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Synthesis of TiO_2 using sol–gel method and comparison of photocatalytic characteristics

Alka[a], K.M. Choi[a,*], Y.H. Kim[a], S.M. Lee[b]

[a]*Department of Electronics & Information Communication Engineering, Kwandong University, Gangwondo 210-701, Korea*
Email: kmchoi@kd.ac.kr
[b]*Department of Environmental Engineering, Kwandong University, Gngneung, Gangwondo 210-701, Korea*

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ABSTRACT

The aim of the present communication is to compare the physical and chemical properties of TiO_2 powder and TiO_2 coated thin film particularly the photochemical degradation of pollutants. TiO_2 Powder was synthesized by the sol–gel method and was annealed with the temperatures ranging from 300 to 1100˚C. TiO_2 coating, about 8 μm thin film, was successfully fabricated by the sol–gel dip process on borosilicate glass used as a substrate having a surface area of 100 mm^2 and was further annealed at the same temperatures 300–1100˚C. TiO_2 films and powder which were annealed at 300˚C for 2 h have the structure of anatase and the particle phase composition was mainly dependent to the annealing temperature which was found to be changed from amorphous to crystalline anatase and rutile by increasing the temperature. These results were demonstrated based on the X-ray diffraction, SEM and UV–visible spectroscopic data. Further, the photocatalytic characteristics of the synthesized powder and film showed that the TiO_2 powder possessed better photocatalytic behavior than the thin film employed.

Keywords: Anatase; Photocatalytic; Amorphous; Titanium oxide

1. Introduction

The development of novel and effective technologies for purifying air and water is an important social goal. Photocatalysts are materials, typically possessed with wide band gap semiconductors, activated by exposure of UV light whose energy exceeds the band gap energy of the material. When the material is activated, electron hole pairs are generated and the life time of these two different types of carriers is different. These two carriers take part in the oxidation and reduction reactions. Photocatalysts have been studied over the years for a variety of applications such as photochemical solar energy conversion, synthetic fuel production, and the decomposition of variety of hazardous/toxic pollutants present in environment particularly in water and air [1].

TiO_2 is fairly photosensitive, stable, and inexpensive which exaggerates its wide applications in photocatalytic processes. Search for new efficient and

*Corresponding author.

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cost-effective materials towards the remediation of polluted environment is one of key issues among the researchers in order to implement the technology to clean up the environmental pollutants effectively/efficiently [2]. In this point, TiO_2-based photocatalysts showed potential use in destruction of organic compounds in polluted environment [3]. The TiO_2 has three main phase—anatase, rutile, and brookite. Anatase is relatively an unstable phase with an optical energy band gap of 3.2 eV, while rutile is a high temperature stable phase and has an optical energy band gap of 3.0 eV. Thus the TiO_2 can be used with the UV light whose energy is greater than the band gap of TiO_2 (~3.2 eV) [2].

The TiO_2-based photocatalyst which has anatase phase showed excellent photocatalytic effect than that of rutile phase [2–5]. The crystal structure, density, and adherence of the coating fabricated by sol–gel dip-coating method depends largely upon the molar ratio of the chemical precursors in the sol, the sol–gel dip-coating process, and thereafter the successive heat treatment as to enhance the growth of titania onto the substrate [5].

The present communication deals the use of anatase phase of TiO_2 thin films and powder as were obtained using the sol–gel preparation method. The characteristics of the materials were discussed by annealing it at temperatures from 300 to 1,100˚C. The changes which occurred with its structure, composition, and optical properties with the annealing were further studied by the X-ray diffraction, SEM, and UV–visible spectroscopic methods. Moreover, the photo-catalytic characteristics of these two solids were optimized with the degradation of acetaldehyde.

2. Materials and methods

The sol–gel process was used in preparation of thin films onto the surface of borosilicate substrate as well to obtain the TiO_2 powder.

2.1. Preparation of TiO_2 thin film

In this experiment, frosted and clear borosilicate glass was used as a substrate having the surface area of 100 mm^2, sonicated for 5 min in presence of distilled water, rinsed with plenty of distilled water followed by acetone in order to remove any pooling or bubble liquid on the surface. It was dried at room temperature. Further, the sol–gel of titanium was prepared at the room temperature and in ambient environment. $Ti(OCH(CH_3)_2)_4$ (titanium isopropoxide: TTIP) was used as the precursor of the TiO_2. The solution of TTIP was obtained by mixing 1.1 g of TTIP in 10 mL of absolute ethanol under continuous stirring. In order to maintain the acidic condition, a drop of 3 M CH_3COOH solution was added to this solution. The solution mixture was kept for ultra-sonication for 12 min. This was then allowed to stand for 12 h at room temperature which resulted in a transparent solution. This solution was coated uniformly over the borosilicate glass substrate surface by dipping the borosilicate sheet into the solution for 60 min and the substrate was lifted at the speed of 1 cm/min from the solution. The sheet was dried in oven at 100˚C for 15 min. The same coating procedure was repeated (four times) until the desired TiO_2 thin film thickness ($d \geq 8$ μm) was obtained. Similarly, the five coated sheets were obtained. These sheets were finally fired at different temperatures (300, 500, 700, 900, and 1,100˚C) for 1 h separately using a muffle furnace. The temperature of muffle furnace was raised with a speed of 5˚C/min.

2.2. Preparation of the TiO_2 powder

The transparent solution prepared by the same sol–gel method described before was centrifuged for 20 min at 8,000 rpm. The supernatants, water, and ethanol were removed by decantation and the wet powder was collected. This wet powder was dried in air at 60˚C for 48 h. The dried powder was gently ground using a mortar and pestle. This powder was slowly heated (1.5˚C/min.) and annealed at 300˚C for 2 h. Further, it was annealed at the annealing temperature of 300, 500, 700, 900, and 1100˚C for 3 h. The temperature was raised with the increasing temperature rate of 20˚C/min. The powder was slowly cooled to room temperature.

The crystal structure of the powder and film was obtained by the X-ray diffraction method using the (Phillips model PW1830 diffractometer). Similarly, the surface morphology of the film and powder was observed using the SEM images (JOEL JSM-6330F).

3. Results and discussion

3.1. Effect of water content in ethanol on the TiO_2 particle size

The water content present with ethanol varied from 0 to 5%, in a view to observe the particle size of the TiO_2 aggregated onto the substrate surface, which may ultimately change the photocatalytic ability of the coated sheet [6]. Further, the change of particle shape and size was assessed using the SEM images. The SEM images obtained are shown in Fig. 1.

The average particle size of the TiO_2 of 0, 1, 2, 3, 4, and 5% was optimized, respectively, to be 15–23, 16–

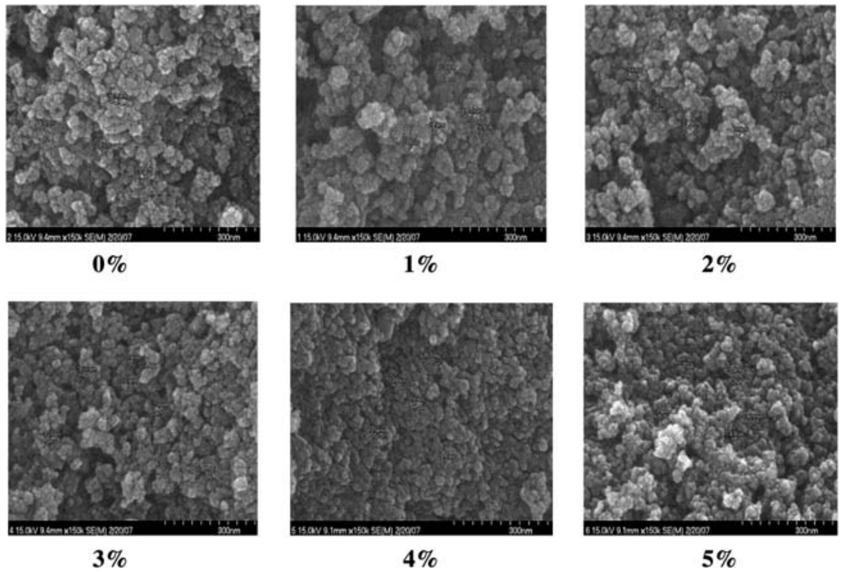

Fig. 1. SEM image of TiO2 powder for water contents (% v/v).

21, 15–24, 16–20, 15–22, and 14–23 nm (cf. Fig. 2). These results clearly indicated that the water content even up to 5% with ethanol was insignificant to affect the particle size of the TiO_2 formed onto substrate, which is in accordance with the previous reports as well [3,5].

3.2. *XRD analysis of the TiO_2 thin film and powder*

XRD data obtained for the thin film and powder of TiO_2 annealed at different temperatures are shown in Figs. 3(a) and (b), respectively. These figures clearly demonstrated that a significant reflection peak of (1 0 1) plane of anatase phase occurred at $2\theta = 25.116$ for all the samples that annealed at different temperatures. Similarly, a characteristic peak of the (1 1 0) plane of rutile phase of TiO_2 occurred at $2\theta = 27.412$. Moreover, it was again observed that the anatase crystal diffraction peak of TiO_2 (1 0 1) became more intensely annealed with increased annealing temperatures [7]. This clearly indicated that the crystallinity of the TiO_2 powder was increased with increasing annealing temperature. However, a new diffraction peak appeared with 700°C annealed sample. This peak referred that TiO_2 powder started a phase transition from anatase to rutile.

Fig. 3(b) shows XRD pattern of TiO_2 thin film at various annealing temperatures. The relative peak intensity of the TiO_2 thin film is weaker than those of the TiO_2 powder. This result showed that the growth

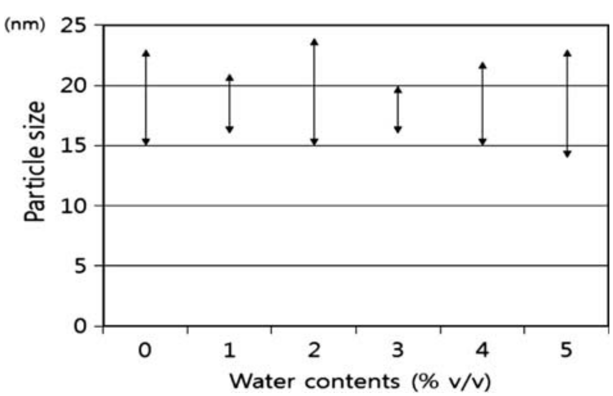

Fig. 2. Average particle size of the TiO_2 powder on 0, 1, 2, 3, 4 and 5% of water content.

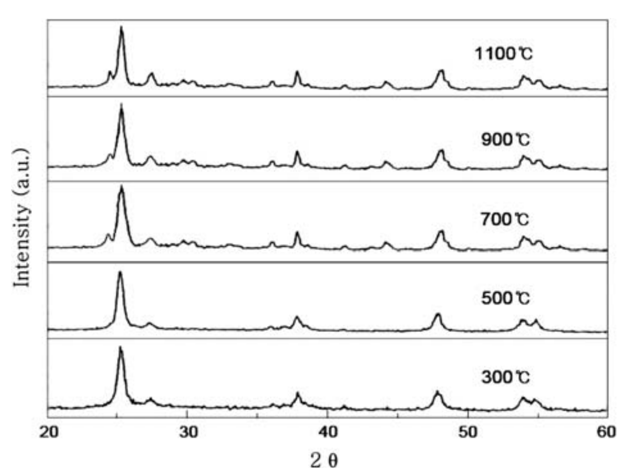

Fig. 3(a). XRD pattern of TiO_2 powder.

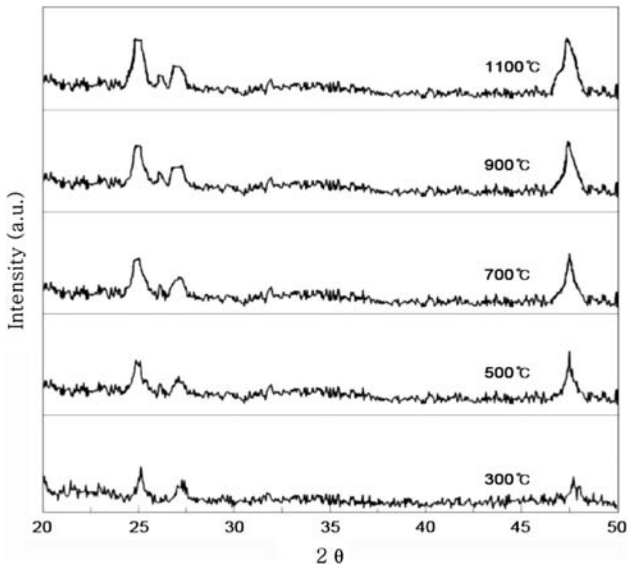

Fig. 3(b). XRD pattern TiO_2 thin film.

of the crystallites of the TiO_2 thin films did not grow well as that of TiO_2 powder. Moreover, the diffraction peak of rutile phase appears in lower annealing temperature than TiO_2 powder.

Moreover, the surface morphology of coated sheet is shown in Fig. 4. This figure clearly indicated that small sized particles of TiO_2 are very orderly arranged onto the surface of substrate.

Fig. 5 showed the reflection characteristics of the TiO_2 powder at varied annealing temperatures. It clearly indicated a red shift tendency with increasing annealing temperature.

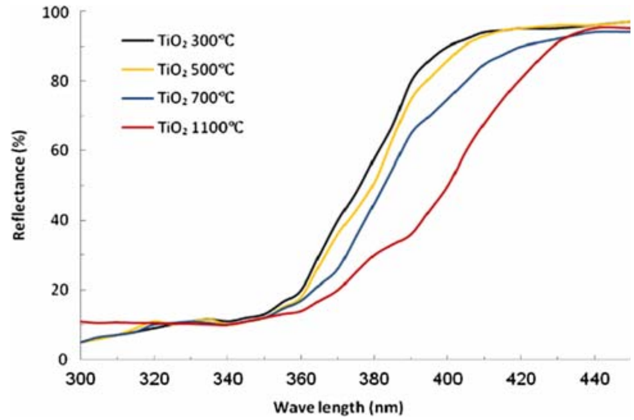

Fig. 5. Reflection characteristics of the TiO_2 powder at varied annealing temperatures.

3.3. Comparison of photocatalytic characteristics

The comparison of the photocatalytic decomposition performance of the TiO_2 powder and TiO_2 thin films was assessed in the reactor fabricated using the Pyrex glass contained with the UV lamp inside. One of the organic pollutant viz. the 100 ppm acetaldehyde was discharged with the flow rate of 300 cc/min and the results obtained are shown in Fig. 6. This clearly indicated that a significant degradation of the pollutant was photocatalytically degraded using either the TiO_2 powder or thin film. These two materials are effective even for prolonged period as assessed for 24 h with the almost same efficiency. Comparing these two materials, the photocatalytic activity of the TiO_2 powder is 32.5% higher than that of the TiO_2 thin film fabricated in this study. This could be ascribed as

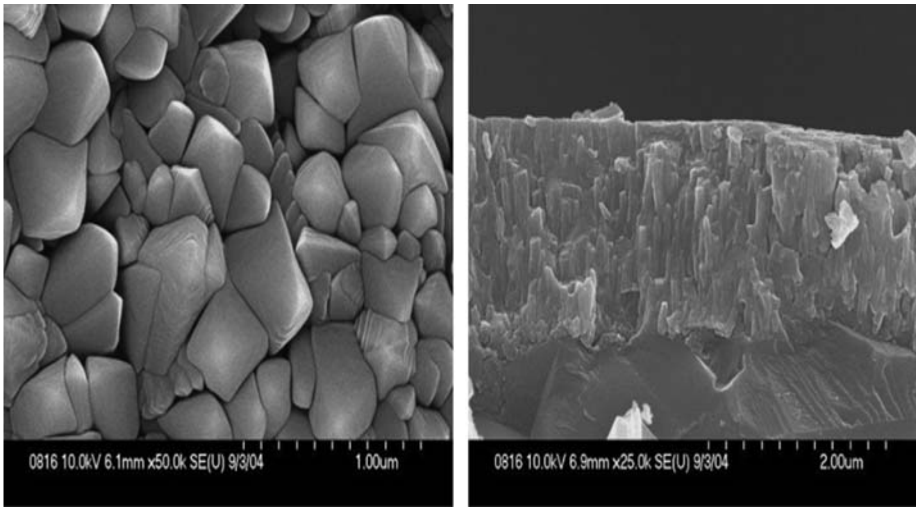

Fig. 4. SEM image of the TiO_2 thin film.

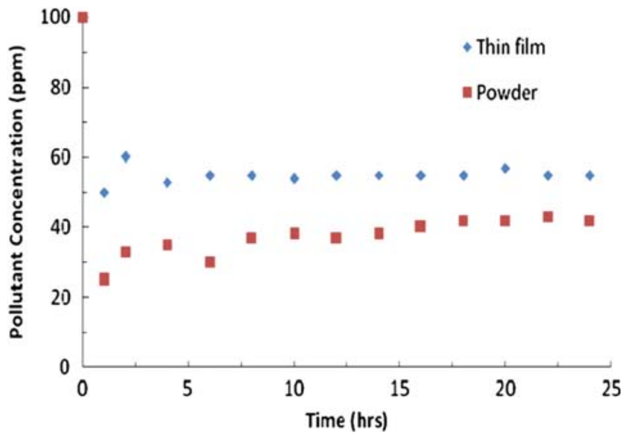

Fig. 6. Photocatalytic decomposition of the pollutant gas using the TiO_2 thin film and powder as a function of time.

more exchange of pollutant could take place using TiO_2 powder, however, the limited space was available with the thin films. Moreover, the surface roughness and heterogeneity of the solid may also enhance the photocatalytic degradation of acetaldehyde. It was also noted that the anatase phase of TiO_2 significantly enhances the photocatalytic behavior [4].

4. Conclusions

Titanium dioxide powder and film deposited onto the borosilicate substrate was obtained by the sol–gel method. Photocatalytic property of the thin film and powder was measured. These results indicated that the photocatalytic properties of the film and powder depend on the surface morphology and roughness as well as on the ratio of two crystalline phases, the anatase (as a main phase) and the rutile (as a secondary phase). Particle size of the synthesized powder was almost unaffected with the presence of water content (maximum 5%) in ethanol. XRD results showed that the crystallinity of the TiO_2 powder increased with increasing annealing temperature but the growth of the crystallites of the TiO_2 thin films has not grown well as that of TiO_2 powder. Moreover, the photocatalytic activity of the TiO_2 powder was higher than that of the TiO_2 thin film.

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