

Effects of N-Doped Titanium Oxide on Photocatalytic Properties

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In this work, N-doped TiO₂ powders were prepared by sol-gel procedure using NH₄NO₃ as the nitrogen source. The photocatalytic activity was evaluated by measuring the decomposition of methyl orange under UV irradiation. X-ray diffractometry and field emission scanning electron microscopy were applied to characterize crystal structure and morphology. The mixtures of rutile and anatase phase co-exist in the resulted N-doped TiO₂ powders. Amounts of nitrogen doping in TiO₂ can effectively improved the photocatalytic activity of TiO₂. The change of phase composition that derived from the different content of nitrogen doping also has influence on photocatalytic activity. Photodegradation of methyl orange in 1 h was about 63 % and the crystallite size was about 60 nm.

Key Words: N-Doped, Titanium oxides, Photocatalytic, Methyl orange.

INTRODUCTION

Photocatalytic activity of TiO₂ has been attracting much attention in view of their practical applications to environmental cleaning such as self cleaning of tiles, glasses and windows. TiO₂ has the advantages of its high chemical stability, nontoxicity and low cost, but it can be activated in the photoexcitation processes only under the UV light that has higher energy than the band gap of TiO₂. Because UV light accounts for only a small fraction (8 %) of the sun's energy compared to visible light (45 %), any shift in the optical response of TiO₂ from the UV to the visible spectral range will have a profound positive effect on the photocatalytic efficiency of the material. Nitrogen doped into TiO₂ has proven to be indispensable for band-gap narrowing^{1,2}. Several groups have succeeded in doping nitrogen into TiO₂ photocatalyst to obtain photo-response at visible light. Asahi *et al.*² showed that TiO₂ films can be doped with nitrogen by sputtering methods and exhibit thereafter enhanced photoactivity in the visible spectral range. Burda *et al.*³ reported that TiO₂ - xNx nanocrystals were catalytically active and absorbed well into the visible region up to 600 nm. The composition of crystalline phase also has influence in the photocatalytic activity. Ohno *et al.*⁴ showed that the mixed structure of anatase and rutile must be the key to the high activity of the P-25 powder. Zhang *et al.*⁵ reported that the phase junction formed between the surface anatase nanoparticles and rutile particles can greatly enhance the photocatalytic activity⁵.

However, there was little information about the studies of interaction between phase composition and photocatalytic activity which both derived from nitrogen doping. We need to investigate the interaction for higher photocatalytic activity. This paper focuses on the interaction and explores the reason.

EXPERIMENTAL

Preparation of N-doped TiO₂ catalysts: N-Doped TiO₂ powders were prepared by sol-gel method. Fig. 1 shows the scheme for the preparation of TiO₂ catalysts by hydrolysis of [CH₃(CH₂)₃O]₄Ti, which was employed as precursor. NH₄NO₃ were used as nitrogen sources for the synthesis of N-TiO₂ powders. [CH₃(CH₂)₃O]₄Ti/C₂H₅OH/H₂O/CH₃COOH molar ratios in the reacting solution were 1/18/2/0.5. [CH₃(CH₂)₃O]₄Ti and parts of C₂H₅OH were vigorously stirred in a reactor in a temperature. Nitrogen precursor, others of C₂H₅OH, acetic acid, H₂O and PEG were added during the above hydrolysis and polycondensation period. The resulting transparent yellow sol was dried at 90 °C and calcined at 600 °C in furnace about 3 h.

Characterization: The crystalline phase was identified by X-ray diffractometry (XRD) with a Bruker D8 Advance XRD-diffractometer (40 kV, 50 mA) using Cu K_α radiation. XRD patterns were obtained for 20-80° (2θ) by stepscanning with a step size of 0.02. To determine the average crystallite size, peak broadening analysis was applied to titanium dioxide diffraction using Scherrer's equation. The size of the titanium dioxide crystalline was calculated by means of

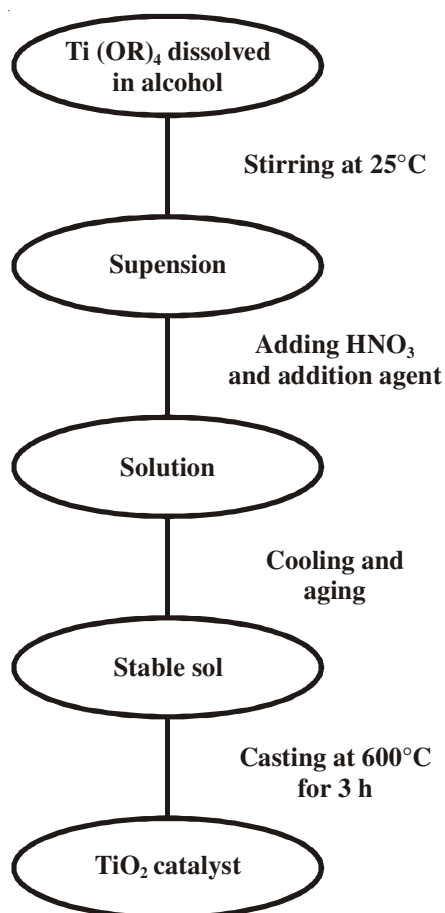


Fig. 1. Schematic representation of the preparation of TiO_2 catalysts

the Scherrer's equation from the broadening of the XRD reflection. A field emission scanning electron microscopy (FESEM) was used to observe the morphology and grain size of the catalyst.

Measurement of photocatalytic activity: The photocatalytic activity of N-doped TiO_2 was characterized by photodegradation of methyl orange under UV-light irradiation. For an examination of the catalytic activity under UV-light irradiation, 100 mL 5 mg/L⁻¹ methyl orange aqueous solution with 0.1 g catalyst was loaded in a glass container and mixed using a magnetic stirrer. The solution was irradiated with a 120 W mercury lamp about 1h. The concentrations of methyl orange were determined by visible spectrophotometer (7230G, Shanghai Precision & Scientific Instrument).

RESULTS AND DISCUSSION

Effect of sol reaction temperature on the degradation rate of TiO_2 : The temperature of sol process was one of the most crucial steps in the formation of TiO_2 powder of which properties were decided by sol particle distribution in the TiO_2 . Fig. 2 shows the effects of TiO_2 degradation rate of methyl orange as a function of sol synthesis temperature. It was indicated that an increase temperature from 20 to 25 °C led to an increase of degradation rate. The degradation rate of methyl orange at 25 °C was much larger than that in the case of temperature being above 25 °C. So during the experimental operation in this study, the temperature of the sol was initially

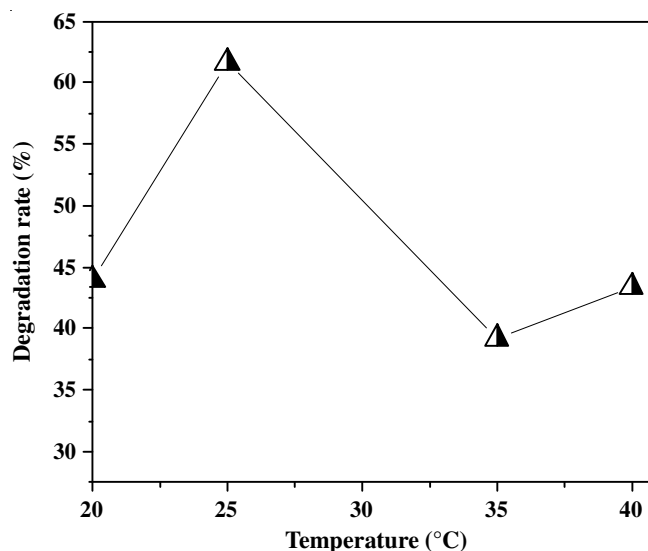


Fig. 2. Photocatalytic degradation rate of methyl orange for various sol synthesis temperature

kept at 25 °C, which was then increased slowly and with sufficient care by trickling the solvent. By doing so, the particle size would get smaller. The phenomena mentioned above can be explained by the principle of the hydrolysis reaction of titania sols. When the temperature of the sol was below 25 °C, hydrolysis of sol was difficult to process. However, if the temperature of the sol was above 25 °C, an amount of titania became available for undergoing condensation reactions, which would produce relatively large particles. If the temperature of the sol was increased slowly and carefully, the rate of condensation reactions could be controlled precisely, which would lead to small particles. It is worthy to note that the temperature of the titania sol should be controlled carefully.

Effect of additives on the degradation rate of TiO_2 :

The additives introduced in a colloidal solution were used to improve properties of the sol-gel because it can avoid particle aggregation and adjust the viscosity of sol. The introduction of measured organic additive to the TiO_2 sol can restrain the hydrolysis of the metal alkoxide and raise the rate of the condensation reaction. Therefore, the gel network was strengthened, which was beneficial for the formation of the membrane. Poly(vinyl alcohol) (PVA) and hydroxypropyl-cellulose (HPC), methyl cellulose could be used as an organic additives. For the sol system in this study, poly(ethylene glycol) was found to be very suitable. As shown in Fig. 3, when the methyl cellulose content was controlled about 1.3 mL, the degradation rate of methyl orange was optimum probably due to the good dispersion of sol particle which will improve the TiO_2 powder size. However, when the additive amount was above 1.3 mL, the degradation rate was decreased slightly mainly owing to the bridging function of high molecular surfactant in sol. This indicated that a little amount of poly(ethylene glycol) was enough to obtain a perfect TiO_2 sol.

Effect of N/Ti ratio on the degradation rate of TiO_2 :

Fig. 4 shows the changes of degradation rate of methyl orange as a function of N/Ti in the presence of N-doped TiO_2 powders while irradiating with UV-light. All of the N- TiO_2 with various ratios showed higher photocatalytic activity than pure TiO_2 .

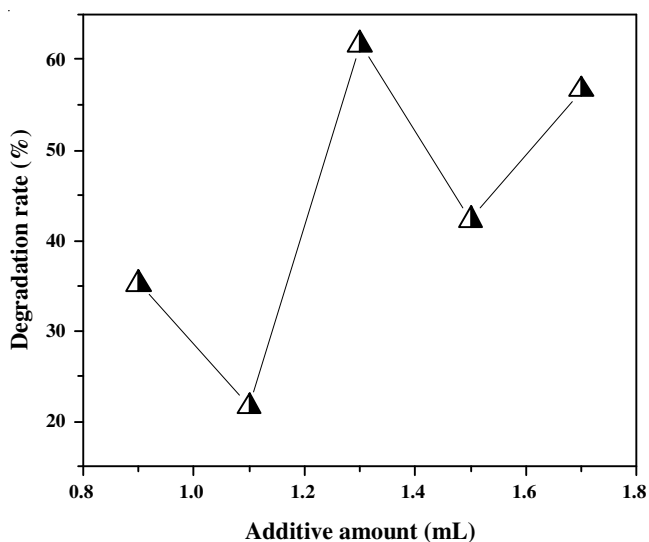
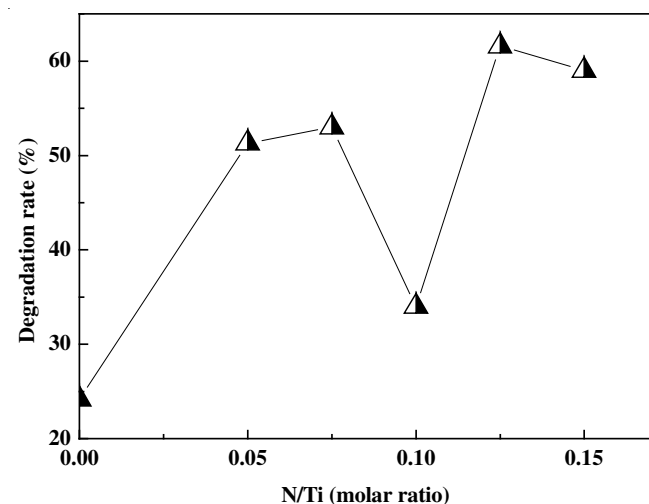
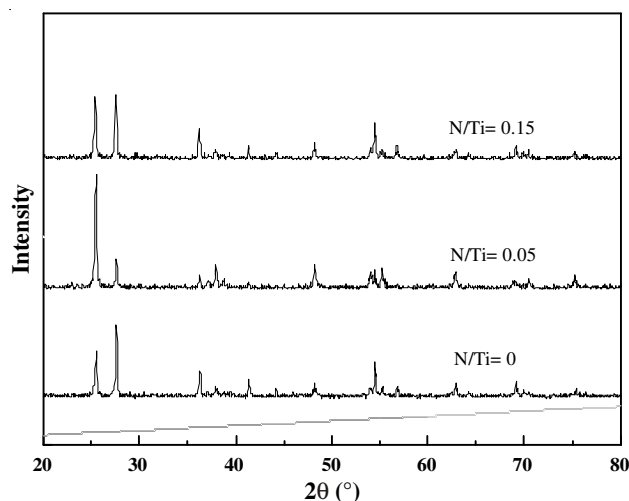


Fig. 3. Photocatalytic degradation rate of methyl orange for PEG additives

Fig. 4. Photocatalytic degradation rate of methyl orange for various N-doped TiO₂ powders

Accession of nitrogen effectively improved the photocatalytic activity of TiO₂. The increase of efficiency of photocatalytic activity was founded in the irradiation of UV-light. This showed that not only narrowing of band gap and expanding of light response region by reason of addition of nitrogen, but also the presence of nitrogen enhanced the photocatalytic activity in UV-light that has been fewly reported in past. *Via* the inclusion of specific dopants it should be possible to improve the efficiency of the photocatalytic behaviour by creating new band structures or by suppressing the recombination of photogenerated electron-hole pairs to improve quantum efficiency^{6,7}. Addition of nitrogen element influenced the electron distribution of TiO₂ crystal. Thus the defect of crystal and oxygen vacancy was formed. The electrons trapped on oxygen vacancies in N-doped TiO₂ were detected under UV- light irradiation.

Fig. 5 showed that the change of crystalline phase owing to nitrogen doping was founded in XRD patterns of samples. There was the different of crystalline phase of TiO₂ with different of N/Ti ratio. The pure TiO₂ showed a mixture of anatase and rutile crystalline forms. When the impurities accumulated to a certain amount (N/Ti = 0.05), the content of anatase was

Fig. 5. XRD profiles of TiO₂ with various N/Ti ratio

increased with increasing of N/Ti ratio while the content of rutile was decreased. And when the N/Ti ratio was to 0.15, the content of anatase gradually decreased with increasing of N/Ti ratio while the rutile was increased. These showed that nitrogen doping was very important to the constituent of crystalline phase of TiO₂.

The reason of above was related to the hydrolysis reaction of tetrabutyl titanate. The process of oxygen elements substituted by nitrogen element competed with the polyreaction of Ti(OH)_x(OBU)_y. In the process of sol-gel, polyreaction of Ti(OH)_x(OBU)_y was greatly vigorous. Therefore, when the N/Ti ratio was lesser, the appearance of substitutional nitrogen was rather difficulty. So the nitrogen element was added in the interstitial site. And the substitutional nitrogen was founded when the N/Ti ratio was higher. In addition, we found the lower degradation at the 0.1 ratio and higher at the 0.05 and 0.15 ratio. This showed that the photocatalytic activity was not always improved by nitrogen doping. And we observed the difference of constitute of crystalline phase in the different N/Ti ratio. So the interactive influence of nitrogen additives between TiO₂ powder crystal structure and photocatalytic activity was existent. At 0.1 ratio, the content of nitrogen doping can induce the change of crystalline phase and the content of rutile should be higher than the 0.05 ratio, but the photocatalytic activity was lower, so we believed that anatase was more important than rutile for photocatalytic activity⁸. And the change of photocatalytic activity that derived from the constitute of crystalline phase was larger than by the only nitrogen doping. When the content of nitrogen doping come to the 0.15 ratio, the photocatalytic activity was increased with the content of rutile increased. This seemed contradictory with above all. But it was considered that the content of nitrogen doping was more important than the constitute of crystalline phase for the photocatalytic activity while the content of nitrogen composite have changed the TiO₂ particle size, which has directivity effects on the photocatalytic performance of TiO₂ (Table-1). Accordingly, the addition of nitrogen in TiO₂ has a complicated effect on the photocatalytic activity. Proper quantities of nitrogen will improve the photocatalytic degradation rate of methyl orange.

TABLE-1
CRYSTALLITE SIZE FROM SCHERRER'S EQUATION

N/Ti ratio	0	0.05	0.15
Crystallite size	76 nm	67.5 nm	67.8 nm

The crystal structure of TiO₂ was changed by nitrogen doping. When nitrogen elements was added in the interstitial site, the crystal structure was so expanded that very difficultly transformed to rutile which was more closed packing than anatase. So while the content of nitrogen doping was lesser, the content of rutile also was lesser. And when the nitrogen elements was added in the substitutional site, because of the atomic radius of nitrogen element was much closed to oxygen atom (N, 0.075 nm, O, 0.074 nm), so the crystal structure was not changed very well. And the rutile was founded when the content of nitrogen higher. Fig. 6 showed the FESEM photograph of N-doped TiO₂. In this photograph, we can see that the anatase distribute in the rutile⁴. And the degree of aggregation anatase was fewer than rutile, this should be the important for the difference of photocatalytic activity between anatase and rutile. The crystallite size from the FESEM photograph was closed to the value from Scherrer's equation.

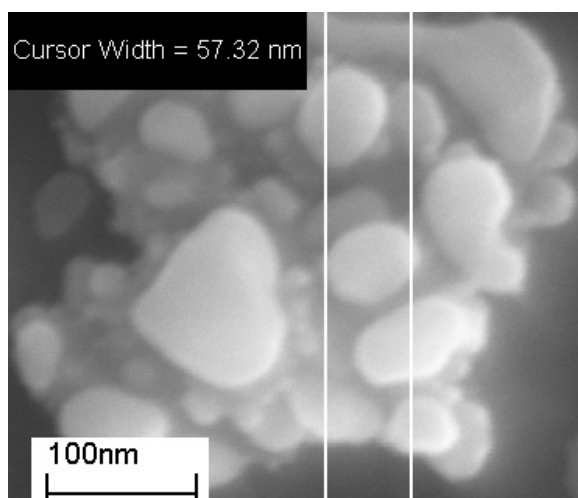


Fig. 6. FESEM photograph of N-doped TiO₂

Conclusion

N-doped TiO₂ powder were prepared by sol-gel procedure using NH₄NO₃ as the nitrogen source and followed by calcination at certain temperature. The photocatalytic activity were evaluated by measuring the decomposition of methyl orange under UV irradiation. XRD and SEM were commanded to characterize crystal structure and morphology. The change of crystal structure was important influenced through additive nitrogen as well as the photocatalytic activity. Photodegradation of methyl orange in 1 h was about 63 % and the crystallite size was about 60 nm.

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