

Highly selective photocatalytic reduction of NO₂ in air to NO using Cu²⁺-loaded TiO₂ thin films

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ABSTRACT

We have discovered that Cu²⁺-loaded TiO₂ films (1.5 μm thick) exhibit a high activity of selective reduction of NO₂ to NO in air under UV light illumination (1 mW cm⁻²). This effect is associated with a reduced NO oxidation to HNO₃. For an increasing amount of Cu²⁺ ions the NO reductions become more stable. Cu²⁺ ions are responsible for the high redox property, playing an important role in adsorption of NO₂/NO₂⁻, electron transfer from the TiO₂ to NO₂/NO₂⁻, and recombination center for positive holes.

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1. Introduction

Photocatalytic destruction of harmful and toxic compounds using TiO₂ photocatalysts has been attracting much attention from the viewpoint of purifying air and water in our environment. [1–3] In the photocatalytic reactions, both an oxidative reaction and a reductive reaction occur on the TiO₂ surface, since the photo-excited electrons and the photo-generated holes will react with surface-adsorbed species, respectively. The photo-generated holes have a strong oxidizing potential, with which most organic compounds can be oxidized to carbon dioxide at ambient temperature and pressure. On the other hand, the photo-excited electrons, e.g., reduction of oxygen molecules (O₂) in air, followed by production of superoxide radicals (O₂^{-•}), hydroperoxyl radicals (HO₂[•]), and hydrogen peroxide (H₂O₂). The generated H₂O₂ will produce hydroxyl radicals (•OH) via electro-reduction (Ti³⁺ + H₂O₂ → Ti⁴⁺ + •OH + OH⁻ or H₂O₂ + O₂^{-•} → Ti⁴⁺ + •OH + OH⁻ + O₂) [4,5] or photolysis (H₂O₂ → 2•OH). [5,6] In this way, the reductive energy of the photo-excited electrons is also devoted to the oxidative action. Therefore, it is considered that

only oxidative reactions efficiently appear in the photocatalytic reactions in air.

Incidentally, protons (H⁺) in an electrolyte are reduced by the photo-excited electrons of TiO₂ and hydrogen gas (H₂) [7,8] can be yielded. Also, silver ions (Ag⁺) [9–11] on TiO₂, not only in solution but also in air, will be reduced to Ag nanoparticles on TiO₂. However, other gaseous species, except for O₂, are not known as oxidizing agents in TiO₂ photocatalysis in air.

The same bias applies in the case of nitrogen oxides (NO_x) removal by TiO₂ photocatalysis. The photocatalytic removal of NO_x has been recognized as one of the important technologies for environmental purification and extensively studied by many researchers. It is possible to decompose nitrogen monoxide (NO) gas to nitrogen (N₂) and oxygen (O₂), activated by the photo-excited electrons of TiO₂, although the reaction is limited in vacuum, [12–14] in the atmosphere without O₂, [15] or with a sacrificial reducing agent, for example, ammonia (NH₃), [16] carbon monoxide (CO), [17] mannitol, [18] and so on. It has been believed that only the oxidation reaction of NO_x to nitrate acid (HNO₃) proceeds on TiO₂ in air [19–24].

In case a reductive reaction in air is possible, while another gaseous product is obtained effectively without using any sacrificial decomposable agent, it is of great interest and importance both in science and technology. Herein, we demonstrate selective reduction of nitrogen dioxide (NO₂) in air to NO using Cu²⁺-loaded

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TiO₂ photocatalysts for the first time. We examined the dependency of the NO production on the Cu²⁺ amount and the reaction of nitrite (NO₂⁻) and nitrate (NO₃⁻) pre-deposited on the Cu²⁺-loaded TiO₂ in air. The morphology of the Cu²⁺-loaded TiO₂ nanoparticles was observed by transmission electron microscopy (TEM), and the reaction mechanism was elucidated.

2. Experimental

A TiO₂ thin film was prepared on a pyrex glass plate (5 × 10 cm²) by a conventional spin coating process, using a TiO₂ anatase aqueous solution (Ishihara Sangyo Kaisha, Ltd., STS-21, 50 m² g⁻¹ surface area, 20 nm particle diameter). [25] The thickness of the TiO₂ film was approximately 1.5 μm. The TiO₂-coated glass plates were immersed in deionized water for more than 24 h under UV light illumination with a black fluorescent lamp (Toshiba Co., FL10BLB-A; wavelength, 300–400 nm; UV intensity, 2 mW cm⁻²) in order to remove residual organic matter and water-soluble inorganic contamination from the TiO₂ surface, as evidenced by ion chromatography (IC; Tosoh, IC-2001).

CuSO₄, Cu(NO₃)₂, NaNO₂, NaNO₃, AgNO₃, FeCl₃ were purchased from Wako Pure Chemical Industry (JIS Special Grade) and used without further purification. To load some chemical reagents on the TiO₂ surface, a small portion of aqueous solution (Milli-Q water) was pipetted and casted on the whole TiO₂ film (5 × 10 cm²), and then dried in air. For example, CuSO₄ aqueous solution (1 mM) was used to load 2 μmol of Cu²⁺ on the TiO₂ film. Cu²⁺-loaded TiO₂ nanoparticles were observed by TEM (Philips CM-30, 200 keV).

All of the photocatalytic reactions were carried out at room temperature (298 K). The reaction gas was prepared from a NO–N₂ gas mixture or a NO₂–N₂ gas mixture (Takachiho Chemicals Co., ~100 ppm each, ~20 mL min⁻¹) as well as purified dry air (1 L min⁻¹) and purified wet air (1 L min⁻¹, created through a humidifier), attained by using thermal mass-flow controllers. The relative humidity (RH) of the reaction gas was adjusted to 50%. The NO as well as the NO₂ concentration were kept at 1 ppm. A typical flow-type reactor for photocatalysis was used, in which the distance between the sample plate and the optical quartz window, in other words, the layer of the reaction gas over the sample, is approx. 5 mm (2 L min⁻¹, laminar flow). [26] The UV light source was a black fluorescent lamp, set over the photo-reactor (1 mW cm⁻²). NO_x (NO and NO₂) in the gas phase was monitored with a chemiluminescent NO–NO_x analyzer (Monitor Labs Inc., Model 9841A). The reaction products remaining on the TiO₂ were extracted by immersing the sample into deionized water (10 mL) for 30 min, and measured using IC (column, TSKgel SuperIC-AZ; eluent, 1.9 mM NaHCO₃ and 3.2 mM Na₂CO₃).

3. Results and discussion

3.1. Photocatalytic reaction with NO₂

Time dependencies of the concentrations of NO, NO₂, and NO_x (=NO+NO₂) and the accumulated amount of HNO₃ on the Cu²⁺-loaded (2 μmol) TiO₂ film are shown in Fig. 1. The concentration change of NO₂ caused by adsorption on the sample was negligible in the dark, due to the small surface area of the sample. Starting UV light illumination, the NO₂ concentration dropped to ~0.5 ppm, while the NO concentration increased to over 0.4 ppm. Afterwards, the NO₂ concentration increased to ~0.9 ppm, while the NO concentration decreased to ~0.1 ppm. Meanwhile, HNO₃ accumulated in the TiO₂ film, and saturated at ~0.4 μmol. The nitrogen mass was balanced between the removed NO_x gas and the recovered HNO₃ from the TiO₂ film during the reaction. As seen from the concentration change of NO_x, NO₂ conversion to HNO₃ diminishes after

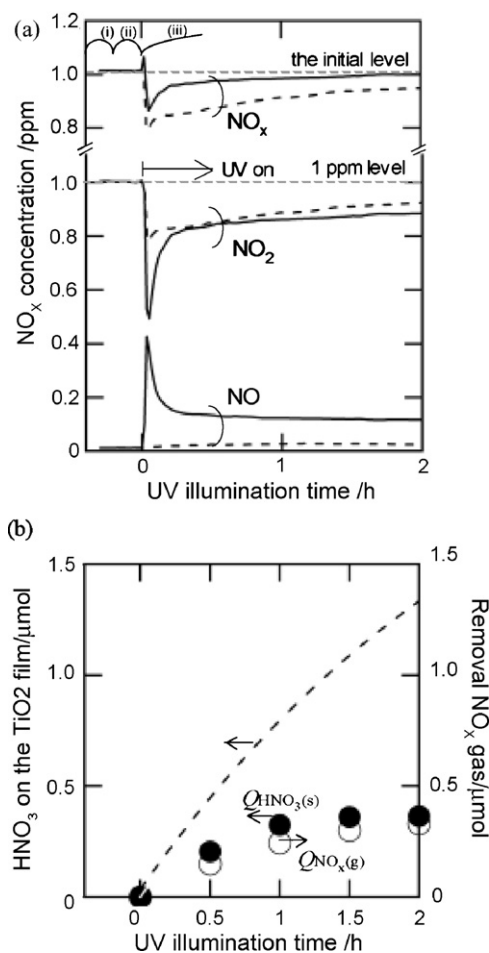
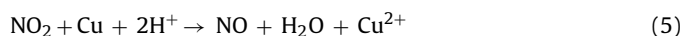
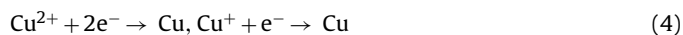
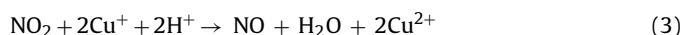


Fig. 1. (a) Concentrations of NO, NO₂ and NO_x (=NO+NO₂) as a function of UV illumination time in the photocatalytic reaction of NO₂ using the Cu²⁺-loaded TiO₂ film (thickness of the TiO₂ film, 1.5 μm; Cu²⁺, 2 μmol; UV intensity, 1 mW cm⁻²; initial NO and NO₂ concentrations, 0.01 and 1 ppm, respectively; time period (i) the reaction gas did not pass through the reactor for measuring the initial concentration of NO₂; time period (ii) the reaction gas passed through the reactor in the dark for measuring the adsorption of NO₂ on the TiO₂ film; time period (iii) the sample was illuminated with UV light for conducting the photocatalytic oxidation of NO₂). (b) The amount of HNO₃ recovered from the TiO₂ film ($Q_{\text{HNO}_3(\text{S})}$) (●) and that of NO_x removed from air ($Q_{\text{NO}_x(\text{g})}$) (○) as a function of UV illumination time (each plot was acquired by repeating a separate experiment in which UV illumination stopped at a given time). The dashed lines indicate the data using the bare TiO₂ film (1.5 μm thick).

2 h, while the reduction of NO₂ to NO was constantly observed over 15 h. The characteristics of NO production from NO₂ using the Cu²⁺-loaded TiO₂ was quite different from that of an ordinary TiO₂. The result obtained using the bare TiO₂ film (1.5 μm) is also shown in Fig. 1 (dashed line). The bare TiO₂ film converted NO₂ to HNO₃ directly (the quantum efficiency, ~0.3%), and the maximum amount of HNO₃ accumulated on the TiO₂ film was ~2.6 μmol. [26] The reduction of NO₂ to NO by the Cu²⁺-loaded TiO₂ is considered as follows:



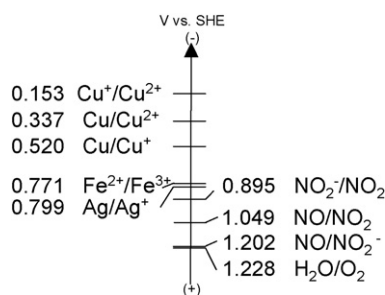


Fig. 2. List of redox potentials of nitrogen oxides, copper ions, and the related materials.

The Cu²⁺-loaded TiO₂ film was found to preferably reduce NO₂ to NO in air, resulting in a suppressed amount of HNO₃ to ~15% compared to the bare TiO₂ film. The apparent deactivation may be caused by the physical inhibition of HNO₃ and H₂O₂ produced on the TiO₂ surface. In addition, the contact of Cu²⁺ to the TiO₂ surface may be weakened during the reaction, since Cu²⁺ ions are easily dissolved into acid solution. [27] When we used Cu(NO₃)₂ instead of CuSO₄, the reduction of NO₂ to NO was similarly observed, so that the role of Cu²⁺ ions was mostly independent of the counter anions. Additionally, we examined a sintered sample (200 °C) in which Cu²⁺ was loaded using a Cu(NO₃)₂ aqueous solution to form CuO. The deactivating behavior was not affected by this method. Arai et al. reported that CuO works as co-catalyst on WO₃ photocatalyst, in which the surface state of CuO is changeable between Cu⁺ and Cu²⁺, though the bulk of CuO is known rather stable. [28] Cu²⁺ compounds alone, deposited on a glass substrate, did not show any reaction for NO₂ under UV light illumination. Ag⁺ ions or Fe³⁺ ions loaded on the TiO₂ did not show the NO₂ reduction like Cu²⁺, although the redox potentials are sufficient for the reduction of NO₂ to NO (Fig. 2). [29] The unique property of Cu²⁺ for reduction of NO₂ is most probably related to the adsorption process and the electron transfer process between NO₂ and Cu²⁺, which will be easily inhibited by O₂ in air in case of the other metallic ions. In contrast, the release of NO in Fig. 1 is considered to be caused by the competitive adsorption of O₂ in air to Cu²⁺.

3.2. Photocatalytic reaction with NO

Fig. 3 shows the time dependencies of the concentrations of NO, NO₂, and NO_x (=NO+NO₂) and the accumulated amount of HNO₃ on the Cu²⁺-loaded (2 μmol) TiO₂ film. The concentration change of NO due to adsorption was negligible in the dark. Under UV light illumination, the NO concentration dropped to ~0.92 ppm, while the NO₂ concentration increased to 0.05 ppm. HNO₃ was produced and accumulated in the TiO₂ film, and saturated at ~0.15 μmol. The nitrogen mass was balanced between the removed NO_x gas and the recovered HNO₃ from the TiO₂ film during the reaction. The concentration change of NO_x and the production of HNO₃ stopped after 1 h, while the oxidation of NO to NO₂ continued over 15 h. The NO oxidation behavior of the Cu²⁺-loaded TiO₂ film is different from that of the bare TiO₂ film, as shown in Fig. 3(dashed line). The bare TiO₂ converted NO to HNO₃ effectively (the quantum efficiency, ~0.7%), and the maximum amount of HNO₃ was ~0.5 μmol. [30] On the other hand, the Cu²⁺-loaded TiO₂ film shows a reduced oxidation activity of NO to HNO₃ in air. The sequence of the photocatalytic oxidation of NO to HNO₃ is considered as follows [5,31–34].

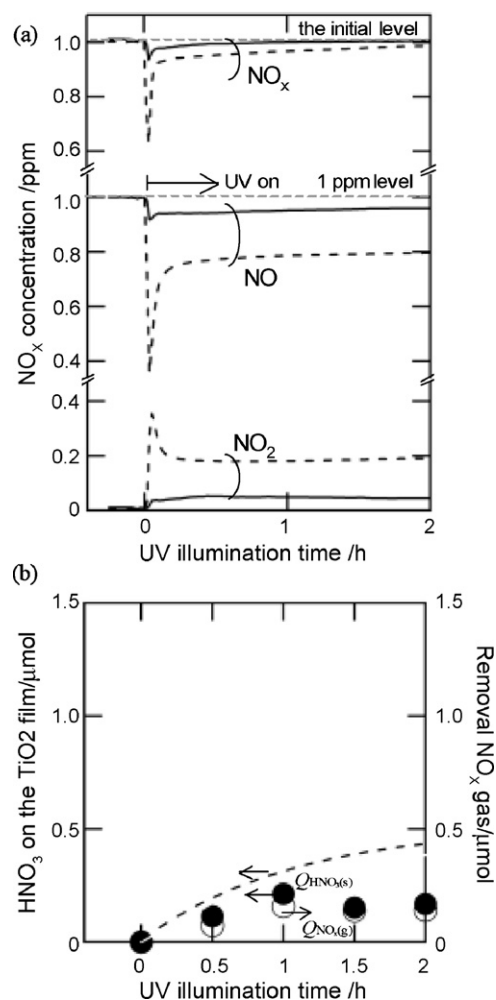
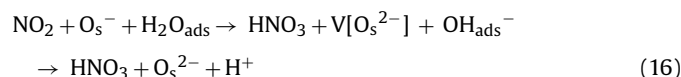
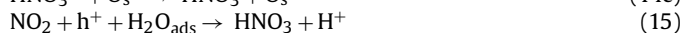
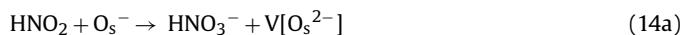
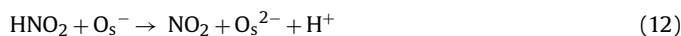
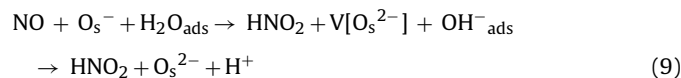


Fig. 3. (a) Concentrations of NO, NO₂, and NO_x (=NO+NO₂) as a function of UV illumination time in the photocatalytic reaction of NO using the Cu²⁺-loaded TiO₂ film (Cu²⁺, 2 μmol; UV intensity, 1 mW cm⁻²; initial NO and NO₂ concentrations, 1 and 0.01 ppm, respectively). (b) The amount of HNO₃ recovered from the TiO₂ film ($Q_{\text{HNO}_3(\text{s})}$) (●) and that of NO_x removed from air ($Q_{\text{NO}_x(\text{g})}$) (○) as a function of UV illumination time. The dashed lines indicate the data using the bare TiO₂ film.



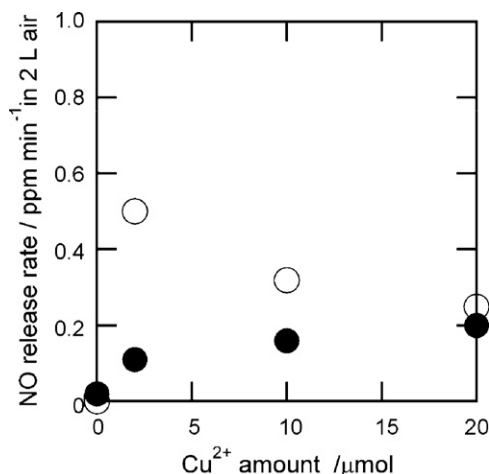


Fig. 4. Dependence of the initial rate (○) and the final steady rate (●) of the NO production in the photocatalytic reaction of NO₂ using the Cu²⁺-loaded TiO₂ films on the amount of Cu²⁺.



where O_s²⁻ represents terminal (bridging) oxygen ions and V[O_s²⁻] are bridging oxygen vacancies. The photo-excited electrons (e⁻) will be captured by O₂ in air, and then produced O₂^{-•} and HO₂[•] also contribute to the NO oxidation, e.g., NO + HO₂[•] → HNO₃, etc.

The low efficiency of the Cu²⁺-loaded TiO₂ for the production of HNO₃ is explained by the action of Cu²⁺ to reduce NO₂ to NO as Eqs. (2)–(5). Assuming that the oxidation of NO proceeds consecutively as Eqs. (7)–(17), it is reasonable that Cu²⁺-loaded TiO₂ is able to revert NO₂, an intermediate species in the NO oxidation, to NO on the way to the HNO₃ production. Therefore, the production of HNO₃ is greatly suppressed when using the Cu²⁺-loaded TiO₂ film.

3.3. Cu²⁺ dependency

Next, we examined the dependency of the NO production rate on the amount of Cu²⁺. Fig. 4 shows the initial- and final rate for NO production under UV light illumination: the initial rate is reduced, while the final rate is enhanced with increasing Cu²⁺ concentration. The result is explained as follows; the photocatalytic reaction is physically inhibited by addition of CuSO₄. However, the Cu²⁺ ions serve as the reductive sites on the TiO₂ film in air. A higher Cu²⁺ ion concentration increases the probability for NO₂ to be reduced in air before being oxidized by photogenerated holes. For the present investigation no sacrificial agent has been used to enhance the reductive reaction. The observed high production rate of NO and the long time stability of the selective reduction of NO₂ to NO are indicative that Cu²⁺ ions act not only as an electron transfer from TiO₂ to NO but also as a hole-scavenger recycling between the states of Cu²⁺ and Cu⁺ or Cu²⁺ and Cu, because Cu²⁺ has a good redox property between the states of Cu²⁺, Cu⁺, and Cu. There was no change in the sample color under UV light illumination. However, the valence state of Cu²⁺ is difficult to examine in the current experiment, since Cu nanoparticles are known to be quickly oxidized in air [27].

3.4. Reaction mechanism

To consider the reaction mechanism more deeply, we examined whether NO₂⁻ or NO₃⁻ will be changed to NO or NO₂ on the Cu²⁺-loaded TiO₂ film. NaNO₂ (2 μmol) or NaNO₃ (2 μmol) was pre-deposited on the Cu²⁺-loaded TiO₂ film. As a result, NO₂⁻ was greatly reduced to NO just on the UV light illumination (Fig. 5a). The production of NO decreased rapidly, while the production of NO₂ continued for a longer time period relative to that of NO. The

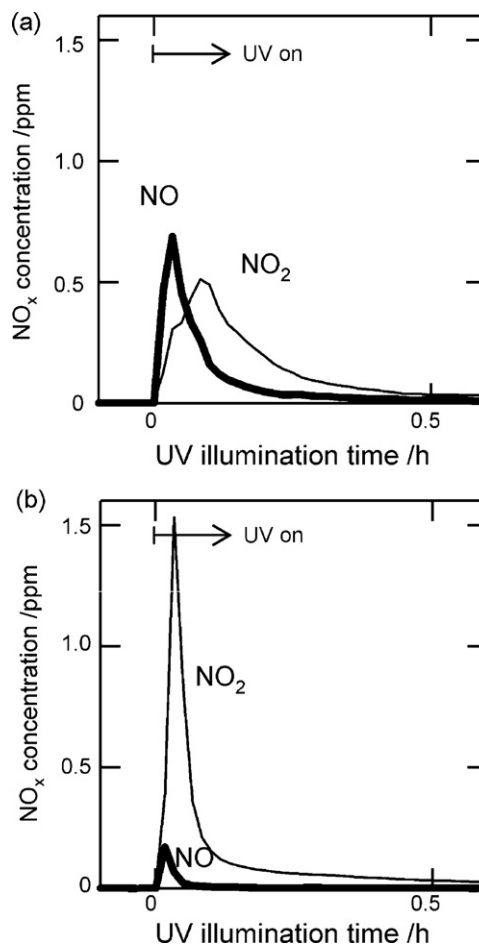
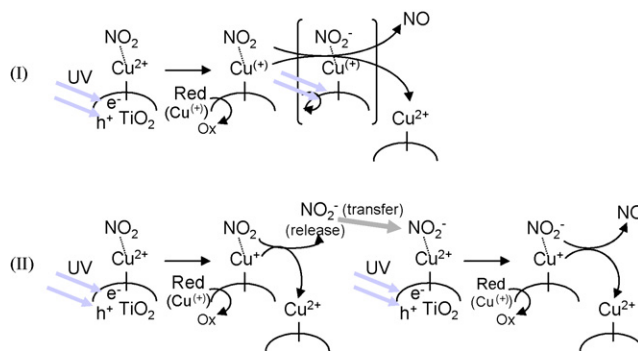


Fig. 5. (a) Concentration changes of NO and NO₂ initiated by UV light illumination when using the Cu²⁺-loaded TiO₂ film (Cu²⁺, 2 μmol) on which ~2 μmol of NaNO₂ was pre-deposited. (b) Concentration changes of NO and NO₂ initiated by UV light illumination when using the bare TiO₂ film on which ~2 μmol of NaNO₂ was pre-deposited.

reaction rates of reduction of NO₂⁻ to NO and oxidation of NO₂⁻ to NO₂ reversed under continuous UV light illumination. The latter NO₂ production may be caused by the normal oxidative reaction for NO₂⁻, or the formation of NO₃ radicals, [30] reacting with NO produced by the effect of Cu²⁺. On the other hand, when we used the bare TiO₂ film, NO₂⁻ was predominantly oxidized to NO₂ (Fig. 5b). NO₃⁻ was merely reduced to NO or NO₂ under UV light illumination for both the samples. This indicates that NO₃⁻ is much more stable and having less interaction with Cu²⁺ than NO₂⁻.



Scheme 1. Suggested Mechanism of NO₂ reduction to NO on the Cu²⁺-loaded TiO₂ photocatalyst.

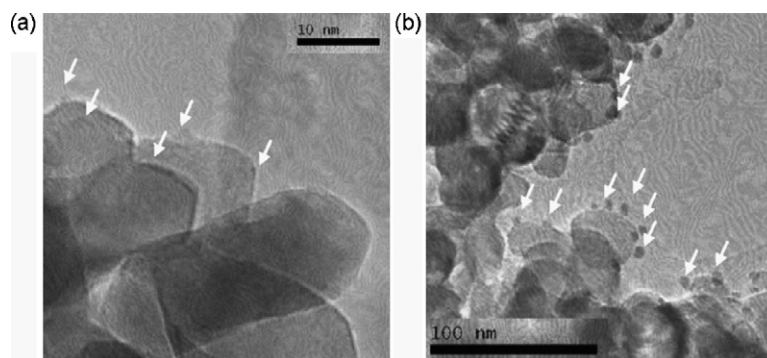


Fig. 6. TEM images of TiO₂ nanoparticles loaded with Cu²⁺ (a) 2 μmol; (b) 20 μmol; Cu²⁺ origin nanoparticles were arrowed.

Based on the results, we propose a reaction mechanism as shown in Scheme 1: (I) NO₂ is reduced to NO on the same Cu²⁺ during the reaction, and (II) NO₂ is reduced to NO₂⁻ on a Cu²⁺. If NO₂⁻ is released from the Cu²⁺, another Cu²⁺ will reduce the NO₂⁻ to NO. A high Cu²⁺ density is therefore favorable to find another Cu²⁺ for the released NO₂⁻. Cu²⁺ may act as recombination center for positive holes because the reduced Cu²⁺ (Cu⁺ and Cu) is formed by photogenerated electrons. The stability increased with increasing the Cu²⁺ amount. In both the mechanisms, it is important to restrain the oxidation reaction to HNO₃.

Nanoparticles of Cu²⁺ compounds were verified on the TiO₂ nanoparticles (~20 nm) by TEM (Fig. 6). The density of nanoparticles of the Cu²⁺ compounds on the sample of Cu²⁺-20 μmol is much higher than that of Cu²⁺-2 μmol. The apparent density of Cu²⁺ on the TiO₂ surface is calculated to be ~1.7 ions per nm² for the Cu²⁺-2 μmol sample, and ~17 ions per nm² for the Cu²⁺-20 μmol sample, according to the surface area of TiO₂ nanoparticles (50 m² g⁻¹) [25] and the weight of the TiO₂ film (~14 mg). The volume of ~17 units of CuSO₄ is ca. 1.1 nm³. The observed Cu²⁺ compounds roughly agreed with the above calculated result. However, it should be mentioned that the TEM observation is conducted in vacuum. The image may be different from that in air, thus some Cu²⁺ must be dissolved from the CuSO₄ into the adsorbed water on the TiO₂ surface in air. In addition, the adsorbed Cu²⁺ on the TiO₂ surface must be considered, which is not possible to show by TEM.

4. Conclusions

In summary, Cu²⁺-loaded on the TiO₂ surface, was found to exhibit a high activity of the selective reduction of NO₂ to NO in air under UV light illumination (1 mW cm⁻²). The behavior for NO₂ is complementary to bare TiO₂, oxidizing NO₂ to HNO₃. The reaction of NO_x gases to HNO₃ was seriously suppressed by Cu²⁺ loading. Similar phenomena were not observed for Fe³⁺ and Ag⁺ loads. It is concluded that Cu²⁺ plays the following roles for the reduction of NO₂: (1) adsorption site for NO₂/NO₂⁻, (2) electron acceptor from the TiO₂, (3) electron donor for NO₂/NO₂⁻, (4) recombination center for positive holes, and (5) recyclable redox agent. The findings will be a typical model to utilize the reductive energy of TiO₂ photocatalysis in the gas-phase for producing another gaseous species in air, except for O₂. It might be possible to make an ideal photocatalysts to reduce NO_x gas to N₂ in air, different from the ordinal type that utilizes only oxidation reactions and deactivates due to the accumulation of the produced HNO₃.

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