

Recovery of visible-light photocatalytic efficiency of N-doped TiO₂ nanoparticulate films

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Abstract

Bare TiO₂ and N-doped TiO₂ nanoparticulate films in anatase phase were prepared on glass substrates by laser ablation of titanium target in O₂, N₂/O₂ and NH₃/N₂/O₂ atmospheres, respectively. The nitrogen dopant concentration increased notably when a small amount of NH₃ was added into the N₂/O₂ mixture. The film prepared in NH₃/N₂/O₂ exhibited enhanced photoabsorption and photocatalytic ability in the visible-light region as compared with that produced in N₂/O₂. However, for all films, rapid deactivations were observed with operating time, leading to a poor reusability of the catalysts. With a simple and effective approach of mild heat treatment, the photocatalytic efficiency was completely recovered and the reusability of the film was greatly improved.

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1. Introduction

Due to the ongoing serious pollution problems and the shortage of energy sources, photoinduced oxidation and reduction reactions at the surface of titanium dioxides (TiO₂) particles or thin films have been attracting much attention in view of their possible applications for solar energy conversion as well as environmental cleaning [1–4]. TiO₂ has a high oxidation power under ultraviolet (UV) illumination and it is chemically stable, nontoxic, and relatively inexpensive. However, how to effectively utilize sunlight as the light source for photocatalysis is one of the challenges for the wide application of TiO₂. TiO₂ with its absorption edge below 380 nm has photoactivity only under UV light [2], while UV light possesses only a small fraction (about 8%) of the solar energy. So, shift in the optical absorption of TiO₂ from UV to the visible will impose a profound positive effect on enhancing the photocatalytic efficiency of the material using sunlight as the energy source [2].

So far, great efforts have been made to prepare N-doped TiO₂ films by using a variety of approaches [5–7]. Mostly,

the doped nitrogen concentrations were below 2%, and the visible-light photocatalytic efficiencies were not high enough. Moreover, the photocatalytic deactivation was often observed for TiO₂ films [8–11], as well as TiO₂ powders [12,13]. The deactivation with operating time was thought to result from the coverage of the surface active sites by the photocatalytic reaction intermediates. The deactivation will result in a poor reusability, which is unfavorable to the practical applications. Because of their porous surfaces, the nanoparticulate films may exhibit higher deactivation rates although the nanostructured surface has advantages for the catalytic reactions. Hence, along with the efforts to improve the photocatalytic efficiency, the recovery of photocatalytic ability is also crucial for TiO₂ to have higher commercial potentials. Although, a few studies were conducted for the regeneration of TiO₂ powders as a photocatalyst [12,14], the methods were proved to be quite impractical and expensive for many instances. However, very few experimental evidences have been reported on the regeneration of N-doped TiO₂ films. In this work, the bare TiO₂ and N-doped TiO₂ nanoparticulate films were prepared by pulsed laser deposition (PLD). The as-deposited films were characterized by atomic force microscope (AFM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and ultraviolet-visible (UV–vis) absorption spectroscopy, respectively. The photocatalytic activities of the produced films

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in the UV and visible region were studied by measuring the decomposition rate of methylene blue (MB) in aqueous solutions. Photocatalytic deactivation was observed for the produced films. The approach to recover the photocatalysis efficiency was explored.

2. Experimental

The details of the preparation of TiO₂ films were described in our previous paper [15]. Briefly, the TiO₂ and N-doped TiO₂ films were grown on glass (1 cm × 1 cm) by laser ablation of a rotating titanium rod in the atmospheres of different gas mixtures. The output beam of a frequency doubled Nd:YAG laser at 10 Hz was focused onto the titanium target surface with a fluence fixed at 4.8 J/cm² and the substrate was placed 3 cm from the target surface. Three films were prepared in the gaseous atmospheres of O₂, N₂/O₂ (19/1) and N₂/NH₃/O₂ (17/2/1) mixtures, respectively, with a total pressure of 27 Pa and denoted as samples A–C.

The surface morphology was examined by AFM (PSIA XE-100). The film thickness was measured with a surface profiler (Zygo NV200HR). The crystalline structures of the films were determined by Raman spectroscopy (LABRAM-1B). The surface composition and bonding configurations were decided by XPS (PHI 5000C ESCA). The UV–vis absorption spectra of the films were acquired with a spectrophotometer (Shimadzu Uv3101pc).

The photocatalytic activities of the samples were evaluated by measuring the changes of the absorbance of an MB solution at 654 nm during the photocatalytic decomposition. Each of the films was placed in a quartz cuvette filled with an aqueous MB solution (2 ml) at a concentration of 0.03 mmol/l. A UV lamp (320–400 nm, centered at 360 nm, 0.1 mW/cm²) was used as the UV light source. Since MB has an absorption band from 500 to 720 nm, a 405 nm semiconductor laser (Coherent, Radius 405) with an output of 15 mW was used as the visible-light source to avoid the direct photolysis of MB. The UV- or visible-light was guided onto the film surface in the solution. The photocatalytic activity was evaluated by comparing the intensities of the absorption spectra of the MB solution with and without the photocatalyst after illumination.

The recovery of the photocatalytic efficiency was evaluated by the following procedure. The film in a MB solution was irradiated with visible- or UV-light for 24 h as one use. After each use, the film was immersed in deionized water for 15 min and then heated at 80 °C for 1 h under nitrogen flow or argon flow. After the treatment, the photocatalytic ability was measured again.

3. Results and discussion

The acquired AFM images and Raman spectra of the produced films are similar to that obtained in our previous work [15]. AFM images show that the three films have the similar uniform structure in the surface composed of round particles of 10–30 nm in diameter. They have a similar thickness of about 0.8 μm as measured by a surface profiler. It was proved that the morphology of the produced film was mainly dependent on the

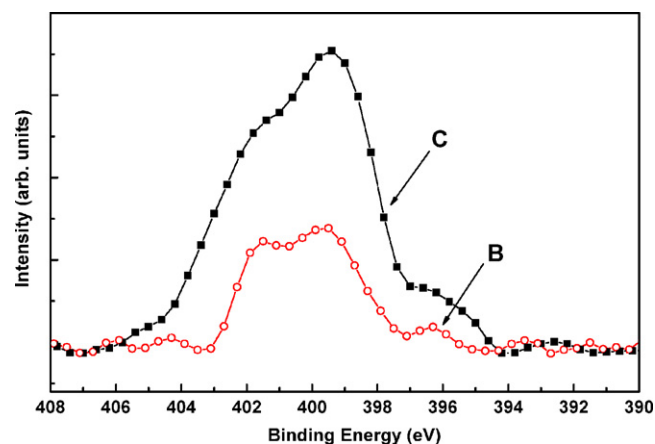


Fig. 1. N 1s XPS spectra of B and C.

total gas pressure, laser fluence and the distance between the target and substrate. The Raman spectra showed that all the three films were in the anatase phase. No other phases such as rutile or TiN were detected, indicating that the doping of nitrogen in this work did not change the crystalline structure.

When measuring the XPS, no N signal was detected for sample A as expected. Fig. 1 shows the high resolution N 1s XPS spectra measured from B and C. The nitrogen dopant concentrations were estimated to be about 2.0% and 4.9% for B and C, respectively, according to the XPS data. They were in some extent overestimated due to the existence of the molecularly chemisorbed γ -N₂. The nitrogen concentration in C was much higher (more than doubled) than that in B although the quantity of N element in the NH₃/N₂/O₂ (2/17/1) mixture was less than that in the N₂/O₂ (19/1) mixture at the same total pressure. The explanation can be found in our previous work that the dissociation of N₂ is enhanced when adding a small amount of ammonia into nitrogen gas [16]. This implies that the atomic nitrogen rather than the molecular nitrogen is possibly easier to be doped into the TiO₂ matrix.

With careful inspections, a three-peak structure at binding energies of 401.6, 399.6, and 396.3 eV was observed in the N 1s spectra for both B and C. However, the nitrogen states in the doped TiO₂ are complicated and the assignments of the N 1s peaks are still under debate. In most cases, the N 1s feature with a binding energy of 396.3 eV was assigned as the substitutional incorporation of nitrogen into the TiO₂ lattice [2,6,17–19]. Other N 1s peaks at higher binding energies in the range of 399–402 eV were observed by several groups [6,19–24]. Saha and Tompkins [25] and Asahi et al. [2] assigned the two peaks at 400 and 402 eV to the molecularly chemisorbed γ -N₂. Suda et al. [6] and Miao et al. [19] attributed the peak at 400 eV to the N–O and N–N bondings. Chen and Burda [23] observed a peak centered at 401.3 eV and Jang et al. [20] observed a peak at 401.5 eV for their N-doped TiO₂ nanoparticles. They both attributed it to the formation of O–Ti–N in the TiO₂ lattice. Di Valentine et al. [21] observed a peak at about 400 eV experimentally and their theoretical calculation results revealed that the interstitial configuration had a higher core level binding energy than the substitutional configuration and the peak was probably at >399 eV. In another

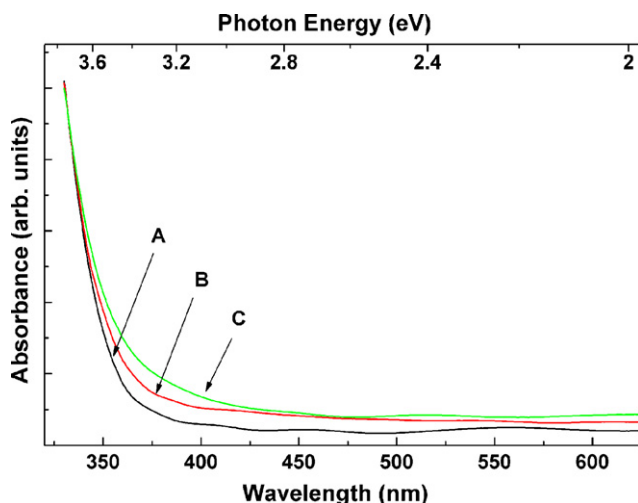


Fig. 2. UV–vis absorption spectra of A, B and C.

study, where NH_3 flow was used for nitrogen doping, the peak at 399.6 eV was assigned to the N–H bonding and interstitial doping into the lattice [17].

In the present work, the broad peak at 399.6 eV could be possibly attributed to both the molecularly chemisorbed $\gamma\text{-N}_2$ and the interstitial nitrogen. And for sample C, the film prepared with NH_3 , this peak could also be assigned to the N–H bonding if hydrogen was incorporated into the film. Although H element cannot be measured by XPS, strong H lines were observed in the emission spectra of the ablation plume as demonstrated in our previous work [15]. Therefore, codoping of nitrogen and hydrogen was possible when NH_3 was used.

The ultimate aim for producing a photocatalyst is its ability for photocatalytic reaction. The doping effects on the visible-light photoactivity were studied in this work. Shown in Fig. 2 are the UV–vis absorption spectra of samples A–C. With respect to the undoped film (A), the photoabsorptions of N-doped films (B and C) were enhanced in the visible-light region.

The photocatalytic ability was evaluated by comparing the absorbances of the MB solution with and without the photocatalyst after illumination. A photograph of four aqueous MB solutions (with samples A–C, and without any photocatalyst) after illumination at 405 nm for 24 h is demonstrated in Fig. 3 as a visual example to show the changes of their colors. The lighter color corresponds to the more decompositions of MB. Noticeable differences can be seen in the photograph for different samples, where C shows the most effective decomposition of MB.

A quantitative comparison of their photocatalytic efficiencies is shown in Fig. 4. The curves were obtained by measuring the absorbance of MB solutions at different moment within 24 h. The lower absorbance corresponds to the more decompositions of MB. As an example, a time evolution of the absorption spectra of the MB solution with sample C under illumination at 405 nm is shown as an inset in Fig. 4b. MB solutions without any photocatalyst were also illuminated under UV and at 405 nm, respectively, as demonstrated in Fig. 4a and b. No significant absorbance changes were detected, indicating that the

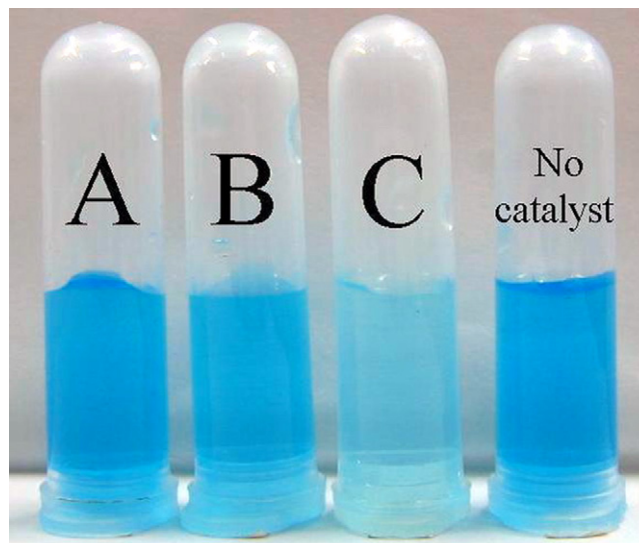


Fig. 3. Photograph of the aqueous MB solutions with photocatalysts A, B and C, as well as the one without any catalyst after an illumination at 405 nm for 24 h.

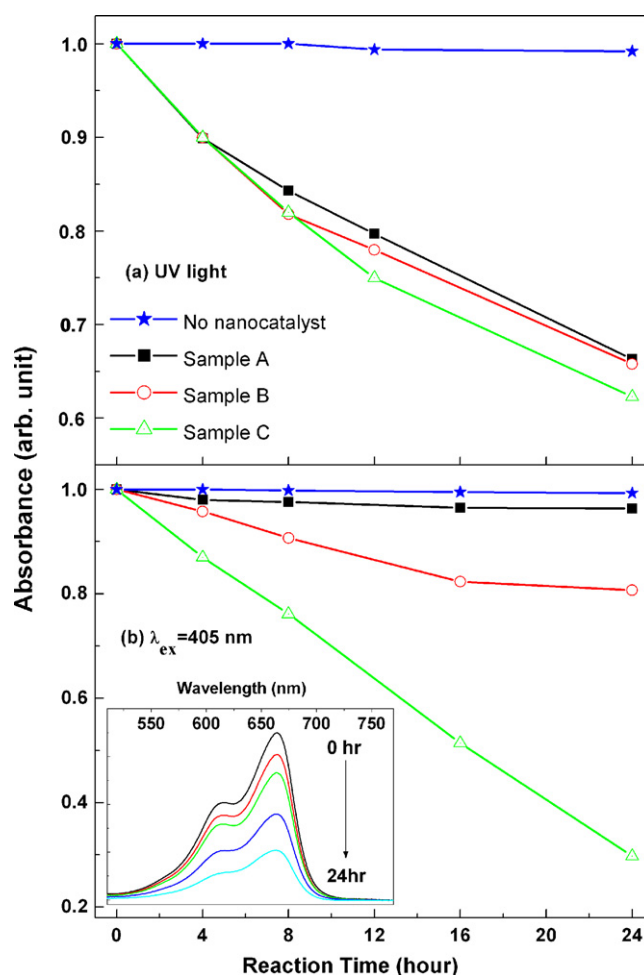


Fig. 4. Photocatalytic decomposition of MB in aqueous solution under UV (a) and 405 nm (b) irradiations as monitored by the decrease in absorbance.

direct photolysis of MB (without any photocatalyst) could be ruled out. Therefore, the absorbance change must be completely originated from the photocatalytic decomposition. As expected, the three samples exhibited almost the same photocatalytic ability under UV illumination (Fig. 4a). However, the situation was entirely different when visible-light was applied as depicted in Fig. 4b. Under the illumination at 405 nm, C exhibited the highest photocatalytic efficiency, while A exhibited no meaningful photocatalytic effect, indicating that doping of nitrogen could greatly promote the photocatalytic efficiency in the visible region.

Note that the photocatalytic efficiency of C is estimated to be about 3.5 times higher than that of B. The stronger absorption of sample C at this wavelength must be an important reason, but when comparing the absorption intensities at 405 nm between sample B and C, the difference is far less than that between the decomposition efficiencies. The photocatalytic activity is determined by the light absorption ability and the quantum efficiency of catalytic reaction. Modification of TiO₂ films with nitrogen would result in the enhancement of the absorption in the visible region as shown in Fig. 2 and therefore promote the visible-light photocatalytic activity. On the other hand, larger surface area and higher crystallization degree of anatase phase would enhance the quantum efficiency of photocatalysis, but these factors could be ruled out in this work since the produced films had the similar particle size distributions and similar crystallization degrees. However, it should be noted that the N atoms in the N-doped TiO₂ are electron deficient, which could serve as an electron trap to inhibit the recombination between photoinduced electrons and holes, thus increase the quantum efficiency of catalytic reaction [26]. And when the film is prepared with NH₃, such as sample C, the formation of surface OH is possible and the OH species might serve as the source for producing photoinduced hydroxyl radicals (\bullet OH) [26], which have strong oxidative decomposing power, and would lead to higher photocatalytic quantum efficiency. Therefore, the incorporation of hydrogen could not only enhance the absorption of visible-light but also promote the photocatalytic quantum efficiency. In fact, many N-doped TiO₂ materials, which showed remarkable improvement in the visible-light photocatalysis, were processed or produced with NH₃ [2,17,18] or H₂ [19]. However, to well understand the mechanism, more experiments and theoretical calculations should be conducted to provide further evidences.

In normal cases, the photocatalytic efficiency of TiO₂ nanoparticulate films reduced with the operating time. The poor reusability resulted from deactivation is a common problem for the photocatalysts to have high commercial potentials. As shown in Fig. 5a, the photocatalytic ability of C declined gradually under 405 nm irradiation and was entirely lost after it was used for four times (24 h each time). Similar situation was found under UV illuminations and for samples A and B as well.

To improve the reusability, an approach of mild heat treatment as described in the experimental section was employed for the regeneration of the deactivated films. Fig. 5b shows the recovery of the photocatalytic ability for sample C where the mild heat treatment under the atmosphere of flowing nitrogen was applied after each use (illumination for 24 h as one use). As shown in

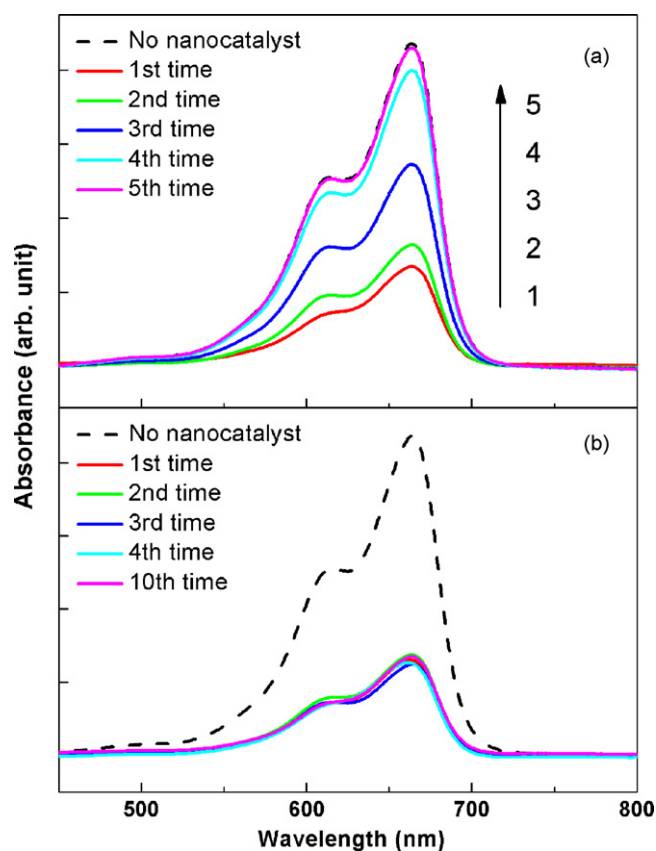


Fig. 5. Absorption spectra of the MB solution with C to show the deactivation of the film (a) and the recovery of the photocatalytic ability (b). The spectrum of the solution without any catalyst (dotted line) is also displayed as a comparison. The spectra in (b) were detected for different times of use. The film was mild heat treated after each use.

the figure, the photocatalytic ability was completely recovered with each treatment. The photocatalytic efficiency kept at the same level even in the tenth time of use. Similar results were obtained for the other two samples under either UV- or visible-light illumination, indicating that this simple and inexpensive method can be applied widely. When the deactivated films were regenerated under argon flow instead of nitrogen flow, similar results were obtained. This means that the recovery was not due to the nitrogenation of the film surface. In fact, such a low treatment temperature of 80 °C could not cause any significant nitrogenation of the films.

The mechanism for the recovery of the photocatalytic ability in this work is not yet well understood. Photocatalysis is based on the reactive properties of an electron-hole pair generated in TiO₂. Under illumination, electrons are excited to the conduction band. Both the hole in valence band and the electron in conduction band migrate to the catalyst surface. When adsorbed water or the TiO₂ surface active OH \bullet group is oxidized by the valence band holes, active hydroxyl radicals (\bullet OH) are formed [27]. Then, the organic matter will be attacked by these active hydroxyl radicals and generate organic radicals or some other intermediates. Meanwhile, the photogenerated electrons in the conduction band are trapped by the dissolved oxygen to form superoxide ions (\bullet O₂⁻), which attach to the intermediate prod-

ucts in the oxidative reaction, forming peroxides or changing to hydrogen peroxides and then to water.

The photocatalyst deactivation was thought to result from the accumulation of the reaction intermediates or by-products on the TiO₂ surface [8–13]. Toluene was sometimes selected as an organic substance that has aromatic rings to test the photocatalytic ability of the TiO₂ films. Irokawa et al. reported that the oxalic acid, acetic acid, formic acid, and pyruvic acid were found on the N-doped TiO₂ surface during the decomposition of toluene [28]. Blount and Falconer suggested that the deactivation observed in their experiment was caused by the accumulation of less-active intermediates such as methylcyclohexane (MCH), benzaldehyde, ethylene and methane on the catalyst surface, while these intermediates would desorb from the TiO₂ surface at high temperatures [8]. Cao et al. explained that the severe deactivation of TiO₂ catalysts observed was due to the accumulation of partially oxidized intermediates from toluene, such as benzaldehyde and benzoic acid, on the active sites of the TiO₂ surface [9]. They found that the deactivated catalysts could be regenerated by burning out the chemisorbed carbon species in air. Complete recovery of catalytic activity occurred only when the regeneration temperature was at or above 420 °C.

During the photocatalytic decomposition of MB, some *N*-demethylated intermediates such as Azure B, Azure A, Azure C or thionine were formed [29]. As elucidated by Lachheb et al. [30], sulfur heteroatoms were converted into innocuous SO₄²⁻ ions. The mineralization of nitrogen was more complex. Nitrogen atoms in the –3 oxidation state, such as in amino-groups, remain at this reduction degree and produced NH₄⁺ cations, subsequently and very slowly converted into NO₃⁻ ions. The aromatic rings were submitted to successive attacks by photogenerated OH• radicals leading to hydroxylated metabolites before the ring opening and the final evolution of CO₂ induced by repeated subsequent “photo-Kolbe” reactions with carboxylic intermediates. In our experiments, small gas bubbles were observed to appear on the catalyst surface during photocatalytic degradation of MB in solution. The intermediates might be adsorbed on the catalyst surface and the coverage of the surface active sites would lead to the decrease of catalytic efficiency. However, the catalytic ability was completely recovered under a very low heating temperature of 80 °C. Such a low temperature could not decompose the aforementioned intermediates and remove them from the catalyst surface. Considering the water solubility of these intermediates, accumulation of the intermediates on the catalyst surface was unlikely the main reason for the deactivation of the catalysts. Since gaseous species such as CO₂ were eventually generated in the oxidation reactions and the nanoparticulate films had porous structures, these gaseous species would be easily adsorbed in the pores and cracks of the nanostructured catalyst surface. The accumulation of the gaseous products on the active sites would cause the photocatalytic deactivation with the operating time. As found by Blount and Falconer [8], the CO and CO₂ could be desorbed over a broad temperatures range. Thus, the removal of gaseous species could easily be achieved through the mild heat treatment, leading to the recovery of the photocatalytic ability.

4. Conclusions

Bare TiO₂ and N-doped TiO₂ nanoparticulate films in anatase phase were synthesized by PLD in O₂, N₂/O₂ and NH₃/N₂/O₂ atmospheres, respectively. Higher nitrogen dopant concentration was achieved by adding a small amount of NH₃ into the N₂/O₂ mixture. The bare and N-doped TiO₂ films had almost the same photocatalytic ability under UV-light irradiation. While under visible-light illumination, only N-doped TiO₂ films exhibited photocatalytic abilities. Compared with the film deposited in N₂/O₂, the one produced in NH₃/N₂/O₂ showed higher photocatalytic efficiency in the visible-light region. All the films exhibited deactivation with operating time. The mild heat treatment was proved to be a simple and effective way for the complete recovery of the photocatalytic ability, which is of particular importance for the practical applications.

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