Decomposition of 2-naphthol in water and antibacterial property by NiO and CeO$_x$ modified TiO$_2$ in the dark or under visible light

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Rutile-type TiO$_2$ was modified with NiO and CeO$_x$ using chemisorption calcination cycle method. Then the decomposition activity of 2-naphthol in water was evaluated in the dark or under visible light at 50°C. Little difference was found in the specific surface area or crystal phase before and after modification. The NiO modification decreased the apparent bandgap and provided photocatalytic decomposition activity under visible light. Results suggest that the formation of a Ti–O–Ni interfacial bond yielding a surface d sub-band plays an important role in this increased activity. Although the NiO-modified TiO$_2$ possessed decomposition activity only under visible light, additional modification of CeO$_x$ onto the material enabled decomposition of 2-naphthol in water in the dark at 50°C. The dark activity was attributed to the Mars–van Krevelen mechanism of Ce in CeO$_x$. The NiO-modified TiO$_2$ exhibited high antibacterial activity against *Escherichia coli* and *Staphylococcus aureus* under visible light at room temperature.

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1. Introduction

Titanium oxide (TiO$_2$), a well-known photocatalyst material, is widely applied for various environmental purification uses.$^{1}$ When ultraviolet (UV) is illuminated on the material, electron–hole pairs are generated. These electrons and holes react with water or oxygen, producing radical species such as OH, O$_2^-$, HO$_2$, and H$_2$O$_2$, which can decompose various organic compounds and bacteria.$^{2-4}$

Although this inexpensive material possesses strong oxidation power, an important shortcoming is its requirement of UV light. Because of its bandgap (3.2 eV for anatase; 3.0 eV for rutile),$^5$ photocatalytic decomposition activity of TiO$_2$ is obtainable only under UV illumination. Consequently, numerous investigations have been conducted to shift the required wavelength range from UV to visible light by doping, modification, or using high pressure.$^{1,6-11}$

However, photocatalysts with activity under visible light do not work in the dark. The combination of visible light photocatalysts with the materials that decompose organic compounds in the dark enables continuous environmental purification all through the day. Recently, Shiohara et al. modified rutile-type TiO$_2$ with MnO$_x$ and CeO$_x$ clusters using chemisorption calcination cycle (CCC) method$^{12,13}$ developed by Tada et al. They demonstrated that this material possesses decomposition activity against 2-naphthol in water, either in the dark or under visible light at 50°C.$^{14}$ They attributed the activity in the dark to the Mars–van Krevelen (MvK) mechanism$^{15-17}$ of MnO$_x$ and CeO$_x$. The activity under visible light was attributed to the apparent bandgap decrease caused by the formation of a Ti–O–Mn interfacial bond yielding a surface d sub-band, which disperses around the energy level to overlap with the valence band (VB) of TiO$_2$. Especially, the additional modification of CeO$_x$ onto MnO$_x$-modified TiO$_2$ was effective for the increase of decomposition activity in the dark. They attributed this result to the synergistic effects between MnO$_x$ and CeO$_x$, which has been reported for these two oxides.$^{18,19}$

Earlier studies of the metal oxide cluster modification onto the TiO$_2$ surface using CCC method have indicated that NiO is among the most effective materials for providing decomposition activity under visible light.$^{13}$ Detailed investigation by Iwaszuk et al. using the density functional theory revealed that the VBs of rutile and anatase arise from electronic states on the NiO cluster, which increases...
photon absorption in the visible light region. Results of that investigation also suggest that new vacant levels are generated near the conduction band (CB) minimum of anatase, which contributes to the increase of charge separation yield for photo-excited electrons.20) Earlier studies of the TiO2 modified with metal oxide cluster by CCC method have been conducted mainly using P25, in which anatase is a major phase. Therefore, they stated this as the dominant reason for the advantage of giving high photocatalytic activity of NiO-modified TiO2 under visible light. However, direct evidence of this charge transfer is still insufficient. Moreover, according to works by Shiohara et al., rutile is more effective than anatase for the combination of MvK mechanism with visible light photocatalytic activity.14),21) Furthermore, antibacterial activity under visible light has not been reported on TiO2 modified with metal oxide clusters using CCC method.

Given this background, we prepared NiO-modified rutile-type TiO2 by CCC method for this study. We additionally modified CeO2 onto the surface of the material using the same method. Then decomposition activity against 2-naphthol was evaluated in the dark and also under visible light under the same conditions as those used for the work conducted by Shiohara et al.14) We also evaluated the antibacterial activity of prepared NiO-modified TiO2 under visible light. Bacteria are classified into two categories: gram-negative bacteria and gram-positive bacteria. Gram-negative bacteria possess a lipopolysaccharide outside of outer membrane and a peptidoglycan layer in a cell wall. Gram-positive bacteria have a thicker peptidoglycan layer in the cell wall. For this study, we used Escherichia coli (E. coli) as gram-negative bacteria and used Staphylococcus aureus (S. aureus) as gram-positive bacteria.

2. Experimental

2.1 Sample preparation and characterization

All starting materials used for this study were reagent-grade. A commercial rutile-type TiO2 powder (MT150A; Taiya Corp., Osaka, Japan) was fired at 600°C for 1 h in air. Then precursors of NiO were impregnated to the TiO2 by CCC process. The TiO2 powder (1 g) was dispersed into an ethanol solution (8.0 mmol/L, 10 mL) of nickel(II) acetylacetonate [Ni(acac)2]; Sigma-Aldrich Corp., U.S.A.] and was stored for 24 h at room temperature. After filtration and washing, the powder was dried in vacuum for 24 h. Then it was fired at 500°C for 1 h in air. This impregnation–calcination cycle was repeated four times for NiO modification. These samples are denoted respectively as NiX in this study. The X in the name signifies the repetition numbers for modification. We also conducted CeO2 modification using cerium(III) acetylacetonate [Ce(acac)3]; Sigma-Aldrich Corp., U.S.A.] as a starting chemical under the same condition against Ni3. In the CeO2 modification, only one impregnation–calcination procedure was conducted. Therefore, this sample is denoted as Ni3–Ce1.

The crystalline phase of the powder was evaluated using X-ray diffraction (XRD, XRD-6100; Shimadzu Corp., Tokyo, Japan) with Cu Kα radiation. Specific surface areas were measured using Brunauer–Emmett–Teller method with N2 (BEL SORP mini; Bel Japan Inc., Tokyo, Japan). Morphological features of the powder were observed using a scanning electron microscope (SEM, JEM-7500F; JEOL Ltd., Tokyo, Japan) and a transmission electron microscope (TEM, JEM-2010F; JEOL Ltd., Tokyo, Japan) with Cu Kα X-ray line (1486.6 eV). The valences of Ni and Ce were ascertained from deconvolution of the Ni2p and Ce3d peaks, as they were in earlier studies,22)23) The electron spin resonance (ESR) spectra were evaluated at 90–100 K using an ESR spectrometer (EMXnanno; Bruker Analytik, Germany). The sample powder was placed in a quartz glass sample tube with a Young vacuum joint and a stopcock, followed by evacuation of air from the sample tube. Measurements were taken in the dark and under UV illumination using a UV illuminator (LA-410UV-1; Hayashi Watch Works, Tokyo, Japan) equipped with a 200 W Hg–Xe lamp. The microwave frequency was approximately 9.62 GHz. The microwave power was fixed at 1 mW. The field modulation was 0.05 mT. The photoluminescence (PL) emission spectra were measured using a fluorescence spectrophotometer (F-7100; Hitachi Ltd., Tokyo, Japan). The PL measurements were taken with 300 nm excitation wavelength using a 150 W Xe lamp with 5.0-nm-wide excitation slits, 1200 nm/min scanning speed, and 700 V PMT voltage.

2.2 Decomposition activity measurement

A solution of 2-naphthol (C10H7OH; Fujifilm Wako Pure Chemical Corp.) was prepared by dissolution into an acetonitrile (C3H3N; Fujifilm Wako Pure Chemical Corp.)–water mixture (1:99 volume ratio) solvent (Initial 2-naphthol concentration C0: 4.0 × 10−5 mol/L). The modified TiO2 powder was dispersed into the solution heated at 50°C (by 0.2 g/100 mL). The suspension was stirred at 300 rpm with air bubbling by 100–120 mL/min. After filtration, the 2-naphthol concentration (C) in the solution was analyzed from absorption at 223 nm, which is characteristic to 2-naphthol,24) using UV–Vis spectra. To evaluate the temperature dependence, similar activity evaluation was also conducted for Ni3–Ce1 at 60 and 70°C.

Illumination experiments were conducted in a square Pyrex glass vessel (5 cm × 5 cm × 8 cm) under the same conditions using a light emitting diode (LPWI-10071II; Hayashi Watch Works, Tokyo, Japan) with a L-42 filter (absorbed light <420 nm (50% transmittance); Asahi Glass Co. Ltd., Japan). Because of this experimental
setup, the contribution of the light within the wavelength range that is feasible for pristine rutile excitation is almost negligible. The light illumination was conducted continuously. Its intensity at the inner front surface of the vessel was 6.8 × 10³ lux.

2.3 Antibacterial activity measurement

For this study, we used \( E. \) \( \text{coli} \) (NBRC 3972) and \( S. \) \( \text{aureus} \) (NBRC 12732). Evaluation of the antibacterial activity was conducted following a film adhesion method described in JIS R 1752. Figure SI-1 in Supporting Information presents a flow diagram of the evaluation procedure of this method.

Powder samples were dispersed into ethanol (sample: ethanol = 1 mg:1 mL). The suspension (0.15 mL) was loaded uniformly on a glass substrate (25 mm × 25 mm) and was dried at 100°C for 30 min. Then the substrate was coated with the sample powder (0.15 mg total amount).

Both \( E. \) \( \text{coli} \) and \( S. \) \( \text{aureus} \) were precultured on nutrient agar (NA; Nissui Pharmaceutical Co. Ltd., Tokyo, Japan) at 37°C for 18 h and were suspended in 1/500 nutrient broth (1/500NB; Eiken Chemical Co. Ltd., Tokyo, Japan) that was 1 × NB 500-fold dilution with sterile water. Then the concentration of these bacteria was fixed to ca. 2.0 × 10⁶ colony forming units (CFU)/mL. A 50 µL (=10⁵ CFU) bacteria suspension was pipetted onto a substrate loaded with the sample powder. The substrate was covered with a transparent film to contact the bacteria suspension with the particles. Then it was incubated under a humid condition at room temperature (ca. 25°C). During this incubation, visible light was illuminated using a Xe lamp with an L-42 filter. The illumination intensity was 7000 lux for \( S. \) \( \text{aureus} \) and 15000 lux for \( E. \) \( \text{coli} \). After a certain period (0–20 h), the bacteria were harvested by shaking with 10 mL soybean casein digest broth with lecithin and polysorbate broth (SCDLP; Eiken Chemical Co. Ltd., Tokyo, Japan) for 2 min to halt the incubation. The bacteria in SCDLP were diluted with phosphate buffered saline (Sigma-Aldrich Corp., USA). Each 1 mL of the diluted bacteria suspension was mixed in NA and was incubated at 37°C for 48 h to form bacterial colonies. The concentrations of viable bacterial cells at each time point \( (N) \) were calculated by multiplying the number of colonies and the dilution ratio. The reference cell concentrations were calculated using the same procedure with a glass substrate without samples. The initial cell concentration \( (N_0) \) is equal to the cell concentration at 0 h for each sample. The antibacterial activity was determined as an inactivation value, defined as \( \log_{10}(N/N_0) \).

3. Results and discussion

Figure 1 presents XRD patterns of samples obtained before and after modification by CCC method. No marked difference in intensity was found among the peaks for all samples. The XRD patterns showed only the peaks attributable to rutile structure with \( P4_2/mnm \) (No. 21-1276) space group. The powder gradually became yellowish with increased NiO modification repetitions; it deepened by CeO₂ modification. The specific surface areas of all samples were almost equivalent (31–35 m²/g), except for Ni3–Ce1, which provided slightly higher specific surface area (40 m²/g), probably because of CeO₂. SEM micrographs of the obtained powders are displayed in Fig. SI-2 in Supporting Information. The rutile particle size was 20–100 nm, but images showed no remarkable morphological change by the modification. Figure 2 presents TEM photographs of the obtained powders. Although the portion of NiO was not identified clearly as in many studies of
the metal oxide modification by CCC process,\textsuperscript{13,14,25} the place that seems CeO\textsubscript{x} was identified in the image. The atomic ratios of the circled portions for O, Ti, Ce, and Ni by energy dispersive X-ray spectrometry in Fig. 2(b) are, respectively, 19.2, 59.1, 21.3, and 0.4\%. This image suggests that CeO\textsubscript{x} is approx. 4 nm. However, because of the very small size of this portion and the tilt angle limitation of the sample in TEM, we were unable to make the zone axis of the sample parallel to the electron beam for high-resolution observation.

Table 1 presents surface chemical compositions obtained from XPS analysis. Although the concentration change is fluctuating, the entire amount of Ni gradually increased concomitantly with increasing repetition number. The valences of Ni and Ce obtained from peak separation of XPS spectra were Ni(II), with mixture of Ce(III) and Ce(IV).

Figure 3 depicts UV–vis spectra of obtained powders. The absorption of NiO-modified TiO\textsubscript{2} was extended to a longer wavelength range than that of pristine TiO\textsubscript{2}. No remarkable difference was observed among Ni2, Ni3, and Ni4. The absorption around 700 nm was derived from d-d transition (737 nm) of Ni.\textsuperscript{20} The apparent bandgap values calculated from Kubelka–Munk function for Ni1, Ni2, Ni3, and Ni4 were, respectively, 2.92, 2.89, 2.86, and 2.86 eV. Figure 4 shows the XPS VB spectra for Ni4 and pristine TiO\textsubscript{2}.

Figure 5 presents the concentration changes of 2-naphthol in water at 50\(^\circ\)C under visible light. The rate of concentration decrease of 2-naphthol increased by NiO modification. Although light is illuminated after the confirmation of adsorption equilibrium in general photocatalytic activity measurement, light illumination was conducted simultaneously with sample addition in this study because decomposition and adsorption might occur simultaneously. Actually, NiO modification did not give a decomposition activity in the dark (described below). Therefore, we also conducted photocatalytic activity measurements of the Ni2 sample following a general procedure (light was illuminated after 2 h from sample addition) and confirmed that results were almost identical (see Fig. SI-3 in Supporting Information). This result corresponds to the negligible adsorption of NiX samples in the dark (described below and displayed in Fig. 9).

Figures 6 and 7 depict PL emission spectra of samples and ESR differential spectra of Ni3 before and during UV illumination. Figure 8 presents a schematic illustration of band structure in this system and expected electron transfer. According to computational calculations presented by Iwaszuk et al.,\textsuperscript{20} NiO forms Ti–O–Ni bonding with TiO\textsubscript{2}. The CCC process,\textsuperscript{12–14,27} Tada et al. proposed the formation of a Ti–O–metal interfacial bond yielding a surface d sub-band. They reported that the band disperses around the energy level to overlap with the VB of TiO\textsubscript{2}.\textsuperscript{12} Their model was supported also by several other more extensive studies, some of which have presented results of computational calculations.\textsuperscript{13,14,20,27–32}

Table 1. Chemical composition and specific surface area of samples

| Atomic ratio | Specific surface area [m\textsuperscript{2}/g] |
|--------------|---------------------------------------------|
| TiO\textsubscript{2} | 100 | — | 34.9 |
| Ni1 | 100 | 3.85 | — | 33.6 |
| Ni2 | 100 | 5.04 | — | 33.3 |
| Ni3 | 100 | 8.54 | — | 33.0 |
| Ni4 | 100 | 10.0 | — | 31.4 |
| Ni3–Ce1 | 100 | 7.38 | 2.86 | 40.2 |
by the electron-filled d-sub band. The energy level of the band in the bonding is more negative than that of VB in the bulk TiO$_2$. Then another vacant d-band for which the energy level is more negative than the CB minimum of TiO$_2$ (rutile) is formed simultaneously. Regions a and b in the PL spectra respectively correspond to the inter-band transition for rutile and trapped electron at oxygen vacancy.\(^{33}\) As described in the Experimental section, the light source for PL is a xenon lamp with approx. 300 nm wavelength. Therefore, inter-band excitation occurs in pristine TiO$_2$. In Fig. 6, compared to pristine TiO$_2$, we can observe a remarkable decrease of PL spectra for Ni$_X$ samples in the wavelengths of 400–500 nm. The degree of the decrease increased concomitantly with increasing surface NiO concentration. Two plausible explanations are expected for this result: (i) Because the light source includes photons with a short wavelength, some electrons excited in TiO$_2$ transferred to the vacant d-band of NiO, which leads to an increase of charge separation yield and resultant decrease of PL spectra. (ii) Some illuminated photons were consumed for the electron excitation from NiO to either the vacant d-band of Ni or the CB of TiO$_2$. Therefore, the amount of inter-band excitation of TiO$_2$ was decreased. The resultant PL spectra were decreased. In this case, the recombination yield of electron excited from NiO is also expected to be small. In the ESR spectra, the signals detected at around $g = 2.000$ are those which originated from the apparatus. Different signals were obtained around $g = 2.23–2.26$ by UV illumination. This signal corresponds to Ni(III).\(^{34,35}\) It is noteworthy that Ni(II) is inert for ESR analysis. This result rules out electron donation to NiO; the probability of (i) above is small. In practical photocatalytic activity measurements, only visible light is illuminated. Also, NiO modification increases decomposition activity remarkably. One can infer that electrons were excited from the d sub-band in Ti–O–Ni bonding to the CB of TiO$_2$. The surface-to-bulk electron transfer enhances charge separation yield, and increases photocatalytic activity.

Figure 9 displays concentration changes of 2-naphthol in water for the samples at 50°C in the dark. Pristine TiO$_2$ and Ni$_1$–Ni$_4$ samples exhibited no decomposition activity in the dark, although dark activity was obtained from Ni$_3$–Ce$_1$. Figure 10 shows concentration changes of 2-naphthol in water for Ni$_3$–Ce$_1$ at 50, 60, and 70°C in the dark, and the corresponding reaction constants (inset). The concentration change during the initial 1 h was greater than that after 1 h for Ni$_3$–Ce$_1$. After 1 h, the rate of concentration change was almost constant. We used data from 1–6 h for the reaction constant calculation by assuming a first-order reaction.

The desorption of molecules adsorbed onto the solid surface is accelerated by temperature increase because of the increase of molecular vibration. However, increasing temperature generally suppresses the adsorption process with negative entropy change.\(^{13}\) Therefore, the equilibrium adsorption amount of the molecule onto solid surface decreases concomitantly with increasing temperature.\(^{36}\)

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**Fig. 6.** PL emission spectra of samples. Regions a and b correspond to the inter-band transition for rutile and trapped electron at oxygen vacancy, respectively.

**Fig. 7.** ESR differential spectra of Ni$_3$ before and during UV illumination.

**Fig. 8.** Schematic illustration of band structure in this system and expected electron transfer.
When only adsorption contributes concentration decrease of the system, the degree of the concentration decrease is expected to decrease concomitantly with increasing temperature. In the present study, the reaction constant of the concentration decrease increases concomitantly with increasing temperature. The reason for the clear difference in the trend of concentration decrease between 0–1 h and 1–6 h cannot be ascertained if the adsorption–desorption equilibrium was not attained within the measurement time (6 h). These trends are difficult to explain solely by adsorption and suggest the involvement of other mechanism such as decomposition. An Arrhenius plot of the reaction constant is shown in Fig. SI-4 in Supporting Information. The calculated activation energy value for Ni3–Ce1 was 39.4 kJ/mol. This value is almost equivalent to that (37.2 kJ/mol) of MnO2 and CeO2 modified TiO2 (Mn3–Ce1) obtained using CCC method, which decomposes 2-naphthol in water by the MvK mechanism. Moreover, XPS analysis revealed that the valence ratio between Ce(III) and Ce(IV) was changed from 67:33 to 83:17 by subsequent heat treatment at 300°C for 4 h in air. The reaction constant of this sample on the 2-naphthol decomposition recovered to approx. 0.011 h⁻¹. These results suggest that reaction constants on the decomposition of 2-naphthol correlate with the valence of Ce in CeO2.

Considering the experimentally obtained results [(i) concentration decreases in the dark, (ii) enhancement of concentration decreases by increasing temperature, (iii) positive correlation between Ce valence change and reaction constant after a dark reaction and subsequent heat treatment, and (iv) similar decomposition trend and the activation energy between Ni3–Ce1 and Mn3–Ce1], we conclude that the dominant mechanism on the decomposition activity of Ni3–Ce1 in the dark was MvK mechanism of Ce in CeO2. Direct modification of CeO2 onto TiO2 does not give decomposition activity but adsorption only (Figs. SI-5 and SI-6 in Supporting Information). Therefore, this result means that MvK mechanism at this temperature appears by the combination of NiO with CeO2. This report is the first describing the effect of this combination at a temperature lower than 100°C. Reoxidation of the reduced CeO2 by dissolving oxygen is an important factor for the MvK mechanism in this system. However, a small (not dominant) contribution of adsorption is not completely deniable in the time range of 1–6 h because it is difficult to evaluate adsorption and decomposition separately in this study. The initial concentration decreases in the time scale of 0–1 h for Ni3–Ce1 suggests of a certain contribution of adsorption. Therefore, in this study, the reaction constant in the dark was calculated after 1 h of sample addition.

The photocatalytic decomposition activity of Ni3 under visible light was decreased slightly by Ce modification (Fig. SI-7 in Supporting Information). According to ESR differential spectra, signals around g = 2.23–2.26, which correspond to Ni(III), exist even in the dark. Their intensity increases by UV illumination (Fig. SI-8 in Supporting Information). This result suggests that Ce in CeO2 on NiO attracts electrons in NiO before UV illumination, which might suppress the excitation of electron from Ti-O-Ni bonding to CB of rutile. Redox potential difference between Ce(III)/Ce(IV) (E0 = 1.74 V vs. NHE, pH = 0) and Ni(II)/Ni(III) (E0 = 0.49 V vs. NHE, pH = 0) also suggests this possibility. Another possibility is the coverage of oxidation (NiO) or reduction sites (TiO2) for photocatalytic activity by CeO2. Detailed investigations of the contribution of these possibilities must be conducted in future work.

Figure 11 presents antibacterial activity against E. coli and S. aureus. The modification of NiO onto TiO2 surface clearly increased antibacterial activity against both bacteria. Especially, Ni4 inactivated more than 99.9% [log10 (N/N0) = −3] of S. aureus cells within 20 h. However, the value on E. coli was −2 despite strong light intensity, probably because E. coli is gram-negative and because it possesses a lipopolysaccharide outside of the outer membrane and a peptidoglycan layer in the cell wall. Practical photographs of colonies for Ni4 against these bacteria are displayed in Fig. 12.
measurements in the dark are depicted in Fig. SI-9 in Supporting Information. No sample including Ni3Ce1 was found to have any antibacterial activity in the dark because the MvK mechanism does not function effectively at room temperature in this system.

4. Summary

For this study, we prepared NiO and CeOx modified rutile TiO2 using CCC method. The NiO modification decreased apparent bandgap and provided photocatalytic decomposition activity under visible light. Electron excitation from Ni in NiO was confirmed from ESR analysis. Formation of a Ti–O–Ni interfacial bond yielding a surface d sub-band is inferred as playing an important role in this increased activity. The NiO-modified TiO2 possessed decomposition activity only under visible light, but additional modification of CeOx onto the material provided decomposition of 2-naphthol in water in the dark at 50°C. The dark activity was attributed to the MvK mechanism of Ce in CeOx from the temperature dependence and valence change. This MvK mechanism is obtainable by the combination of NiO and CeOx. The NiO-modified TiO2 exhibited antibacterial activity against E. coli and S. aureus under visible light at room temperature.

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