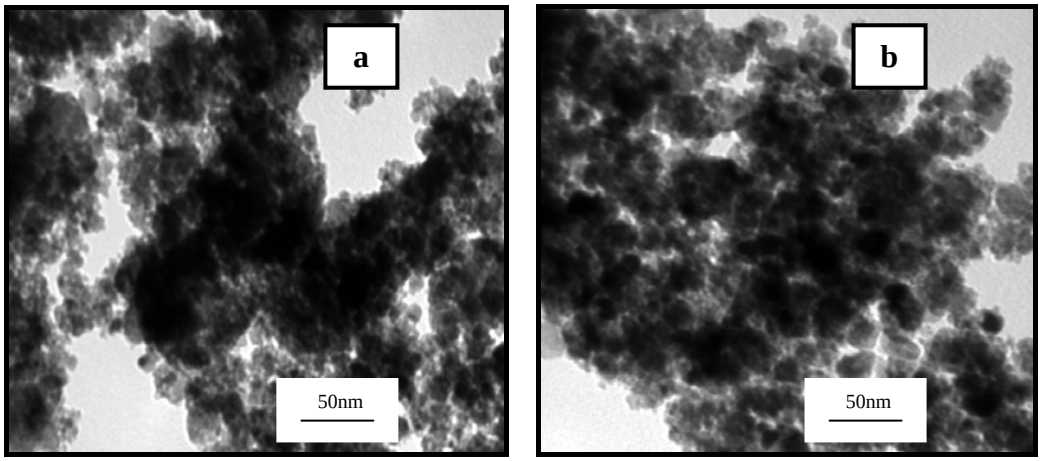

Figure 2. TEM photographs of O-TiO2 (a)and N-TiO2(b)

Fig 2 shows the TEM images of O-TiO2 and N-TiO2 catalyst, indicating that these two kinds of catalysts are all in nano size. It agrees with the value determined from XRD analyses. It can be seen that the micrograph of N-TiO2 nanocomposites reveals significant morphological differences compared to O-TiO2.The TEM images indicated that the N-TiO2 particles were in a dispersed state,thus，the O-TiO2 particles prepared without ultrasonication aggregate in dense groups. This indicates that lower ultrasound frequency is favorable for the crystallinity of N-TiO2, which is in accordance with the result of XRD.

UV- visible diffuse reflectance spectroscopy

Fig.3 shows UV-Vis diffuse reflectance spectra of O-TiO2 (a)and N-TiO2(b). The wavelength maxima observed for O-TiO2 and N-TiO2 are 387 nm and 410 nm respectively. N-TiO2 nanocrystals absorb well into the visible region up to 600 nm.N-TiO2 shows remarkable red shift to visible wavelength region and stronger absorption in the visible light as compared to O-TiO2 . Band gap energy has been calculated for photoca-talysts by using the formula:Eg=1240/λg(eV),Where λg(nm) is the wavelength value obtained from UV-DRS spectra, Eg is the band gap (eV) of the sample.These results confirm lowering of band gap energy due to ultrasound doping of nitrogen in titania. It is thought that newly formed N2p band locates above O2p valence band [Asahi ,2001].

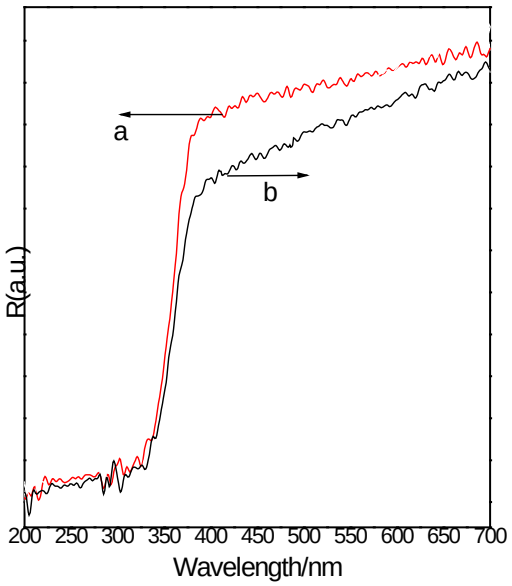

Figure 3. UV-Vis diffuse reflectance spectra of O-TiO_2 and N-TiO_2

XPS

In order to identify the chemical status of N in the nitrogen-doped TiO2 samples, Fig.4 shows the high-resolution XPS spectra of the N1s region of the N-TiO2 sample.As Irie and Saha reported,the peaks of N1s can be decomposed into two contributions corresponding to the different chemical status, respectively. One contribution is attributed to β-N1s (binding energy at about 397eV) belonging to the N1s of TiN,the other is attributed to chemical adsorption γ-N1s (binding energy at about 400eV) [Irie,2003] [Saha,1992].

In later studies, the peak at about 399.7 eV was frequently observed for N-doped TiO2 materials[Gole, 2004] [Liu G,2008]. Fig.4 shows a peaks of N1s at binding energy 399.8 eV. Therefore, it was believed that nitrogen doping of the N-TiO2 sample was responsible for the visible light photoactivity.

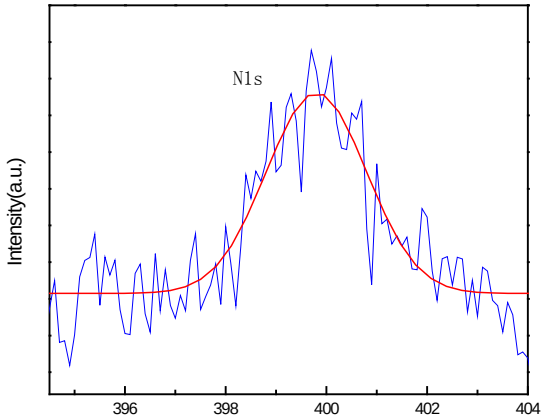

Figure 4. Peak fitting of N_{1s} XPS spectra taken on the surfaces of N-TiO_2

Photocatalytic activity

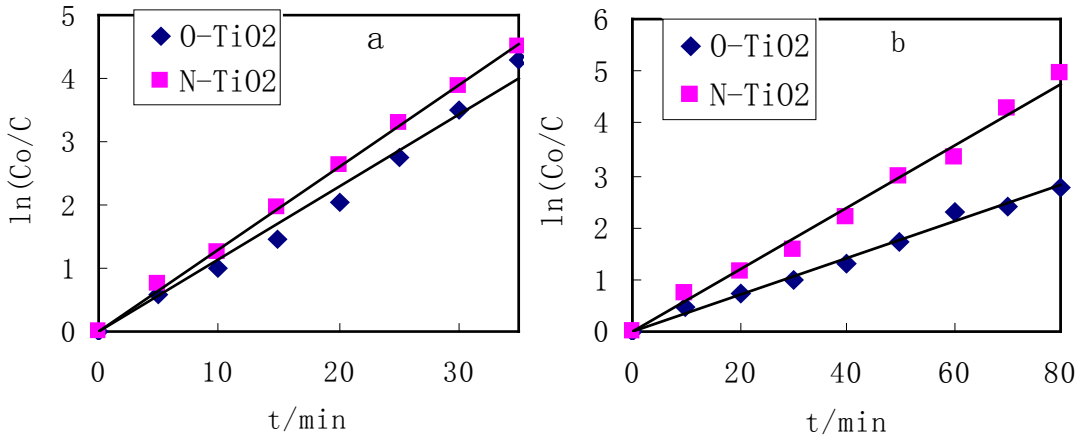

Figure 5. Dynamics curves of photodegradation of samples at ultraviolet lamp（a）and xenon lamp（b）

The photocatalytic degradation of methyl orange is chosen as a model reaction to evaluate the photocatalytic activities of the present N-doped TiO2, and it is compared with that of the pristine TiO2 without doping(Fig. 5).According to the Langmuire Hinshel-wood kinetics model , the apparent rate order equation can be expressed as ln (C0/C) = kt, where C is the concentration of the organic pollutant, t is the irradiation time and C0 corresponding to the initial concentration of the organic pollutant. The apparent first order rate constant (kapp) are given by the slope of ln (C0/C) versus t. As shown in Fig. 5 ,the degradation rate of N-TiO2 on methyl orange under the visible light irradiation as well as UV light irradiation is signicantly enhanced compared to O-TiO2. In particular, the apparent decomposition rate under visible light of N TiO2 is 0.1296 min-1 and it is 1.699 times higher than that of O-TiO2 .The enhanced UV photocatalytic performance of N-TiO2

could be attributed to ultrasonication decreases the size of TiO2 grain and particle, and increases surface area as indicated by the TEM results in Fig.2,So the lifetime of photogenerated electrons and holes can be increased, which is beneficial to enhance the photocatalytic efficiency. The high visible phtotcatalytic activity of the sample is due to the nitrogen doping which is responsible for the red-shifted absorption edge of N-TiO2 as indicated by the DRS results in Fig.3.

CONCLUSION

N-TiO2 were prepared by sol-gel method using triethylamine as nitrogen raw material under ultrasonic irradiation. Ultrasonication does not only reduce the particle size but also enhances the hydrolysis of titanium alkoxide for faster and better crystallization of anatase nanoparticles.Given its wide light absorption range,small particlesize and high surface area, N-TiO2 shows higher photocatalytic activity under both ultraviolet and visible irradiation compared to O-TiO2. In particular, the degradation rate of N-TiO2 on methyl orange under visible light was 1.69 times as fast as O-TiO2 prepared without nitrogen doping or ultrasonication. Thus exemplifying the use of a ultrasonication -based synthesis as a means of producing novel photocatalytic materials.

Acknowledgements

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