

## Visible-light Photocatalyst - Nitrogen-doped Titanium Dioxide -

Takeshi Morikawa, Ryoji Asahi, Takeshi Ohwaki, Koyu Aoki,  
Kenichi Suzuki, Yasunori Taga

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### Abstract

A new photocatalyst, known as nitrogen-doped  $\text{TiO}_2$  ( $\text{TiO}_{2-x}\text{N}_x$ ), yielding high reactivity under visible light irradiation, together with high potential for mass-productivity, has been developed by using a highly time-efficient development technique that combines computational materials design with experimental syntheses. Under visible light irradiation,  $\text{TiO}_{2-x}\text{N}_x$  films and powders exhibit significant advantages over commercially-available  $\text{TiO}_2$  in terms of optical absorption and photocatalytic decomposition rates with respect to gaseous acetaldehyde and toluene, etc. The active wavelength range of  $\text{TiO}_{2-x}\text{N}_x$  (below 520 nm) covers a wider irradiation energy range for white fluorescent and incandescent light than that of

$\text{TiO}_2$ . As a result,  $\text{TiO}_{2-x}\text{N}_x$  exhibits a photodecomposition rate for gaseous acetaldehyde that is more than 5 times higher than that of  $\text{TiO}_2$  under interior illumination (300-600 lux). It also exhibits significant antibacterial properties.  $\text{TiO}_{2-x}\text{N}_x$  is therefore a promising photocatalytic material, and it possesses other desirable features; it shows highly reproducible photocatalytic activity, it has a potential for mass-production, and it is environmentally benign (no toxic ingredients). Further development of this material is now underway, so it should be available to contribute to the human environment by reducing indoor VOCs (Volatile Organic Compounds) in the very near future.

#### Keywords

Photocatalyst, Visible light, Titanium dioxide, Doping, Anion, Nitrogen, FLAPW, Band-gap, Acetaldehyde, Toluene

## 1. Preface

It is well-known that the discovery of photo-electrochemical water-splitting on reduced TiO<sub>2</sub> surfaces during '70s<sup>1)</sup> was instrumental in establishing a research field centered round the generation of hydrogen from water ( $\text{H}_2\text{O} \rightarrow \text{H}_2 + 1/2\text{O}_2$ ) by using photo-energy from sunlight absorbed onto the photoelectric or photocatalytic surfaces of oxide materials.<sup>2-4)</sup> Prior to this discovery, the photo-oxidation of organic substances on TiO<sub>2</sub> had already been recognized.<sup>5)</sup> However, since the publication of the paper on the photo-induced splitting of water, TiO<sub>2</sub> has been considered to be a particularly promising materials, and hence its photochemical properties have been studied extensively.<sup>6-8)</sup> From the viewpoint of the practical applications of TiO<sub>2</sub>, engineers in Japan, in particular, have focused on the three main photo-induced effects that it exhibits as a photocatalyst: its deodorizing,<sup>5)</sup> self-cleaning,<sup>9)</sup> and antibacterial effects.<sup>6)</sup> As a result, TiO<sub>2</sub> photocatalysts have recently been put into practical use. Some examples are air purification systems in hospitals, houses and automobile cabins, and self-cleaning tiles and canvases for buildings and tents. As a specific use in the field of automobiles, hydrophilic side mirrors coated with a combination of silica-titania are now installed on a number of cars, contributing to improvements in safety in wet weather.

The market for TiO<sub>2</sub> photocatalysts has been growing. However, there are still some technological problems that need to be solved. In particular, the development of visible-light responsive photocatalysts suited to mass production has been considered to be indispensable, because TiO<sub>2</sub> can only be activated by UV light. It is therefore usually impractical to apply TiO<sub>2</sub> to interior living spaces where the lighting contains little UV.

In this paper, a new photocatalyst, known as nitrogen-doped TiO<sub>2</sub> (TiO<sub>2-x</sub>N<sub>x</sub>), which exhibits high reactivity under visible light irradiation, will be reported.

## 2. Photocatalysis on TiO<sub>2</sub>

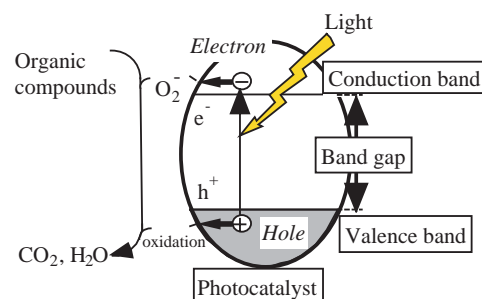
### 2.1 Mechanism

The general mechanism for photocatalytic

reactions on semiconductor TiO<sub>2</sub> can be explained as shown in **Fig. 1**. The absorption of light in TiO<sub>2</sub> at the wavelengths of less than 387 nm (for the anatase crystal with a band gap of 3.2 eV) leads to the promotion of an electron from the valence band to the conduction band of the semiconductor. This excitation process creates an electron in the conduction band and an electron vacancy (a hole) in the valence band. The electron-hole pairs that are generated in this way migrate toward the surface where they can initiate the redox reactions with adsorbates. Because the valence band edge of TiO<sub>2</sub> is located at approximately +3.2 V with respect to a normal hydrogen electrode (NHE) at pH 0 (the position of the band edge is pH dependent), these holes are very powerful oxidizing agents and are capable of oxidizing a variety of organic molecules, leading to the formation of mainly CO<sub>2</sub> and H<sub>2</sub>O. However, the main issue to be taken into consideration is that TiO<sub>2</sub> photocatalysts can only be excited by UV light because of their wide band gap.

### 2.2 Past research into 'visible-light-responsive' TiO<sub>2</sub>

A large number of researches aimed at activating TiO<sub>2</sub> photocatalysts using visible light have been carried out over the last 20 years or more. Three main methods have been studied to achieve this purpose: doping TiO<sub>2</sub> with transition metal ions to produce intermediate states in the band-gap of TiO<sub>2</sub>,<sup>10)</sup> attaching photo-sensitizers such as another semiconductors<sup>11)</sup> or organic substances<sup>12)</sup> that absorb visible light; and the formation of reduced TiO<sub>x</sub> photocatalysts.<sup>13)</sup> However, the former two methods suffered from thermal or photo-induced instability, poor reproducibility of photoactivity, and



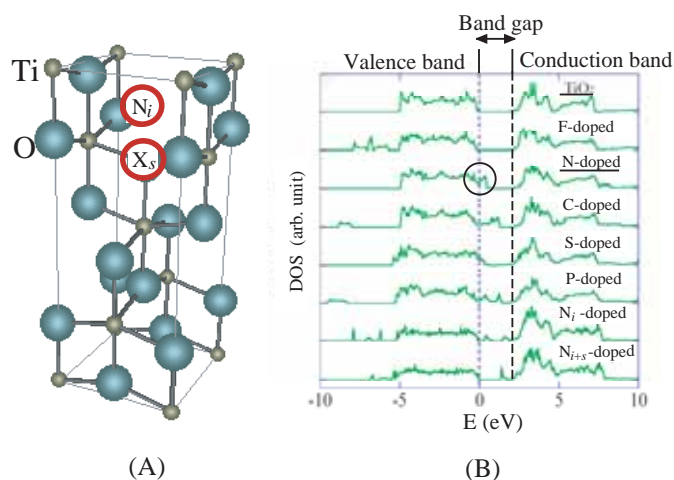
**Fig. 1** Mechanism of photocatalysis.

increases in the density of carrier-recombination centers which significantly deteriorates photocatalytic activity. In the case of the third method mentioned above, productivity rates and the durability of the material are low. Furthermore the process introduces localized oxygen vacancy states that are located at 0.75 - 1.18 eV below the conduction band minimum (CBM) of  $\text{TiO}_2$ , and these vacancy states have the effect of degrading photocatalysis.<sup>14)</sup> Hence, all three of these methods are generally considered as being impractical for industrial applications.

### 3. Material design by FLAPW calculation

Instead of the three methods mentioned above, which many researchers have been investigating for decades, we postulated that an uncommon anion-doped system might possess the potential to yield visible-light activated photocatalysts.<sup>14, 15)</sup>

We have calculated the densities of states (DOS) for the substitutional doping of (C, N, F, P, or S) to replace O in the anatase-phase  $\text{TiO}_2$  crystal (Fig. 2A). We used a technique based on the noble full-potential linearized augmented plane wave (FLAPW) formalism in the framework of the local density approximation (LDA). As a result, some anionic species such as N and S were identified that could potentially form new impurity levels near the valence band maximum in the band gap as shown in Fig. 2B. Among the possible candidates, we became



**Fig. 2** (A) Anion doping into  $\text{TiO}_2$  ( $X_s$ : substitutional doping into oxygen site,  $N_i$ : interstitial doping of nitrogen). (B) Calculated density of state.

convinced that substitutional doping with N would prove to be most effective, because its  $p$  states contribute to band-gap narrowing by mixing with the  $p$  states of oxygen.

## 4. Nitrogen-doped $\text{TiO}_2(\text{TiO}_{2-x}\text{N}_x)$ photocatalyst

### 4.1 Synthesizing $\text{TiO}_{2-x}\text{N}_x$ films and powders

$\text{TiO}_{2-x}\text{N}_x$  films were prepared on glass substrates by sputtering a  $\text{TiO}_2$  target in an  $\text{N}_2(40\%)/\text{Ar}$  gas atmosphere. After annealing at  $550^\circ\text{C}$  in  $\text{N}_2$  gas for 4 hrs, the amorphous films crystallized with features assignable to a mixed structure of the anatase and rutile crystalline phases, as determined by X-ray diffraction (XRD). The  $\text{TiO}_{2-x}\text{N}_x$  films were yellowish in color and were also transparent.

$\text{TiO}_{2-x}\text{N}_x$  powders were prepared by treating anatase  $\text{TiO}_2$  powder in an  $\text{NH}_3(67\%)/\text{Ar}$  atmosphere at  $600^\circ\text{C}$  for 3 hrs. The white-colored  $\text{TiO}_2$  turned into yellowish  $\text{TiO}_{2-x}\text{N}_x$  with the anatase structure. The average crystalline size as estimated by XRD and the measured BET surface area were 19 nm and  $67 \text{ m}^2/\text{g}$ , respectively. We developed another method that was suitable for mass production by annealing a mixture of urea (and/or thiourea) and  $\text{TiO}_2$ .<sup>16)</sup> By using this method,  $\text{TiO}_{2-x}\text{N}_x$  powders can be synthesized without diminishing the specific surface area of the original  $\text{TiO}_2$  (ca.  $280 \text{ m}^2/\text{g}$ ).

### 4.2 N states in $\text{TiO}_{2-x}\text{N}_x$

In order to examine the state of N in the  $\text{TiO}_{2-x}\text{N}_x$  films, we measured the N1s core levels by X-ray photoelectron spectroscopy (XPS). Three peaks were observed at binding energies of 402 eV, 400 eV, and 396 eV. Although the original  $\text{TiO}_2$  films also included a small amount of N, no peak was observed at 396 eV. Therefore, the peak at 396 eV is unique to the  $\text{TiO}_{2-x}\text{N}_x$  films. According to the literature regarding oxidative annealing processes of TiN (a Ti-N-O system), this peak can be assigned to atomic  $\beta\text{-N}$  (396 eV).<sup>17)</sup> In contrast, only the anatase and/or rutile phases are observed in  $\text{TiO}_{2-x}\text{N}_x$  films, whereas metallic Ti and TiN are not. Theoretical core-level shift analyses also confirmed that the substitutional N is located in the lowest energy region in N1s (i.e. the strongest possibility for 396 eV).<sup>18)</sup> These results, combined with the theoretical and experimental analyses described above, consistently suggest that the atomic  $\beta\text{-N}$  (substituted)

states that are responsible for the peak at 396 eV in the XPS spectra are a specific feature of  $\text{TiO}_{2-x}\text{N}_x$  photocatalysts.

### 4.3 Photocatalytic properties

#### 4.3.1 Optical properties

The optical absorption spectra (Fig. 3A) show that  $\text{TiO}_{2-x}\text{N}_x$  films noticeably absorb light at less than 520 nm, while  $\text{TiO}_2$  films do not. This is in good agreement with the theoretical results: the calculated imaginary parts of the dielectric functions of  $\text{TiO}_{2-x}\text{N}_x$  indeed show a shift in the absorption edge to a lower energy due to the N doping.<sup>14, 15)</sup> The dominant transitions at the absorption edge have been identified as those from N  $2p_\pi$  to Ti  $d_{xy}$ , instead of those from O  $2p_\pi$  as in  $\text{TiO}_2$ .<sup>14)</sup>

#### 4.3.2 Action spectrum

The photocatalytic activity of the material was initially evaluated by measuring the decomposition rates of methylene blue (MB) as a function of the cut-off wavelength of the optical high-pass filters under fluorescent light (Fig. 3B). The detailed experimental conditions are described elsewhere.<sup>14, 19)</sup> Significant photocatalytic activity below 520 nm is observed for the  $\text{TiO}_{2-x}\text{N}_x$  films, and the cut-off wavelength where photocatalytic activity emerges corresponds well with the optical absorption spectra shown in Fig. 3A. By contrast, both the  $\text{TiO}_{2-x}\text{N}_x$  and  $\text{TiO}_2$  films exhibit similar activity with respect to UV light (represented by the results under black light (BL) illumination).

#### 4.3.3 Photooxidation of volatile organic compounds

We evaluated the photodecomposition of gaseous acetaldehyde, a well-known volatile organic compound (VOC) that causes the so-called sick building syndrome.

Figure 4A shows the  $\text{CO}_2$  concentrations that were evolved by the photodecomposition of acetaldehyde (485ppm in a 1 liter bottle) as a function of irradiation time. While both the  $\text{TiO}_{2-x}\text{N}_x$  and  $\text{TiO}_2$  exhibit similar activity in the UV irradiation range, under visible light (> 410 nm), the  $\text{CO}_2$  evolution rate of  $\text{TiO}_{2-x}\text{N}_x$  is more than 5 times greater than that of  $\text{TiO}_2$ .

Figure 4B shows the data for long-term

irradiation. The data indicate that acetaldehyde molecules have been completely oxidized to  $\text{CO}_2$  by visible light only.

Hence,  $\text{TiO}_{2-x}\text{N}_x$  is considered to maintain sufficient oxidation power, despite the narrowing of the band-gap of  $\text{TiO}_2$ . It was also found that  $\text{TiO}_{2-x}\text{N}_x$  is able to photooxidize other VOCs such as toluene, xylene, acetone, isopropyl alcohol, etc. These results suggest that  $\text{TiO}_{2-x}\text{N}_x$  can be effectively used to reduce indoor VOCs by using only typical interior illumination.

#### 4.3.4 Antibacterial properties

Figure 5 exhibits the antibacterial activities of  $\text{TiO}_{2-x}\text{N}_x$  films, which were photoirradiated using

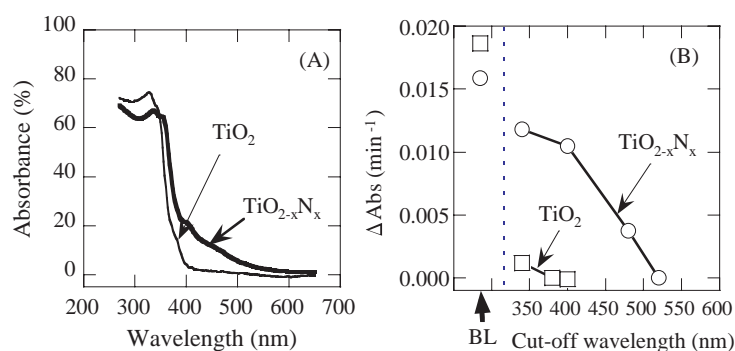


Fig. 3 Properties of sputter-deposited  $\text{TiO}_{2-x}\text{N}_x$  films measured as a function of wavelength : optical absorbance (A), and photocatalytic methylene blue decomposition (absorbance change ratio of embrocated methylene blue during illumination) (B).

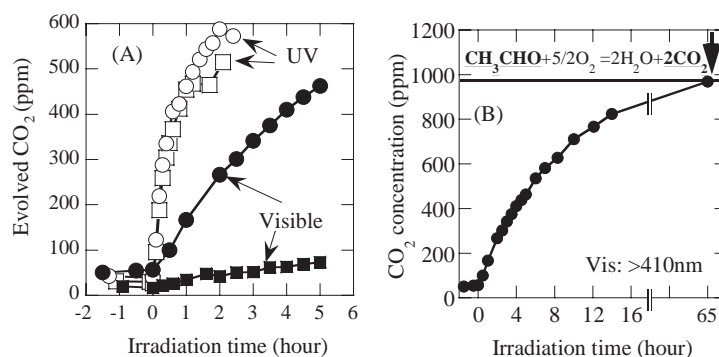


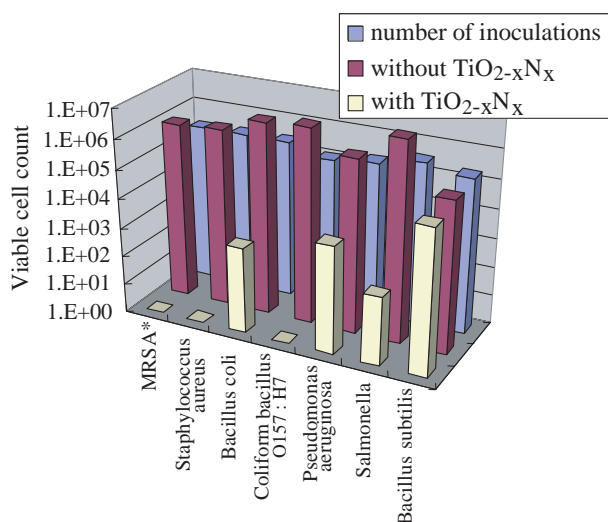
Fig. 4 Photodecomposition of gaseous acetaldehyde on  $\text{TiO}_{2-x}\text{N}_x$  powder : evolved  $\text{CO}_2$  concentration (○, ● :  $\text{TiO}_{2-x}\text{N}_x$ , □, ■ :  $\text{TiO}_2$ ) (A) and complete oxidation to  $\text{CO}_2$  under visible light (B).

white fluorescent light at a luminance of 2000 lux for 24 hrs. While all of the fungi increase in abundance after illumination in the absence of  $\text{TiO}_{2-x}\text{N}_x$ , all apart from *Bacillus subtilis* are obviously diminished on the surface of irradiated  $\text{TiO}_{2-x}\text{N}_x$  films. In particular, significant antibacterial effects are observed in the case of MRSA (*methicillin-resistant Staphylococcus aureus*), *staphylococcus aureus*, and *coliform bacillus* O157, because their numbers declined by 6 orders of magnitude down to an almost undetectable level.

## 5. Summary

We have developed  $\text{TiO}_{2-x}\text{N}_x$  films and powders that exhibit significant superiority over  $\text{TiO}_2$  in terms of their photocatalytic and antibacterial properties under visible light. The active wavelength range of  $\text{TiO}_{2-x}\text{N}_x$  (less than 520 nm) covers a wider irradiation energy range for white fluorescent and incandescent lights than  $\text{TiO}_2$ . In fact,  $\text{TiO}_{2-x}\text{N}_x$  exhibits a photodecomposition rate for gaseous acetaldehyde that is 5 times higher than  $\text{TiO}_2$  under interior illumination (300-600 lux).

$\text{TiO}_{2-x}\text{N}_x$  is a promising photocatalytic material that has several special features; it has highly-



**Fig. 5** Antibacterial properties on  $\text{TiO}_{2-x}\text{N}_x$  film after irradiation at a luminance of 2000 lux for 24 hours. The experiment was operated at Japan Food Research Laboratories pursuant to the method provided by the Society of Industrial-Technology for Antimicrobial Articles.

reproducible activity, it is compatible with mass-production techniques, and it is environmentally benign (no toxic ingredients). Further development of these properties to a practical level is now taking place. We believe that this visible-light-responsive photocatalyst will be accepted as an indispensable material for the human environment in the very near future.

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**Takeshi Morikawa**

Research field : Photocatalysis,  
Magnetics  
Academic degree : Dr. Eng.  
Academic society : Chem. Soc. Jpn.,  
Mag. Soc. Jpn., IEEE  
Awards : R&D 100 Award, 1993  
Technical Award of Jpn. Fine  
Ceram. Assoc., 2003  
Award of Outstanding Papers of  
Ceram. Soc. Jpn., 2005


**Ryoji Asahi**

Research field : Computational physics  
and materials design of functional  
materials  
Academic degree : Ph. D.  
Academic society : Jpn. Soc. Appl. Phys.,  
Phys. Soc. of Jpn., Am. Phys. Soc.  
Awards : Technical Award of Jpn. Fine  
Ceram. Assoc., 2003


**Takeshi Ohwaki**

Research field : Photocatalysts, thin  
films and surfaces  
Academic degree : Dr. Eng.  
Academic society : Jpn. Soc. Appl. Phys.,  
Surf. Sci. Soc. Jpn., Chem. Soc.  
Jpn.  
Awards : Technical Award of Jpn. Fine  
Ceram. Assoc., 2003  
Award of Outstanding Papers of  
Ceram. Soc. Jpn., 2005


**Koyu Aoki**

Research field : Photocatalysis,  
Environmental analysis (Air)  
Academic society : Jpn. Soc. Appl. Phys.  
Awards : Technical Award of Jpn. Fine  
Ceram. Assoc., 2003


**Kenichi Suzuki**

Research field : Applied  
electrochemistry, Surface finishing  
Academic society : Electrochem. Soc.  
Jpn., Chem. Soc. Jpn., Surf. Finish.  
Soc. Jpn., Jpn. Soc. Corr. Eng.  
Awards : Technical Award of Jpn. Fine  
Ceram. Assoc., 2003


**Yasunori Taga**

Research field : Thin film materials  
Academic degree : Dr. Eng.  
Academic society : Am. Vacuum Soc.,  
Soc. Inf. Displays, Eur. Mater. Res.  
Soc., Jpn. Inst. Metals  
Awards : R&D 100 Award, 1998  
Jpn. Inst. Metals, 2002  
ASM Award, 2002  
Technical Award of Jpn. Fine  
Ceram. Assoc., 2003, etc.