Research Article

Ni-Doped Protonated Layered Titanate/TiO₂ Composite with Efficient Photocatalytic Activity for NO_x Decomposition Reactions

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A unique structural transformation of a lepidocrocite-type layered titanate, K_{0.8}Ti_{1.73}Li_{0.27}O₄, into a rutile-type TiO₂ has recently been realized *via* dilute HCl treatment and subsequent drying at room temperature for producing rutile-nanoparticle-decorated protonated layered titanate exhibiting highly efficient photocatalytic activity. Herein, the authors report synthesis of a lepidocrocite-type layered cesium titanate with nominal compositions of Cs_{0.7}Ti_{1.825-x/2}Ni_x□_{0.175-x/2}O₄ ($x = 0, 0.05, 0.1$, and 0.35) through solid-state reactions of Cs₂CO₃, TiO₂, and Ni(CH₃COO)₂·4H₂O at different temperatures (600 or 800°C), followed by treatment with dilute HCl and subsequent drying to produce a Ni-doped protonated layered titanate/TiO₂ composite. Cs_{0.7}Ti_{1.825-x/2}Ni_x□_{0.175-x/2}O₄ with an optimized Ni content obtained at a lower temperature was converted into a Ni-doped protonated layered titanate/TiO₂ composite to exhibit high photocatalytic activity for NO_x decomposition reactions.

1. Introduction

Fuel production, environmental purification, and fine chemical synthesis using a semiconductor photocatalyst with solar light have attracted tremendous attention for developing sustainable photoenergy conversion processes [1–5]. Efforts have thus been made to modify conventional semiconductor photocatalysts as well as to synthesize new state-of-the-art versions, in terms of improved charge-separation efficiency, photoabsorption properties, and specific surface area. Layered transition metal oxides have been used to design highly efficient photocatalysts, due to their ability to provide

expandable 2D nanospaces to accommodate reactants and such functional species as cocatalysts and sensitizers [6–8]. The interlayer structures have been controlled to induce unique photocatalytic reactions, moreover, such as substrates or product-selective reactions [9, 10].

Among layered transition metal oxides, lepidocrocite-type layered titanates are characterized by swelling properties as well as compositional versatility [11]. These make them extremely promising candidates for designing highly efficient functional hybrid photocatalysts. The general formula for lepidocrocite-type layered titanate is A_xTi_{2-y}M_yO₄ (A: interlayer alkali metal ion; M: metal ion or vacancy). Alkali metal

ions are located in the interlayer spaces between titanate sheets to compensate for the negative charge of the layers, which arises from isomorphous substitution of Ti with low-valent metal species or vacancies. We recently reported that a lepidocrocite-type layered titanate with a composition of $\text{K}_{0.8}\text{Ti}_{1.73}\text{Li}_{0.27}\text{O}_4$ (referred to as “KTLO”) exhibited a unique transformation into rutile with dilute HCl treatment and subsequent drying at room temperature (even at 60°C to accelerate the transformation) [12, 13]. Rutile nanoparticles were formed on the outer surface (not in the interlayer space) of protonated layered titanate particles ($\text{H}_{1.07}\text{Ti}_{1.73}\square_{0.27}\text{O}_4$; $\square$ denotes a vacancy) during the drying process. After Pt loading, the protonated layered titanate/rutile composite showed higher photocatalytic H_2 evolution activity from water when compared with Pt-loaded P25 (a benchmark photocatalyst for the reaction). The high photocatalytic activity was explained by a transfer of photoexcited electrons from the protonated layered titanate phase to rutile for enhancing charge separation efficiency. It should be noted that photocatalytic activity of the protonated layered titanate was remarkably enhanced without any interlayer modification, which often requires multiple complicated steps.

Doping of transition metal ions into a TiO_2 framework often results in improved photocatalytic activity due to enhanced-charge separation efficiency and/or development of visible-light responsivity [14–19]. In the case of acid treatment of KTLO, the Li^+ ions in the layers were completely extracted to leave defects in the titanate sheet [12], while the negative charge was likely to be balanced by accommodating H^+ (or in the form of H_3O^+). On the other hand, negligible extraction of Ni^{2+} was observed for $\text{Cs}_{0.7}\text{Ti}_{1.65}\text{Ni}_{0.35}\text{O}_4$ under the same experimental conditions as those for KTLO, possibly due to a stronger electrostatic interaction between metal ions with higher valences and oxide anions [20]. In the present study, we selected Ni-doped lepidocrocite-type layered cesium titanates with different Ni contents as starting materials, and the effects of the Ni-doping on the photocatalytic activity of the layered cesium titanate after dilute HCl treatment and subsequent drying for NO_x decomposition reactions was investigated.

2. Experimental

2.1. Materials. Potassium carbonate (K_2CO_3 , 99.95%) was purchased from Kanto Chemical Co., Ltd. Cesium carbonate (Cs_2CO_3 , 95.0–102%) and nickel acetate tetrahydrate ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 98.0%) were obtained from FUJIFILM Wako Pure Chemical Corporation. Titanium dioxide (P25 TiO_2 , $\geq 99.5\%$) was kindly donated by Nippon Aerosil Co., Ltd. Anatase-type TiO_2 (JRC-TIO-1) and rutile-type TiO_2 (JRC-TIO-16) were supplied by the Catalysis Society of Japan. Hydrochloric acid (HCl, 35.0–37.0%) was purchased from Nacalai Tesque, Inc.

2.2. Sample Preparation. A layered cesium titanate with nominal compositions of $\text{Cs}_{0.7}\text{Ti}_{1.825-x/2}\text{Ni}_x\square_{0.175-x/2}\text{O}_4$ ($x = 0, 0.05, 0.1, \text{ and } 0.35$) was synthesized by solid-state reactions with stoichiometric ratios of Cs_2CO_3 , TiO_2 , and $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$. TiO_2 was suspended in an aqueous solution of Cs_2CO_3 with/without $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ by ultrasoni-

cation for 5 min, and the suspension was stirred at 100°C to evaporate the water. The powder mixture was collected and then calcined at 600°C for 30 min in air. After cooling to room temperature, the sample was mixed again with acetone using a planetary ball mill (Planet M2-3, Gokin Planetaring Inc.). After evaporation of the acetone at room temperature, the samples were calcined at 600°C or 800°C for 20 h in air. The samples obtained by the solid-state reactions were referred to as CTNO (x) $_T$, where T represents the calcination temperature. CTNO (x) $_T$ was suspended in dilute HCl (0.5 M), and the suspension was stirred at room temperature for 3 days. After centrifugation, the solid phase was collected and dried at 60°C overnight without washing with water, resulting in retention of HCl on the outer particle surface. The samples prepared by dilute HCl treatment and subsequent drying of CTNO (x) $_T$ were referred to as HTNO (x) $_T$.

2.3. Characterization. X-ray powder diffraction (XRD) patterns of the samples were recorded with a Rigaku Ultima IV diffractometer operated at 40 mA and 40 kV with monochromatic $\text{CuK}\alpha$ radiation. UV-vis diffuse reflectance (UV-vis DR) spectra of the samples were obtained with a JASCO V-750 spectrophotometer equipped with an integrating sphere (ISV-722 attachment). X-ray photoelectron spectroscopy (XPS) analyses were performed with an ULVAC-PHI PHI5600. Raman spectra were recorded with a Renishaw in Via reflex spectrometer using a 532 nm laser. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurement was performed with an SPS 5510 (SII Nano-Technology, Inc.). The extraction rate (%) of Ti and Ni from the samples during the dilute HCl treatment was determined by the following equation:

$$\text{Extraction rate (\%)} = \frac{\text{Amount of element extracted}}{\text{Amount of element in the sample}} \times 100 \quad (1)$$

2.4. Photocatalytic Reaction. The photocatalytic activity of the samples was evaluated by a NO_x decomposition reaction in the gas phase under light irradiation ($\lambda > 290 \text{ nm}$) at room temperature using a continuous flow-type reactor. A high-pressure mercury lamp (Ushio 450 W) was used as a light source. The initial concentration of NO was set to 1 ppm with compressed air, and the NO_x concentration after photocatalytic decomposition was estimated using an NO_x analyzer (Yanaco, ECL-88A). Note that NO_2 formed by photocatalytic oxidation of NO is also counted as an NO_x species. The NO conversion ratio was calculated using the measured NO_x concentration.

3. Results and Discussions

Figure 1 shows XRD patterns of CTNO (0) $_800$, CTNO (0.05) $_800$, HTNO (0) $_800$, and HTNO (0.05) $_800$. Note that the layered cesium titanate with a composition of $\text{Cs}_{0.7}\text{Ti}_{1.825}\square_{0.175}\text{O}_4$, which is equivalent to the nominal composition of CTNO (0) $_800$, has previously been prepared by a solid-state reaction of Cs_2CO_3 and TiO_2 at above 700°C.

FIGURE 1: XRD patterns of (a) CTNO (0)_800, (b) CTNO (0.05)_800, (c) HTNO (0)_800, and (d) HTNO (0.05)_800: ∇ : $\text{Cs}_{0.7}\text{Ti}_{1.825}\square_{0.175}\text{O}_4$, $\blacktriangledown$: $\text{H}_{0.7}\text{Ti}_{1.825}\square_{0.175}\text{O}_4$, $\blacksquare$: TiO_2 (rutile), and $\circ$: unknown.

Both the XRD patterns of CTNO (0)_800 and CTNO (0.05)_800 (Figures 1(a) and 1(b)) were assignable to that of $\text{Cs}_{0.7}\text{Ti}_{1.825}\square_{0.175}\text{O}_4$ [21], indicating that layered cesium titanate with/without Ni was successfully obtained. The visible-light absorption at a wavelength shorter than 500 nm by Ni addition (Figure 2) supports successful Ni-doping into the titanate sheet framework, since transition metals including Ni can develop visible-light absorption by formation of localized energy states in the band gap of TiO_2 [14] and since the local structure of lepidocrocite-type layered titanates is similar to that of TiO_2 [22]. The tail of the visible-light absorption was located at a position closely similar to that observed for Ni-doped TiO_2 in previous reports [23, 24]. In the XRD pattern of HTNO (0)_800 (Figure 1(c)), peaks attributable to rutile were observed at $2\theta = 27.4$, 36.1 , and 41.2° , while peaks in other positions were assignable to $\text{H}_{0.7}\text{Ti}_{1.825}\square_{0.175}\text{O}_4$ [21], the protonated form of $\text{Cs}_{0.7}\text{Ti}_{1.825}\square_{0.175}\text{O}_4$, revealing that the partial transformation of titanate sheets to rutile observed for KTLO in the previous report also occurred in CTNO (0)_800. On the other hand, no rutile formation was observed in HTNO (0.05)_800 (Figure 1(d)), indicating that doping with a small Ni content suppressed the transformation of the titanate sheets into rutile.

Figure 3(a) shows XRD patterns of CTNO (x)_600. Although a very weak XRD peak ascribable to anatase was observed at $2\theta = 25.4^\circ$, the XRD pattern of CTNO (0)_600 was almost identical to that of $\text{Cs}_{0.7}\text{Ti}_{1.825}\square_{0.175}\text{O}_4$ [21]. This indicates that $\text{Cs}_{0.7}\text{Ti}_{1.825}\square_{0.175}\text{O}_4$ was obtained even at 600°C , while it has been prepared by solid-state reactions only at above 700°C [21, 25–28]. Weak peaks at $2\theta = 25.4^\circ$ ascribable to anatase were observed in the cases of CTNO (0.05)_600 and CTNO (0.1)_600, while an unknown weak peak was observed at $2\theta = 29.7^\circ$ in the case of CTNO (0.35)_600. It should be noted, however, that all the peaks at other positions were assignable to $\text{Cs}_{0.7}\text{Ti}_{1.825}\square_{0.175}\text{O}_4$ [21], indicating that the desired layered cesium titanate phase was obtained as the main phase in every case. Although we

FIGURE 2: UV-vis DR spectra of CTNO (0)_800 and CTNO (0.05)_800.

anticipated that the XRD peaks would shift to smaller 2θ values due to doping in the octahedral site with Ni^{2+} with a larger ion radius (0.0690 nm) than that of Ti^{4+} (0.0605 nm) [29], no such shift was observed. As shown in Figure 4, the lattice constants of the Ni-doped samples were almost identical to that of CTNO (0)_600. This indicates that Ni-doping did not affect the crystal structure of CTNO (0)_600.

Figure 3(b) shows XRD patterns of HTNO (x)_600. XRD peaks assignable to $\text{H}_{0.7}\text{Ti}_{1.825}\square_{0.175}\text{O}_4$ and rutile were observed in all the samples, while that assignable to anatase was additionally observed in the case of $x = 0 - 0.1$. Given that no transformation occurred in CTNO (0.05)_800 after dilute HCl treatment and subsequent drying, it was apparent that a structural transformation of the Ni-doped layered cesium titanate into rutile as well as anatase was promoted by posttreatment when a sample prepared at a lower temperature was used as the starting material. The intensity of the peak at $2\theta = 10.2^\circ$ attributable to the (020) plane of $\text{H}_{0.7}\text{Ti}_{1.825}\square_{0.175}\text{O}_4$ increased with increases in the Ni content, while the intensity of the peak at $2\theta = 27.6^\circ$ attributable to the (110) plane of rutile decreased remarkably when the x value increased from 0.1 to 0.35. These results further confirm that the transformation of titanate sheets into rutile was suppressed by Ni-doping. The counter anion of the acids has been reported to affect the crystal phase of TiO_2 obtained from KTLO [22], and the structural transformation of KTLO into rutile by dilute HCl treatment and subsequent drying was explained by the effect of the chloride ion in the previous study [12]. In the present study, on the other hand, formation of anatase in addition to rutile was observed after posttreatment of CTNO (x)_600, except for the x value of 0.35. The composition of the starting material is likely to affect the TiO_2 phase transformed from titanate sheets, although the mechanism remains unclear.

Figure 5 displays Raman spectra of standard TiO_2 samples (anatase and rutile), HTNO (0.1)_600, and HTNO (0.35)_600. The Raman bands at 143 , 394 , 513 , and 634 cm^{-1} of anatase were ascribable to the E_g , A_{1g} , B_{1g} , and E_g modes,

FIGURE 3: XRD patterns of (a) CTNO (x)_600 and (b) HTNO (x)_600: ∇ : $\text{Cs}_{0.7}\text{Ti}_{1.825}\square_{0.175}\text{O}_4$, $\blacktriangledown$: $\text{H}_{0.7}\text{Ti}_{1.825}\square_{0.175}\text{O}_4$, $\square$: TiO_2 (anatase), $\blacksquare$: TiO_2 (rutile), and $\circ$: unknown.

FIGURE 4: Lattice constant of CTNO (x)_600.

respectively, while those at 432 and 600 cm^{-1} of rutile were assigned to the E_g and A_{1g} modes, respectively [30]. In the case of HTNO (0.1)_600, the peaks at 136 cm^{-1} and 595 cm^{-1} were attributable to anatase and rutile, respectively, while the position of the band at 440 cm^{-1} was similar to that of the typical Raman band of $\text{H}_{0.7}\text{Ti}_{1.825}\square_{0.175}\text{O}_4$ (449 cm^{-1}) [31], further confirming that HTNO (0.1)_600 is a mixed phase of protonated layered titanate, anatase, and rutile. On the other hand, in the case of HTNO (0.35)_600, the Raman bands at 268 , 435 , and 710 cm^{-1} were attributable to $\text{H}_{0.7}\text{Ti}_{1.825}\square_{0.175}\text{O}_4$, while that at 594 cm^{-1} was attributable to rutile. The fact that no Raman bands attributable to anatase were observed correlates well with the results of the XRD analysis.

Figure 6(a) shows UV-vis DR spectra of CTNO (x)_600. The light absorption edge at a wavelength of 350 nm observed for CTNO (0)_600 shifted to longer wavelengths with increases in the Ni content. As shown in Table 1, the band gap energy of CTNO (0)_600 calculated by the Tauc plot [32] (Figure 6(b)) was 3.52 eV , which is slightly smaller

FIGURE 5: Raman spectra of (a) anatase (JRC-TIO-1), (b) rutile (JRC-TIO-16), (c) HTNO (0.1)_600, and (d) HTNO (0.35)_600.

than the value previously reported for layered cesium titanate (3.62 eV) whose composition ($\text{Cs}_{0.68}\text{Ti}_{1.83}\square_{0.17}\text{O}_4$) is similar to that of CTNO (0)_600 ($\text{Cs}_{0.7}\text{Ti}_{1.825}\square_{0.175}\text{O}_4$) [33]. The band gap energy decreased with increases in the Ni content. On the other hand, visible-light absorption at wavelengths shorter than 500 nm was introduced by Ni-doping, and the absorption increased with increases in the Ni content. The visible-light absorption changes are ascribable to the

FIGURE 6: (a) UV-vis DR spectra and (b) Tauc plots of CTNO (x)₆₀₀; $x = 0, 0.05, 0.1$, and 0.35 .

TABLE 1: Band gap energies of different samples.

Sample	Band gap energy (eV)
CTNO (0) ₆₀₀	3.52
CTNO (0.05) ₆₀₀	2.88
CTNO (0.1) ₆₀₀	2.83
CTNO (0.35) ₆₀₀	2.73
HTNO (0) ₆₀₀	3.28
HTNO (0.05) ₆₀₀	3.08
HTNO (0.1) ₆₀₀	2.95
HTNO (0.35) ₆₀₀	2.81

introduction of localized energy states into the band gap by Ni-doping as mentioned above. As shown in Figure 7(a), the visible-light absorption attributable to the Ni-doping was observed in the samples even after dilute HCl treatment and subsequent drying, although the absorption intensity decreased, indicating that doped Ni was retained in the titanate sheets, whereas the majority of the doped Ni was extracted during dilute HCl treatment, as revealed by ICP-AES measurement (details to be presented later). As shown in the XPS spectrum of the Ni 2p region of HTNO (0.35)₆₀₀ (Figure 8), two peaks at 856.3 and 874.0 eV were observed, confirming the retention of Ni as a divalent form [34]. As shown in Table 1, the band gap energy of HTNO (0)₆₀₀ (3.28 eV) was smaller than that of CTNO (0)₆₀₀ (3.52 eV). A decreased band gap energy of a layered cesium titanate *via* interlayer protonation has previously been observed for $\text{Cs}_{0.68}\text{Ti}_{1.83}\text{O}_{4}$ (3.62 to 3.47 eV) using dilute HCl treatment [33]. On the other hand, in the case of the Ni-doped samples, the band gap energy increased after dilute HCl treatment and subsequent drying. This correlates well with the blue shift of the light absorption edge of $\text{Cs}_{0.7}\text{Ti}_{1.65}\text{Ni}_{0.35}\text{O}_4$ after dilute HCl treatment in the previous report [20].

Table 2 shows the extraction rates of Ti and Ni from CTNO (x)₆₀₀ during dilute HCl treatment and the residual Ni/Ti ratios in the samples after dilute HCl treatment. While the Ni extraction rates were almost constant at 80-90%, those of Ti increased from 13.4 to 57.6% with increases in the Ni content. Accordingly, the residual Ni/Ti ratio in CTNO (x)₆₀₀ after dilute HCl treatment increased with increases in Ni content. The larger extraction rate for Ni compared with that reported for $\text{C}_{0.7}\text{Ti}_{1.65}\text{Ni}_{0.35}\text{O}_4$ under the same experimental conditions (0.5 M and 3 days for the HCl concentration and reaction time period, respectively) [20] was likely attributable to the smaller particle size of the sample in this study. This is because the preparation temperature of CTNO (x)₆₀₀ (600°C) in this study is lower than that of $\text{C}_{0.7}\text{Ti}_{1.65}\text{Ni}_{0.35}\text{O}_4$ in the previous report (800°C).

Figure 9 shows the photocatalytic NO conversion ratios over CTNO (x)₆₀₀ and HTNO (x)₆₀₀. Because the Ni-doped samples showed negligible photocatalytic activity under visible-light ($\lambda > 420$ nm) irradiation in spite of their visible-light absorption properties, the photocatalytic performance of the samples was evaluated under irradiation by light with a wavelength longer than 290 nm. In the presence of water and oxygen, photooxidation was dominant for the mechanism of the NO_x decomposition reaction. The hydroxyl radical, $\cdot\text{OH}$, produced by photooxidation of H_2O , and the hydroperoxyl radical, $\cdot\text{OOH}$, generated by the reaction between H^+ and photoreduced oxygen (O^{2-}) were involved in the oxidation of NO to form HNO_3 [35–37]. Considering that water and oxygen were contained in the compressed air in the present study, NO was likely to have been decomposed by the photooxidation process. All the CTNO (x)₆₀₀ samples showed a NO conversion ratio approximately 1.8 times higher than P25, which is often used as a benchmark TiO_2 photocatalyst [38, 39]. The NO conversion ratio at CTNO (x)₆₀₀ was almost constant for all the Ni contents, indicating that the photocatalytic activity of CTNO (x)₆₀₀ was not dependent on the amount of doped Ni. After

FIGURE 7: (a) UV-vis DR spectra and (b) Tauc plots of HTNO (x)₆₀₀, $x = 0, 0.05, 0.1$, and 0.35 .

FIGURE 8: XPS spectrum of the Ni 2p region of HTNO (0.35)₆₀₀.

TABLE 2: Extraction rates of Ti and Ni and the corresponding residual Ni/Ti ratios in the CTNO (x)₆₀₀ samples after dilute HCl treatment.

Sample	Extraction rate Ni	Ti	Residual Ni/Ti ratio
CTNO (0) ₆₀₀	N. D.	13.4	0
CTNO (0.05) ₆₀₀	84.1	24.9	5.9×10^{-3}
CTNO (0.1) ₆₀₀	89.5	55.3	13.2×10^{-3}
CTNO (0.35) ₆₀₀	80.5	57.6	97.6×10^{-3}

dilute HCl treatment and subsequent drying, the NO conversion ratio over CTNO (x)₆₀₀ decreased, except for the x value of 0.1, resulting in the highest NO conversion rate over HTNO (0.1)₆₀₀ among the HTNO (x)₆₀₀ samples. The photocat-

FIGURE 9: NO conversion ratios at (a) P25, CTNO (x)₆₀₀ with x values of (b) 0, (c) 0.05, (d) 0.1, and (e) 0.35, and HTNO (x)₆₀₀ with x values of (f) 0, (g) 0.05, (h) 0.1, and (i) 0.35.

lytic NO conversion rate over HTNO (0.1)₆₀₀ was twice as higher as that of P25. It should be noted that the design of a semiconductor photocatalyst for a NO_x decomposition reaction superior to that of P25 remains challenging [35] and that the activity of HTNO (0.1)₆₀₀ was comparable to that of a smart TiO₂-based composite photocatalyst with excellent photocatalytic performance reported previously [40]. The best photocatalytic activity of HTNO (0.1)₆₀₀ among the HTNO (x)₆₀₀ samples was probably caused by a suitable ratio of protonated layered titanate and TiO₂, because the interparticle charge transfer followed by enhanced photocatalytic activity depended largely on the phase composition of the TiO₂-based composites [41–44]. As deduced from the XRD analyses, a layered titanate with low Ni content is likely to be transformed easily into TiO₂ (both anatase and rutile) to decrease the residual layered titanate phase. In light of the fact that the high photocatalytic

performance of the protonated layered titanate/rutile composite in the previous report was attributable to an electron transfer between two components [12], excess conversion of titanate sheets into TiO_2 to reduce the protonated layered titanate- TiO_2 interfaces is considered to be detrimental to photocatalytic performance. Accordingly, the photocatalytic activities of CTNO (0)_600 and CTNO (0.05)_600 decreased remarkably after dilute HCl treatment and subsequent drying. On the other hand, in the case of CTNO (0.35)_600, a relatively small decrease in the NO conversion ratio *via* dilute HCl treatment and the subsequent drying was attributable to the fact that the transformation of titanate sheets into TiO_2 was suppressed by Ni-doping, as mentioned above, and thus, almost no charge transfer occurred between the components. The mechanism of the improved photocatalytic activity of CTNO (0.1)_600 *via* posttreatment is possibly explained by the fact that the Ni-doped protonated layered titanate/ TiO_2 ratio was optimized to induce an efficient interparticle charge transfer and improve the charge separation efficiency. Also, doping with Ni can be effective for decreasing the number of Ti defect sites in layered titanate, which can induce charge recombination [45].

4. Conclusions

The lepidocrocite-type layered cesium titanate with nominal compositions of $\text{Cs}_{0.7}\text{Ti}_{1.825-x/2}\text{Ni}_x\text{O}_{0.175-x/2}\text{O}_4$ ($x = 0, 0.05, 0.1, \text{ and } 0.35$) was synthesized by solid-state reactions of Cs_2CO_3 , TiO_2 , and $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ at different temperatures (600 or 800°C). The layered cesium titanate obtained by the solid-state reactions was treated with dilute HCl and subsequently dried to induce partial transformation into anatase and rutile-type TiO_2 . When the solid-state reaction was conducted at 800°C, no structural transformation into TiO_2 was observed for the Ni-doped sample after posttreatment, while the sample obtained at 600°C was transformed into anatase and/or rutile for all the composition. The photocatalytic activity for the NO_x decomposition reaction of the samples obtained by the solid-state reaction at 600°C was not dependent on the doped Ni content. On the other hand, the layered cesium titanate with an x value of 0.1 after dilute HCl treatment and subsequent drying showed the highest photocatalytic activity among the samples, and the activity was twice as higher as that of P25, a benchmark photocatalyst for the reaction. This was likely attributable to the optimized Ni-doped protonated layered titanate/ TiO_2 phase ratio in the composite to induce an efficient interparticle electron transfer between these two components. Careful selection of the composition of the starting lepidocrocite-type layered titanate seems to be effective for designing layered titanate-based composite photocatalysts with improved photocatalytic performance.

Data Availability

The data used to support the findings of this paper are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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