



Crystal growth of titania by photocatalytic reaction

Hiromasa Nishikiori^{a,b,c,*}, Shunpei Fujiwara^b, Syuhei Miyagawa^a, Nobuyuki Zettsu^{a,b,c}, Katsuya Teshima^{a,b,c}

^a Department of Materials Chemistry, Graduate School of Science and Technology, Shinshu University, 4-17-1 Wakasato, Nagano, 380-8553 Japan

^b Department of Environmental Science and Technology, Graduate School of Science and Technology, Shinshu University, 4-17-1 Wakasato, Nagano, 380-8553 Japan

^c Center for Energy and Environmental Science, Shinshu University, 4-17-1 Wakasato, Nagano, 380-8553 Japan

ARTICLE INFO

Article history:

Received 18 March 2017

Received in revised form 22 May 2017

Accepted 25 May 2017

Available online 26 May 2017

Keywords:

Crystal growth

Titania

Titanium hydroxide

Dehydration

Photocatalysis

Nitrate ion

ABSTRACT

Substrate plates coated with anatase-type titania thin films were immersed in a solution of titanium (IV) chloride and lithium nitrate at 353 K during UV irradiation. About 20 nm-sized anatase-type titania crystals were formed on the original titania film consisting of almost the same sized particles. Nitrate ions in the solution were reduced to nitrite ions, and water was transformed into hydroxide ions by a photocatalytic reaction on the original titania film. The pH value increased on the titania surface, which caused the titanium hydroxide formation. The titanium hydroxide was then dehydrated and transformed into titania. The titania particles formed on the substrate exhibited a photocatalytic activity similar to the original titania.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Titania is one of the most important photocatalysts that is widely investigated by many researchers all over the world because it is highly stable and easy to prepare from commercially available materials [1,2]. The original titania can be transformed into visible light-active materials by certain chemical and physical doping techniques although it can absorb only UV light [2]. Its photocatalytic activity can be improved by surface modification of the original photocatalyst particles. Nanoparticles or nanoclusters of metal oxides are used as modifiers in order to increase the visible light activity, efficiency, and lifetime of the charge separation [3].

Zinc oxide particles were previously deposited from an aqueous solution of zinc nitrate at 323–358 K on a titania thin film by a photocatalytic reaction [4,5]. The zinc oxide films are also prepared by an electrodeposition [6–8] or electroless deposition [9–12] by chemical reactions. However, the photocatalytic reaction can control the amount and size of the deposited particles by changing the amount of the irradiated photons, suitable for forming nanoparticles on the original photocatalyst particles.

The amorphous or low crystalline zinc hydroxide aggregates were deposited at a low temperature. The zinc oxide crystals with about 1–2 μm-sized hexagonal columns and 10 nm-sized spheres were formed at 338–358 K. The formation process can be expressed as follows [13–15]: Nitrate ions in the solution were reduced to nitrite ions, and water was transformed into hydroxide ions by a photocatalytic reaction on the titania film. The pH value increased on the substrate surface with the titania film, which caused the zinc hydroxide formation on the film. The zinc hydroxides were then dehydrated and transformed into zinc oxide. The average crystallite size of the zinc oxide decreased with an increase in the reaction temperature because the reaction rates of the formation and dehydration of the zinc hydroxides increased which resulted in an increase in the formation rate of the crystal zinc oxide nuclei.

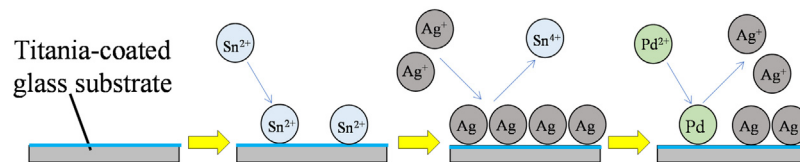
An electrodeposition and chemical deposition cannot easily produce anatase-type titania films due to difficulty in the reaction control. Photocatalytic reaction can produce active nanoparticles or nanoclusters of titania on the original titania particles. The titania growth is a model of formation of metal oxide nanoparticles as the modifiers which can improve the photocatalytic activity.

In this study, based on such a preparation method of zinc oxide, titania nanoparticles were also attempted to be formed from an aqueous solution of titanium (IV) chloride containing nitrate ions on a substrate plate with a titania thin film by a photocatalytic reaction. Titanium is easier to form its hydroxide than zinc and more difficult to be dehydrated. The activation energy of dehydration and

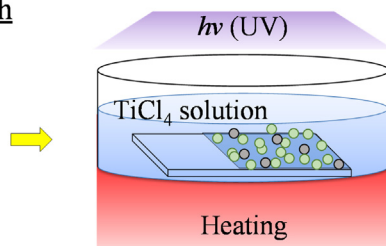
* Corresponding author at: Department of Materials Chemistry, Graduate School of Science and Technology, Shinshu University, 4-17-1 Wakasato, Nagano, 380-8553 Japan.

E-mail address: nishiki@shinshu-u.ac.jp (H. Nishikiori).

Pretreatment (Ag and Pd particle formation)



Titania growth



Scheme 1. Diagrammatic illustration of pretreatment and titania crystal growth.

crystallization for titanium hydroxide (ca. 150 kJ mol⁻¹) is generally higher than that for zinc hydroxide (ca. 40–140 kJ mol⁻¹, depending on the coexisting anion) [16,17]. It is an important point that the dehydration of the titanium hydroxide can occur in the aqueous solution. We investigated the growth of the titania nanocrystals using its photocatalytic activity in order to apply the reaction conditions to the formation of the other metal oxide nanoparticles.

2. Experimental section

2.1. Materials

Titanium tetraisopropoxide, a titanium (IV) chloride solution, ethanol, 2-propanol, diethyleneglycol, polyethyleneglycol (M.W. = 20,000), nitric acid, hydrochloric acid, sodium hydroxide, tin (II) chloride, silver nitrate, palladium (II) chloride, and lithium nitrate (Wako, S or reagent grade) were used without further purification. Water was ion-exchanged and distilled by a distiller (Yamato WG23). The Ti plates (Takeuchi Kinzoku-Hakufun Kogyo), glass plates (Matsunami S-1111), and glass plates with ITO films (AGC Fabritech, 14 Ω cm⁻²) were used after washing with ethanol.

2.2. Sample preparation

The titanium metal, glass, and ITO glass substrates were coated with a very thin titania film by the sol–gel method. The sol was prepared by mixing 25.0 cm³ of ethanol, 0.21 cm³ of nitric acid, and 0.21 cm³ of water, then adding 5.0 cm³ of titanium tetraisopropoxide in a dry nitrogen atmosphere. The anatase-type titania films were prepared by three or ten dip-coatings using the sol, then heating at 773 K for 30 min. The thickness of the ten-layered film was ca. 300 nm. The substrates with the titania film were rinsed in 2-propanol and 0.10 wt% polyethyleneglycol aqueous solutions along with ultrasonication for 5 min each. Furthermore, they were rinsed in water with ultrasonication for 1 min, then immersed in 1.0 mol dm⁻³ hydrochloric acid containing 0.24 mol dm⁻³ SnCl₂ as the sensitizer, 4.4 mmol dm⁻³ AgCl as the first activator, and 5.9 mmol dm⁻³ PdCl₂ as the second activator for 10 min each. Sn²⁺ was adsorbed on the substrate surface, then substituted with Ag and Pd because Sn²⁺ reduced Pd²⁺. Consequently, Ag and Pd particles were formed on the surface as the nuclei for the titania crystal growth and as the promoter for the titania photocatalyst [4,5].

A material solution was prepared with 5.0 cm³ of the titanium (IV) chloride solution, 16.2 cm³ of water, 18.8 cm³ of 1.0 mol dm⁻³

hydrochloric acid, and 20 mmol lithium nitrate or nitric acid of which the pH value was ca. 6. The substrates were immersed in the material solution maintained at 353 K in the dark or during light irradiation using a high-pressure mercury lamp (SEN LIGHTS HB-100-A, 100 W) without stirring. The distance between the substrate and lamp was ca. 2 cm. After the irradiation for 4 h, the samples were washed with water, then dried at room temperature. Scheme 1 shows the diagrammatic illustration of the Ag and Pd particle formation and the titania crystal growth.

2.3. Measurements

A Micromorphology study of the samples was done using a field emission scanning electron microscope (FE-SEM, Hitachi SU8000). The X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer (Rigaku SmartLab). The UV–vis absorption spectra were measured using a spectrophotometer (Shimadzu UV-3150). The Fourier transform infrared–reflection absorption spectroscopy (FTIR–RAS) for the film samples were conducted using an FTIR spectrophotometer (Shimadzu IRPrestige-21) with an RAS accessory. The X-ray photoelectron spectroscopy (XPS) was conducted by AlKα radiation using an X-ray photoelectron spectrophotometer (Shimadzu/Kratos AXIS-HS3.5). For examination of the photocatalytic properties, the samples were prepared on the ITO glass substrates by the method described above. The electrolyte solution consisting of diethyleneglycol containing 0.50 mol dm⁻³ LiI and 50 mmol dm⁻³ I₂ was allowed to soak into the space between the sample and the counter Pt electrode. The samples were irradiated using monochromatic light generated by a fluorescence spectrophotometer (Shimadzu RF-5300) equipped with a Xe short arc lamp. During the light irradiation, the short circuit current was measured in the range from 350 to 400 nm by a digital multimeter (ADC 7461A).

3. Results and discussion

3.1. Titania crystal growth during UV irradiation

The material solutions became turbid after the UV irradiation. The particle formation can occur not only on the substrate surface, but also in the solution. The XRD patterns of the substrate and precipitates were observed in order to identify the reactions and products. Fig. 1 shows the XRD patterns of the Ti substrate with the very thin titania foundation film and that on which the film

Download English Version:

<https://daneshyari.com/en/article/6453947>

Download Persian Version:

<https://daneshyari.com/article/6453947>

[Daneshyari.com](https://daneshyari.com)