Pt/N Co-doped Titanium Dioxide Visible-Light-Active Photocatalyst: Preparation and Characterization

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Abstract: Platinum and nitrogen co-doped TiO2 (denoted as Pt/TiO2-xNx) visible-light-active photocatalysts were prepared via hydrothermal method using nanotubular titanate acid (denoted as NTA) as precursor. The prepared Pt/TiO2-xNx samples displayed a better photocatalytic activity toward the oxidation of propylene than P25 under visible light irradiation. It is suggested that a fresh sub-band nearby the conduction band was induced due to the formation of single-electron-trapped oxygen vacancies, resulting in the visible light response of Pt/TiO2-xNx sample. Dopants nitrogen or platinum play an important role in separating photogenerated electrons and holes. The synergistic effect between oxygen vacancies and nitrogen as well as platinum is responsible for the enhanced photocatalytic property.

1. Introduction
Titanium dioxide co-doped of cation along with nitrogen could enhance visible light photocatalytic activity. Liu (2011) synthesized V-N co-doped titania nanocatalysts using a novel two-phase hydrothermal method [1]. The synergetic effects of vanadium and nitrogen incorporation was attributed to the activity improvement of V-N co-doped TiO2. Hua (2005) reported that photocatalytic activity of N-TiO2 would be significantly increased by co-doping with platinum toward the photo-degradation of trichloroacetic acid [2]. It is suggested that doping nitrogen in TiO2 reduces the band gap of anatase, while dopant platinum plays an important role in retarding the recombination of the photo-exited charge carriers and improve interfacial charge transfer. Li (2008) has been successfully prepared a bifunctional photocatalyst Pt/TiO2-xNx by wet impregnation. The results demonstrated that nitrogen-doped and platinum-modified TiO2 in a H2-O2 atmosphere could enormously increase the quantum efficiency of the photocatalytic system with excellent photocatalytic activity and high catalytic stability [3]. It was proposed that the enhanced separation efficiency of photogenerated electron–hole pairs, higher interface electron transfer rate, and an increased number of surface hydroxyl radicals in the photocatalytic process can account for its excellent photocatalytic activity.

Among these methods, the process of preparation of co-doped TiO2 mainly includes two types: one-step approach and two-step approach. The one-step method usually involves directly synthesizing co-doped TiO2 using sol–gel technique or hydrothermal method, while the two-step approach normally involves either synthesizing N-doped TiO2 followed by co-doping with other metal elements [4].
A facile, one-pot synthesis of platinum and nitrogen co-doped TiO$_2$ in association with enhanced visible light photocatalytic activity is reported in this paper. In the previous work [5-6], NTA was prepared and selected as the most promising materials for designing visible-light-active photocatalyst. To the best of our knowledge, this is the first time that NTA was used as precursor as well as by means of one-pot method to prepare Pt/TiO$_{2-x}$N$_x$ samples.

The physicochemical nature of various Pt/TiO$_{2-x}$N$_x$ samples was investigated by means of fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), diffuse reflectance spectra (DRS), and electron spin resonance (ESR) spectroscopy. The photocatalytic activities of resultant Pt/TiO$_{2-x}$N$_x$ samples in visible light region were quantitatively evaluated by monitoring photocatalytic oxidation of propylene.

2. Experimental
NTA was prepared according to the method reported elsewhere [6]. Briefly, the preparing procedure of NTA is as follows: P25 was thermally treated in a 10mol•L$^{-1}$ NaOH solution under magnetic stirring at 110$^\circ$C for 24h. After naturally cooled down to room temperature, it was washed with de-ionized water to a pH of ca. 7.0 ~ 8.0, and then immersed in 0.1mol•L$^{-1}$ HCl solution for 5 h under magnetic stirring, washed again with de-ionized water to remove Cl- followed by drying under vacuum at room temperature, yielding the product of NTA.

Then a mixture of NTA and urea with the ratio of 1:2 (mass ratio) was simultaneously dissolved in 2 wt.% hydrogen peroxide aqueous solutions, followed by addition of a predetermined amount of chloroplatinic acid (H$_2$PtCl$_6$) solution. Then it is refluxed at 40$^\circ$C for 4h in rotary evaporator followed by vacuum distillation, yielding ready-for-use precursors. In this step, we initially hoped to obtain ultrahigh crystalline TiO$_2$ nanotubes with homogeneously dispersed of urea and H$_2$PtCl$_6$ at low temperature. However, the XRD results showed that the as-prepared precursors still belongs to orthorhombic or rhombic system before calcinations at temperature ≤ 500$^\circ$C. According to the XRD results as well as visible light photocatalytic activity, we have optimized the catalyst preparation conditions with the thermal treatment temperature at 700$^\circ$C. Therefore, the ready-for-use precursors were thermally treated at 700$^\circ$C for 4h in argon flowing to prepare Pt/TiO$_{2-x}$N$_x$.

Fourier transform infrared spectroscopy (FTIR) patterns were measured in the range 400–4000 cm$^{-1}$ on an Alpha Centauri FTIR spectrophotometer. X-ray diffraction (XRD) patterns were measured on an X’Pert Philips diffractometer. Diffusion reflectance spectra (DRS) were obtained on a Shimadzu UV-3010 spectrometer, using BaSO$_4$ as a reference. Electron spin resonance (ESR) spectra were obtained on a Brüker ESP 300E apparatus. Chemical characterization of the sample surface was recorded with scanning X-ray photoelectron spectroscopy (XPS, ULVAC-PHI, Quantera).

The photocatalytic activity of P25 and Pt/TiO$_{2-x}$N$_x$ was evaluated by monitoring the oxidation of propylene under visible light irradiation. About 30 mg of each sample was spread on one side of a roughened glass plate located in a flat quartz tube reactor. A 300 W xenon lamp was used as the visible light source. A cut filter ($\lambda\geq420$ nm) and a water cell were inserted between the xenon lamp and reactor to eliminate ultraviolet and infrared light. Pure C$_3$H$_6$ mixed with air stored in a high-pressure cylinder was used as the feed gas and the flow rate of the feed gas was adjusted to 150 mL•h$^{-1}$. The concentration of C$_3$H$_6$, C, was determined at a sensitivity of 1 ppmV by using a chromatograph. The removal rate of C$_3$H$_6$ was calculated as ($C_0$-C)/$C_0\times100\%$; where $C_0$ refers to the concentration of feed gas C3H6 and is equal to 600 ppmV.

3. Results and Discussion
Figure 1 shows the FTIR spectra of urea, as-prepared precursor and Pt/TiO$_{2-x}$N$_x$, respectively. As
for the urea sample in the IR region, the characteristic antisymmetric and symmetric N—H stretching vibrations at 3446.0 and 3343.3 cm\(^{-1}\) as well as N—H bending vibrations at 1612.8 cm\(^{-1}\) are observed on the spectra. In terms of absorption peaks at 1683.8 and 1155.1 cm\(^{-1}\), they can be assigned as the stretching vibrations of C=O bond and C—N bond, respectively. As can be seen, the deformation vibration peaks of as-prepared precursor were extensively similar to urea, indicating that the surface of NTA were coated uniformly by urea, which was expected to be benefit to the nitrogen doping during its dehydration process. After thermal treated at 700°C for 4h in argon flowing, the characteristics of urea in the IR region have almost disappeared for the platinum and nitrogen co-doped Pt/TiO\(_2\)\(_x\)N\(_x\) samples. It seems that urea was completely decomposed and nitrogen doping was performed. The IR band at 2363.2 cm\(^{-1}\) is reported the characteristic of the stretching vibrations of N—H bond, which results from nitrogen doping\(^{[7]}\), while the presence of the IR band of 1384.8 cm\(^{-1}\) is an evidence of the absorbed molecular oxygen\(^{[7,8]}\).

The XRD patterns of NTA, as-prepared precursor and the Pt/TiO\(_2\)\(_x\)N\(_x\) samples are shown in Figure 2. The diffraction peaks at 2\(\theta\) of 9.0\(^{\circ}\), 24.6\(^{\circ}\), 27.5\(^{\circ}\), and 48.6\(^{\circ}\) (marked with triangle) are the characteristics of
NTA corresponding to (200), (110), (600), and (020) crystal planes, respectively, demonstrating that the NTA were presented in the form of orthorhombic system in terms of crystal structure. The as-prepared precursor exhibited mainly the characteristic diffraction peaks of urea indicating that the surface of NTA were well homogeneously wrapped by urea, which was in accordance with the FTIR results. After as-prepared precursor was annealed in argon flowing at 700°C for 4h, the Pt/TiO$_2$,$\text{N}_x$ samples are composed of anatase as the major phase and rutile as the minor phase, while the characteristic diffraction peaks of urea completely disappeared.

The optical absorption spectra of P25 and Pt/TiO$_2$,$\text{N}_x$ are given in Figure 3. On the one hand, P25 nanoparticles show a dramatic decrease between 320 and 380 nm, which is consistent with the well-known band gap of anatase TiO$_2$ bulk. Additionally, it has no absorbance for visible light due to the larger band gap. On the other hand, it can be seen that the absorption threshold of Pt/TiO$_2$,$\text{N}_x$ is slightly red-shifted as compared to that of sample P25, accompanied with significantly increased absorbance throughout the detected region. It can be clearly seen that a broad absorption bands in the range of 410 ~ 480nm appeared, which might be closely related to the intra-band contributed by the formation of oxygen vacancy (see ESR results below). In our previous studies, we further proved that the origin of visible light absorption of doped samples can be attributed to the existence of oxygen vacancies [6].

In order to analyze the chemical states of the prepared samples, XPS spectra were detected and the core levels of N 1s and Pt 4f of Pt/TiO$_2$,$\text{N}_x$ are shown in Figure 4a and b, respectively. As Figure 4a displayed, the chemical states of dopants nitrogen in the present paper should be composed of two structurally different nitrogen impurities: substitutional N atoms in the form of Ti–N bonds as well as interstitial N atoms in the form of Ti–O–N bonds corresponding to binding energy at 395.7 eV and 399.6 eV, respectively [9–11].
Figure 4b shows the Pt 4f XPS spectra of Pt/TiO$_2$$_x$N$_x$, which can be fitted by two coupling peaks corresponding to the binding energy of 70.5 ~ 73.9 eV and 71.7 ~75.7 eV, respectively. The former and dominant doublets would be associated to metallic Pt (0), while the later and subordinate doublets can be ascribed as oxidized Pt(II).

We have performed the ESR measurements of Pt/TiO$_2$$_x$N$_x$ as well as NTA and P25 at room temperature in air and the results are shown in Figure 5. No ESR signals were observed for NTA and P25, indicating that they are free of paramagnetic species. However, a single peak with $g = 2.004$, the characteristic of single-electron-trapped oxygen vacancies (denoted as SETOVs,$^6$,$^8$), was observed in the detected region of Pt/TiO$_2$$_x$N$_x$. A large amounts of SETOVs generated in TiO$_2$ matrix resulted in a new energy level below the conduction band, which played an important role on the origin of visible light absorption and photocatalytic activity.$^{12}$ Nakamura et al. prepared visible light active TiO$_2$ by hydrogen plasma treatment and found that the saturated intensity of the ESR signal at $g = 2.004$ (i.e., the concentration of SETOVs) was proportional to the removal percentage of nitrogen oxides.$^{13}$ They ascribed the visible light activity to the newly formed oxygen vacancy state between the valence and the conduction bands in the TiO$_2$ band structure. In our previous reports, the formation of SETOVs in TiO$_2$ matrix was suggested to result in visible light sensitization, while doped-N functions to prevent photoinduced electrons and holes from recombination, resulting in visible light photocatalytic activity.$^6$

Figure 6 shows the photodegradation of propylene over P25 and Pt/TiO$_2$$_x$N$_x$ samples as well as the CO$_2$ production as a function of irradiation time under visible light irradiation. It can be seen from Figure 6a that the concentration of propylene together with corresponding CO$_2$ production (see Figure 6b) almost unchanged over P25 under visible light irradiation or not, which can be inferred that P25 samples were inert toward visible light photocatalytic oxidation of propylene due to its larger band gap. In contrast, in the case of Pt/TiO$_2$$_x$N$_x$ samples, the concentration of propylene was dramatically decreased achieving to a constant value after several minutes when irradiated under visible light and the calculated photocatalytic activity was ca. 40%. Turn off the light, the concentration of propylene was gradually going back to the initial level. It can be inferred that propylene was indeed photocatalyzed over Pt/TiO$_2$$_x$N$_x$ samples under visible light irradiation. Noticing that 1 mole C$_3$H$_6$ should produce 3 moles CO$_2$ under
Figure 6. Visible light photodegradation of propylene over P25 and Pt/TiO$_2$-xN$_x$ as well as the CO$_2$ production as a function of irradiation time.

condition of complete oxidation, the CO$_2$ yield shown in Figure 6b indicated that only a part of propylene was mineralized but not completely. There may be some intermediate products were not detected by gas chromatograph and also may be the methanization of CO$_2$ was not complete on the reactor loaded with Ni catalyst.

Papers available on Pt and N co-doped TiO$_2$ indicated that N doping of TiO$_2$ resulted in the visible light sensitization, while metallic Pt on the surface of TiO$_2$ can enhance the separation of photogenerated charges \cite{2,3,14}. The extensive enhancement in photocatalytic activity was attributed to the synergistic effect between dopants N and Pt. In the presence of visible light irradiation, electrons are excited from valence band (VB) first to intra-band offered by SETOVs and then arrive at construction band (CB). On the one hand, the excited electrons on CB were transferred to dopants Pt and then captured by oxygen adsorbed on the surface of Pt, yielding superoxide anion radicals (i.e., O$_2^-$), which is capable of degrading organic compounds. On the other hand, dopants nitrogen played a role in preventing photoinduced electrons and holes from recombination by cutting off the route that the electrons jump back to valence band \cite{12}.

In conclusion, visible-light-active Pt/TiO$_2$-xN$_x$ photocatalyst has been successfully obtained by a facile method using NTA as precursor. The Pt/TiO$_2$-xN$_x$ sample displayed a better visible light photocatalytic oxidation of propylene than P25. The visible light sensitization can be attributed to the formation of SETOVs during doping process, while dopants nitrogen or platinum played an important role not only in improving visible light absorption but also in suppressing the recombination of photo-
generated electrons and holes. The higher visible light activity was proposed due to the synergistic effect between oxygen vacancies and dopants nitrogen as well as platinum.

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References
[1] Liu J. 2011. Enhanced Photoactivity of V−N codoped TiO$_2$ derived from a two-step hydrothermal procedure for the degradation of PCP under visible light irradiation. J. Phys. Chem. C 115:4507-4515.
[2] Hua N. 2005. Titanium dioxide nanoparticles codoped with Pt and N for photodegradation of Cl$_2$CCOOH. Acta Phys. -Chim. Sin. 21:1081-1085.
[3] Li D. 2008. A new route for degradation of volatile organic compounds under visible light: using the photocatalyst Pt/TiO$_2$-N$_x$ in H$_2$O$_2$ atmosphere. Environ. Sci. Technol 42:2130-2135.
[4] Yu J. 2006. Effects of calcination temperature on the microstructures and photocatalytic activity of titanate nanotubes. J. Mole. Catal.s A: Chem 249:135-142.
[5] Wang Y. 2006. A novel N-doped TiO$_2$ with high visible light photocatalytic activity. J. Mole. Catal.s A: Chem 260:1-3.
[6] Wang Y. 2010. Enhanced visible light photocatalytic activity of N-doped TiO$_2$ in relation to single-electron-trapped oxygen vacancy and doped-nitrogen. Appl. Catal. B: Environ 100:84-90.
[7] Kasuga T. 1998. Formation of titanium oxide nanotube. Langmuir 14:3160-3163.
[8] Sato S. 2005. Visible-light sensitization of TiO$_2$ photocatalysts by wet-method N doping. Appl. Catal. A: Gen 284:131-137.
[9] Saha N.C. 1992. Titanium nitride oxidation chemistry: An x-ray photoelectron spectroscopy study. J. Appl. Phys. 72:3072-3079.
[10] Spadavecchia F. 2010. Solar photoactivity of nano-N-TiO2 from tertiary amine: role of defects and paramagnetic species. Appl. Catal. B: Environ 96:314-322.
[11] Liu G. 2008. Electron field emission of a nitrogen-doped TiO$_2$ nanotube array. Nanotechnology 19:025606.
[12] Wang Y. 2011. Visible light active N-doped TiO$_2$ prepared from different precursors: Origin of the visible light absorption and photoactivity. Appl. Catal. B: Environ 104:268-274.
[13] Nakamura I. 2000. Role of oxygen vacancy in the plasma-treated TiO$_2$ photocatalyst with visible light activity for NO removal. J. Mole. Catal.s A: Chem 161:205-212.
[14] Huang L. 2007. Pt/N-codoped TiO$_2$ nanotubes and its photocatalytic activity under visible light. Appl. Surf. Sci. 253:7029-7035.