

# Mechanochemical Synthesis of Visible-light Induced Photocatalyst with Nitrogen and Carbon Doping

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**Abstract:** Nitrogen and/or carbon doped titania photocatalysts were prepared by a novel mechanochemical method. The prepared powders possessed two absorption edges around 400 and 540 nm wavelengths and showed excellent photocatalytic ability for nitrogen monoxide oxidation under visible light irradiation. Under the irradiation of visible light of wavelength >510 nm, 37% of nitrogen monoxide could be continuously removed by the carbon and nitrogen co-doped titania prepared by planetary ball milling of P-25 titania–10% hexamethylenetetramine mixture followed by calcination in air at 400 °C.

**Key words:** mechanochemical synthesis; titania photocatalyst; carbon and nitrogen doping; nitrogen monoxide; oxidation

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## 1 INTRODUCTION

Titania is the most effective photocatalyst and widely applied in purification of air and water, deodorization, antibacterial and self-cleaning coating, and other environmental applications<sup>[1–4]</sup>. However, titania can only be excited by UV light because of its large band gap value of ca. 3 eV. In photocatalyst research, anatase titania is usually considered to be more active than rutile crystalline phase<sup>[5,6]</sup>. Generally, the photocatalytic activities are strongly related to the crystallinity and the specific surface area of the photocatalyst<sup>[7,8]</sup>. In our recent research<sup>[9]</sup>, it was found that nanosize rutile particles with large specific surface area prepared by a low temperature dissolution-precipitation process at 60 °C showed higher photocatalytic activity than anatase particles. It is probably due to the smaller band gap of 3.0 eV, which results in better absorption of visible light. More efficient utilization of solar energy requires more smaller band gap formation in photocatalyst. Asahi et al.<sup>[10]</sup> reported that nitrogen doped titania with very high visible light photocatalytic activity could be prepared by heat treatment of titania in NH<sub>3</sub> (67%)–Ar atmosphere at 600 °C or sputtering TiO<sub>2</sub> target in an N<sub>2</sub> (40%)–Ar gas mixture followed by annealing in N<sub>2</sub> gas at 550 °C for 4 h. Recently, we firstly found that nitrogen doped titania particles with different phase compositions could be synthesized by soft solution process<sup>[12–14]</sup> and

mechanochemical technology<sup>[15]</sup>. In the present research, nitrogen and/or carbon doped titania was prepared by planetary milling of P-25 titania with ammonium carbonate, admantane, and hexamethylenetetramine. The effects of reaction conditions were investigated in detail. It is a low-temperature process for the synthesis of anion doped photocatalyst.

## 2 EXPERIMENTAL

Commercial titania powder P-25 (Degussa) was mixed with 10% (*w*) ammonium carbonate [(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, NHC], admantane (C<sub>10</sub>H<sub>12</sub>, ADM), and hexamethylenetetramine (C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>, HMT) before being introduced into a reaction vessel. A planetary ball mill (Fritsch P-7) was used for grinding of the samples. Seven zirconia balls of 15 mm diameter and 4 g of mixed powder were put in a zirconia vessel of 45 cm<sup>3</sup> inner volume. The grinding was operated at 700 r/min of rotation speed for desired time, followed by calcination in air at 400 °C for 1 h. The phase constitution of the product was determined by X-ray diffraction analysis (XRD) (Shimadzu XD-D1, Japan). The molar ratio of anatase to rutile was determined by the XRD peak intensity ratio according to Spurr and Myers's method<sup>[16]</sup>. The absorption edge and band gap energy of the products were determined from the onset of diffuse reflectance spectrum of the sample measured using a UV–VIS spectrophotometer (Shmadzu UV-2000, Japan). The photocatalytic activity for nitrogen

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monoxide oxidation was determined by measuring the concentration of NO gas at the outlet of the reactor ( $373 \text{ cm}^3$ ) during the photo-irradiation of constant flowing of  $1 \times 10^{-6}$  NO 50% ( $\varphi$ ) air mixed (with balance of  $\text{N}_2$ ) gas ( $200 \text{ cm}^3/\text{min}$ ). The photocatalyst sample was placed in a hollow place of  $20 \text{ mm} \times 15 \text{ mm} \times 0.5 \text{ mm}$  on a glass holder plate and set in the bottom center of the reactor. A 450 W high-pressure mercury lamp was used as the light source, where the light wavelength was controlled by selecting various filters, i.e., Pyrex glass for cutting off the light of wavelength  $< 290 \text{ nm}$ , Kenko L41 Super Pro (W) filter  $< 400 \text{ nm}$  and Fuji triacetyl cellulose filter  $< 510 \text{ nm}$ <sup>[9]</sup>. The amount of nitrogen doped in titania was determined by an oxygen–nitrogen analyzer (HORIBA EMGA-2800, Japan). The binding energy values of  $\text{N}_{1s}$  and  $\text{C}_{1s}$  were measured using an X-ray electron spectrometer (Pekin Elmer PHI5600, USA).

### 3 RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the starting P-25 powder and the titania powders prepared by mechanochemical doping. The P-25 powder contains anatase and rutile at a ratio of 77:23. The amount of rutile gradually increased with planetary milling, and a small amount of brookite was also formed. The vessel temperature increased, but did not exceed  $50^\circ\text{C}$  even after a prolonged milling. Considering that the anatase to rutile transformation temperature is generally higher than  $700^\circ\text{C}$ , the present results may indicate that the

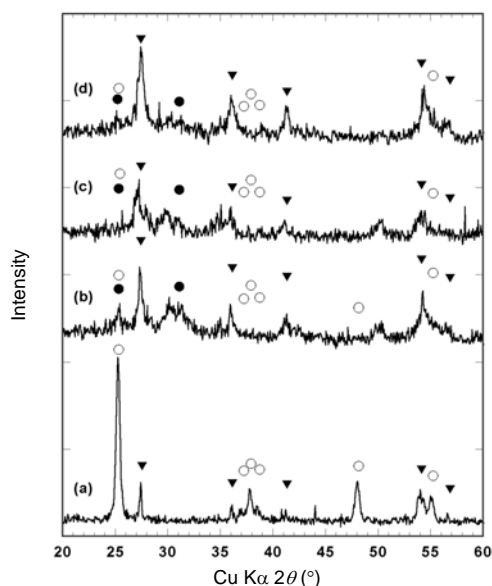


Fig.1 XRD patterns of P-25 titania (a) and the samples prepared by planetary ball milling of P-25 with 10% ( $\omega$ ) of  $(\text{NH}_4)_2\text{CO}_3$  (NHC) (b),  $\text{C}_{10}\text{H}_{12}$  (ADM) (c), and  $\text{C}_6\text{H}_{12}\text{N}_4$  (HMT) (d) at 700 r/m for 60 min [(O) anatase, (●) brookite, (▼) rutile]

high mechanical energy accelerated the phase transformation.

Figure 2 shows the diffuse reflectance spectra of the P-25 titania and the experimental products. The P-25 titania showed an absorption edge at 408 nm corresponding to the band energy gap of rutile (3.04 eV). The yellowish sample prepared with NHC showed two absorption edges at 400~408 nm (3.04~3.10 eV) and 530~550 nm (2.21~2.34 eV). The first edge is the same as that of the original titania, while the second edge seems to indicate the formation of a new  $\text{N}_{2p}$ -based band, which locates above the  $\text{O}_{2p}$ -based valence band<sup>[10,11]</sup>. In the case of using ADM as a reaction reagent, the prepared grayish powders showed good absorption up to the visible light range of 400~700 nm. In the case of using HMT as a reaction reagent, further absorption could be observed. Under the same mechanochemical conditions, the absorption ability in the visible light range increased slightly in the order of HMT>NHC>ADM. The band gap could be greatly narrowed by the present mechanochemical doping of titania with nitrogen and carbon.

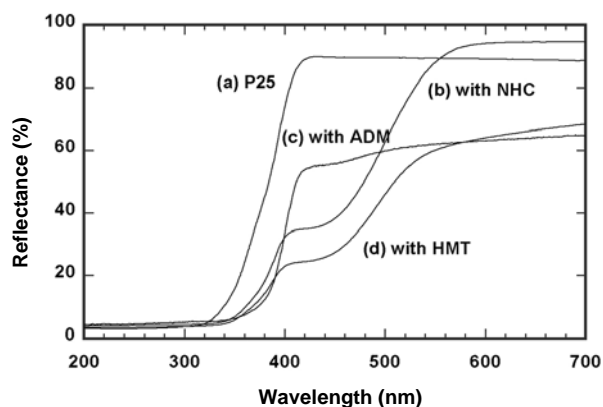


Fig.2 Diffuse reflectance spectra of P-25 titania (a) and the samples prepared by planetary ball milling of P-25 titania with 10% ( $\omega$ ) NHC (b), ADM (c), and HMT (d) at 700 r/min for 60 min, followed by calcination in air at  $400^\circ\text{C}$

Figure 3 shows the  $\text{N}_{1s}$  and  $\text{C}_{1s}$  spectra of P-25, and the products prepared by mechanochemical doping. No peaks of N–Ti and C–Ti bonding were observed in the commercial P-25 powder, indicating that no nitrogen or carbon was doped in the P-25 powder. The binding energy around 396 eV which is related to the existence of N–Ti was confirmed in the  $\text{TiO}_{2-x}\text{N}_y$  samples prepared by using NHC and HMT, indicating that Ti–N bonding was actually formed in the lattice of the titania crystal during the mechanochemical treatment. It was also found that the binding energy around 282 eV which is related to the existence of C–Ti was confirmed in the

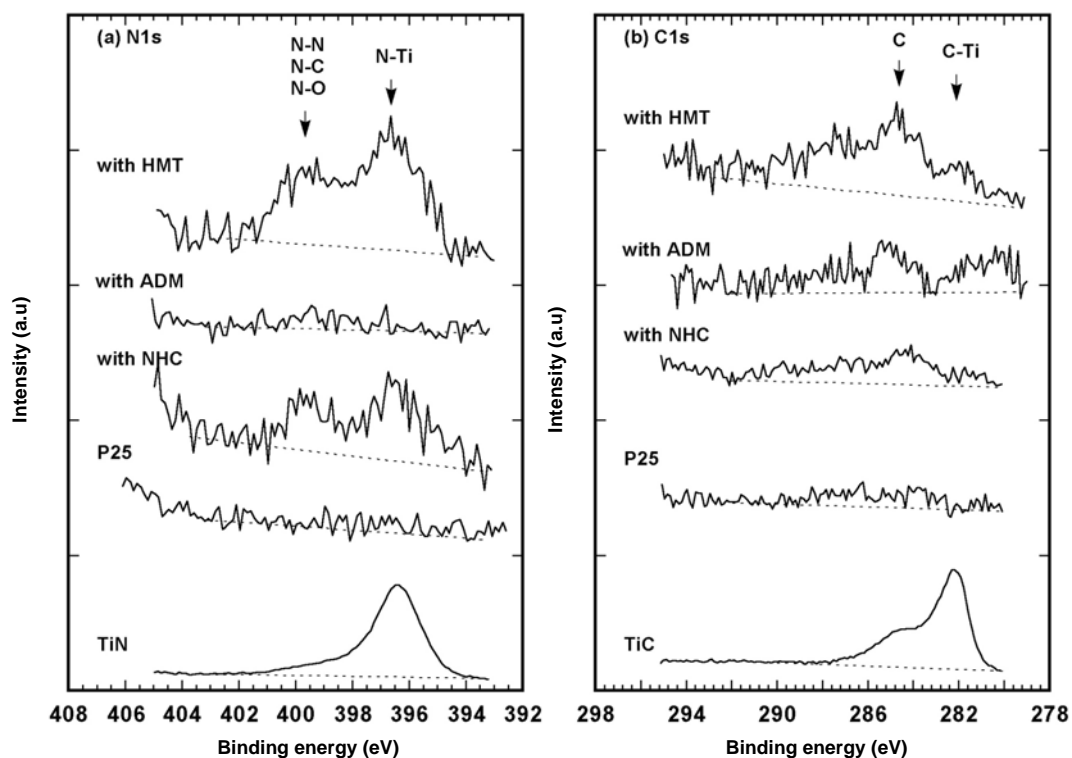


Fig.3 N<sub>1s</sub> (a), and C<sub>1s</sub> (b) XPS spectra of the commercial powder P-25, and the powders prepared by the planetary ball milling of P-25 with 10 % ( $\omega$ ) NHC, ADM, and HMT, followed by calcination in air at 400 °C (The measurement was carried out after Ar<sup>+</sup> ion sputtering for 3 min; for comparison, the spectra of TiN and TiC reagents were also recorded.)

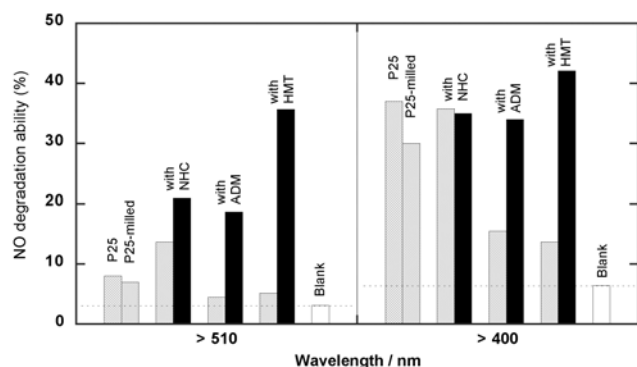


Fig.4 NO<sub>x</sub> degradation ability of the titania powders prepared by mechanochemical doping process using NHC, ADM and HMT as reaction reagents (Open dotted bars: the samples prepared by mechanochemical doping; solid bars: the samples calcined at 400 °C for 1 h. The photocatalytic activity was tested under light irradiation of  $\lambda > 510$  nm and  $\lambda > 400$  nm. For comparison, the results of P-25 before and after ball-milling were also plotted.)

titania samples prepared by using ADM and HMT. It is obvious that both nitrogen and carbon were doped in the lattice of the titania crystal during the mechanochemical treatment using HMT as a reaction reagent.

Figure 4 shows the relationship between the wavelength of light irradiated and the photocatalytic

ability for the oxidative destruction of nitrogen monoxide. It was found that the photocatalytic activity of P-25 decreased by ca. 10%~20% after the milling without any additive at 700 r/min. It may be due to the introduction of crystal defects or phase transformation from anatase to rutile. It is obvious that the nitrogen or carbon-doped titania prepared with NHC and ADM possessed relatively higher photocatalytic activities than that of non-doped titania under the visible light with wavelength  $> 510$  nm. The powder prepared with HMT showed about 2 times higher photocatalytic activity than that with NHC and ADM, i.e., nearly 37% of nitrogen monoxide could be continuously removed by the nitrogen/carbon co-doped titania prepared with 10% ( $\omega$ ) HMT mixture. The activity was ca. 6~7 times higher than that of P-25 as estimated taking the blank result into consideration. This result indicated that nitrogen and carbon co-doping played a multiplier effect on the improvement of visible light photocatalytic activity, agreeing well with the visible light absorption in Fig.2.

Figure 5 shows the dependence of the doped nitrogen amount, phase composition and photocatalytic activity on the milling time. It is obvious that the nitrogen content and rutile fraction increased with milling time. Not only in the visible light region, but

also in the UV-light region, the photocatalytic activity of the prepared sample increased at first with the planetary milling time up to 120 min and then decreased. The decrease after long time milling might be caused by the formation of crystalline defects during the excess planetary milling. It is thought that chemical reaction between titania and nitrogen source proceeds at the same time with phase transformation. It is known that mechanical stressing can make fresh oxygen-rich

surface exposed, on which electron transfer from the surface oxide ion to organic molecules can lead to strong bonding of nonmetallic elements of the organic origin to the oxide surface<sup>[17,18]</sup>. Considering that HMT possesses an adamantane-like structure and that the C–N bond is weaker than the C–O, H–N, and C–H bonds<sup>[19,20]</sup>, it may be supposed that the C–N bond is easily cut on the activated titania surface and nitrogen/carbon co-doped titania forms as a result.

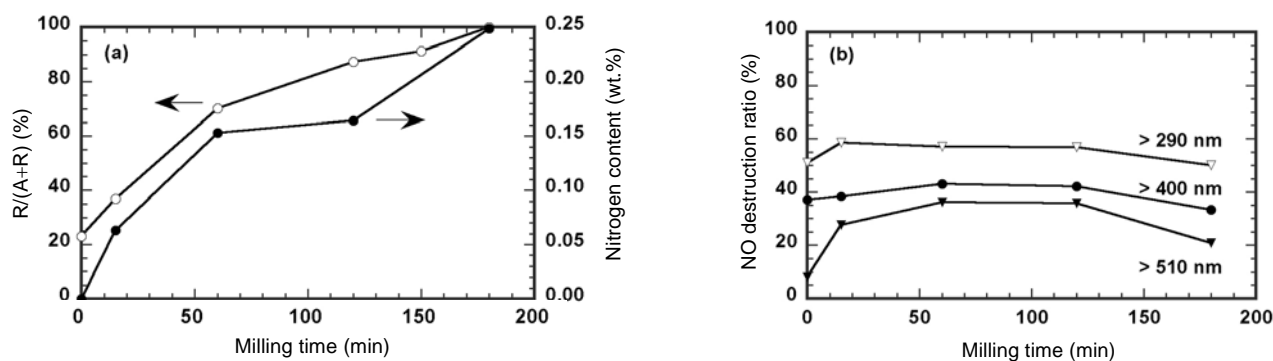


Fig.5 Effect of ball-milling time of P-25 titania with 10% ( $\omega$ ) HMT on nitrogen content and the mole fraction of rutile phase in titania powders (a), and photocatalytic  $\text{NO}_x$  degradation ability (b) under irradiation of light  $\lambda > 510$  nm,  $\lambda > 400$  nm and  $\lambda > 290$  nm

The present work shows that mechanochemically prepared nitrogen and/or carbon doped titania possesses excellent visible-light photocatalytic activities. This kind of mechanochemical treatment might be an effective method for doping oxides and other inorganic compounds with nonmetallic elements.

## 4 CONCLUSIONS

Based on the above results, the following conclusions may be drawn:

(1) Nitrogen and/or carbon doped titania powders were successfully prepared by the mechanochemical reactions of titania with various nitrogen and carbon sources at low temperature.

(2) The prolonging of planetary ball milling time accelerated the phase transformation of anatase to rutile and the increment of nitrogen doped amount, but also introduced lattice defects in the crystals.

(3) The nitrogen/carbon co-doped yellowish titania had two absorption edges at around 400–408 nm and 520–560 nm and showed excellent visible light-induced catalytic ability for the wavelength  $> 510$  nm.

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