

Synthesis of visible-light responsive nitrogen/carbon doped titania photocatalyst by mechanochemical doping

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Abstract Nitrogen and/or carbon doped titania photocatalysts $\text{TiO}_{2-x}\text{A}_y$ ($\text{A} = \text{N}, \text{C}$) were prepared by a novel mechanochemical method. The samples were prepared by a high-energy ball milling of P25 titania with different nitrogen/carbon sources such as hexamethylenetetramine, admantane or ammonium carbonate, followed by calcination in air at 400 °C. The high mechanical energy accelerated the phase transformation of anatase to rutile, while the existence of the chemical reagents tended to block the transformation. The prepared powders possessed two absorption edges around 400 and 540 nm 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 P25 titania–10% hexamethylenetetramine mixture followed by calcination in air at 400 °C. This mechanochemical technique might be widely useful for doping oxides with nonmetallic elements.

Introduction

Titania is the most effective photocatalyst and widely applied in purification of air and water, deodorization,

antibacterial and self-cleaning coating and other environment applications [1–4]. However, titania can only be encouraged by ultraviolet (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 [5, 6]. In order to utilize the solar energy efficiently for photocatalytic reactions, it is necessary to develop photocatalysts highly activated by visible rays. Generally, the photocatalytic activities strongly related to the crystallinity and the specific surface area of the photocatalyst [7, 8]. In our recent research [9], it was found that nanosize rutile particles with large specific surface area prepared by a low temperature dissolution–reprecipitation 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. [10] reported that nitrogen doped titania with very high visible light photocatalytic activity could be prepared by heat treatment of titania in NH_3 (67%)–Ar atmosphere at 600 °C or sputtering TiO_2 target in an N_2 (40%)–Ar gas mixture followed by annealing in N_2 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 [12–14] and mechanochemical technology [15]. In the present research, nitrogen and/or carbon doped titania was prepared by planetary milling of P25 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. The effects of reaction conditions

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on phase composition, particle size, microstructure, specific surface area and photocatalytic activity were investigated in detail.

Experimental section

Synthesis of photocatalyst

Commercial titania powder P25 (Degussa) was mixed with 10 wt.% ammonium carbonate ((NH₄)₂CO₃, NHC), adamantane (C₁₀H₁₂, ADM), and hexamethylenetetramine (C₆H₁₂N₄, HMT) (Kanto Chem, Japan) before being introduced into a reaction vessel. A planetary ball mill (Fritsch, P-7) was used for grinding. Seven zirconia balls of 15 mm in diameter and 4 g of the mixed powder were introduced to the zirconia vessel of 45 cm³ in inner volume. The grinding was operated at 100–700 rpm for desired durations. In order to remove the residual nitrogen reagent and organic byproducts in the final product, the samples were calcined at 400 °C for 1 h.

Analysis

The phase constitution of the products was determined by X-ray diffraction analysis (XRD) (Shimadzu, XD-D1). The molar ratio of anatase and rutile was determined from the XRD peak intensity ratio following Spurr and Myers's method [16]:

$$W_R = 1/(1 + 0.8(I_A/I_R)) \quad (1)$$

$$W_A = 1 - W_R \quad (2)$$

where W_A and W_R are the mole fractions of anatase and rutile, respectively, and I_A and I_R are the peak intensities of anatase (101) and rutile (110).

The absorption edge and the band gap of the products were determined from the onset of the diffuse reflectance spectrum measured using an UV–VIS spectrophotometer (Shimadzu, UV-2000). The particle size distribution was measured with a laser diffraction particle size analyzer (Shimadzu, SALD-7000). The photocatalytic activity for nitrogen monoxide oxidation was determined by measuring the concentration of NO at the outlet of a reactor of 373 cm³ in volume through which a 1:1 mixed gas of air and nitrogen containing 1 ppm of NO was flown at 200 cm³ min⁻¹ under photo-irradiation. The sample was spread to 20 × 15 × 0.5 mm³ on a glass plate and was placed at 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 using filters such as Pyrex glass, Kenko L41 Super Pro (W) filter, and Fuji, triacetyl cellulose filter for cutting off the light of <290 nm, <400 nm, and <510 nm, respectively [9]. The amount of nitrogen in titania was determined by an oxygen–nitrogen analyzer (HORIBA, EMGA-2800). The sensitivity of this measurement was about 0.1 ppm. The binding energy of N 1s was measured using an X-ray electron spectrometer (Pekin Elmer PHI5600).

Results and discussion

Phase transformation

Figure 1a–d show the XRD patterns of the starting P25 powder and the experimental products from the mixture with 10 wt.% of (NH₄)₂CO₃ milled at 700 rpm for different periods. The P25 powder contains anatase and rutile at a ratio of 77:23. The amount of rutile gradually increased with milling time, and also a small amount of brookite was formed. The vessel temperature increased but did not exceed 50 °C even after a prolonged milling. Considering that the anatase to rutile transformation temperature is generally much higher than 700 °C, the present results may be taken as indicating that the high mechanical energy accelerated the phase transformation. Similar results were observed for the cases of ADM and HMT also (see Fig. 1f, g).

Figure 2 shows the rutile fraction in some products, $R/(A + R)$, where the presence of a very small amount of brookite was disregarded. It is clear that the fraction increased with milling time and milling speed, but decreased with increasing amount of the nitrogen source. Single phase rutile could be obtained at low nitrogen source contents. The nitrogen source reagent seems to have eased the mechanical stress on the titania powder. The effect of (NH₄)₂CO₃ was slightly stronger than those of HMT. We think that chemical reactions between titania and nitrogen source proceeds at the same time with phase transformation. All the samples, except for single phase rutile, showed yellowish color, indicating the formation of nitrogen-doped titania during the planetary milling.

Optical properties of the TiO_{2-x}A_y (A = N, C)

Compared in Fig. 3 are the diffuse reflectance spectra of the P25 titania and the experimental products. The absorption edge of the sample was determined by the following equation

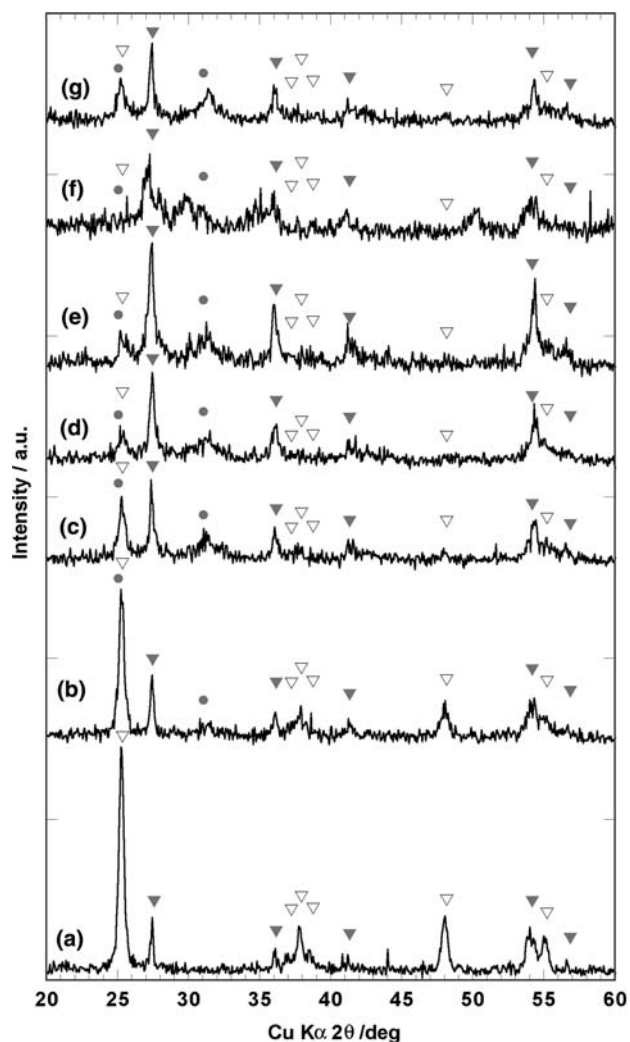


Fig. 1 XRD patterns of (a) P25 titania and the samples prepared from P25 mixed with 10 wt.% of $(\text{NH}_4)_2\text{CO}_3$ milled for (b) 15 min, (c) 60 min, (d) 120 min, (e) 180 min, and from P25 mixed with (f) 10 wt.% of ADM, (g) 10 wt.% of HMT milled for 60 min at 700 rpm. All the samples were calcined in air at 400 °C for 60 min after milling. (V) anatase, (●) brookite, (▼) rutile

$$E_g = 1239.8/\lambda \quad (3)$$

where E_g is the band gap (eV) of the sample and λ (nm) is the wavelength of the onset of the spectrum. The P25 titania showed an absorption edge at 408 nm corresponding to the band gap of 3.04 eV (Fig. 3a). The yellowish samples, however, showed two absorption edges at 400–408 nm [3.04–3.10 eV] and 530–550 nm [2.21–2.34 eV] (Fig. 3b–d), although the second absorption of (c) was not clear enough. The first edge is the same as for the original titania, while the second edge seems to indicate the formation of Ti–N and Ti–C bands which are located above the O2p-based valence

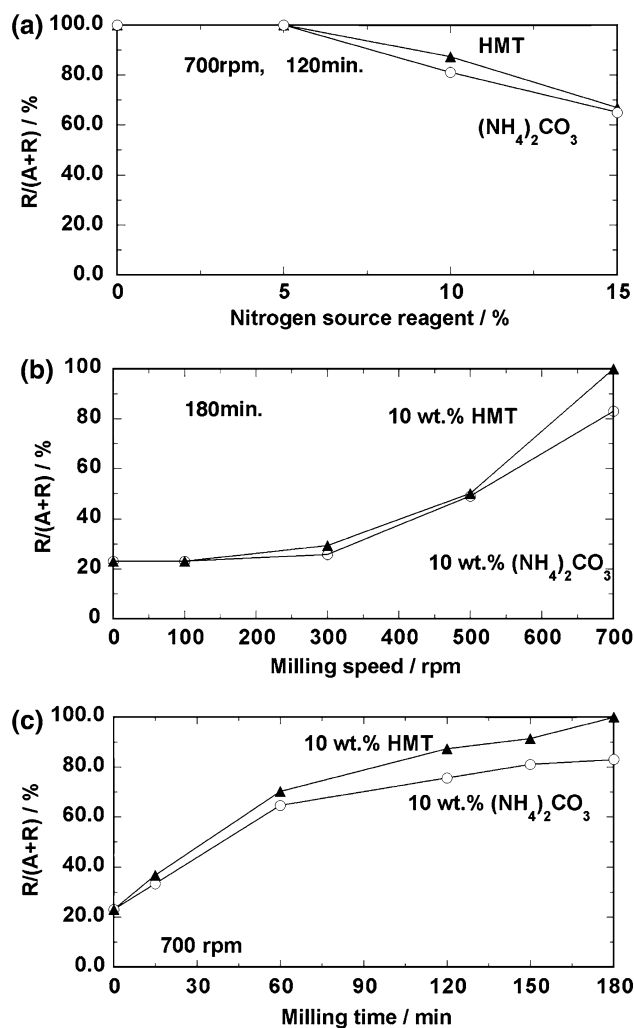


Fig. 2 Effects of (a) milling time, (b) milling speed, and (c) amount of nitrogen source on the mole fraction of rutile in the products from P25 titania mixed with HMT and $(\text{NH}_4)_2\text{CO}_3$

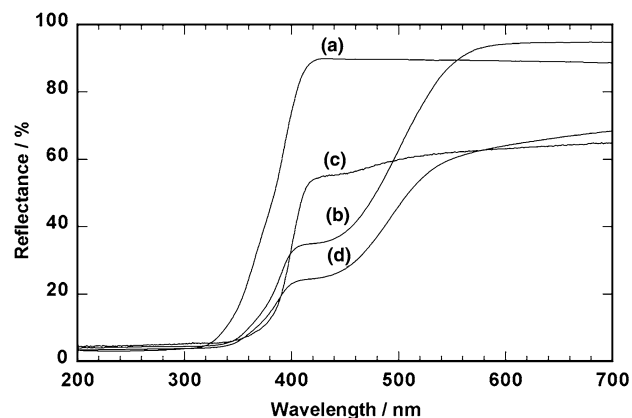


Fig. 3 Diffuse reflectance spectra of (a) P25 titania and the samples prepared by planetary ball milling from mixtures of P25 titania with 10 wt.% of (b) $(\text{NH}_4)_2\text{CO}_3$, (c) ADM and (d) HMT at 700 rpm for 60 min, followed by calcination in air at 400 °C for 60 min

band [10, 11]. The band gap could be greatly narrowed by the present mechanochemical doping of titania with nitrogen. With increasing mechanochemical stress, red shift and band gap narrowing were observed. Under the same mechanochemical conditions (700 rpm, 60 min), the powders possessed absorption ability in order of $\text{HMT} > (\text{NH}_4)_2\text{CO}_3 > \text{ADM}$ in the visible light range. It was also found that nitrogen content increased with milling time and milling speed, although the result was not showed here.

Agglomeration and surface state of the $\text{TiO}_{2-x}\text{A}_y$ (A = N, C)

Figure 4 shows the particle size distribution of the P25 powder before and after the planetary ball milling at 700 rpm for 60 min. The values of medium diameter, 50% D, of titania powders were also indicated in the Fig. 4. The original P25 powder was well-defined particles of 20–40 nm in diameter. The agglomeration of the particles proceeded, indicating fresh surfaces exposed by the milling lowers their high surface energy by agglomeration. The particle size distribution analysis indicated that P25 as received possessed a medium diameter (50% D) of around 0.023 μm . After the milling without any additive, the peak of 50% D shifted to around 0.074 μm , indicating that the particle agglomeration was promoted by the mechanochemical treatment. Similarly, in the case of milling with 10 wt.% nitrogen/carbon reagents mixed, the 50% D values changed to about 0.056–0.075 μm .

Figure 5 shows the N 1s and C 1s spectra of P25, and the $\text{TiO}_{2-x}\text{A}_y$ (A = N, C) products prepared by mechanochemical doping. No peak of N–Ti and C–Ti

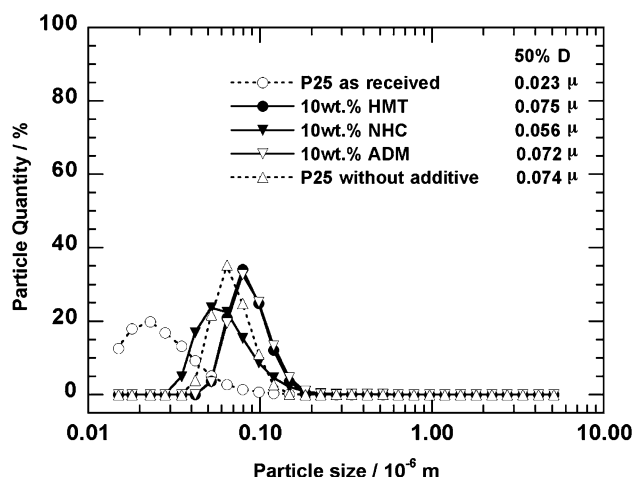


Fig. 4 Particle size distribution and the medium diameter, 50%D, of titania powders prepared by planetary ball milling at 700 rpm for 60 min with or without 10 wt.% additives

bonding was observed in the commercial P25 powders, indicating that no nitrogen or carbon was doped in the P25 powders. The binding energy around 396 eV which 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 binding was actually formed in the lattice of the titania crystal during the mechanochemical treatment. It is known that the peak around 400 eV is related to the N–N, N–O or N–C binding, and that around 402 eV is related to the N–H binding [10, 11]. According to the integral intensity of the peaks around 396 and 400 eV, it could be calculated that about 63% and 58% of the nitrogen consisted in the samples were really incorporated into the TiO_2 lattices (peak at 396 eV) by using HMT and $(\text{NH}_4)_2\text{CO}_3$. It was also found that the binding energy around 282 eV which related to the existence of C–Ti was confirmed in the titania samples prepared by using ADM and HMT. It is obvious that both nitrogen and carbon was co-doped in the lattice of the titania crystal during the mechanochemical treatment using HMT as a reaction reagent.

Photocatalytic activity for NO destruction

Figure 6 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 P25 decreased by ca. 10–20% after the milling without any additive at 700 rpm. It may be due to the introduction of crystal defects or the 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 of >510 nm. The powders prepared with HMT showed about two 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 wt.% HMT mixture. The activity was ca. 6–7 times higher than that of P25 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, which agreed well with the visible light absorption result of Figs. 3 and 5. For the wavelength of >400 nm similar results were observed, although the difference among the samples were not so clear. It was also obvious that the photocatalytic activity of the prepared sample increased with milling time up to 120 min at first and then decreased a little.

Fig. 5 (a) C1s, and (b) N1s XPS spectra of the commercial powder P25, and the powders prepared by the planetary ball milling of P25 with 10 wt.% NHC, ADM, and HMT, followed by calcination in air at 400 °C. The measurement was carried out after Ar⁺ ions sputtering for 3 min

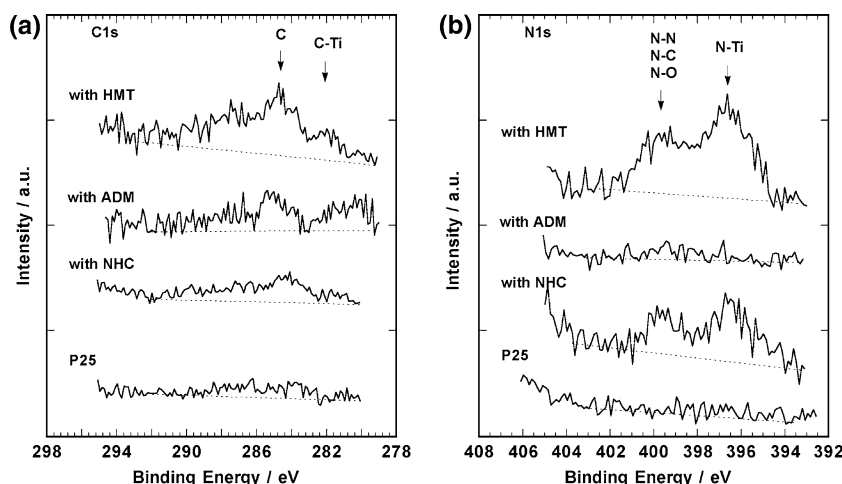
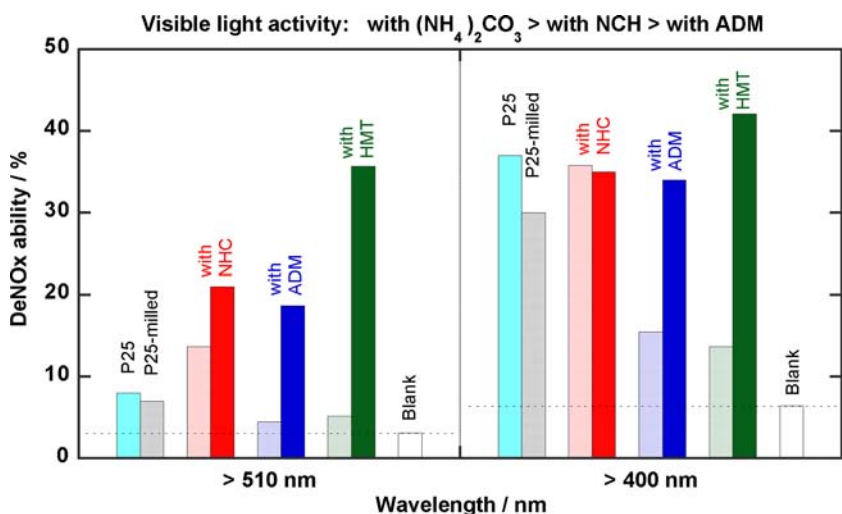


Fig. 6 DeNO_x ability of the titania powders prepared by mechanochemical doping process using NHC, ADM, and HMT as reaction reagents. Open dotted bars: as prepared by mechanochemical doping; Solid bars: calcined at 400 °C for 1 h. The photocatalytic activity is carried out under light irradiation of λ > 510 nm and 400 nm. For comparison, the results of P25 before and after ball-milling are also plotted



The decrease after long time milling might be caused by the formation of crystal defects during the excess planetary milling. It is thought that chemical reaction between titania and nitrogen/carbon 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 [17, 18]. 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 [19, 20], 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.

Figure 7 shows the relationship between the nitrogen content and the photocatalytic activity. The nitrogen amount doped in TiO_{2-x}A_y could be realized by

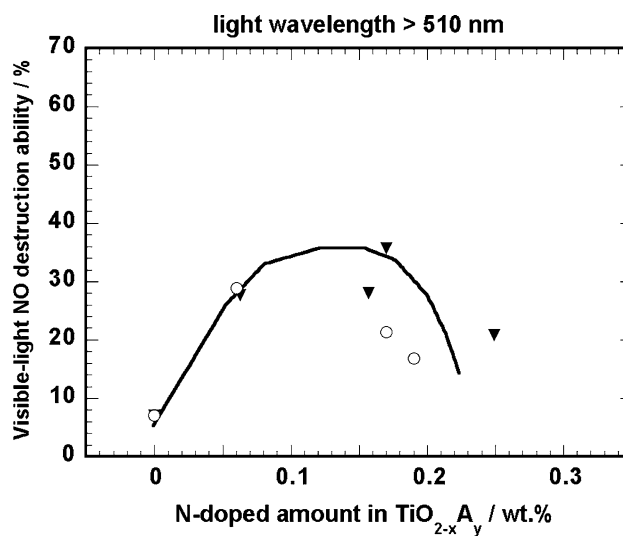


Fig. 7 Relationship between the nitrogen content and the visible-light photocatalytic activity for the wavelength of >510 nm. The samples were prepared by mechanochemical reactions of titania with (▼) HMT, and (○) (NH₄)₂CO₃

changing the preparation conditions such as milling time, milling speed and using various amount of nitrogen additives. It is clear that 0.15–0.17 wt.% of nitrogen is good for the activity for the range of $\lambda > 510$ nm. The decrease of activity for higher nitrogen contents might be caused by the increase of oxygen defects resulting from excessive mechanochemical treatments.

The present work showed 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.

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/carbon sources at low temperature.
- (2) The prolong 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 possessed two absorption edges at around 400–408 nm and 520–560 nm and showed excellent visible light-induced catalytic ability for the wavelength of >510 nm.

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