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Perspective Article

Photocatalytic activity under UV/Visible light range of Nb-doped titanate nanostructures synthesized with Nb oxide

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ABSTRACT

In this work, using economical and stable niobium oxide (Nb_2O_5) powder as niobium source, visible light responsive Nb-doped titanate nanostructures were synthesized by hydrothermal process. The synthesized Nb-doped titanate nanostructures were composed of two types of titanate nanostructures (nanotubes and nanosheets) and TiO_2 nanoparticles. They have a smaller band gap energy of 3.24 eV compared to pure TNTs that were synthesized under the same experimental conditions. The photocatalytic activity of the synthesized Nb-doped titanate nanostructures was evaluated under visible light irradiation through the degradation of methylene blue (MB) and rhodamine B (RhB). Consequently, the synthesized Nb-doped titanate nanostructures exhibited much higher photocatalytic activity under visible light irradiation than pure TNTs. The photocatalytic activity of the synthesized Nb-doped titanate nanostructures was 1.4 times (MB) and 3.1 times (RhB) higher than of pure TNTs because the Nb-doping narrowed the band gap and it accelerated the separation of photo-induced electron-hole pairs.

1. Introduction

Photocatalytic reaction with solar energy and semiconductors is of great importance in solving global energy and environmental issues [1–3]. Various semiconductors, such as TiO_2, ZnO, WO_3, CdS, and NiO, have been attempted to apply the photocatalysts, and it is generally accepted that TiO_2 is the most reliable material due to its relatively low cost, nontoxicity, high reactivity and chemical stability under ultraviolet light (< 387 nm), whose energy exceeds the band gap of 3.0 ~ 3.3 eV in the anatase or rutile crystalline phase [4,5]. Despite such advantages, however, the practical application of TiO_2 for photovoltaics and photocatalysts is extremely limited because of its poor absorption capability under visible light (> 400 nm) due to its intrinsically large energy band gap and low quantum yield caused by the rapid recombination of photogenerated electrons and holes [6,7]. Therefore, there have been several attempts to develop modified TiO_2 that exhibits high reactivity under visible light irradiation. As a result, several approaches for TiO_2 modification have been proposed, including metal-ion doped TiO_2 using transition metals [8], reduced TiO_x photocatalysts [9,10], non-metal doped TiO_2 [11–13], composites with TiO_2 and other semiconductors having lower band gap energy [14,15], and sensitizing of TiO_2 with dyes [16].

Among these approaches, it is well-known that the metal-ion doping is a widely used and effective way to improve the photocatalytic activity and stability of a semiconductor. In particular, niobium (Nb) doping is thought to be a promising approach to improve the photocatalytic activity of TiO_2 under visible light irradiation. Nb can easily form a solid solution in the lattice of TiO_2 because the ionic radius of Nb^{5+} (0.64 Å) is similar to that of Ti^{4+} (0.605 Å) [17]. The effect of Nb on the photocatalytic activity of TiO_2 has been demonstrated in many existing studies. Michalow et al. fabricated Nb-doped TiO_2 powder by a flame spray synthesis using titanium tetraisopropoxide ($Ti(C_3H_7O)_4$) and niobium chloride ($NbCl_5$). To form the Nb-doped TiO_2 powder, Nb and Ti precursors were dissolved in a solvent and sprayed into a high temperature acetylene-oxygen flame using a reactive atomizing gas (oxygen). The photocatalytic activity of the Nb-doped TiO_2 powder was assessed by the photo-degradation of a methylene blue solution under a UV irradiation. TiO_2 with Nb concentration up to 1 at.% showed higher first-order photodecomposition kinetic rate constant towards MB decomposition under irradiation, than commercial P25 [18]. Also, Kaleji et al. prepared an Nb-doped TiO_2 thin film by a sol-gel method using titanium butoxide ($Ti(OC_4H_9)_4$) and

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niobium chloride ($NbCl_5$). To fabricate the Nb-doped TiO_2 thin film, the solution of two starting materials was aged for 24 h in order to complete all reactions, and calcined at 400 °C for 1 h. The photocatalytic activity of the film was tested using the degradation of methylene blue. The 1 mol% Nb-doped TiO_2 sample indicated higher photocatalytic activity than the on-doped TiO_2 in the UV light region [19].

However, these methods, which is used for synthesizing various metal oxide nanostructures, expensive and unstable niobium alkoxide or niobium chloride ($NbCl_5$) is required as a precursor of Nb. Also, complex processing such as flame experimental setup and calcination at higher than 400 °C is necessary. Therefore, economical and easy processes should be examined for the synthesis of Nb-doped TiO_2.

In this study, Nb-doped titanate nanostructures with improved reactivity under visible light irradiation were synthesized by a hydrothermal process using economical TiO_2 and Nb_2O_5 powders as an Nb precursor. Photocatalytic activity under UV/visible light range of synthesized Nb-doped titanate nanostructures was also investigated.

2. Experimental

2.1. Synthesis of Nb-doped titanate nanostructures

In this study, Nb-doped titanate nanostructures were synthesized by a hydrothermal process. Commercial anatase TiO_2 (99.9%, Kojundo Chemical Lab. Co., Japan) and Nb_2O_5 (99.9%, Wako Pure Chemical Industries Ltd., Japan) powders were used as starting materials. Nb_2O_5 powder at a concentration of 3 mol% was mixed with TiO_2 powder, and then the mixed powders were homogeneously dispersed in a 10 M NaOH aqueous solution by ultrasonification for 30 min to form an amorphous Ti-Na-O. The mixture was refluxed at 135 °C for 24 h. The resulting product was washed with deionized water until it reached pH 7 ~ 8. Next, the product was treated with 0.1 M HCl to exchange sodium ions. The treated product was washed repeatedly with deionized water and ethyl alcohol until the solution conductivity reached below 10 µS/cm. Finally, the synthesized powder was dried in an oven at 70 °C for 48 h.

2.2. Characterization

The phase analysis of synthesized Nb-doped titanate nanostructures was conducted by X-ray diffractometer (XRD, D8 Advance, Bruker AXS GmbH) using Cu Kα radiation. Microstructure observation and composition analysis of synthesized Nb-doped titanate nanostructures were performed by a field emission scanning electron microscopy (FESEM, NanoSEM 450, FEI) and transmission electron microscopy (TEM, JEM-2100F, JEOL Co.) with an accelerating voltage of 200 kV equipped with an energy dispersive spectroscopy (EDS). The optical properties were analyzed with UV–vis spectrophotometer (V-650 spectrophotometer, Jasco Co.) equipped with the integrating sphere accessory for diffuse reflectance spectra. $BaSO_4$ was used as a reference.

2.3. Photocatalytic activity

The adsorptive and degradative properties of synthesized Nb-doped titanate nanostructures were analyzed using methylene blue (MB, Wako Pure Chemical Industries Ltd.) and rhodamine B (RhB, Wako Pure Chemical Industries Ltd.). The photocatalytic activity of the synthesized Nb-doped titanate nanostructures was compared with that of commercial Degussa P-25 and TNTs synthesized under the same experimental conditions. MB and RhB solutions were prepared at a concentration of 20 mg/L. Then, 20 mg of synthesized Nb-doped titanate nanostructures was suspended in 100 mL of this solution. The degradation of MB and RhB under UV irradiation was evaluated after exposure to UV light (mercury–xenon lamp with a center wavelength of 365 nm, UVF-204S, SAN-EI Electric Co.) and degradations under visible light was performed by exposure to visible light (solar simulator with cutoff glass filter under 400 nm) at room temperature. Also, the adsorption capacity of TNTs and Nb-doped titanate nanostructures for MB and RhB dye was compared with Degussa P-25 under dark condition over 6 h. The concentrations of MB and RhB solutions were analyzed with a UV–vis spectrophotometer (UV mini-1240, Shimadzu Co.) by measuring the absorption band at 663 and 552 nm, respectively.

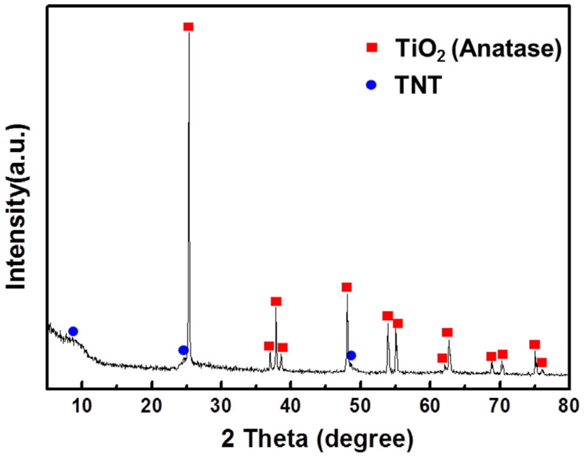

Fig. 1. XRD pattern of synthesized Nb-doped titanate nanostructures.

3. Results and discussion

Fig. 1 shows the XRD pattern of the synthesized Nb-doped titanate nanostructures. It clearly showed the peaks of anatase TiO_2 and titanate ($H_2Ti_4O_9{\cdot}H_2O$), which indicates that the nanotubes were synthesized through a solution chemical route, such as pure TNTs. In particular, Nb_2O_5 peaks could not be found in the XRD pattern of synthesized Nb-doped titanate nanostructures. It was considered that the Nb_2O_5 powder was completely dissolved in the NaOH aqueous solution and Nb ion (Nb^{5+}) might have been substituted for the Ti ion (Ti^{4+}) site in titanate [20].

Fig. 2 shows the high-resolution XPS spectra of pure TNTs and synthesized Nb-doped titanate nanostructures, confirming the presence of Ti 2p, O 1s, and Nb 3d in the samples. For both samples, two peaks at about 458–464 eV correspond to the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ states, indicating that Ti is present in a valence state of 4^+, and the at 529 eV, which is attributed to bulk oxygen bonded to titanium, were observed as shown in Fig. 2(a) and (b). In particular, for synthesized Nb-doped titanate nanostructures, two peaks at about 206–209 eV correspond to the Nb $3d_{5/2}$ and Nb $3d_{3/2}$ states, confirming that Nb is present in the 5^+ valence state [21].

The shape and morphology of synthesized Nb-doped titanate nanostructures observed using FE-SEM are shown in Fig. 3. In general, non-doped titanate nanostructures are known to exist as nanotubes with large aspect ratio [22]. However, Nb-doped titanate nanostructures were found to exist as a mixture of agglomerated nanotubes and nanosheets. The reason for the poor yield of nanotubes is that the additives, including Nb ions, interfere with the rolling of nanosheets into nanotubes during the hydrothermal process [23]. Also, it is thought that the separation of layered nanosheets was limited because of complicated interconnection. Therefore, some platelet TiO_2 nanoparticles (NPs) with diameters of about 100–200 nm were present.

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