N-doped TiO₂ Nanotubes with Visible Light Photo-Activity for Degradation of Methyl Orange in Water

可視光活性を有する N ドープ TiO₂ ナノチューブのメチルオレンジ分解

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N-doped TiO₂ nanotubes were prepared by a wet process and with an additional thermal treatment. Firstly, titanate nanotubes were prepared by a hydrothermal chemical method. Then the obtained nanotubes were immersed in a 0.5 mol/L NH₃ solution for different periods. Finally, the resulted products were calcinated at high temperature to complete the substitution of O by N. The prepared N-doped nanotubes had an anatase structure and a large specific surface area. For those N-doped TiO₂ nanotubes, a significant shift of the absorption edge to a lower energy region and a notable decomposition of methyl orange in an aqueous solution under visible light irradiation were observed. The most visible light active catalysts were those immersed in a 0.5 mol/L NH₃ solution for 10 h and then calcinated at 400°C for 1 h.

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1. Introduction

Titanium dioxide (TiO₂), as an efficient photocatalyst has been applied to various items such as air purification, deodorant, sterilization, and anti-fouling.¹⁾ Recently, its tubular structure—TiO₂ nanotubes receive more attentions because of their unique shape, size confinement in radial-direction and large surface-to-volume ratio.^{2),3)} Pure anatase TiO₂ has a wide band gap (3.0–3.2 eV) and it can only be excited by ultraviolet light with wavelength shorter than 390 nm. In recent years, many efforts have been made to enhance the visible light sensitization of TiO₂. Doping with impurities, e.g. transition metals^{4)–7)} or anions, including C, N, F, P, S,⁸⁾ is one of the typical methods. Among all impurities doping, we are most interested in nitrogen doping. Asahi et al.⁸⁾ reported that N-doped TiO₂ showed higher visible light activity. They made theoretical densities-of-states (DOS) calculations for the substitution of O in TiO₂ lattice with C, N, F, S dopants, then concluded N-doping was the most effective method for increasing the visual light sensitization. Moreover, they considered the valence band edge shifted to the negative direction by mixing the N 2p and O 2p states, thus as a result of it, the band gap narrowed. Other groups also have succeeded in doping N into the TiO₂ lattice to obtain photo-response at visible light region.^{9)–19)} However, those reports were mainly aimed at TiO₂ powders.

The aim of this paper was to obtain visible-light-active TiO₂ nanotubes by doping with N. The visible light activity of N-doped TiO₂ nanotubes was evaluated on the basis of decomposition of methyl orange under visible light irradiation.

2. Experimental section

2.1 Synthesis of titanate nanotubes

The titanate nanotubes were synthesized by a hydrothermal chemical process:²⁰⁾ 0.5 g pure TiO₂ powders of anatase phase were mixed with a 10 mol/L NaOH aqueous solution in a Teflon vessel at 120°C for 24 h. The resulted products were washed off with a 0.1 mol/L HCl aqueous solution and further washed with distilled water until the PH=7.

2.2 Synthesis of N-doped TiO₂ nanotubes

The N-doped TiO₂ nanotubes were prepared according to the following procedure: such obtained titanate nanotubes in 2.1 were immersed in an aqueous HNO₃ solution (0.5 mol/L) for 12 h to protonate the surface. The products then were immersed in a 0.5 mol/L NH₃ solution for different periods at room temperature. Finally, the resulted products were calcinated at 400°C for 1 h, which resulted in N-doped TiO₂ nanotubes.

2.3 Characterization of TiO₂ nanotubes

The diffuse reflectance spectra (DRS) were determined by a SHIMACZU UV-2501PC spectrometer equipped with integrating sphere accessory. The X-ray powder diffraction (XRD) patterns were recorded by a X-ray diffractometer (MSAL-XDII) using a Cu K α radiation. The transmission electron microscopy (TEM) investigations were taken on a PHILIPS TECNAI-10 instrument. The BET surface area was calculated from the adsorption-desorption isotherm of N₂ at 77 K (Micromeritics ASAP 2010). The X-ray photoelectron spectroscopy (XPS) measurements were performed on a X-ray photoelectron spectrometer (PHI Quantum 2000) using the Al K α X-ray beam. The fluorescence spectra were recorded on a F-4500 HITACHI fluorometry.

2.4 Measurement of photocatalytic activity

The photocatalytic activity was evaluated by measuring the photo-degradation of a 100 ml methyl orange solution with an initial concentration of 20 mg/L. The weight of the photocatalysts used in each measurement was kept at 0.2 g. The visible light was obtained by a 100 W xenon lamp, which mainly emitted visible light in the range of 400–800 nm. The cut-off-filters were used to obtain the visible light. The concentrations of methyl orange solution were quantified by a TU-1900 spectrophotometer at 464 nm.

3. Results and discussions

The visible light activity of TiO₂ was dependent on N-doping levels sensitively. Changes in N-doping levels could give significant effects on the visible light activity. For nanotubes, calcination at higher temperature would destroy the tubular structure. So in this paper the doping temperature was 400°C and we mainly discussed the effects of immersion periods on

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Fig. 1. Diffuse reflectance spectra of non-doped TiO₂ nanotubes (S0), *N*-doped TiO₂ nanotubes prepared by immersing in a 0.5 mol/L NH₃ solution for 5 h (S5), 10 h (S10), 15 h (S15) and 20 h (S20) respectively. All the nanotubes were calcinated at 400°C for 1 hour.

Table 1. Band Gap Values (E_g) for Different Photocatalyst

photocatalyst	S0	S5	S10	S15	S20
$\lambda_{\max}(\text{nm})$	375	393	405	430	431
$E_g(\text{eV})$	3.31	3.15	3.06	2.89	2.88

N-doping levels.

For evaluating the influences of immersion periods, the pure titanate nanotubes were immersed in a 0.5 mol/L aqueous NH₃ solution for different periods, namely 5, 10, 15, and 20 h, then calcinated at 400°C for 1 h. The diffuse reflectance spectra of obtained specimens (referred to as S5, S10, S15, and S20 respectively), as well as the non-doped nanotubes which were also calcinated at 400°C for 1 h (referred to as S0), are shown in Fig. 1.

As shown in Fig. 1, S0 do not absorb visible light above 390 nm. For S5, an obvious shift of the absorption edge to the longer wavelength region can be observed. By increasing the immersion periods in NH₃ solution, the mentioned shift becomes more and more significant. The most significant shift is obtained for S15 and S20 (no significant difference between them). The estimated band gap values of these specimens are presented in Table 1.

In this paper, *N*-doped TiO₂ nanotubes were prepared by a two-steps approach. Firstly, titanate nanotubes were immersed in a NH₃ solution. During this wet process, titanate nanotubes absorbed NH₄⁺ and then reacted with NH₄⁺ to form ammonium titanate nanotubes. The absorbing amount of NH₄⁺ increased with the increase of immersion periods until the adsorbing reached saturation. Next, the crystal phase of nanotubes changed from amorphous to anatase during the following calcination process. Obviously, the more NH₄⁺ were adsorbed during the wet process, the more nitrogen were doped into the lattice during the calcination process. But when

Fig. 2. TEM images of TiO₂ nanotubes: (a) S0, (b) S10.

Fig. 3. XRD patterns of S0 and S10.

the immersion periods increased up to 20 h, the adsorbing of NH₄⁺ reached saturation. As a result of it, the visible light shift and the *N* doping levels of S20 were similar with those of S15.

Figure 2(a) shows the TEM image of S0 and Fig. 2(b) shows that of S10. From Fig. 2, it can be seen that S10 are in good tubular structure and there are no damages caused by immersion and high temperature calcination.

We also analyzed the XRD patterns of S0 and S10, as shown in Fig. 3. Their crystal form are both anatase, which indicates *N*-doping has no effects on the crystal phase. The atomic compositions of S10 were analyzed with XPS, as shown in Fig. 4. We can observe a peak with the binding energy of 397 eV. Asahi et al.⁸⁾ analyzed their *N*-doping TiO₂ with XPS and observed three *N* 1S peaks with the binding energy of 402, 400, and 396 eV. They assigned these peaks as atomic β -N (396 eV) and molecularly chemisorbed γ -N₂ (400 and 402 eV). Sato et al.,⁹⁾ prepared *N*-doped TiO₂ by NH₃ solution treatment and their XPS analysis revealed that the *N* 1S peak did not exist at 396 eV but at 400 eV. They pointed out that *N* doping by wet method was similar to impurity sensitization and doped *N* might exist as NO. H. Irie et al.¹⁰⁾ also prepared *N*-doped TiO₂ by NH₃-treatment method. They observed *N* 1S peaks at 396 eV and 400 eV in XPS analysis and they ascribed the 396 eV

Fig. 4. XPS spectra of S10.

Fig. 6. Removal of methyl orange under UV-light for S0, S10, and P-25.

Fig. 5. Removal of methyl orange under visible light.

Fig. 7. Fluorescent spectra of S0, S10, and P-25.

peak to visible light sensitization. For our *N*-doped specimens S10, the *N* 1S peak at 397 eV can be observed. This peak is assigned to Ti–N bond. But the *N* 1S peak at 400 eV which assigned as molecular nitrogen by Asahi does not exist.

Figure 5 shows the obtained results of the decomposition of methyl orange under visible light irradiation over various samples. Common feature is *N*-doped samples are visible active. And the best decomposition results are obtained with S10. In the case of S10, the methyl orange removal is equal to 20, 33, 40, 52, and 66% after the irradiation of 30, 60, 90, 120, and 150 min. While for S0, the removal of methyl orange is 2, 3, 5, 7, 9% after the same irradiation time. The observed results indicate that *N*-doped TiO₂ nanotubes are more visible light active than non-doped nanotubes. It should be noted that S15 show lower photocatalytic activity. In this case, the removal of methyl orange is 15, 25, 37, 44, and 58% after the same irradiation time. As was mentioned before, the band gap value of S10 is 3.06 eV and that of S15 is 2.89 eV. Although the band gap of S15 is significantly narrowed in comparison with that of S10, the visible light activity decreases. The fact that the presented activity does not correlate with the absorption spectra suggests that several factors influence the visible light

activity. On the one hand, *N* doped into the lattice lead to the narrowing of band gap by mixing the N 2p and O 2p states, resulting in visible light activity. On the other hand, higher amount of *N* doped into the TiO₂ lattice might cause excessive defects that would act as recombination centers of photoinduced electron-hole pairs, resulting in decreasing the activity. Another explanation might be attributed to a change in the crystal structure caused by high doping amount of N.²¹⁾ Although the observed crystal phase of S15 is anatase, we can not rule out the possibility that there are other phases that are difficult to detect within the sensitivity of the XRD machine. In order to explain in detail the obtained results, further investigations are needed.

To compare the photocatalytic activity under UV-light irradiation, S0, S10 and P25 were evaluated under the same experimental conditions mentioned in 2.4, except that the 300 W medium pressure mercury lamp was used as UV-light source. As shown in **Fig. 6**, both S0 and S10 are more active than P-25. There maybe two reasons. On the one hand, the specific surface area of S0 (324 m²/g) and S10 (311 m²/g) are larger than that of P-25 (138 m²/g), which implies the adsorptive powers of nanotubes are stronger than those of P-25. Excellent adsorptive powers will contribute to high photocata-

lytic activity. On the other hand, it is well known that the quantum yield is of vital importance to the photocatalytic activity. **Figure 7** shows the fluorescent spectra of S0, S10, and P-25. The intensity of the fluorescent signals has direct relation with the recombination rate of photo-generated pairs. The stronger the fluorescent signals are, the higher the recombination efficiency are. As shown in Fig. 7, the fluorescent signals of P-25 are stronger than those of S0 and S10, which indicates the recombination efficiency of photo-generated hole and electron in P-25 are higher than in nanotubes. In other words, the separation efficiency of hole and electron in nanotubes are higher than in P-25. As a result of it, S0 and S10 show higher photocatalytic ability. In the case of S10, its fluorescent signals are stronger than those of S0. This phenomenon might be due partly to the defects caused by *N* doping and the defects would act as recombination centers. However, both the specific surface area and the intensity of fluorescent signals show no significant difference between S0 and S10. So their activities are almost equal. The results indicate that the loss of photocatalytic activity due to *N* doping is little.

4. Conclusions

N-doped TiO₂ nanotubes with visible light activity can be prepared by immersing the titanate nanotubes in a 0.5 mol/L NH₃ solution and then by calcination at 400°C for 1 h. The *N*-doped TiO₂ nanotubes have an anatase structure. XPS analysis confirms that N atoms are directly bond to Ti in the TiO₂ lattice. TEM results show that *N*-doping has no effects on the tubular microstructure. The shift of the absorption edge to a lower energy region does not correlate with the visible light activity and higher doping of *N* decreases the activity. The most visible light active catalysts are those immersed in a 0.5 mol/L NH₃ for 10 h and then calcinated at 400°C for 1 h.

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