N-doped TiO_2 Nanotube with Visible Light Activity

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Nitrogen-doped TiO_2 nanotubes were synthesized by a wet process. The nanotubes have an anatase crystal structure with nitrogen atoms substituted into oxygen sites of TiO_2. These nanotubes exhibited photocatalytic oxidation activity of gaseous isopropanol into acetone and carbon dioxide when illuminating with visible light.

Titanium dioxide (TiO_2) is an efficient photocatalyst that has been applied to various industrial items because of its strong oxidation activity[1] and superhydrophilicity.[2] However, titanium dioxide has a wide band gap (3.0–3.2 eV). Thus, photocatalytic reactions do not proceed when illuminating with visible light. Numerous studies have attempted to extend the photosensitivity of TiO_2 towards the visible light region by coupling or doping with other materials.[3] Recently, visible light responses were reported when nitrogen was doped into a TiO_2 lattice.[4] The design of the electronic structure is very important for controlling the light absorbing property, also the microstructure is a key factor for developing new functional photocatalysts. Recently, titanate nanotubes have received a lot of attention owing to their unique one-dimensional (1-D) nanostructure and economic fabrication process.[5] We reported a thin film of titanate nanotubes and its photochemical reactions such as photocatalytic oxidation activity and photoinduced hydrophilicity.[6] However, the band gap of a titanate nanotube is larger than that of the bulk TiO_2 materials because of its quantum size effect. Thus, it is not active when illuminating with visible light. The previous study reported that the N-doped TiO_2 nanotubes were synthesized by annealing titanate nanotubes in gaseous NH_3,[7] but this process is very reductive and generates defects in the crystal.[4b,4f] In this study, nitrogen-doped TiO_2 nanotubes (anatase) were synthesized by a soft chemical process and visible light responses for decomposing gaseous isopropanol were evaluated.

Our N-doped TiO_2 nanotubes were synthesized from titanate nanotubes by protonating the surface, then immersing into aqueous NH_3 solution, and annealing in air. The starting materials (titanate nanotubes) were synthesized by a previously reported hydrothermal method.[5a] After the hydrothermal reaction, a white precipitate was filtered and washed with 0.1 M HNO_3 aq solution to neutralize it. Then the precipitate was washed with distilled water. Next, the obtained powder was immersed in an aqueous HNO_3 solution (0.5 M) for 15 h at room temperature to protonate the surface. This protonation procedure enables the nitrogen dopant (NH_4^+) to easily diffuse into the layered titanate structure. After surface protonation, a white precipitate was obtained by centrifuging and then this precipitate was immersed into an aqueous NH_3 solution (1.0 M) for 15 h to dope with nitrogen. The obtained powders were dried and annealed in air at 673 K for 1 h, which resulted in light-yellow powder.

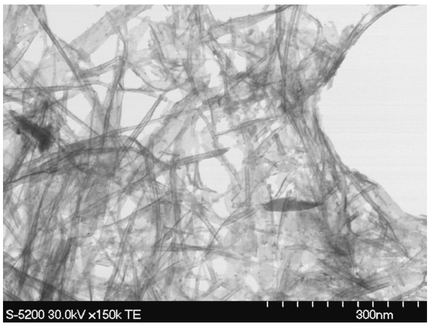

Figure 1. TEM images of the nanotubes.

Figure 1 shows the TEM image of the light-yellow powder. Nanotubular structures were observed and this powder contained sheet-like structures similar to previously reported titanate nanotubes.[5b,5e] The BET surface area of this powder was 204 m^2/g and the pore size distribution exhibited a 3.5 nm pore, which corresponds to the inner diameter of nanotubes. We also evaluated the XRD patterns for this powder and the crystal structure was pure anatase, while the hydrothermally synthesized starting materials exhibited the titanate nature similar to the previous report.[5b] After immersing into NH_3 solution, the titanate structure was maintained. Thus, the annealing procedure caused the crystal transformation into anatase. Furthermore, XPS for N (1s) orbital revealed that the anatase nanotubes have a peak with the binding energy of 396 eV, although titanate nanotubes did not have a peak of N (1s) orbital. The peak at 396 eV has been previously assigned to Ti–N bonding.[8] These results indicate that the nitrogen atoms were doped into lattice oxygen of TiO_2 anatase nanotubes. The doping density of nitrogen atoms analyzed by XPS was 0.4%.

Figure 2 shows the UV–vis spectra. Among these powders, the N-doped TiO_2 nanotube can absorb visible light above the wavelength of 400 nm. The inset in the figure shows the square root of the absorption coefficient (α) vs photon energies. Since the electronic structure of anatase TiO_2 gives an indirect transition,[9] the square root of α is linear with photon energy, and the intercept with the x axis estimates the band gap energy. The estimated band gap values for N-doped TiO_2 nanotube, pure anatase, and titanate nanotube were 3.17 eV (λ: 391 nm), 3.22 eV (385 nm), and 3.42 eV (363 nm), respectively. Asahi et al. reported that substitutionally nitrogen doping into lattice oxygen causes the band gap narrowing.[4a] In contrast, Irie et al. recently reported that the visible light activity in N-doped TiO_2 was caused by the isolated N(2p) narrow band above the O(2p) valence band under a low nitrogen doping density ($<2\%$).[4b] Our UV–vis spectra revealed that the band gap of N-doped TiO_2 nanotube (3.17 eV, λ: 391 nm) was slightly narrower than that of pure anatase. On the other hand, broad light absorption above 400 nm was observed in N-doped TiO_2 nanotube (Figure 2). This light absorption above 400 nm is not attributed to the interband transition but to the isolated states of N(2p) orbitals. On the basis

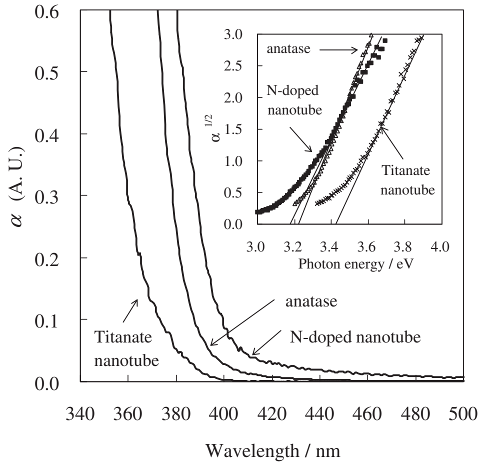

Figure 2. UV–vis spectra for powders analyzed by the diffuse reflectance method. Absorption coefficient (α) was obtained by the Kubelka–Munk method. The inset shows the square root of absorption coefficient versus photon energy.

of these results, the substitutional nitrogen doping into lattice oxygen causes the slight band gap narrowing as well as the isolated states between the band gap.

Figure 3 shows the concentration changes of gaseous isopropanol, acetone, and CO_2 for the N-doped TiO_2 nanotube when illuminating with visible light (410–500 nm). Under these conditions, the photogenerated holes in the N-doped TiO_2 nanotube would exist in isolated states between the band gap, but the N-doped TiO_2 nanotubes exhibited visible light activity. Gaseous isopropanol was directly oxidized to CO_2, or oxidized through an acetone intermediate to CO_2. The visible light responses for pure anatase and titanate nanotube were also evaluated, but they did not exhibit activity. We have also evaluated the photocatalytic activity under the visible light illumination with the wavelength above 500 nm by using a cut-off filter. And as a result, the N-doped TiO_2 nanotube did not exhibit any activity under this illumination condition. As is shown in Figure 2, the N-doped TiO_2 nanotube did not absorb the light above 500 nm, thus the light absorption below 500 nm is indispensable for the photocatalytic activity. In addition, photocatalytic activity of the N-doped TiO_2 nanotube under UV illumination (λ: 365 nm) was as high as the pure anatase. Furthermore, the photocatalytic activity under a fluorescent light bulb, which contains both UV and visible light, was evaluated. Consequently, the N-doped TiO_2 nanotube exhibited the highest activity among these samples. The titanate nanotube exhibited the lowest activity in these powders, owing to its wide band gap, bad crystallinity, and/or defects in the crystal.

In summary, the N-doped TiO_2 nanotube exhibited visible light activity. The N-doped TiO_2 nanotube is stable, and its activity did not decrease under exposure to UV illumination in air as well as in water. N-doped TiO_2 nanotubes have a unique 1-D nanostructure with a high photocatalytic activity. This nanotube should be a new photocatalyst material with novel functions, such as molecular size recognition and selectively decomposing organic contaminants.

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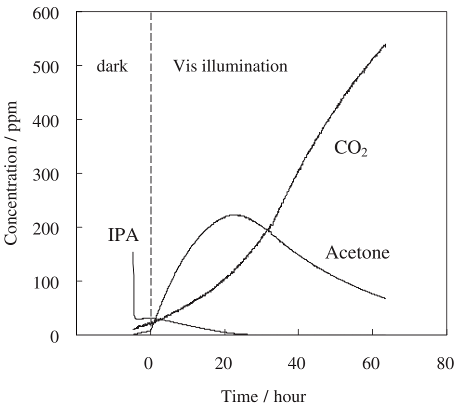

Figure 3. Photocatalytic decomposition of gaseous isopropanol when illuminating with visible light (relative humidity: 50%). The initial concentration of isopropanol was 500 ppm. The light source was 250-W Xe lamp (LA-250Xe, Hayashi Watch Works), which was used in conjunction with UV and IR cutting filter. The wavelength ranged between 410 and 500 nm.

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