Enhancing Visible Light Absorption of Yellow-Colored Peroxo-Titanate Nanotubes Prepared Using Peroxo Titanium Complex Ions

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ABSTRACT: Visible light-activated yellow titanate nanotubes (TNTs) modified by peroxy groups were directly synthesized via a facile chemical reaction route using peroxy titanium complex ions as a precursor. Obtained peroxy-modified TNTs (PTNTs) possessed a cylindrical-shaped tubular morphology with an outer diameter of approximately 10 nm. The peroxy titanium functional group (Ti−O−O) was formed between the interlayers of the lepidocrocite-type titanate crystal that was the base structure of TNTs, with the interlayer distance estimated at approximately 10.02 Å. The formation of the peroxy functional groups reduced the electron density adjacent to the titanium atom, raising the valence band to 1.35 eV and forming a band gap of 2.50 eV, which is lower than that of TNTs (3.19 eV). In addition, the peroxy titanium functional group had a negative potential, which increased the chemical adsorption performances with positively charged rhodamine B molecules in water. Meanwhile, the photocatalytic investigation indicated that the PTNTs have enhanced the photocatalytic performance for RhB decolorization under visible light irradiating in comparison with TNTs. These findings show not only the improvement in the photocatalytic performance but also the potential of processing design by selecting the precursor with arbitrary characteristics.

INTRODUCTION

Titanate nanotubes (TNTs) are known to have been formed by rolling up the layered titanate crystal nanosheets and have a cylindrical-shaped tubular morphology with a high aspect ratio. Therefore, this structure has a relatively large specific surface area and large pore volume, internal pores. In particular, considering the wide optical band gap energy of the TNTs originated from TiO₆ octahedrons, they can show photocatalytic characteristics through excellent oxidation–reduction reaction. TNTs also have the advantage of low product costs, so they have been utilized for various applications such as solar cells, photocatalysts, gas sensors, ion absorbents, and biomedical materials in various industries. These days, the number of applications has been expanding not only outdoors but also indoors. For an application that uses light, such as solar cells or photocatalysts, light absorption is important. In order to excite the electrons from the valence band to the conduction band in the electrical band structure of the semiconductor, light irradiation above the band gap energy is required. However, a typical TNT powder has high light reflectivity due to its white color and has a wide optical band gap energy of approximately 3.1 eV or more than it, requiring irradiation light with high energy such as an ultraviolet (UV) light region to excite the electrons. However, this ultraviolet light region is less than 5% of the entire solar spectrum. Further, because indoor light does not include sufficient light in the ultraviolet range, an additional ultraviolet light generator is required to operate a photocatalytic cleaning system, wallpaper, painting, or coating indoors. Nowadays, the extension of its photocatalytic properties to a broader part of the solar spectrum is key.

Recently, investigations aimed to improve the photocatalytic performance of oxides by enhancing the light absorption through expanding the absorption spectra of the structure to the visible light region. As a typical method, heterostructures with noble metals such as gold or silver have been reported. Although conductive metal nanoparticles serve to absorb light and provide the resulting electrons to titanate, contact surfaces can act as defect sites, which degrade the photocatalytic performance. Considering the drawbacks of the heterostructure, the formation of visible activated catalysts through nonmetal nitrogen doping received more attention. This is achieved by expanding the absorption light range to the visible light region and reducing the optical band gap energy. The doping process has been conducted through heat treatment using materials such as trimethylamine or hexamethylenetetramine with an oxide photocatalyst such as titania, for nitrogen supply. The extension in light absorption to the visible range could be assigned to the band gap narrowing phenomenon in accordance with the reports. However, because this method requires heat treatment at harsh
temperatures or using an inert gas atmosphere to obtain a pure and uniformly doped photocatalyst, if the method is applied to TNTs, they may collapse the nanotubular structure, or the crystal structure may be transformed.\textsuperscript{21} In particular, in the case of nitrogen doping, oxygen vacancy can occur in the oxide structure, which can also act as a defect and increase the electron–hole recombination, resulting in reduced photocatalytic performance.\textsuperscript{22} Another method to prepare the yellow photocatalyst is the treatment method using hydrogen peroxide.\textsuperscript{23} When the spherical white anatase or rutile TiO\textsubscript{2} crystalline powder is treated with hydrogen peroxide, it becomes a yellow powder. The peroxo (O–O) functional group forms the peroxo titanium bond (Ti–O–O) through the interaction with a titanium atom, which is known to present a yellow color.\textsuperscript{24} This bond affects the optical band gap energy of the photocatalyst, and the band gap reduction phenomenon due to valence band uplifting in the band structure was reported.\textsuperscript{16} Therefore, the photocatalyst is considered to show activity in the visible light range by reducing optical band gap energy.\textsuperscript{23}

Based on this mechanism, previously many studies attempted the synthesis of hydrogen peroxide-treated TNTs or titania compounds for photocatalytic applications.\textsuperscript{16,25–28} However, the surface treatment is not only difficult to be achieved sufficiently inside the solid crystals but also requires the processing of highly concentrated hydrogen peroxide for an extended time to achieve a uniform treatment. In addition, the crystal might be broken down, or the nanotube structure might be destroyed by the heat treatment. In contrast, the direct synthesis of highly active and visible light responsible TNT photocatalysts is considered not to require post-treatment, and thus, many attempts have been proposed and reported.\textsuperscript{29,30} Zhao et al.\textsuperscript{29} reported the synthesis of cobalt-modified TNTs by the hydrothermal reaction, in which cobalt ions were incorporated into the TNT lattice to add visible light responsibility. Eom et al.\textsuperscript{30} synthesized nanocomposites consisting of carbon nanotubes (CNTs) and TNTs, which were formed through a one-step solution chemical process by using TiO\textsubscript{2} powder as a precursor mixed with CNTs. However, these were prepared in the high-concentration alkaline solution of 10 M, and thus, the use of large amounts of alkali species may cause negative effects on mass production.

Therefore, we suggested a novel bottom-up process for the synthesis of hydrogen peroxide-treated TNTs via a solution chemical route that does not require high-temperature treatment. The introduction of the bottom-up method may be a solution to uniformly create peroxo titanium bonds (Ti–
O–O) into crystals as well as surfaces during the formation process of the TNTs at a sufficiently low temperature.

In this study, visible-activated yellow peroxo-TNTs (PTNTs) were successfully synthesized by a facile method using peroxo titanium complex ions ([Ti(OH)2O2]–) as a precursor without any dopant, heat treatment, or postchemical treatment. This aimed to minimize the structural degradation of nanotubes during the synthesis process. To the best of our knowledge, there are no studies reported on the direct synthesis of visible light-active TNTs, including peroxo titanium bonds, by the simple and low alkaline bottom-up process using peroxo-titanium complex ion precursors. The presence and state of the peroxo titanium bond in the structure are investigated, and the effect they have on the reflectivity and optical band gap energy is also investigated. Finally, the effects of optical, structural, and electrical characteristics of the structure on the decolorization of rhodamine B (RhB) under visible-light irradiation are studied.

RESULTS AND DISCUSSION

Structural Features of TNTs and PTNTs. Scanning electron microscopy (SEM) images show the agglomerates with 1 μm size in both TNTs and PTNTs as shown in Figure 1a.b. Transmission electron microscopy (TEM) images show the tubular structure with an approximately 10 nm diameter in both samples (Figure 1c,d). In the case of PTNTs, the tube structure was maintained without any destruction. Figure 1e,f shows N2 adsorption−desorption isotherms corresponding to TNTs and PTNTs. Both isotherms display the type IV isotherm with the H3 type hysteresis loop (IUPAC classification), meaning that they have slit-like pores. The S BET and pore volumes of the TNTs were calculated to be 300.7 m2/g and 1.706 cm3/g, and in the case of PTNTs, the values were calculated to be 183.1 m2/g and 0.344 cm3/g, respectively. The insets of each figure show the pore size distribution graphs. They show that TNTs have a pore size of 12.3 nm and PTNTs have 9.9 nm size.

Figure 2 shows the X-ray diffraction (XRD) pattern of TNTs and PTNTs. They are basically the same implying an identical structure origin. Both are indexed as the 200, 110, 310, 020, and 002 reflection of protonated dittitanate (H3Ti2O7) with the lepidocrocite-related layered phase (PDF card# 00-047-0124).31,32 The PTNTs were synthesized using a simple process with low NaOH concentration, low temperature, and short duration by using the peroxo titanium complex ion, compared to TNTs. However, the peak position corresponding to the 200 plane is slightly different. The 200 diffraction peaks were observed at 9.96 and 8.66° for the TNTs and PTNTs, respectively. Its crystal plane corresponds to the interlayer distance of the lepidocrocite titanate crystal.6 As in the case of PTNTs, the fact that the 200 plane peak is found at lower diffraction angle than TNTs shows that the interlayer spacing value of PTNTs (10.02 Å) is wider than that of TNTs (8.89 Å). Although it is known that if a sodium ion (Na+) exists in its interlayer, then a peak can be found at low angles; it is believed that the sodium ion would be effectively exchanged with the proton (H+) when the acid treatment was introduced. Table S1 shows the Ti and Na molar ratio of TNTs and PTNTs measured by the X-ray fluorescence (XRF) elemental analysis. Sodium was considered to exist as an ion (Na+) in the nanotube structures with a proportion of approximately 1%, showing that the sodium concentration decreased approximately 99% from the theoretical value (1:1 for Na2Ti2O5) by the washing process. Kong et al.16 reported that the gap of the interlayer may be extended if the peroxide bond is present in the interlayer of the layered titanium oxide. The explanation is that the hydrogen peroxide molecules can enter between the crystals of lepidocrocite titanate and form a new Ti−O−O−H bond from the Ti−O−H bond. This will result in an interlayer distance increase of 0.56 Å. In the results of this experiment, the d-value from the 200 plane peak of TNTs and PTNTs is calculated as 8.89 and 10.02 Å with a difference of 1.13 Å. A similar phenomenon of larger interlayer distance was also observed from the TEM investigation as shown in Figure S1. Both TNTs and PTNTs showed a periodic lattice image that corresponds to the 200 plane of lepidocrocite-type titanate, whose values were 8.55 and 9.65 Å, respectively. The difference in the interlayer distance observed by TEM was 1.10 Å, which is in good agreement with the XRD analysis result (1.13 Å). This extension of the interlayer can be hypothesized to be connected with a peroxide bond interlayer of the crystal. Considering that the difference of interlayer spacings between pristine and peroxo-modified titanate was greater in this report than that of the previously reported value,16 this implies that a large number of peroxo titanium bonds exist inside the crystal prepared directly from the peroxo titanate complex ion solution. In the TNT case, a peak assigned to the 004 reflection of anatase (PDF card# 00-021-1272) is observed at 40°. In this study, the P25-TiO2 powder was used as a precursor to prepare the TNTs, which consists of anatase and rutile crystals. This was not fully reactive, and the precursor may still have remained in the TNT structure, whereas a pure lepidocrocite titanate structure was formed for the PTNTs.

Raman spectra analysis was used to further investigate the structural analysis and the existence of the peroxide bond in the structure. Figure 3 shows the Raman spectra of the TNTs and PTNTs. They show similar Raman patterns with peak positions to the patterns of the hydrogen titanate structure.33 In both patterns, anatase A1g (antisymmetric bending vibration of Ti−O−Ti in TiO2),34 Ti−O−35 anatase B1g (Symmetric bending vibration of O−Ti−O in TiO2),34 Ti−O−Ti36 and covalent Ti−O−H35 bonds were observed at 186, 275 (PTNT case is 276 cm−1), 387, 444, and 821 cm−1 of the Raman shift, respectively. However, there are some differences between each pattern. In the case of TNTs, the different pattern observed at 146 cm−1 is assigned to anatase E g (symmetric stretch vibration of O−Ti−O in TiO2).38 Additionally, a broad peak is observed at 638–700 cm−1, which is expected to
overlap the peaks assigned to rutile $A_{1g}$ (antisymmetric bending vibration of Ti$-\text{O}$-Ti in TiO$_2$),$^{37}$ Ti$-\text{O}$-Ti (edge-shared TiO$_6$),$^{38}$ and Ti$-\text{O}$-H$^{39}$ at 638, 668, and 700 cm$^{-1}$, respectively. However, in the PTNT case, the peak assigned to rutile $A_{1g}$ is not observed. It is estimated that the peak assigned to rutile $A_{1g}$ was detected in the TNT Raman pattern. This is considered that the chemical bonding between Ti and O and the TiO$_6$ octahedron configuration such as edge-sharing in TNTs was essentially similar to the common TiO$_2$ crystal structure. Because TNTs were synthesized using P25-TiO$_2$ as a starting material, the coordination and bonding configuration of Ti$-\text{O}$ structures might tend to be retained as a primary unit through the chemical reaction route and then remained in the final TNT structure. Furthermore, for PTNTs, a slight difference is observed at 915 cm$^{-1}$ assigned to the peroxo functional group.$^{40}$ If sodium is present in the TNT interlayer, it is reported that a peak assigned to Na$-\text{O}$ is observed at 130 cm$^{-1}$ of the Raman pattern.$^{53}$ This is not observed in both patterns, which allows us to expect that sodium was exchanged with protons via ion exchange. The XRF measurement of the samples showed that the molar ratio of titanium:sodium was 1:0.015 (Table S1). Compared to the theoretical ratio of the Na$_2$Ti$_3$O$_5$ structure, it can be expected that the sodium ions were removed approximately 98.5% in their structure after washing.

To further investigate the existence of the peroxo titanium group, X-ray photoelectron spectroscopy (XPS) analysis was introduced in the Ti$_{2p}$ and O$_{1s}$ of the TNTs and PTNTs (Figure 4). In Figure 4a, the Ti$_{2p}$ spectra of the TNTs and PTNTs are composed of the same two peaks assigned to Ti$_{2p_{3/2}}$ and Ti$_{2p_{1/2}}$ at 457.8 and 463.5 eV, respectively, meaning that Ti ions are in an octahedral structure.$^{41}$ The peak separation of 5.7 eV between the Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ signals is in excellent agreement with other values reported in the literature.$^{42}$ In the O$_{1s}$ XPS spectra of the TNTs, as shown in Figure 4c, the peaks were separated only two other peaks assigned to Ti$-\text{O}$ and H$_2$O at 529.3 and 531.7 eV, respectively. Compared with TNTs in Figure 4d, the PTNTs O$_{1s}$ XPS spectrum shows that the same peaks assigned to the Ti$-\text{O}$ bond and H$_2$O bond are also observed at 529.2 and 531.6 eV, respectively. The separated new peak observed at 533.1 eV is assigned to the Ti$-\text{O}$-O bond$^{40}$ with a proportion contribution of 11.5%.

The optical property and the electronic structure of the prepared samples were studied by UV−vis spectroscopy and by measuring the valence band potential by XPS (Figure 5). Figure 5a shows the reflectance of TNTs and PTNTs. In the case of white color TNTs, the inset picture shows a high reflectance under the visible light range above 400 nm wavelength. Moreover, from a 400 nm wavelength, the TNT reflectance begins to decrease, showing a high absorption under UV region light. This spectrum shows typical absorption due to strong excitation in the UV light region, which is assigned to band gap absorption by electron transition (O$_2p$−Ti$3d$) from the valence band to the conduction band.$^{20}$ In the case of yellow PTNTs in the inset picture, the reflectance begins to decrease from 650 nm wavelength to a very low reflectance for the wavelengths under 500 nm. The decrease in reflectance in the visible light range which is expected to be due to a decrease in the band gap results in increased absorption. The inset shows the optical band gap energy
obtained for the TNTs and PTNTs. These were estimated using the Kubelka–Munk model to be 3.19 and 2.50 eV for TNTs and PTNTs, respectively. The band gap reduction from pristine TNTs to PTNTs could be due to the variation in the lattice parameter from the formation of the peroxo titanium bond. The downward shifting of the conduction band is related to the presence of an oxygen vacancy, and because the valence band is known to uplift the excess oxygen doping, the reduced band gap can be considered a result of valence band uplift.

**Photocatalytic Properties of TNTs and PTNTs.** Figure 7a,b shows the results of the photocatalytic activity test for TNTs and PTNTs under visible light (>420 nm) irradiation. Both peak tops are degraded with a wavelength shift toward a lower wavelength region. The peaks are shifted from 554 nm wavelength to 544 nm for TNTs and 495 nm for PTNTs during the 6 h irradiation time as shown in Figure 7c. It is well-known that the RhB absorption peak is shifted with the degradation by the photocatalytic reaction as follows: RhB (554 nm) is degraded to N,N,N′-triethyl rhodamine (539 nm), N,N′-diethyl rhodamine (522 nm), N-ethyl rhodamine (498 nm), and rhodamine. It is estimated that RhB degraded to N,N,N′-triethyl rhodamine for TNTs and to rhodamine for PTNTs. Figure 7d shows the photocatalytic performance (C/Co) versus the visible light irradiation time of TNTs and PTNTs for the decolorization of RhB. After soaking under a dark condition for 30 min, 14.6% of RhB for TNTs and 22.4% of RhB for PTNTs were absorbed. In addition, the RhB absorption test under a dark condition up to 6 h was carried out, and the result (shown in Figure S2) exhibited a similar RhB absorption rate after 30 min for both PTNTs (22.3%) and TNTs (13.8%), which implied that RhB absorption was almost saturated up to 30 min. Typically, it is known that the absorption is related to surface area and increases as the surface area of the structure increases. A larger specific surface area may involve more active sites and absorption areas for the dye molecule. However, what we found is contradictory to these observations. Although TNTs have a wider absorption area than PTNTs, the absorption rate under the dark condition of PTNTs is better than TNTs, and this can be explained by surface electrical potential. The zeta-potential of TNTs was −22.2 ± 0.9 mV, while the value of PTNTs was −28.0 ± 0.3 mV. The RhB molecule has a positive potential, so it allows for easy absorption to the negative surface for the catalyst. Therefore, in the case of PTNTs, it is expected that the more negative potential of the peroxo titanium bond made the dye absorption easier.

We assume that the surface potential is one of the most important factors to improve dye absorption onto the surface. The TNTs display a relatively unstable degraded curve pattern during the photocatalytic reaction compared to PTNTs. It is assumed that TNTs are not only less affected under visible light irradiation because of their wide band gap but also the adsorption and desorption are repeated because of the relatively weak surface absorption characteristics coming from the weak negative zeta-potential compared to the PTNTs. The TNTs have a decolorization efficiency of approximately 35.4% after irradiation for 6 h under visible light.
light. Nevertheless, it is surprising that the PTNTs take approximately 6 h to reach a decolorization efficiency of approximately 64.3% with a stable degraded curve pattern under visible light irradiation.

It is plausible to suggest probable mechanisms of chemical absorption and photocatalytic reaction for PTNTs based on our experimental results. RhB as the positively charged cationic dye can be absorbed into the negatively charged surface of PTNTs. PTNTs have a lower band gap of 2.50 eV compared to that of TNTs (3.19 eV), which allows the electron to be easily excited by visible light irradiation above 420 nm (corresponds to 2.95 eV). The resultant excitons might contribute to form the active radicals such as hydroxyl radicals or superoxide radicals by oxygen. These species lead to the chemical reaction to promote the decolorization of RhB. RhB degraded to \( N,N,N' \)-triethyl rhodamine in the case of TNTs and to rhodamine in the case of PTNTs under visible light irradiation (Figure 8). From these results, we successfully synthesized yellow PTNTs in the presence of peroxo bonds on the surface, which show the visible-light response characteristics by simple bottom-up processing. In other words, this study shows the potential of bottom-up processing which can synthesize more sophisticated materials by selecting the precursor with arbitrary characteristics.

**CONCLUSIONS**

Yellow PTNTs were synthesized by facile one-step bottom-up processing using the peroxo titanium complex ion with further acid and ultrapure water washing. This process allowed us not only to minimize the use of alkaline such as NaOH but also to form uniformly structure-modified low-dimensional nanostructured titanate with enhanced photocatalytic properties. PTNTs exhibited a nanotube structure with approximately 10 nm in the outer diameter and an average pore size of 9.9 nm. Various optical analyses revealed that the present PTNTs contained a large amount of peroxo groups in the lepidocrocite-based crystalline structures homogeneously: the peroxo titanium bonds were formed in the interlayers of the lepidocrocite titanate crystal, which resulted in the increase in the interlayer distance of two-dimensional TiO\(_6\)-based octahedron network layers to 10.02 Å in PTNTs compared with that of TNTs (8.89 Å). This structural modification exhibited the change of the titanate’s color from white for usual titanate to yellow one in the present PTNTs, and the color change contributed to enhancing the optical absorption in the visible light region. As a result, by comparing TNTs, a great decrease in optical band gap energy, down to 2.50 eV, was confirmed which was caused by peroxo titanium bond formation and followed a change in the crystalline and electrical band structure with the valence band raising to 1.35 eV. The surface chemistry of PTNTs was greatly affected by the introduction of peroxo functional groups to titanate structures; a negative zeta potential of \(-28.0 \text{ mV}\) for PTNTs was higher than that of TNTs (\(-22.2 \text{ mV}\)). Although the PTNTs had lower specific surface area, the difference of such a chemical characteristic is considered to be a reason why the cationic RhB dye molecule was absorbed more on the PTNTs than on the pure TNTs. The optical response for PTNTs was
extended to the visible light range compared to pure TNTs, resulting in enhanced photocatalytic degradation performance of RhB. By replacing the precursor of nanostructured titanate from TiO₂ powders to a water-soluble peroxy titanium complex ion, homogeneous and high-density introduction of the peroxy titanium bonding unit (Ti−O−O) into the titanate nanomaterials takes place, which is due to the precious bottom-up formation of titanate-based inorganic structures from molecularly controlled peroxy titanium complex precursors through the present solution chemical route. Therefore, we believe that the interesting bottom-up process used herein might be extendable to synthesize the visible-activated titanate nanostructured materials with various structures with advanced chemical and photochemical properties.

■ EXPERIMENTAL SECTION

Yellow TNT Preparation. As a precursor, the peroxy titanium complex ion ([Ti(OH)₃O₂]⁻)⁴⁸ was synthesized by the following methods of the previous study: initially, 0.63 g of TiH₂ (>99%, Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan) was dissolved in 62.46 mL of mixed solution with pH 10 containing H₂O₂ (30%, FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan) and NaOH (97%, FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan) aqueous solution for 2 h at 10 °C. The pH of the mixed solution was adjusted by adding 10 M concentrated NaOH solution to the hydrogen peroxide solution. To synthesize PTNTs, the prepared peroxy titanium complex ion solution was heated in a refluxing vessel at 100 °C for 12 h with 200 rpm stirring speed. Then, the precipitates were treated by 5 M HCl (30%, FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan) solution until the pH stabilized at 5 and washed by distilled water until the ion conductivity of the filtrate became less than 5 μS/cm using a vacuum pump (MDA-020C, ULVAC, Inc., Kanagawa, Japan) solution until the pH stabilized at 5 and washed by distilled water until the ion conductivity of the filtrate became less than 5 μS/cm using a vacuum pump (MDA-020C, ULVAC, Inc., Kanagawa, Japan) to exchange the sodium ion (Na⁺) to the proton (H⁺). They were dried by a freeze dryer (EYELA FDU-2200, TOKYO RIKAKIKAI Co., Ltd., Tokyo, Japan) and are named PTNTs. Furthermore, to synthesize pristine TNTs⁴⁹ as a reference sample, 1 g of P25 TiO₂ powder as a precursor was mixed with 100 mL of 10 M concentrated NaOH solution and then heated in the refluxing vessel at 115 °C for 24 h with 200 rpm stirring speed. Afterward, prepared precipitates were also acid-treated for the ion exchange (i.e. protonation of titanate), washed, and freeze-dried.

Characterization. The morphology and particle size were observed using field emission SEM (SEM) (SU-9000, Hitachi High-Technologies Corporation, Tokyo, Japan) at 30 kV acceleration voltage and TEM (JEM-2100, JEOL, Tokyo, Japan) at 200 kV acceleration voltage. N₂ adsorption−desorption experiments (NOVA 4200e, Quantachrome Instruments, United States) were evaluated to determine the pore volume and pore size distribution for the samples. The specific surface area was calculated using the Brunauer−Emmett−Teller (BET) method considering the adsorption isotherm at a P/P₀ range of 0.1−0.3. The crystal structure and purity information were examined by XRD (D8 ADVANCE, Bruker AXS Co. Ltd., Karlsruhe, Germany). Diffraction patterns of structures were collected using a Scintag diffractometer, operating in the Bragg configuration using Cu Kα radiation (λ = 1.54 Å) from 5 to 85° at 0.02° scanning rate. Raman spectra were acquired with a Raman microspectrometer (HR 800, HORIBA, Kyoto, Japan) using an Ar ion laser (514.5 nm). Spectra were collected in the range of 1000−100 cm⁻¹ with a resolution of 1 cm⁻¹. The XPS (JPS-9010MX JEOL Ltd., Tokyo, Japan) patterns were measured in O₁s, Ti₃p, and valence range. The binding energy was standardized with C₁s energy. The reflectivity of the prepared powder was evaluated using the solid sample measurement mode in ultraviolet−visible (UV−vis) DRS (V-650, JASCO Co., Tokyo, Japan), and the optical band gap energy was measured by the Tauc−plot method using Kubelka−Munk transformation. The UV−vis absorption spectrum was obtained using the spectrophotometer (UVmini-1240, SHIMADZU Corporation, Tokyo, Japan). The zeta potential was evaluated using a dynamic light scattering analyzer coupled with a laser doppler micro−electrophoresis method (Zetasizer, Nano-ZS MALVERN Panalytical, Worcestershire, United Kingdom) by repeating the measurement three times for each sample.

Photocatalytic Reaction. The photocatalytic properties of the prepared photocatalysts were evaluated in the photo-decolorization reaction using RhB as an organic compound. RhB solution was prepared with 10 mg/L concentration. The test was carried out in an aqueous phase in a stirred batch reactor containing 2 g/L photocatalysts suspended in 50 mL of the substrate solution. The solution containing the photocatalyst was stirred with 300 rpm speed in the dark for 30 min to an adsorption−desorption equilibrium of the dye molecule on the catalyst surface; afterward, the solution was visible light irradiated. The light from the solar simulator (OTENTO-SUN III, Bunkoh-Keiki Co., Ltd, Tokyo, Japan) was calibrated under standard air mass (A.M.) 1.5 and 1000 W/m² and filtered with cut filter L-42 (<420 ± 5 nm, Hoya Corporation, Tokyo, Japan). The samples were obtained at reaction time intervals of 30 min and filtered using a 0.2 μm pore-sized filter to remove the catalyst powder, and their UV−vis absorption spectra were recorded. The decolorization⁵⁰ of RhB was calculated using the formula: decolorization = (A₀ − A)/A₀, where A₀ and A were the absorbance of the RhB before and after the reaction, respectively.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02734.

Experimental data of the XRF elemental analysis; high-resolution TEM images; and changes in optical absorption spectra of RhB solutions after 6 h soaking under the dark condition for TNTs and PTNTs (PDF)

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Author Contributions
The manuscript was written through the contributions of all authors. H.P. and T.S. conceived and designed the present study; H.P. performed the experiments, analyzed the data, and wrote the paper; T.G., S.H.C., and H.N. contributed the experiment and analysis methods. All authors discussed the results and the implications of this manuscript.

Notes
The authors declare no competing financial interest.

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