



Research Report

Enhanced Visible-light Photocatalysis over N-doped TiO₂ by Loading with Fe, Cu, or Pt Cocatalysts

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■ABSTRACT■ The rates of visible-light-induced photocatalytic oxidation of gaseous formic acid, acetic acid, acetaldehyde, and toluene over N-doped TiO₂ (N-TiO₂) were enhanced by surface-loading with Fe, Cu, or Pt. It was found that Cu and Pt gave the highest rates of acetic acid and toluene oxidation, respectively. It was also confirmed that the rate of formic acid photooxidation was enhanced by factors of 5 and 22 upon loading with Fe and Pt, respectively. The extreme rate enhancement of formic acid oxidation over Pt-loaded N-TiO₂ was found to result from a combined effect of photocatalysis and thermal catalysis at room temperature, facilitated by nanoscale (1-2 nm) Pt. N-TiO₂ photocatalysts loaded with Fe, Cu, and Pt were applied to textiles to provide antibacterial and odor-eliminating properties for use in products such as air-purifying window blinds and tooth-whitening systems to enhance the health and comfort of human life.

■KEYWORDS■ Photocatalysis, Visible light, Titanium dioxide, Nitrogen doping, Iron, Copper, Platinum, Acetaldehyde, Carbon dioxide

1. Preface

TiO₂ photocatalysts are known to exhibit excellent activity for the oxidative detoxification of organic pollutants and for their self-cleaning properties.^(1,2) However, a crucial issue to be taken into consideration is whether TiO₂ can be used only outdoors or with a UV light source, because of its wide bandgap (3.2 eV). To widen the area of practical applications to include indoor use, photocatalysts that can be activated under visible light irradiation with high yields are considered indispensable.

2. N-doped TiO₂

As was reported previously, we developed nitrogen-doped TiO₂ (N-TiO₂), in which nitrogen atoms substitute some oxygen sites in the anatase TiO₂ lattice (**Fig. 1** (a)).^(3,4) We reported that N-TiO₂ was promising, because it responds to visible light at wavelengths below 520 nm and has demonstrated antibacterial activity under interior lighting conditions.⁽⁴⁾ N-TiO₂ can photodegrade formaldehyde under very-low concentration (100 ppb flow) and weak illumination (at 150 lux under a fluorescent lamp, which corresponds to a typical indoor lighting environment).⁽⁵⁾

However, in many practical applications, a higher

reaction rate is required. Furthermore, some researchers raised an uncertain alert that the photogenerated holes in N-TiO₂ fail to oxidize methanol, formic acid, and ethylene glycol in aqueous media because of the lower potential of visible photons.⁽⁶⁻⁸⁾ Among these organic substances, the oxidation of formic acid is the most significant because almost all organic pollutants must undergo formic acid formation before being completely photooxidized to CO₂ and H₂O, as we demonstrated in an *in-situ* DRIFT-GC analysis of the photooxidation of toluene over N-TiO₂.⁽⁹⁾ Accordingly, we have confirmed that formic acid can also be decomposed into CO₂ and H₂O

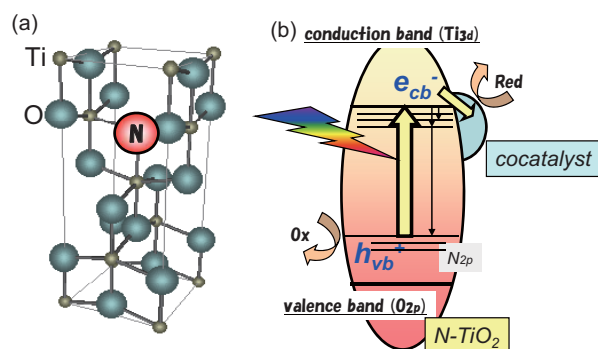


Fig. 1 Crystalline structure of anatase N-TiO₂ (a) and a simplified photocatalytic mechanism for N-TiO₂ loaded with cocatalysts (b).

in air, since CO₂ at 960 ppm was stoichiometrically generated from acetaldehyde at 480 ppm (2CH₃CHO + 5O₂ → 4CO₂ + 4H₂O). However, it was unclear whether the rate of photooxidation of formic acid was equivalent to that of acetaldehyde, *etc.* If the photooxidation of formic acid were slower, it would be the rate-determining step for many photodegradation processes over N-TiO₂ under visible light irradiation. Elucidating the rate-limiting step is crucial to improve the rate of photodegradation of organic substances over N-TiO₂.

3. N-doped TiO₂ loaded with Cu, Fe, or Pt cocatalysts

3.1 Synthesis and structure

The loading of metallic species onto the surface of N-TiO₂ is one realistic method of enhancing photocatalytic activity under visible light. Besides the specific chemical reaction at the cocatalyst surfaces, it is generally believed that charges in a photoexcited state (electrons and holes) can be separated by loading of cocatalysts, extending a lifetime of the carriers (Fig. 1 (b)). Bare N-TiO₂ powders with an anatase crystalline phase were synthesized according to the previous literature.^(3,9) Cocatalysts were loaded by impregnation of N-TiO₂ with aqueous solutions of Fe(NO₃)₃, Cu(NO₃)₂, or Pt(NH₃)₂(NO₂)₂ at room temperature, followed by stirring for 1 hour and heating at 150°C for water evaporation. Finally, the catalysts were calcined at 300°C for 2 hours for Fe and Cu, and 400°C for Pt. The optimum temperatures were carefully chosen from post-annealing conditions between 150 and 500°C. 0.5 wt% of Cu, Fe or Pt was loaded. In the XRD patterns of Fe, Cu, or Pt loaded N-TiO₂, diffraction peaks derived from the loaded particles were not detected. In a TEM photograph of a sample loaded with 0.5 wt%-Pt, nanoscale Pt particles (1 - 2 nm in size) were clearly observed on the surface of the N-TiO₂. On the contrary, particles were not observed on the Fe or Cu loaded samples, presumably because of their small particle sizes.⁽¹⁰⁾ As a result, the yellow-colored N-TiO₂ turned light-brown, light-green, or brown after modification with Fe, Cu, or Pt, respectively, as shown in Fig. 2.

In order to investigate the chemical states of Fe, Cu, and Pt, XPS measurements were performed. In the XPS spectrum of 0.5 wt% Cu loaded N-TiO₂, the binding energies of Cu 2p_{3/2} and 2p_{1/2} were

found to be 932.6 eV and 952.4 eV, respectively, suggesting that Cu, Cu₂O, or Cu hydroxides were present on the catalyst surface.⁽¹¹⁾ Furthermore, the Cu LMM Auger region was shifted to a higher binding energy (338.5 eV) than that of metallic copper (334.9 eV), indicating that Cu₂O, Cu hydroxides, or clusters containing Cu-O bonds were probably present on the catalyst surface.⁽¹²⁾ Among these, clusters containing Cu-O bonds were most likely, judging from the results of XAFS. Similarly, in the XPS spectrum of 0.5 wt% Fe loaded N-TiO₂, the binding energy of the Fe 2p band was 709.5 eV, suggesting that clusters containing Fe-O bonds or Fe²⁺ hydroxide were present on the catalyst surface. The peak at 710.9 eV corresponding to Fe³⁺ was negligible (less than the XPS resolution of 0.05 at%) and the ESR signal corresponding to Fe³⁺ was also very small.⁽¹³⁾ XAFS spectra suggested the existence of clusters containing Fe-O bonds. As for Pt, the binding energies of the Pt 4f band were 71.9 eV and 75.4 eV, respectively, suggesting that nanoscale Pt particles 1-2 nm in size comprised a mixture of metallic Pt (71.2 eV⁽¹⁴⁾) and PtO (72.4 eV⁽¹⁴⁾) on the catalyst surface.

3.2 Photocatalytic activity over N-TiO₂ loaded with Cu, Fe, or Pt

Figure 3 illustrates the photocatalytic oxidation of gaseous acetaldehyde over TiO₂ (ST01, Ishihara Sangyo), bare N-TiO₂, Fe-loaded, Cu-loaded, and Pt-loaded N-TiO₂ under visible light (> 410 nm). In this experiment, 1200 ppm acetaldehyde and 0.1 g of photocatalyst were placed in a 1-liter glass-vessel reactor irradiated by visible light (> 410 nm, 0.9 mW/cm²).^(12,13) In Fig. 3 (a), the scattering observed at the initial concentrations of acetaldehyde was attributable to the adsorption characteristics of each

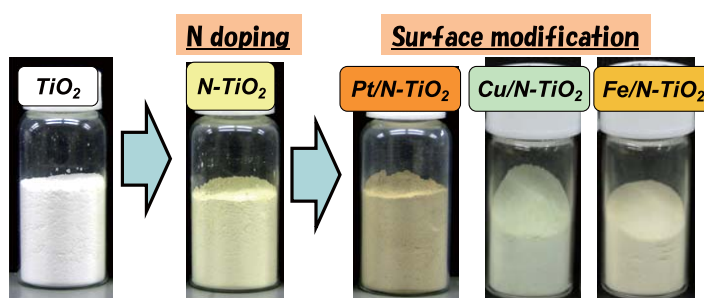


Fig. 2 Powders of TiO₂, bare N-TiO₂, Pt-loaded N-TiO₂, Cu-loaded N-TiO₂, and Fe-loaded N-TiO₂.

sample. It is obvious that TiO₂ (ST01) adsorbed more acetaldehyde molecules than bare N-TiO₂, and that the loading of cocatalysts did not improve the adsorption. From Fig. 3 (a), it was found that Fe or Cu loading markedly enhanced the rate of acetaldehyde photodegradation, as indicated by the dramatic decrease in the acetaldehyde concentration. In Fig. 3 (b), no significant CO₂ evolution was observed over

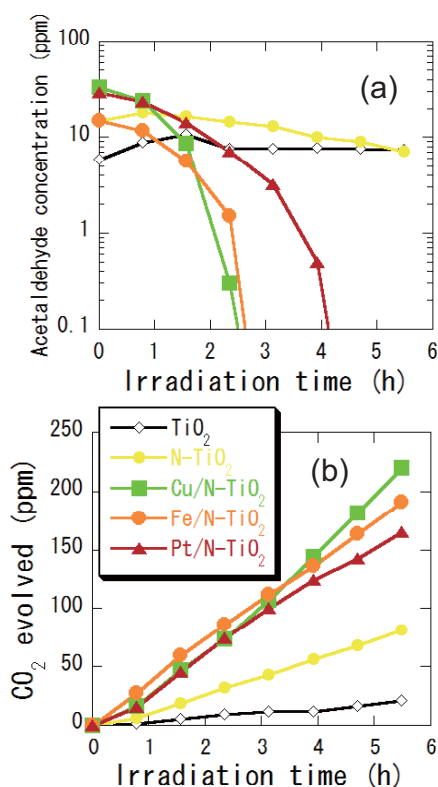


Fig. 3 Concentration of gaseous acetaldehyde (a) and CO₂ (b) in glass-vessel reactors as a function of visible-light irradiation time (> 410 nm). CO₂ was generated by the photooxidation of acetaldehyde over the photocatalysts ($2\text{CH}_3\text{CHO} + 5\text{O}_2 \rightarrow 4\text{CO}_2 + 4\text{H}_2\text{O}$).

TiO₂, indicating that acetaldehyde was not appreciably photooxidized to CO₂ over TiO₂ under visible light. On the contrary, the acetaldehyde oxidation rate was greatly improved by N-doping, and was then nearly doubled by loading Cu, Fe, or Pt.^(13,14) These photocatalysts can stoichiometrically decompose acetaldehyde into CO₂ and H₂O under visible light irradiation.

Table 1 summarizes the rates of CO₂ generation from formic acid, acetic acid, acetaldehyde, and toluene over various photocatalysts irradiated with visible light. The measurement of catalytic oxidation of the samples was performed three or more times for each set of experimental conditions. The acetaldehyde oxidation rate over bare N-TiO₂ was about 6 times higher than over TiO₂, as described in a previous paper.⁽³⁾ On the contrary, the effect of N-doping on acetic acid oxidation was low compared to its effect on acetaldehyde oxidation, and the rate was only 2.2 times that of undoped TiO₂. However, Fe, Cu, and Pt loading improved the rate of acetic acid oxidation over bare N-TiO₂. Among these, Cu loading caused a significant acceleration of acetic acid oxidation, enhancing the rate by a factor of 4.2. Formic acid was confirmed to be oxidized to CO₂ over bare N-TiO₂, and the rate was improved to nearly that of acetaldehyde oxidation by the loading of Cu, Fe, or Pt. The detailed reaction mechanism will be discussed in section 3.3.

As for the long-term stability, more than 2300 micromoles of CO₂ was produced from acetaldehyde under continuous photooxidation for 110 days over 1100 micromoles of Fe/N-TiO₂ under visible light irradiation. This would correspond to an exposure time of 6.7 consecutive years at 150 lux, assuming a linear dependence of the CO₂ generation rate on the illuminance (or number of incident photons) between 0.9 mW/cm² (this experiment) and 44 μW/cm²

Table 1 Rates of CO₂ generation from formic acid, acetic acid, acetaldehyde, and toluene over TiO₂, bare N-TiO₂, Fe/N-TiO₂, Cu/N-TiO₂, and Pt/N-TiO₂ under visible light irradiation (> 410 nm). The rates of CO₂ generation from formic acid in the dark are also listed.

Organic substance	Rate of CO ₂ generation under visible light (> 410 nm) (ppm/h)				
	N-TiO ₂	Pt/N-TiO ₂	Fe/N-TiO ₂	Cu/N-TiO ₂	TiO ₂
HCOOH (Darkness)	0.0	16.7	0.0	0.0	0.0
HCOOH	5.5	123.6	28.5	34.6	0.5
CH ₃ COOH (Darkness)	0.0	0.0	0.0	0.0	0.0
CH ₃ COOH	6.0	15.0	12.4	25.0	2.7
CH ₃ CHO	20.1	30.6	32.7	33.1	3.6
C ₇ H ₈	9.8	14.5	10.4	9.9	0.5

(at 150 lux). After this long-term stability test, the CO₂ generation rates for bare N-TiO₂ and Fe-loaded N-TiO₂ decreased to 51% and 70% of the initial rates, respectively. This suggests that the loading of Fe not only enhanced the photooxidation rate, but also helped prevent the long-term deactivation of N-TiO₂.

3.3 Mechanistic insights into photocatalysis over cocatalyst-loaded N-TiO₂

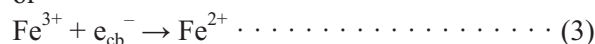
N-doped TiO₂ can be excited by visible light due to an Ti 3d ← N 2p transition.^(3,15) This raised concerns that N-TiO₂ would be unable to oxidize certain organic compounds such as formic acid in liquid regime reactions due to the low oxidative power of visible photons (i.e. holes induced by visible light). However, the present results demonstrated the successful decomposition of formic acid into CO₂ over N-TiO₂ in ambient air under visible light. This means that the concerns were unfounded and that the problem was legitimately solved. A basic reaction pathway over bare TiO₂ has been clearly summarized in the literature.⁽¹⁶⁾ Adsorbed O₂ molecules and photogenerated electrons can form superoxide radical anions (O₂⁻) and singlet oxygens (¹O₂) through triplet-triplet energy transfer,⁽¹⁷⁾ presumably followed by the formation of hydrogen peroxide or other radical species such as •OH.⁽¹⁸⁾ Accordingly, over N-TiO₂, the adsorbed gaseous O₂ molecules and conduction band electrons (e_{cb}⁻) play important roles in photocatalytic oxidation over N-doped TiO₂ because visible-light excitation from N 2p to Ti 3d generates e_{cb}⁻, in which the final state of the optical transition induced by visible excitation (Ti 3d ← N 2p transition) is the same as that induced by UV excitation (Ti 3d ← O 2p transition).⁽¹⁹⁾

As for the effect of cocatalyst loading, certain amounts of O vacancies are generated by the doping of N³⁻, when two N atoms stoichiometrically substitute for three O atoms in the TiO₂ lattice, while the chemical state of the Ti atoms remains Ti⁴⁺. Because the O vacancies cause recombination of photogenerated electrons and holes, it is important to facilitate the rapid separation of these charges to improve the photocatalytic reaction efficiency. A time-resolved microwave conductivity study of Cu-loaded N-TiO₂ indicated that mobile conduction-band electrons (e_{cb}⁻) in the photoexcited state vanish from N-TiO₂ within <500 ns in the case of Cu/N-TiO₂, but last much longer in bare N-TiO₂. This suggests fast electron transfer from N-TiO₂ to the Cu cocatalyst.⁽¹⁹⁾

This fast electron transfer is cause of the enhanced photocatalytic reaction rates (Fig. 1(b)). The same goes for Fe- or Pt-loading, which is consistent with the previously-reported Pt/TiO₂.⁽²⁰⁾ A prolonged lifetime of valence-band holes (h_{vb}⁺) in N-TiO₂ after the loading of cocatalysts was also suggested by transient optical spectroscopy. In addition to the fast charge separation, another important factor for enhanced activity is photocatalysis over Cu, Fe, and Pt cocatalysts. Pt-loaded N-TiO₂ shows an outstandingly high rate of CO₂ generation from formic acid because formic acid can be oxidized even in darkness. This is due to a well-known effect by which nanoscale noble metals supported on oxides exhibit a catalytic reaction without light irradiation at ambient atmospheric temperature.^(21,22) With Cu and Fe cocatalysts, Cu¹⁺ and Fe²⁺ ions may facilitate the production of hydroxyl radicals (•OH) by the photo-Fenton effect from hydrogen peroxide generated from superoxide anions (O₂⁻) derived from e_{cb}⁻, as described by Eqs. (1)-(3),^(23,24) because the loading of Ni, Zn, or La did not improve the acetaldehyde photodegradation rate⁽¹²⁾



or



Singlet oxygen (¹O₂), which can be produced by the recombination of O₂⁻ and h_{vb}⁺, is also considered to be an active species for oxidation over TiO₂ in the photoexcited state.⁽¹⁷⁾ However, this mechanism is not applicable because the ¹O₂ concentration was decreased by the loading of these cocatalysts according to chemiluminescence measurements. This is presumably responsible for the enhanced spatial separation of O₂⁻ (from e_{cb}⁻) and h_{vb}⁺.⁽²⁵⁾ The speculated total reaction scheme is illustrated in **Fig. 4**.

In addition to the properties discussed above, N-TiO₂ loaded with Cu, Fe, or Pt was found to be active under LED irradiation, and was capable of NO_x elimination.⁽²⁵⁾ Cu-loaded N-TiO₂ showed highly improved antibacterial capabilities.⁽¹²⁾

4. Practical application of N-TiO₂ photocatalysts

To boost the performance of these photocatalysts for practical use, we have also developed precipitation-free slurries and coating solutions that can produce

transparent films of N-TiO₂s. Through collaborative research and development with many companies possessing specific commodities applicable to photocatalysts, N-TiO₂, both bare and loaded with Fe, Cu, or Pt, has been successfully utilized on textiles functionalized with antibacterial and odor-eliminating properties, air-purifying indoor goods such as window blinds, and tooth-whitening systems for dental esthetics, and other applications, as shown in **Fig. 5**.

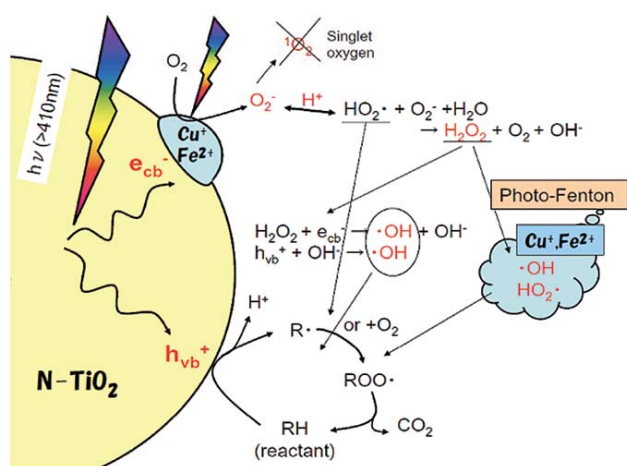


Fig. 4 Speculated photocatalytic reaction mechanism over Fe- or Cu-loaded N-TiO₂ irradiated with visible light. This figure is based on our research results with Cu/N-TiO₂ and Fe/N-TiO₂, which is complemented over the reaction pathways for oxidation of organic matter over bare TiO₂ photocatalyst.⁽¹⁶⁾

5. Summary

Loading Fe²⁺ or Cu¹⁺ ions or nanoscale Pt onto the surface of N-TiO₂ improved the rates of photocatalytic oxidation of gaseous toluene, acetaldehyde, acetic acid, and formic acid under visible light irradiation (> 410 nm). Cu and Pt loading provided the highest rates of acetic acid and toluene oxidation, respectively. The rate of formic acid photooxidation was enhanced by factors of 5 and 22 after loading with Fe and Pt, respectively. Commercial products making use of these photocatalysts are currently available, and are already making human lives healthier and more comfortable.

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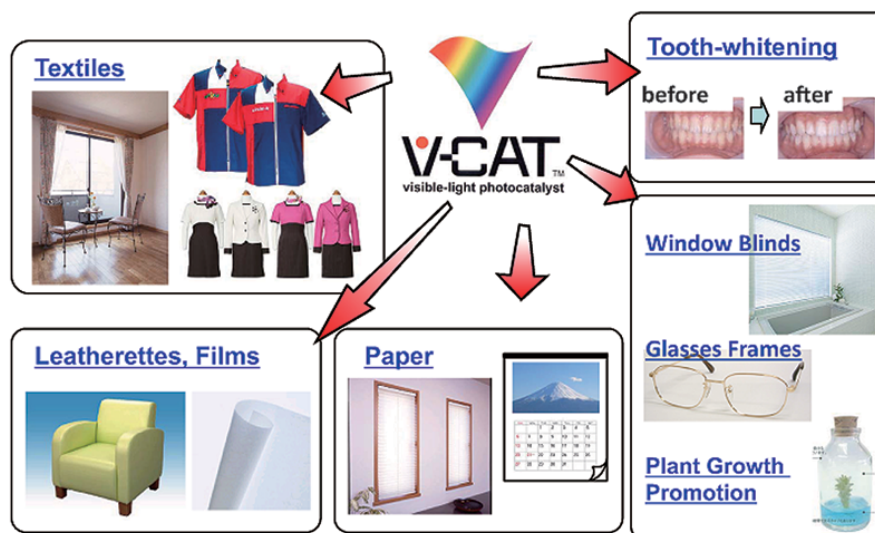


Fig. 5 Practical applications of N-TiO₂ and cocatalyst-loaded N-TiO₂ photocatalysts.

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Fig. 3 and Table 1

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Award :
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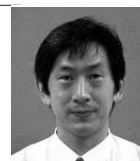
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 - Award of Outstanding papers of Ceram. Soc. Jpn., 2005
 - Ceram. Soc. Jpn. Technology Award, 2006
 - The Am. Ceram. Soc. Corporate Environmental Achievement Award, 2006
 - The Chem. Soc. Jpn., Award for Technical Development, 2007

*Retired