

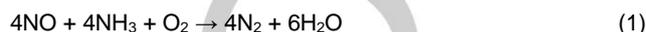
Visible-Light-Assisted Selective Catalytic Reduction of NO with NH₃ over Dye-Modified TiO₂ Photocatalysts

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Abstract: Dye-modified TiO₂ photocatalysts showed high photocatalytic activity for the selective catalytic reduction of NO with NH₃ in the presence of O₂ under visible-light irradiation. Among the 15 dyes investigated, the maximum conversion was achieved using a Ru(2,2'-bipyridyl-4,4'-dicarboxylic acid)₂(NCS)₂ complex (N3-dye) for the modification of TiO₂ (NO conversion > 99%, N₂ selectivity > 99%). Diffuse reflectance infrared Fourier transform (DRIFT) investigation showed that nitrite (NO₂⁻) and nitrate (NO₃⁻) species were generated on the N3-TiO₂ surface under visible-light irradiation. In gas switch reactions, NO₂⁻ on the N3-TiO₂ surface became N₂ by a reaction with adsorbed NH₃ under visible-light irradiation, although NO₃⁻ reacted with NH₃ to form N₂ and N₂O. Based on the reactivity with NH₃, we concluded that the NO₂⁻ species is an intermediate in photo-SCR and reacts with NH₃ adsorbed on the surface of N3-TiO₂ under visible-light irradiation to selectively form N₂.

Introduction

Nitrogen oxides (NO_x) are air pollutants and cause serious environmental problems, including acid rain and town smog. The removal of NO_x in exhaust gases that contain excess O₂ is an important process in air purification. Typically, NO_x are decomposed to harmless N₂ using selective catalytic reduction with ammonia (NH₃-SCR) over vanadium oxide-based catalysts^[1] and Fe- or Cu-zeolite catalysts,^[2] according to eq. 1.



These catalysts, however, cannot efficiently remove NO_x from diesel engines during cold start condition (< 473 K).^[3] Therefore, novel catalysts that can perform NH₃-SCR at low temperatures are strongly required.

We have reported photocatalysts that show activity for NH₃-SCR at low temperatures in the presence of excess O₂ (referred to as photo-SCR).^[4] The reaction mechanism of photo-SCR has been investigated by us and other groups using spectroscopic,^[5] kinetic,^[4b, 6] and theoretical^[7] methods. Over TiO₂ photocatalyst, the conversion of NO and the selectivity to N₂ becomes 90% and 99%, respectively, at a gas hourly space velocity (GHSV) of 8000 h⁻¹, which is sufficient for the De-NO_x process in typical stationary sources such as power plants, blast furnaces, and incinerators. However, higher GHSV values (>50000 h⁻¹) are required in diesel engines owing to the limited installation space of the De-NO_x process and a high flow rate of the exhaust gas.

Recently, we reported that porphyrin-sensitized TiO₂ functions as a visible-light-sensitive photocatalyst for NH₃-SCR. This reaction proceeds via electron injection from photo-excited dyes into the conduction band of TiO₂ (dye-sensitization mechanism),^[8] although a detailed mechanism of the reaction is unclear. The electron injection process from photo-excited dyes into the conduction band of a semiconductor is an important step in dye-sensitized solar cells (DSSCs)^[9] and dye-sensitized photocatalysts,^[10] and has been previously investigated.^[11] Many researchers have tested various dyes, including Ru complexes,^[12] porphyrins,^[13] phthalocyanines,^[14] and other organic dyes,^[9b, 10c, 15] to improve the performance of DSSCs and dye-sensitized photocatalysts. The type of dye used for the modification of semiconductors has a great impact on the performance of DSSCs and dye-sensitized photocatalysts, and thus, should have a significant effect on the activity in photo-SCR under visible-light irradiation. A major problem of the dye-sensitization system is the stability of the dyes; moreover, optimization of the dye is essential to evaluate and improve the performance of photo-SCR over dye-modified TiO₂ photocatalysts. Herein, we investigated photo-SCR under visible-light irradiation using TiO₂ photocatalysts modified with 15 different dyes (Fig. 1). The reactivity of the adsorbed intermediates generated over the dye-modified TiO₂ photocatalyst were also investigated by means of *in situ* diffuse reflectance infrared Fourier transform (DRIFT) and UV-Vis diffuse reflectance (DR) spectroscopies to elucidate the reaction mechanism.

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Results and Discussion

Screening of dyes. Fig. 2 shows the results of photo-SCR over dye-modified TiO₂ photocatalysts. The reaction proceeded to some extent (ca. 5%) over a bare TiO₂ photocatalyst under visible-light irradiation, as reported in the previous paper.^[16] Modification of TiO₂ with various dyes greatly enhanced photo-SCR activities. The maximum conversion of NO (>99%) was obtained using an N3-dye (**1** in Fig. 1)-modified TiO₂ photocatalyst (N3-TiO₂) after 30 min. The conversion of NO was significantly higher than those of other photocatalysts (e.g., UV-light irradiated TiO₂)^[4d, 8] and conventional catalysts (e.g., Fe- and Cu-zeolite catalysts)^[17] at low temperatures. N₂O was not detected in all reactions shown in Fig. 2. The high selectivity to N₂ is consistent with our previous reports of photo-SCR over porphyrin-modified TiO₂ photocatalysts under visible-light irradiation.^[8] The order of activities is discussed in the last section.

The conversion of NO was almost stable over 180 min of visible-light irradiation over the TiO₂ photocatalysts modified with Ru(bpy)₃Cl₂ **4**, TCPP **7**, phthalocyanines **9** and **11**, and RhCl₃ **12**. A relatively high stability was observed in the case of N3-dye (**1**), and the N3-TiO₂ photocatalyst showed the highest conversion of NO even at 180 min (95%). When xanthenes dyes were used, relatively high conversions of NO were obtained after 30 min; rose bengal **2** (81%), eosin Y **3** (80%), and rhodamine B **5** (63%). However, as shown by the time course of photo-SCR (Fig. 3), conversions gradually decreased over 180 min of the reaction. Bleaching of the catalyst colors was observed after the reaction, which suggests that the decrease in the activity was due to dye decomposition. The low stability of xanthenes dyes was consistent with previously reported DSSCs.^[9b, 18] Thus, the xanthenes dyes were deemed unsuitable for photo-SCR.

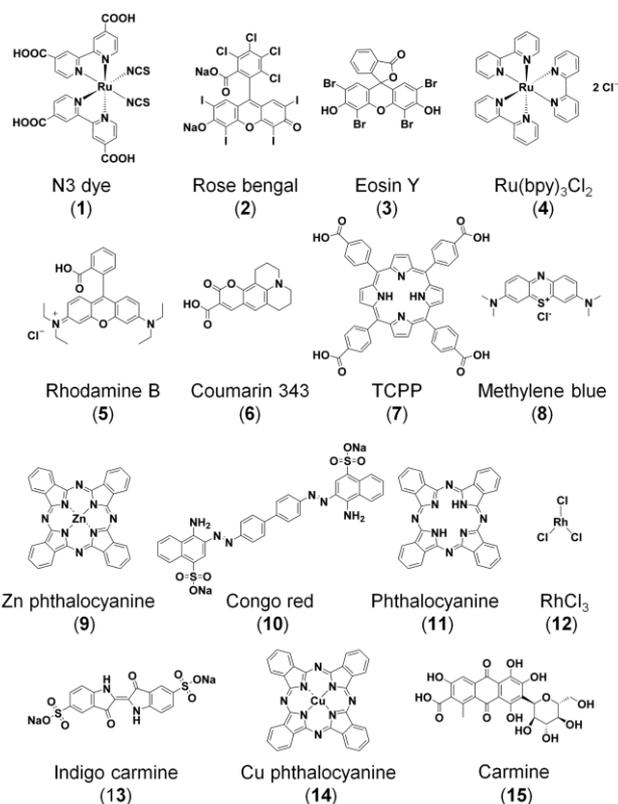


Figure 1. Schematic representation of dyes.

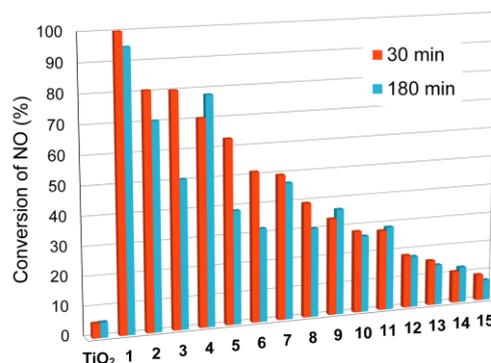


Figure 2. Conversion of NO in photo-SCR over the dye-modified TiO₂ photocatalysts under visible-light irradiation. Dye loading: 12.5 μmol g⁻¹. GHSV: 100000 h⁻¹. The numbers in the bottom axis correspond to those in Fig. 1.

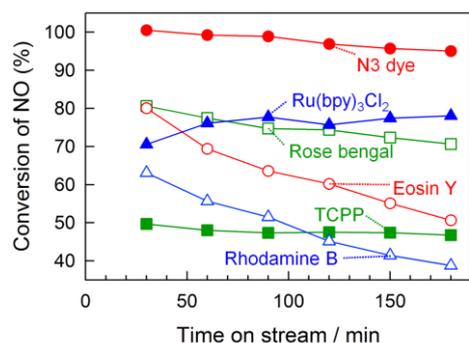


Figure 3. Time course of the conversion of NO in photo-SCR over the dye-modified TiO₂ photocatalysts under visible-light irradiation. Dye loading: 12.5 μmol g⁻¹. GHSV: 100000 h⁻¹.

Reactivity of adsorbed species of NH₃ and NO. Table 1 lists the results of reactions under various conditions. Efficient N₂ formation was observed over N3-TiO₂ in the presence of NO, NH₃, and O₂ under visible-light irradiation (640 ppm, entry 2). The activity of N3-TiO₂ was significantly higher than that of a bare TiO₂ photocatalyst under UV and visible light irradiation (290 ppm, entry 1). Product formation was greatly diminished without NO, NH₃, or O₂ (entries 3, 4, and 5), which indicated that all the gases are involved in the formation of N₂. Furthermore, visible-light irradiation drastically promoted photo-SCR over N3-TiO₂ (entry 6).

A couple of gas switch experiments were carried out to investigate the reactivity of the adsorbed species of NH₃ and NO on the N3-TiO₂ surface. In the first experiment, NH₃/He gas was flowed in the first 120 min in the dark (Fig. 4(A)), and no product was observed. Subsequently, the feed gas was switched to NO/O₂/He gas and visible-light irradiation was started. Selective formation of N₂ (910 ppm, selectivity to N₂ > 99%) was observed after 5 min of visible-light irradiation. The concentration of N₂ in the outlet gas gradually decreased with increasing visible-light irradiation time and dropped to 24 ppm after 270 min. This formation of N₂ presumably derived from the reaction between the initially adsorbed NH₃ and NO in the gas phase, because low amounts N₂ were formed via a reaction between NO and O₂ under visible-light irradiation (Table 1, entry 4).

In the second experiment, NO/O₂/He gas was flowed under visible-light irradiation for 90 min, and then the feed gas was switched to NH₃/He gas in the dark (Fig. 4(B)). During this period, a small amount of N₂ was formed and N₂O was not detected. After 120 min of the NH₃/He gas flow in the dark, visible-light irradiation was started and N₂ (780 ppm) and N₂O (130 ppm) were observed (selectivity to N₂: 86%) after 5 min; the concentrations gradually decreased as the irradiation time was increased. The blank test results showed that NH₃ did not decompose to N₂ over N3-TiO₂ under visible-light irradiation (Table 1, entry 3). Accordingly, this formation of N₂ and N₂O was due to the reaction between the adsorbed NH₃ and the surface NO_x species formed by the addition of NO/O₂/He gas under visible-light irradiation. The NO_x species on the surface of N3-TiO₂ did not react with NH₃ without visible-light irradiation, which

indicated that visible-light was essential for this surface reaction. Based on the gas switch experiment, we concluded that surface NO_x species became N₂ and N₂O by a reaction with adsorbed NH₃ on the N3-TiO₂ surface under visible-light irradiation (Langmuir-Hinshelwood mechanism).

Table 1. Result of photo-SCR under various reaction conditions.

Entry	Catalyst	Inlet (%) ^[a]			Lamp ^[b]	Outlet (ppm) ^[c]	
		NO	NH ₃	O ₂		N ₂	N ₂ O
1	TiO ₂	0.1	0.1	2	UV+Vis.	290	4
2	N3-TiO ₂ ^[d]	0.1	0.1	2	Vis.	640	n.d. ^[e]
3	N3-TiO ₂ ^[d]	0	0.1	2	Vis.	14	n.d. ^[e]
4	N3-TiO ₂ ^[d]	0.1	0	2	Vis.	10	n.d. ^[e]
5	N3-TiO ₂ ^[d]	0.1	0.1	0	Vis.	35	7
6	N3-TiO ₂ ^[d]	0.1	0.1	2	OFF	15	n.d. ^[e]
7	N3-SiO ₂ ^[d]	0.1	0.1	2	Vis.	16	n.d. ^[e]

[a] Concentration of N₂ and N₂O in the inlet gas. [b] Light source, UV+Vis: 300 W Xe lamp without cut-off filter, Vis: 300 W Xe lamp with L-42 cut-off filter. [c] Concentration of N₂ and N₂O in the outlet gas. GHSV: 250000 h⁻¹, total flow rate: 500 ml min⁻¹, catalyst amount: 110 mg. [d] Loading of N3-dye: 37.5 μmol g⁻¹. [e] Not detected.

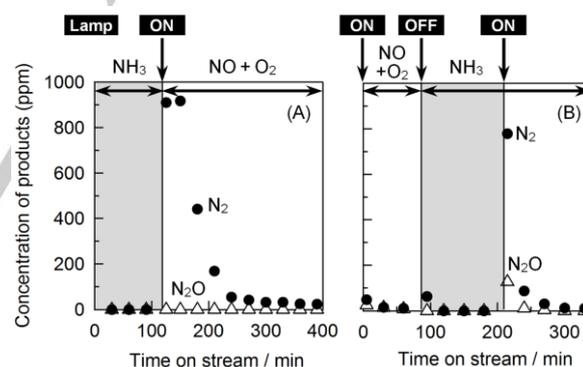


Figure 4. Time course of concentration of N₂ and N₂O in the outlet gas in the gas switch reactions. Catalyst: 37.5 μmol g⁻¹ N3-TiO₂, NO: 1000 ppm, NH₃: 1000 ppm, O₂: 2 %, He: balance. GHSV: 8000 h⁻¹, Light source: 300 W Xe lamp equipped with a L42 cut-off filter.

DRIFT investigations of surface NO_x species. Fig. 5 represents the DRIFT spectra before and after the addition of NO/O₂/He gas in the dark. The spectrum before the addition was used as the baseline. Two peaks, at 1478 and 1198 cm⁻¹, gradually increased with increasing the exposure time (Fig. 5(A)). The peak at 1478 cm⁻¹ was assigned to a ν₃ vibration of monodentate NO₂⁻ adsorbed on the surface of N3-TiO₂. This species is also expected to have a ν₁ vibration band between 1065 and 1050 cm⁻¹.^[19] In the DRIFT experiment, a shoulder band was observed around that region, which supports its

proposed generation. The peak at 1198 cm^{-1} was assigned to a bridged bidentate NO_2^- in a previous paper.^[19] Three negative peaks at 3697 , 3659 , and 3631 cm^{-1} , and a broad positive peak around 3500 cm^{-1} appeared after the addition of $\text{NO}/\text{O}_2/\text{He}$ gas (Fig. 5(B)). The negative peaks were assigned to isolated OH groups in different surroundings (e.g., number of coordinated Ti atom, valence of coordinated Ti atom, surface sites of TiO_2)^[20] and the broad positive peak was attributed to a hydrogen-bonded OH group. We did not observe a characteristic band of deformation vibration of water molecules around 1640 cm^{-1} , which indicated that the amount of adsorbed water did not change by the co-adsorption of NO and O_2 . Thus, the increase of the band intensity centered at 3500 cm^{-1} is not due to the adsorption of water molecules generated. The change in the OH region suggests that the adsorbed NO_2^- species interacted with the isolated OH groups through hydrogen bonding, thus reducing the band intensities of the isolated OH groups and increasing the hydrogen-bond-related band intensity. Both NO_2^- species (monodentate and bridged bidentate) were generated on the surface of N3-TiO_2 by the co-adsorption of NO and O_2 in the dark.

After 30 min of NO/O_2 gas flow, O_2/He gas was introduced to the DRIFT cell, and then visible-light irradiation was started across the KBr window. As shown in Fig. 6(A), the band at 1478 cm^{-1} decreased with visible-light irradiation, which indicated that the NO_2^- species were consumed by the reaction with O_2 under visible-light irradiation. New bands at 1605 , 1583 , 1297 , and 1253 cm^{-1} increased with increasing irradiation time. Bands at 1605 and 1253 cm^{-1} were attributed to a ν_3 vibration of the bridging bidentate nitrate (NO_3^-), and a set of bands at 1583 and 1297 cm^{-1} was assigned to the chelating bidentate NO_3^- .^[19] Thus, the NO_2^- species was oxidized into the NO_3^- species under visible-light irradiation. In the OH region (Fig. 6(B)), the isolated OH bands at 3697 , 3659 , and 3631 cm^{-1} decreased with visible-light irradiation, suggesting that the surface OH groups reacted with the adsorbed NO_2^- to form NO_3^- . The DRIFT investigation revealed that the NO_2^- species appeared after the co-adsorption of NO and O_2 in the dark, and were oxidized into NO_3^- by O_2 under visible-light irradiation (Scheme 1).

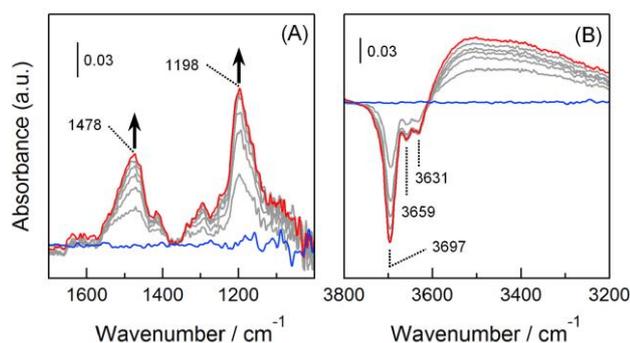


Figure 5. DRIFT spectra of N3-TiO_2 in the dark before addition of $\text{NO}/\text{O}_2/\text{He}$ gas (blue line), and after 5, 10, 15, 20, 25 (grey lines), and 30 min (red line).

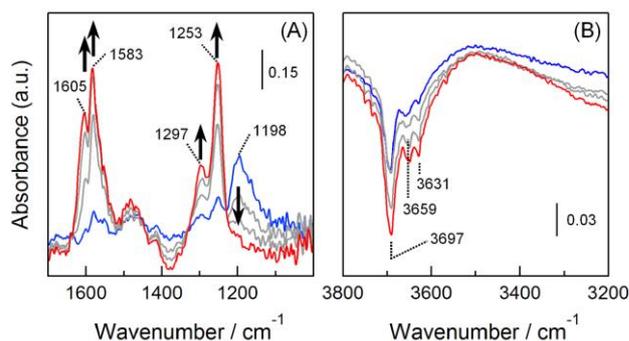


Figure 6. DRIFT spectra of N3-TiO_2 in O_2/He gas before visible-light irradiation (blue line), and after 20 min, 40 min (grey lines), and 60 min (red line) from the start of visible-light irradiation.

Reactivity of the NO_2^- and NO_3^- species with NH_3 under visible-light irradiation.

Either NaNO_2 or NaNO_3 was impregnated over N3-TiO_2 in order to investigate the reactivity of NO_2^- and NO_3^- on the surface of N3-TiO_2 . NH_3 was flowed into the reactor filled with the NaNO_3 - or NaNO_2 -impregnated catalysts (Fig. 7). In the dark, N_2 and N_2O were not detected in an NH_3/He gas flow for both catalysts. For the NaNO_3 -impregnated N3-TiO_2 , N_2 (2020 ppm) and N_2O (1420 ppm) were observed after 5 min of visible-light irradiation. Not much N_2 was observed in the NH_3/He gas flow under visible-light irradiation in the blank tests (Table 1, entry 3). Thus, the generated N_2 shown in Fig. 7(A) is derived from a reaction between NH_3 in the gas phase and NO_3^- species on the surface of N3-TiO_2 . Surprisingly, a large amount of N_2O was detected in this experiment (selectivity to $\text{N}_2 = 59\%$). In contrast, selective formation of N_2 was observed from the NaNO_2 -impregnated N3-TiO_2 under visible-light irradiation (Fig. 7(B), selectivity to $\text{N}_2 = 94\%$), which suggested that NO_2^- became N_2 on reacting with NH_3 . As shown above, the reactivity of NO_2^- with NH_3 was significantly different from that of NO_3^- in terms of selectivity to N_2 (Scheme 1), which could explain the relatively low selectivity to N_2 (selectivity to $\text{N}_2 = 86\%$) in the gas switch reaction shown in Fig. 4(B); both the NO_2^- and NO_3^- species were formed in $\text{NO}/\text{O}_2/\text{He}$ gas under visible-light irradiation on the surface of N3-TiO_2 and reacted with NH_3 . High selectivity to N_2 (>99%) in photo-SCR in the presence of NO , NH_3 , and O_2 (Table 1, entry 1) over N3-TiO_2 strongly indicated that an intermediate in photo-SCR was NO_2^- was adsorbed on the surface of N3-TiO_2 on the basis of the difference in their reactivity.

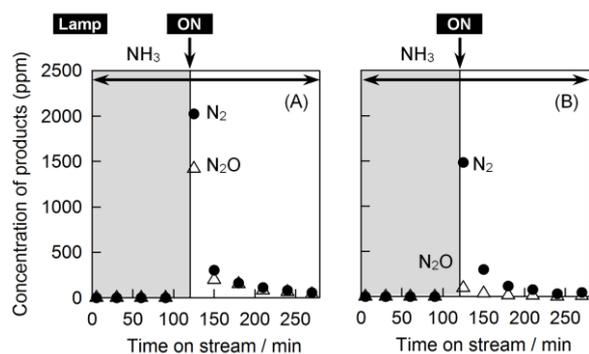
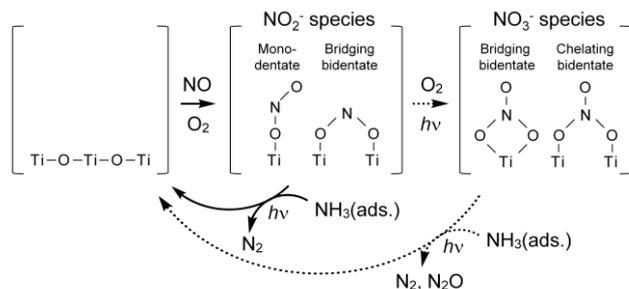


Figure 7. Time course of concentration of N_2 and N_2O in the outlet gas over (A) $NaNO_3$ -impregnated $N3-TiO_2$ and (B) $NaNO_2$ -impregnated $N3-TiO_2$. Loading of $NaNO_3$ or $NaNO_2$: $1000 \mu mol g^{-1}$. Loading of $N3$ -dye: $37.5 \mu mol g^{-1}$. Reaction gas: $1000 ppm NH_3/He$. GHSV: $8000 h^{-1}$, light source: $300 W$ Xe lamp equipped with a L42 cut-off filter.



Scheme 1. Surface NO_x species on $N3-TiO_2$ catalyst and its reactivity with NH_3 under visible light irradiation.

Role of dyes. As shown in Table 1, the activity of $N3-SiO_2$ catalyst was very low (conversion of NO : 1.6%, entry 7), which indicated that the $N3$ -dye did not function independently of the support (i.e., TiO_2). Thus, the reaction over $N3-TiO_2$ proceeds via a dye-sensitization mechanism: visible-light irradiation induces the electron injection from photo-excited dyes to the conduction band of TiO_2 . A similar result was obtained in porphyrin-modified TiO_2 photocatalysts.^[8] After the electron injection, the oxidation product of $N3$ -dye and an electron in the conduction band of TiO_2 should be generated as shown in eq. 2:



Based on eq. 2, we investigated the reactivity of the oxidation product of $N3$ -dye with NH_3 . In a previous report,^[21] the one-electron oxidation product of $Ru^{2+}(bpy)_3$ (i.e., $Ru^{3+}(bpy)_3$) in zeolite was prepared using Cl_2 as an oxidant, and we attempted the corresponding oxidation of $N3$ -dye. However, $N3\text{-dye}^+$ could not be prepared because of its instability, although an oxidized $N3$ -dye species, which underwent further transformations from $N3\text{-dye}^+$, reacted with NH_3 and returned to the initial state (for details, see ESI). Therefore, we used the TiO_2 photocatalyst modified with $Ru^{2+}(bpy)_3Cl_2$ (4 in Fig. 1) in the UV-Vis spectroscopic study and investigated the reactivity of $Ru^{3+}(bpy)_3$ with NH_3 (Fig. 8). After the evacuation of $Ru(bpy)_3Cl_2/TiO_2$, an

adsorption band at 455 nm was observed (spectrum (a) in Fig. 8) and attributed to an MLCT band of $Ru^{2+}(bpy)_3$. After the addition of Cl_2 , the catalyst color changed from light orange to slightly greyish orange and the adsorption at 600–800 nm increased (spectra (b)), which was assigned to an LMCT band of $Ru^{3+}(bpy)_3$.^[21] As previously mentioned, $Ru^{3+}(bpy)_3$ was successfully prepared on the TiO_2 surface by using Cl_2 as an oxidant. Subsequent introduction of NH_3 to the cell resulted in a decrease in the adsorption at 600–800 nm (spectra (c)), which clearly showed the reaction of $Ru^{3+}(bpy)_3$ with NH_3 and reduction to the initial $Ru^{2+}(bpy)_3$ species. The UV-Vis spectroscopic result shows that $Ru^{3+}(bpy)_3$ has the potential to oxidize NH_3 . We concluded that $Ru^{3+}(bpy)_3$, generated after the electron injection, activates NH_3 to an NH_2 radical (eq. 3),^[16] which reacts with NO_2^- to form N_2 selectively.^[4b, 16]

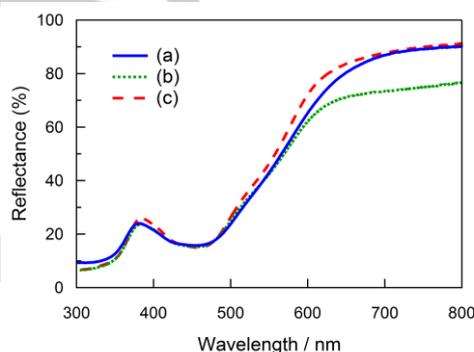
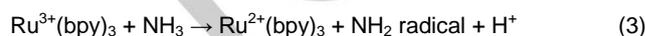
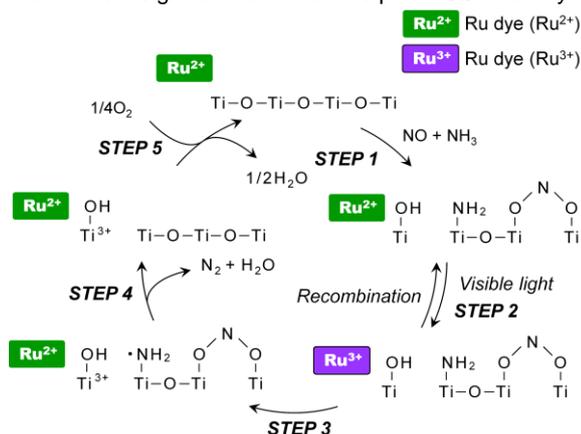


Figure 8. UV-Vis DR spectra of the TiO_2 photocatalyst modified with $Ru(bpy)_3Cl_2$ after evacuation (a), after addition of Cl_2 , and after addition of NH_3 . Dye loading: $37.5 \mu mol g^{-1}$.

Proposed reaction mechanism and effects of dyes on the activity. Based on the results obtained thus far, we proposed the reaction mechanism of photo-SCR over Ru -dye-modified TiO_2 photocatalysts under visible-light irradiation (Scheme 2). The mechanism is composed of five steps: (1) adsorption of NO and NH_3 on the catalyst surface, (2) electron injection from photo-excited Ru dyes into the conduction band of TiO_2 , (3) activation of NH_3 by oxidized Ru dyes, (4) surface reaction between an NH_2 radical and NO_2^- , and (5) re-oxidation of Ti^{3+} sites by O_2 .

In DSSCs, Ru complexes have shown the best photovoltaic properties among a huge number of dyes,^[9b] and $N3$ -dye was known to be an effective Ru dye for DSSCs due to 1) the wide adsorption range to 800 nm, 2) strong adsorption on the semiconductor surface due to binding with up to four carboxyl groups, and 3) sufficiently long excited state life-time ($\sim 20 ns$)^[9b]. In our research, $N3$ -dye showed the highest activity in photo-SCR under visible-light irradiation among the 15 dyes studied. The adsorption of $N3$ -dye was not larger than other dyes as shown in Fig. 9 (UV-Vis adsorption spectra of other dyes studied are shown in Fig. S2). This result indicated that the highest activity was not due to the adsorption amount in the

visible region, although this should be a significant factor. In the case of DSSCs, carboxylic groups were necessary in terms of the strong adsorption of dyes on the semiconductor surface, and the strong adsorption led to strong photovoltaic properties. In this research, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ dye, which does not possess a carboxylic group, also showed high activity (conversion of $\text{NO} = 70.5\%$). A similar result for photo-SCR was obtained in our previous reports using the porphyrin-modified TiO_2 photocatalysts with different functional groups.^[8] Therefore, carboxylic groups were not important to improve the activity, unlike the DSSCs system. Thus, the life-time of the photo-excited state and the reactivity of the oxidized product of dyes with NH_3 , which should affect reaction steps 2 and 3 in Scheme 2, would have a significant effect on the photo-SCR activity.



Scheme 2. Proposed reaction mechanism of photo-SCR under visible-light irradiation over Ru complexes modified TiO_2 photocatalyst.

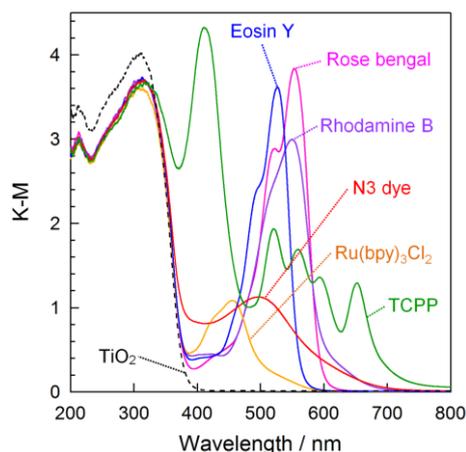


Figure 9. UV-Vis DR spectra of the dye-modified TiO_2 photocatalysts. Dye loading: $12.5 \mu\text{mol g}^{-1}$.

Conclusions

We demonstrated high-performance photocatalysts for NH_3 -SCR under visible-light irradiation by combining popular dyes with

TiO_2 photocatalysts. The screening of 15 dyes displayed that N3-dye was most effective for the modification of TiO_2 . Complete conversion of NO and selectivity to N_2 were achieved over N3- TiO_2 at a high GHSV of 100000 h^{-1} after 30 min of visible-light irradiation. We proposed a reasonable reaction mechanism of the photo-SCR over dye-modified TiO_2 photocatalysts under visible light irradiation by using *in situ* DRIFT and UV-Vis DR spectroscopies. The reaction proceeds via electron injection from dyes excited by visible-light irradiation into the conduction band of TiO_2 (dye-sensitization). The dye oxidation product, generated after the electron injection, oxidatively activates NH_3 , which then reacts with surface NO_2^- through the Langmuir-Hinshelwood mechanism, to provide selective formation of N_2 .

Experimental Section

Catalyst preparation. All dyes were used without further purification, and their structures are shown in Fig. 1. The dyes were impregnated on a TiO_2 powder (ST-01, anatase, $273 \text{ m}^2 \text{ g}^{-1}$), purchased from Ishihara Sangyo Kaisha, Ltd., using appropriate solvents (see ESI). Sodium nitrite (NaNO_2) and sodium nitrate (NaNO_3) were impregnated on the N3-dye-modified photocatalyst using water as the solvent (loading of NaNO_2 or NaNO_3 : $1000 \mu\text{mol g}^{-1}$).

Photocatalytic reaction. Photo-SCR was carried out in a conventional fixed-bed flow system at atmospheric pressure, the details of which we have previously reported.^[4b, 8] In brief, two types of a quartz reactor were used in this research: reactor 1 ($12 \text{ mm} \times 10 \text{ mm} \times 1.0 \text{ mm}$, catalyst amount: 110 mg) for a GHSV of 100000 and 250000 h^{-1} , and reactor 2 ($50 \text{ mm} \times 15 \text{ mm} \times 1.0 \text{ mm}$, catalyst amount: 420 mg) for a GHSV of 8000 h^{-1} . The reaction gas (NO 1000 ppm , NH_3 1000 ppm , O_2 2% , He balance) was introduced to the reactors at a flow rate of $100\text{--}500 \text{ mL min}^{-1}$. A 300 W Xe lamp (PERKIN-ELMER PE300BF) equipped with an L42 cut-off filter was used as a light source ($\lambda > 400 \text{ nm}$). N_2 and nitrous oxide (N_2O) were analyzed using two SHIMADZU GC-8A TCD gas chromatographs.

Characterization. *In situ* DRIFT measurements were performed with a JASCO ISDR-600 FTIR spectrometer equipped with a mercury-cadmium-tellurium (MCT) detector cooled by liquid N_2 at a resolution of 4 cm^{-1} and with 16 co-added scans. The sample powder (50 mg) was placed in a DR cell, which was fitted with a KBr window at the top. The catalyst was pretreated at 353 K under a He gas flow (100 mL min^{-1}) for 1 h , and was then cooled to room temperature. Concentrations of gases were the same as in the reaction. The background spectrum was measured after the pretreatment in a He gas flow at room temperature. A 200 W Hg-Xe lamp equipped with a collective lens (San-Ei Electric Co. Ltd., UVF-204S type C) was used as a light source, and light was irradiated through an L42 cut-off filter. UV-Vis DR spectra were measured using a UV-Vis spectrometer (JASCO V-650) with an integrating sphere. A BaSO_4 plate was used as a reference. A sample powder was added to a quartz cell with flat facets and evacuated at 373 K for 1 h before the measurement. Cl_2 and NH_3 gas were added to the cell using a vacuum line.

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Keywords: Photocatalysis • Nitrogen oxides • Dyes • Environmental chemistry • NH_3 -SCR

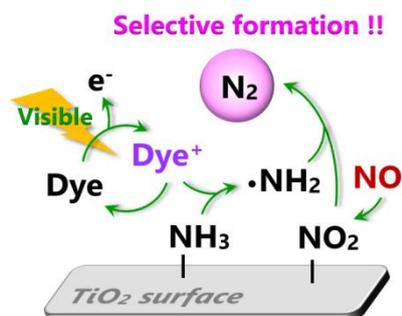
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Entry for the Table of Contents

Layout 1:

FULL PAPER

Dye-sensitized TiO₂ photocatalysts showed high photocatalytic activity for selective catalytic reduction of NO with NH₃ (NH₃-SCR) under visible-light irradiation. DRIFT and reactions under various conditions revealed that surface NO₂⁻ species is an intermediate in the reaction and reacts with adsorbed NH₃ under visible-light irradiation to selectively form N₂.

*Author(s), Corresponding Author(s)***Page No. – Page No.**Title*

Supporting Information

1. Preparation of catalyst

The dye-modified TiO₂ photocatalysts were prepared by a simple impregnation method using organic solvent as shown Table S1.

Table S1. Solvent used for the impregnation

Entry	Dye	Solvent used for the impregnation
1	N3 dye ^[a]	Methanol
2	Rose bengal	Methanol
3	Eosin Y	Methanol
4	Ru(bpy) ₃ Cl ₂	Methanol
5	Rhodamine B	Methanol
6	Coumarin 343	Methanol
7	TCPP ^[b]	Methanol
8	Methylene blue	Methanol
9	Zn phthalocyanine	Trifluoroacetic acid
10	Congo red	Water
11	Phthalocyanine	Trifluoroacetic acid
12	RhCl ₃	Water
13	Indigo carmine	Water
14	Cu phthalocyanine	Trifluoroacetic acid
15	Carmine	10 mmol L ⁻¹ NaOH aq.

^[a] Ru(4,4'-dicarboxy-2,2'-bipyridine)₂(NCS)₂

^[b] Tetrakis(4-carboxyphenyl)porphyrin

2. Reactivity of oxidation product of N3 dye

As shown in the main text, we tried to prepare the one electron oxidation product of N3-dye using Cl_2 as an oxidant. Figure S1 shows the UV-Vis DR spectra of N3-dye and the photographs of the catalysts. After evacuation, the catalyst color was the dark purple (a), and an absorption band at 515 nm was observed. The band is assigned to a MLCT band of the ground state N3-dye (Ru^{2+}). After addition of Cl_2 , the catalyst color changed from dark purple into ochre (b), and the absorption peak was shifted to 420 nm. The band at 420 nm is not attributed to the one electron oxidation products (Ru^{3+}) of N3-dye because the one electron oxidation product have an adsorption band around 740 nm, which was observed in several transient adsorption experiment.^[1,2]

S. Das and P. V. Kamat^[2] investigated the oxidized form of N3-dye by using transient absorption spectroscopy using azide ($\text{N}_3\bullet$) radical generated by γ -Radiolysis as an oxidant. Their results provided the spectral evidence for the formation of two different species that follow the oxidation of N3 dye. One oxidized product (species 1, abs. max: 740 nm) was attributed to the one-electron oxidation product of N3-dye, and is undergone further transformations to the other oxidized form (species 2, abs. max: 440 nm) at room temperature. The identification of species 2 was not made in their report. The ochre products (abs. max: 420 nm) observed in our UV-Vis DR experiments can be assigned to the species 2 judging from the position of adsorption maximum.

To examine the reactivity of species 2, NH_3 was introduced to the cell. After addition of NH_3 , the catalyst color changed into the initial dark purple as shown in Figure S1(c). This result clearly indicates that species 2 can react with NH_3 and returned to the initial ground state of N3 dye (eq. 3 in the main text). Although the identification is not made, and which oxidation products (species 1 or 2) activate NH_3 in the in situ reaction condition is unclear, the UV-Vis DR spectroscopy revealed that oxidized products (at least, species 2) of N3-dye have a potential to activate NH_3 .

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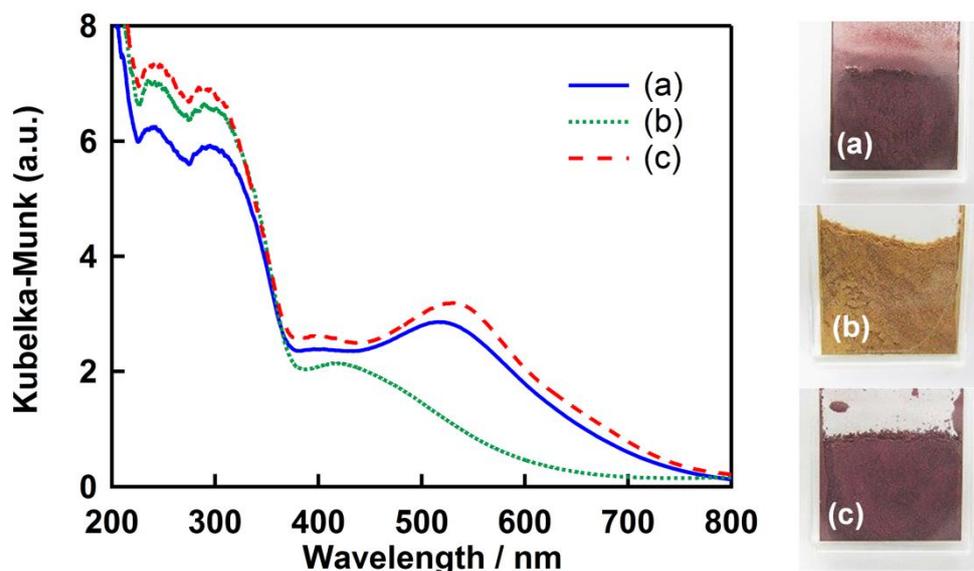


Figure S1. UV-Vis DR spectra and photographs of $37.5 \mu\text{mol g}^{-1}$ N3-TiO₂ photocatalyst after evacuation (a), after addition of Cl₂ (b), and after addition of NH₃ (c).

3. UV-Vis DR spectra of dye-modified TiO₂ photocatalysts

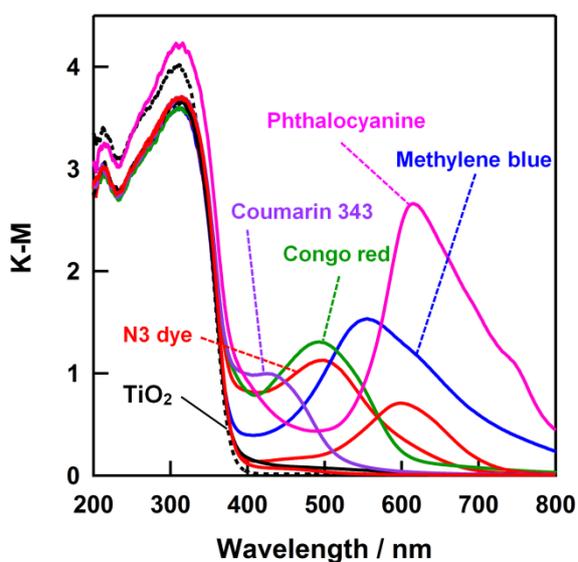


Figure S2. UV-Vis DR spectra of the dye-modified TiO₂ photocatalysts. Dye loading: $12.5 \mu\text{mol g}^{-1}$.