Preparation and Characterization of TiO$_{2-x}$N$_x$ with High Visible Light Activity

Abstract: Nitrogen doped TiO$_2$ with high visible light activity were prepared by annealing nanotubular titanic acid (H$_2$Ti$_2$O$_4$(OH)$_2$, denoted as NTA) in NH$_3$ flow at different temperature for 2h. Diffusion reflectance spectra (DRS) show that all the TiO$_{2-x}$N$_x$ samples have apparently visible light absorption over the entire region. X-ray diffraction (XRD) patterns indicate that the samples are completely consisted of anatase TiO$_2$, no rutile phase was detected. The chemical states of nitrogen atoms in TiO$_{2-x}$N$_x$ samples were investigated by X-ray photoelectron spectroscopy (XPS), and the XPS results show that only one N 1s peak appeares in the spectra, demonstrating that doped-N is present in the interstitial site in the form of Ti–O–N bond. The photoactivities were evaluated by decomposition of propylene under visible light (λ ≥ 420 nm). The results show that the TiO$_{2-x}$N$_x$ samples annealed at 700 ºC possess the best photoactivity.

Keywords: Nanotubular titanic acid, Visible light photocatalysis, Nitrogen doping, Propylene

1 Introduction

Titanium dioxide has been proven to be the most promising photocatalyst for its low cost, non-toxicity, high stability and high efficiency in the field of degradation of difficult-to-remove pollutants. But titanium dioxide is activated only by irradiating with ultraviolet (UV) light because the band gap energies is 3.0 eV for rutile and 3.2 eV for anatase, respectively. To use solar irradiation or interior lighting, several attempts have been made to extend the absorption range of TiO$_2$ from the ultraviolet to the visible light region using transition metal doping [1–4] or synthesis of reduced TiO$_x$ [5,6]. However, the metal-doped materials suffer from a thermal instability [2], an increase of carrier-recombination centers, or the requirement of an expensive ion-implantation facility [3]. Recently, N-doped TiO$_2$ has attracted widely attention for its photocatalytic activity in the visible light region [7–21]. The recent research in
2001 by Asahi et al [10] has rekindled a great interest in TiO₂ for its high visible light photoactivity, though the visible light response of N-doped TiO₂ was discovered in 1986 by Sato [11]. In conclusion, N-doped TiO₂ has been prepared by a variety of methods such as sputtering, ion implantation, chemical vapor deposition, sol-gel, oxidation of TiN, direct nitridation of TiO₂ and decomposition of N-containing metal organic precursors.

In the present paper, a simple method was found easily to dope nitrogen into TiO₂ and the TiO₂₋ₓNx samples prepared by thermal treatment of NTA at different temperatures in the NH₃ flow for 2 h show apparently visible light photocatalytic activity for decomposition of propylene.

2 Experimental Section

NTA was synthesized from nanotubed sodium titanate (Na₂Ti₄O₉(OH)₂) by an ion exchange reaction with 0.1 mol/L.HCl solution [22]. Then about 1 g NTA was treated in the NH₃ flow for 2 h at 400 ~ 700 °C. From the typical procedure, the TiO₂₋ₓNx samples were obtained and denoted as N-NTA(4002–7002), respectively. P25-TiO₂ was selected as the reference.

The physicochemical properties of resultant N-doped TiO₂ samples were investigated by means of transmission electron microscopic (TEM), diffusion reflectance spectra (DRS), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). TEM images were taken on a JEM-2010 electron microscope. XRD patterns were measured on a Philips X’Pert Pro X-ray diffractometer. DRS were recorded on a Shimadzu U-3010 spectrometer. XPS characterizations were performed using a Escalab210 X-ray photoelectron spectrometer. The energy scale of XPS spectra was corrected using the binding energy of the adventitious carbon as C 1s = 284.8 eV.

The photocatalytic activity of the samples was evaluated by oxidation of propylene. The propylene gas (about 600 ppmV) was passed through the quartz reactor where the glass plate (1 cm × 10 cm) with the photocatalyst was placed at the flow rate of 100 mL/h. The photocatalyst was irradiated with visible light from a Xe lamp passed through a cutoff filter (λ ≥ 420 nm) and the propylene concentration were analyzed by the gas chromatograph (Shimadzu GAS CHROMATOGRAPH GC-9A), which was equipped with a GDX-502 column and a Fire Ion detector (FID).
Fig. 1: TEM images of NTA and relevant TiO$_{2-x}$N$_x$ samples prepared by treating NTA at different temperature in NH$_3$ flowing for 2h, respectively: (a) 400 °C; (b) 500 °C; (c) 600 °C; (d) 700 °C

3 Results and Discussion

Fig. 1 display the morphology of the relevant TiO$_{2-x}$N$_x$ samples and the inset in Fig. 1 (a) shows the typical TEM image of precursor NTA. As can be seen, NTA is hollow with a diameter of 5 ~ 10 nm and a length of several hundreds nanometers, which is well in agreement with our previous results [22]. However, after thermal treatment of NTA in NH$_3$ flowing, the resultant TiO$_{2-x}$N$_x$ samples could not keep the nanotubular morphology but were broken and gradually agglomerated into nanoparticles. With the temperature increasing, the particle size became gradually bigger and bigger.

Shown in Fig. 2 is the diffusion reflectance spectrum of NTA, P25 and the samples produced by treating NTA in NH$_3$ atmosphere at different temperature for 2h. It is obvious that all the TiO$_{2-x}$N$_x$ samples showed visible-light absorption over the entire range, while NTA and P25 show no visible-light absorption as a result of the white color. Also it can be obviously seen that the fundamental absorption edge of TiO$_{2-x}$N$_x$ samples did not shift into visible light region compared with P25, indicating that the N-doping into TiO$_2$ did not change the band gap of TiO$_2$. As shown in Fig. 1, it must be pointed out that the visible light absorption of TiO$_{2-x}$N$_x$ samples has not direct relationship with the thermal treatment temperature. Samples prepared at 400 °C or 600 °C possess hardly the same light absorption ability.
Fig. 2: Reflection spectrum of P25, NTA and relevant TiO$_2$–N$_x$ samples prepared by treating NTA at different temperature in NH$_3$ flowing for 2h, respectively: (a) 400 °C; (b) 500 °C; (c) 600 °C; (d) 700 °C

The XRD patterns of N-NTA(4002–7002) samples prepared by NH$_3$-thermal treatment of NTA were shown in Fig. 3. It shows the effect of calcination temperature on the phase change of the TiO$_2$–N$_x$ samples. As-prepared NTA materials belong to an orthorhombic system [22] (Figure not given here) As can be seen, the orthorhombic system gradually converted into anatase phase at 400 °C and all the samples were present in the anatase phase accompanying with the treating temperature increasing, no rutile phase corresponding to 2θ around 32.0° appeared even the treatment temperature enhanced to 700 °C. Furthermore, the intensity of A(101) peaks became more and more sharper and higher accompanying with the treating temperature increasing, meaning that the better crystallization degree of anatase of the TiO$_2$–N$_x$ samples.
Fig. 3: XRD patterns of TiO$_{2-x}$N$_x$ samples prepared by treating NTA at different temperature in NH$_3$ flowing for 2h, respectively.

Fig. 4 demonstrates the N 1s XPS spectra of the relevant TiO$_{2-x}$N$_x$ samples prepared by NH$_3$-thermal treatment of NTA at different temperatures for 2h. No N 1s XPS signals were detected on the surface of NTA (figures are not given here). After doping nitrogen, one could see that only one N 1s XPS peak with a core level binding energy of 400.0 eV was observed from the spectrum of the every TiO$_{2-x}$N$_x$ samples. It can be inferred that doped-N was present only in one form. Up to now, the N 1s chemical state in TiO$_{2-x}$N$_x$ samples was often divided into substitutional-N and interstitial-N depending on the binding energy of 396 ~397 eV and ca. 400.0 eV, respectively [7 – 22]. Therefore, the XPS results show that only one N 1s peak appears in the spectra, demonstrating that doped-N is present in the interstitial site in the form of Ti–O–N bond.
Fig. 4: N 1s XPS spectra of TiO$_{2-x}$N$_x$ samples prepared by treating NTA at different temperature in NH$_3$ flowing for 2h, respectively: (a) 400 °C; (b) 500 °C; (c) 600 °C; (d) 700 °C
Fig. 5 shows the photocatalytic ability for the decomposition of propylene under visible light ($\lambda \geq 420\text{nm}$). NTA and Degussa-P25 showed no vis-light-photoactivity (not given in Fig. 5). With the calcination temperature increasing from 400 °C to 700 °C, the photoactivity gradually increased from 29.7% for TiO$_{2-x}$N$_x$ samples prepared at 400 °C to 42.8% prepared at 700 °C. It can be seen that the TiO$_{2-x}$N$_x$ samples prepared at 700 °C showed the best photoactivity at this flow system. Furthermore, the removed propylene was converted into CO$_2$, which can be detected by the gas chromatograph, although we did not show the data here. From the data, it is obviously seen that the TiO$_{2-x}$N$_x$ samples prepared by annealing NTA in NH$_3$ flowing showed highly visible light photocatalytic activity.

4 Conclusion

Visible-light-active TiO$_{2-x}$N$_x$ samples were obtained by treating NTA at different temperature in NH$_3$ flowing for 2h. The physicochemical properties of resultant TiO$_{2-x}$N$_x$ samples were investigated by means of TEM, DRS, XRD, and XPS. The results showed that the nanotubular morphology of was destroyed into nanoparticles after thermal treatment, accompanying with its phase converted into anatase TiO$_{2-x}$N$_x$ samples from orthorhombic system of NTA. After nitrogen doping, doped-N was present in the interstitial site in the form of Ti–O–N bond. It was found that TiO$_{2-x}$N$_x$ samples obtained by annealing of NTA at 700 °C possessed the highest visible light
photocatalytic activity for propylene oxidation. It could be concluded that NTA is one of the most promising precursors for designing and preparing visible-light-active photocatalyst.

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References