IOP Conference Series: Materials Science and Engineering

Formation and Characteristics of Anatase-Type Titania Solid Solution Nanoparticles Doped with Nb^{5+} M (M = Ga^{3+}, Al^{3+}, Sc^{3+})

To cite this article: Masanori Hirano and Takaharu Ito 2011 *IOP Conf. Ser.: Mater. Sci. Eng.* **18** 062010

IOP Conf. Series: Materials Science and Engineering **18** (2011) 062010 doi:10.1088/1757-899X/18/6/062010

Formation and Characteristics of Anatase-Type Titania Solid Solution Nanoparticles Doped with Nb^{5+} and M ($M=Ga^{3+}$, Al^{3+}, Sc^{3+})

Masanori Hirano[1] **and Takaharu Ito**
Department of Applied Chemistry, Faculty of Engineering,
Aichi Institute of Technology, Yakusa, Toyota, 470-0392, Japan

E-mail: hirano@aitech.ac.jp

Abstract. Anatase-type titania solid solutions co-doped with Nb^{5+} and cation M ($M=Ga^{3+}$, Al^{3+}, Sc^{3+}) with composition $Ti_{1-2X}Nb_XM_XO_2$ were directly formed as nanoparticles from precursor solutions of $TiOSO_4$, $NbCl_5$, and metal salts ($Ga(SO_4)_3$, $Al(NO_3)_3$, and $Sc(NO_3)_3$) under mild hydrothermal conditions at 180 °C for 5 h using the hydrolysis of urea. The effect of co-doped cation M on the formation and properties of anatase-type titania solid solutions was investigated. The region of anatse-type solid solution depended on the co-doped cation M. The composition range of anatase-type titania solid solution in the case of $M= Sc^{3+}$ was much wider than that in the case of $M= Ga^{3+}$ and Al^{3+}. The increase in the amount of co-doped cation $M=Ga^{3+}$, Al^{3+} enhanced the crystallite growth of anatase solid solutions under the hydrothermal conditions. The solid solutions co-doped with $M= Al^{3+}$ showed the most improved photocatalytic activity in the three cations. The anatase-to-rutile phase transformation of solid solutions was promoted at lower temperature via the presence of co-doped cation $M=Ga^{3+}$.

1. Introduction
Titania (TiO_2) has attracted attention as a promising material for photocatalysts [1] and electrodes for dye-sensitized solar cell. Among three polymorhs (rutile, anatase, and brookite) the metastable phase of anatase exhibits high photocatalytic activities. The metastable anatase transforms to a thermodynamically stable rutile phase at elevated temperatures through heat treatment. In general, the properties such as the anatase-to-rutile phase transformation behaviour as well as photoactivity are affected by their grain size, impurities, compositions, the nature and the amount of dopant, specific surface area, etc. The precursor materials and processing also influence the properties and performance of resultant material. Hydrothermal treatment is well known to be able to directly synthesize homogeneous nanometer-sized metal-oxide solid solutions from aqueous precursor solutions at relatively low temperatures [2]. The formation of solid solutions containing zirconium [3] and niobium [4] is effective for the enhancement of photocatalytic activity, although there are many studies on doped TiO_2 catalysts. The ionic radii of niobium Nb(V), aluminum Al(III), gallium Ga(III), and scandium Sc(III) are close to that of titanium Ti(IV).

[1] To whom any correspondence should be addressed.

The present study was concerned with the effect of the co-dopant M (M = Ga, Al, and Sc) on the formation, crystallite growth, optical band gap, photocatalytic activity, and phase stability of anatase-type titania solid solutions with compositions $Ti_{1-2X}Nb_XM_XO_2$ that were directly formed as nanoparticles under hydrothermal conditions at 180 °C.

2. Experimental

2.1. Preparation of samples

A mixture (0.5 mol/dm^3) of an aqueous solution of $TiOSO_4$, ethanol solution of $NbCl_5$, and either of $Al(NO_3)_3$, $Ga(NO_3)_3$, and $Sc(NO_3)_3$ in different ratios of Ti/Nb/M, M = Al, Ga, and Sc was prepared in a Teflon container (20 ~ 100 dm^3). The solution mixture with compositions $Ti_{1-2X}Nb_XM_X$ and X = 0.10 ~ 0.35 added with aqueous solution of urea in the Teflon container was controlled to become weakly basic after hydrothermal treatment. After the Teflon container was placed in a stainless-steel vessel, it was heated at 180 °C for 5 h. After hydrothermal treatment, the precipitates were washed with distilled water, separated from the solution, and dried in at 60 °C. The powder thus prepared was heated in an alumina crucible at heating rate 200 °C/h, held at 800 – 1050 °C for 1 h in air. Commercially available pure TiO_2 (ST-01, anatase-type, Ishihara Sangyo Kaisha Ltd., Japan) was used as the reference.

2.2. Characterization

The phases of the as-prepared and heat-treated powders were examined by X-ray diffractometry (XRD) using CuKα radiation. The morphology of the as-prepared samples was observed by transmission electron microscopy (TEM). The crystallite size of anatase was estimated from the line broadening of 200 diffraction peaks, according to the Scherrer equation. The lattice parameters were measured using silicon as the internal standard. The diffuse reflectance spectra measurements for powder samples have been made. The optical absorption of these prepared powders was measured using an ultraviolet-visible spectrophotometer.

The photocatalytic activity and adsorptivity of these prepared powders were separately estimated from the change in the concentration of methylene blue ($C_{16}H_{18}N_3S$, MB) both under ultraviolet ray (UV) irradiation from black light (20 W) and in the dark, respectively. After the dispersed sample powders in the solution adsorbed MB to the full by holding in the dark for 24 h under stirring, the sample in the solution was maintained for 0-5 h under irradiation of ultraviolet ray with an intensity of 1mW/cm^2 under stirring. Thus, the UV-light irradiation time dependence of MB concentration decomposed by the sample powders was estimated by the measurement of the concentration of MB remained in the solution based on the absorbance change using the spectrophotometer.

3. Results and discussion

3.1. Formation of anatase-type solid solutions

Figure 1 shows the XRD patterns of the precipitates obtained from the precursor solution mixtures in a ratio of Ti/Nb/M = 0.80/0.10/0.10. The yields were close to 95 % of the theoretical amounts. All the precipitates were detected as a single-phase anatase-type structure, and no trace of diffraction peaks due to another phase were detected. Figure 2 shows the TEM image of the precipitate formed from the precursor solution mixture in a ratio of Ti/Nb/Sc = 0.80/0.10/0.10 under hydrothermal condition at 180 °C. The anatase-type precipitates grew to approximately the same diameter. Though the particle size of the precipitates ranges from 10 to 20 nm in diameter, relatively high homogeneity in particle size scattering is observed. The lattice parameters a_0 and c_0 of the as-prepared tetragonal anatase-type TiO_2, as determined via XRD using silicon as the internal standard increased gradually with the increase of the content (X) of dopants. A single phase of metastable anatase-type solid solution can exist up to the composition $ScTiNbO_6$ via the substitution of Ti by Nb and Sc. The optical band gap of the anatase depended on the amounts and kinds of co-dopant, and it was increased in order of M = Ga, Al, and Sc.

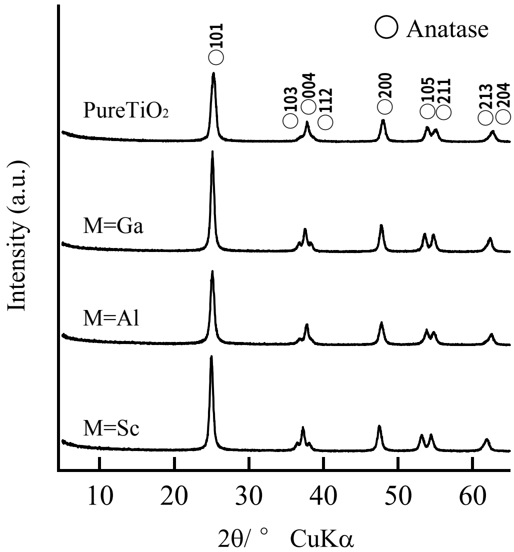

Figure 1. XRD patterns of precipitates formed at the composition of X = 0.10 in $Ti_{1-2X}Nb_XM_XO_2$ (M = Ga, Al, and Sc) under hydrothermal condition at 180 °C for 5 h.

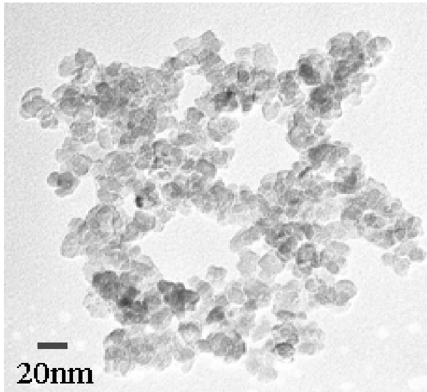

Figure 2. TEM image of precipitate hydrothermally formed at the composition of X = 0.10 in $Ti_{1-2X}Nb_XSc_XO_2$.

3.2. Photocatalytic activity

The changes in the concentration of MB with time in the dark and under UV-light irradiation are indicated for the samples ($Ti_{0.80}Nb_{0.10}M_{0.10}O_2$) in addition to the sample with pure TiO_2 composition that was prepared under the same hydrothermal condition and reference powder ST-01 (pure TiO_2) are shown in Figure 3.

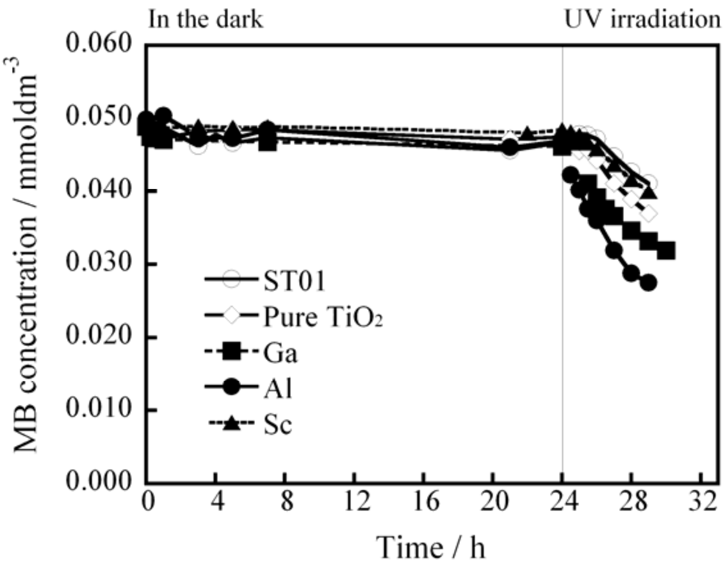

Figure 3. Change in methylene blue concentration for the samples $Ti_{0.80}Nb_{0.10}M_{0.10}O_2$ (M = Ga, Al, and Sc) and pure TiO_2 prepared under hydrothermal condition at 180 °C for 5 h and reference sample ST-01 with stirring time in the dark and under UV irradiation.

The anatase solid solutions co-doped with Nb and either of Al or Ga showed rapid decrease in MB concentration under UV irradiation. The formation of anatase-type solid solutions via the substitution of Ti by Nb and other co-dopant Ga or Al is seen to be effective for the improvement of photocatalytic activity.

3.3. Phase stability

The XRD patterns of the anatase-type solid solutions with compositions $Ti_{0.70}Nb_{0.15}Al_{0.15}O_2$ and $Ti_{0.33}Nb_{0.33}Sc_{0.33}O_2$ before and after heating in air are shown in Figures 4 and 5, respectively. The anatase solid solutions with composition $Ti_{0.70}Nb_{0.15}M_{0.15}O_2$ transformed into a single phase of rutile ones. A α-PbO_2 phase was precipitated from anatase-type solid solutions $Ti_{1-2X}Nb_XSc_XO_2$ in the composition range $0.33 > X \geq 0.20$ via the phase transformation.

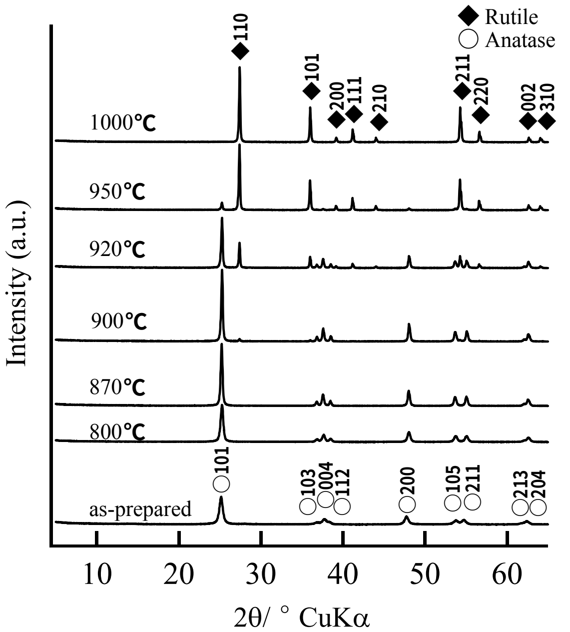

Figure 4. XRD patterns of $Ti_{0.70}Nb_{0.15}Al_{0.15}O_2$ solid solutions as-prepared and after being heated at 800-1000 °C for 1 h.

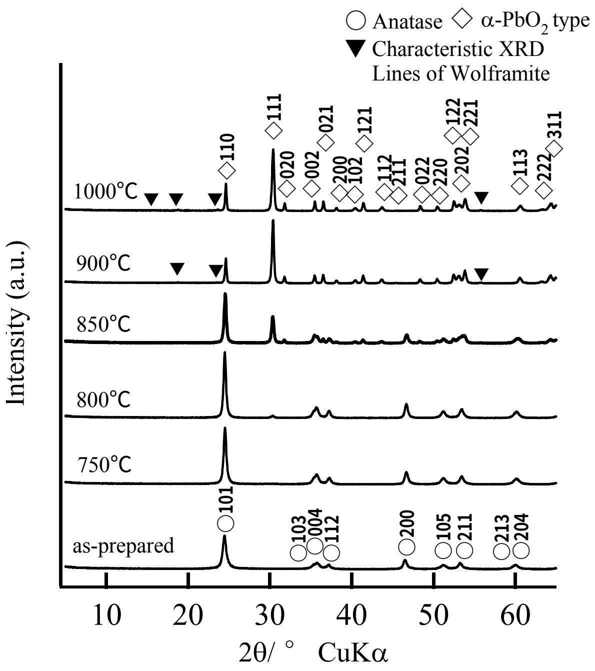

Figure 5. XRD patterns of $Ti_{0.33}Nb_{0.33}Sc_{0.33}O_2$ solid solutions as-prepared and after being heated at 750-1000 °C for 1 h.

4. Summary

The effect of co-dopant M (Ga, Al, and Sc) on the formation and properties of anatase-type titana solid solutions ($Ti_{1-2X}Nb_XM_XO_2$) that were directly formed as nanoparticles under hydrothermal conditions at 180 °C for 5 h was investigated. The solid solution range X of anatase-type titania ($Ti_{1-2X}Nb_XM_XO_2$) depended on the co-dopant M. The titanium dioxide co-doped with Nb and Sc can form the metastable anatase-type solid solutions with wide solid solution ranges. The formation of the solid solutions was effective for the improvement of photocatalytic activity. The anatase solid solutions with composition $Ti_{0.70}Nb_{0.15}M_{0.15}O_2$ transformed into a single phase of rutile ones.

References

[1] Carp O, Huisman C L and Reller A 2004 *Prog. Solid State Chem.* **32** 33
[2] Komarneni S 2003 *Current Science* **85** 1730
[3] Hirano M, Nakahara C, Ota K, Tanaike O and Inagaki M 2003 *J. Solid State Chem.* **170** 39
[4] Hirano M and Matsushima K 2006 *J. Am. Ceram. Soc.* **89** 110