Preparation and Characterization of Cerium Doped Titanium Dioxide Nano Powder for Photocatalyst

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Abstract This study was aimed at synthesizing and characterizing cerium-doped titania. Cerium-doped anatase titania powders were prepared by sol-gel process, with ammonium (IV) nitrate and titanium (IV) butoxide as the raw materials. The characteristics of pure TiO₂ and cerium-doped TiO₂ were investigated by XRD, TG/DTA, FE-SEM, and UV-vis spectroscopy. The results of this study show that anatase type of TiO₂ was obtained in as-prepared and calcined TiO₂ and Ce-TiO₂ powder. A DTA curve was also observed as the crystallization temperature decreased with increasing cerium contents. We found that the crystallite size of the obtained anatase particles decreased from 55 nm to 25 nm and the particle size decreased with increasing cerium contents. Moreover, UV-vis spectra showed that anatase titania powders with various cerium contents effectively extend the light absorption properties to the visible region.

Key words cerium, TBT, sol-gel process, anatase titania, photocatalyst.

1. Introduction

The development of nanocrystalline photocatalytic materials is rapidly a growing field of science and technology. This fact relates to the unique physical and chemical properties of TiO₂. TiO₂ bears tremendous hope in tackling the environmental issues we are currently facing. TiO₂ is regarded as the most efficient material and environmentally benign photocatalyst: it has a wide range of potential applications and specially its materials exhibit photocatalytic activities. One drawback is unmodified TiO₂ photocatalyst that works only with energies to operate in the UV wavelength (380 nm, 3.2 eV) range and below which is the required energy wavelength to excite normal TiO₂.^{1,2)} This range is well below visible wavelength, which limits its indoor use or using effectively solar energy.³⁻⁵⁾ In addition, these materials may also exhibit photocatalytically induced super hydrophilicity that converts the hydrophobic character of the surface to hydrophilic when exposed to UV light. This causes the formation of uniform water films on the surface of these materials, which prevent the adhesion of inorganic or organic compounds and thus retain a clean surface on the photocatalyst.⁶⁾ Hence these photocatalytic materials may

be deployed on surfaces of various substrates such as glass, ceramics or metals to provide layers that exhibit self sterilization and self cleaning properties.^{7,8)}

For effective utilization of solar energy, development efforts towards enlarging the absorption scope of TiO₂ emerge as an appealing challenge.^{9,10)} Therefore, the development of a new generation of photocatalyst is very important. There are many methods for preparation of visible light responsive photocatalyst such as doping of titania with metals and non metals.^{4,10,11)} Recently, doping TiO₂ with rare earth ions has also attracted much attention. Doping the impurity ion is known as one of the most effective ways to manipulate the internal properties of host material such as crystallite size and the crystalline structure.^{12,13)} The sol-gel route^{14,15)} has been developed in our laboratory for elaboration of TiO₂ and properties of sol-gel derived TiO₂ materials have been reported recently.¹⁶⁾ Therefore, Cerium doping TiO₂ introduces a new energy level into the band gap of nano TiO₂ making it possible to utilize light with a wavelength over 380 nm (visible light).

In this study, pure TiO₂ and cerium doped TiO₂ were prepared by sol-gel method. The presence of cerium ions in the titania matrix caused a significant absorption shift

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to the visible region compared to the pure TiO_2 .

2. Experimental procedure

The following commercial reagents were used without further purification. Titanium (IV) butoxide (97 %, Sigma Aldrich) was used as precursor for synthesizing TiO_2 particles. Ethyl alcohol (99.9 %, Ducksan reagents) was used as a solvent, Acetic acid, (99.5 %, Samchun chemical) was used as the catalyst. Ammonium cerium (IV) nitrate (98 %, Sigma Aldrich) was used as the source of cerium for doping TiO_2 . Distilled water was used in all of these experiments. We reported previously using the sol-gel process¹⁶⁾, pure TiO_2 and Ce- TiO_2 synthesized with various Ce contents.

A series of TiO_2 and Ce- TiO_2 samples were prepared according to the following procedures: 1 mole of TBT (97 %, Aldrich) diluted with 25 ml $\text{C}_2\text{H}_5\text{OH}$ was added in drop, vigorously stirring into 80 ml distilled water. The solution was stirred for 45 minutes at 70 °C, and then 3 ml CH_3COOH was added in drops. The resulting solution was continuously stirred for 1 hour at 70 °C. A clear sol was obtained and aged for 12 hours at room temperature to obtain gel. The gel was dried at 70 °C for 5 hours and then calcined at 550 °C for 2 hours to obtain anatase TiO_2 . Cerium doped titania was prepared similarly to pure titania: solution containing 1 mole of TBT, 25 ml $\text{C}_2\text{H}_5\text{OH}$, and 80 ml H_2O was prepared and solution containing 3 ml CH_3COOH , 10 ml $\text{C}_2\text{H}_5\text{OH}$, 10 ml H_2O and Ammonium cerium (IV) nitrate, was added in drops, vigorously stirring. The subsequent characterization procedure was as mentioned below.

Crystalline phases of the as-prepared samples were revealed by powder X-ray diffraction (D/Max-2200, Rigaku, Japan). The microstructure of the powders were observed with FE-SEM (JSM-6701F, Japan). The thermal behavior of the dried gel was investigated using TG-DTA (STA 409, Netzsch, Germany), and carried out at up to 800 °C in air at a constant heating rate of 5 °C/min using Al_2O_3 as the reference material. UV-vis spectrometer (V-550, JASCO, Japan) showed the wavelength of the powders.

3. Results and Discussion

The XRD patterns of TiO_2 and Ce- TiO_2 are shown in Fig. 1. In all samples, to be pure anatase phase, the most intense diffraction at $2\theta = 25^\circ$ is assigned to anatase (d_{101}). The powders showed the crystalline pattern and the observed d-lines matched the reported values for anatase phase. A single-phase anatase type of structure was detected for the cerium doped samples, and no trace of cerium diffraction peaks. Upon calcinations, the intensity of diffraction peaks is broader and weaker compared to

Fig. 1. X-ray diffraction patterns of (a) 0.44wt%Ce- TiO_2 , (b) 0.09wt% Ce- TiO_2 , and (c) TiO_2 powder calcined at 550 °C.

Fig. 2. Crystallite size of TiO_2 powder with cerium contents calcined at 550 °C.

pure TiO_2 .¹⁷⁾ The high stability of anatase phase can be attributed to the formation and interaction of Ti-O-Ce bonds by inhibiting the transition of anatase phase, additionally inhibiting the growth of crystal grains. Moreover, rare earth ions have been used by other groups as stabilizing agents of materials especially mesoporous TiO_2 .¹⁸⁾

The size of the crystallites of the cerium doped TiO_2 powders were determined from the broadening of corresponding X-ray diffraction peaks by using Debye-scherrer's formula on the anatase (101) diffraction peaks,

$$D = (\kappa\lambda)/\beta\cos\theta,$$

Where D is the average crystallite size, λ is the wavelength of the x-ray radiation, κ is the scherrer's constant ($\kappa = 0.9$). β is x-ray diffraction peak and θ is the full-width at half maximum (FWHM).^{2,10)}

The crystallite size of Ce-TiO₂ are shown in Fig. 2. It was found that the crystallite size of the obtained anatase particles decreased from 55 nm to 25 nm and the particle size decreased with increasing cerium contents.

DTA curves in Fig. 3 show a small endothermic peak below 100 °C, which is attributed to desorption of water. Some other small peaks appear at 120 °C and 225 °C, which are ascribed to the combustion decomposition of organic matters. A sharp endothermic reaction peak appeared between 250 °C and 359 °C, indicating a phase change of the powder from amorphous to anatase phase. It was noted that as the cerium content was increased, the crystallization temperature decreased. Fig. 4 shows a three-step weight loss pattern for Ce-TiO₂ powders. All powders show first weight loss at temperatures below 100 °C, indicating that water started to evaporate from the powders. The next loss at temperatures between 120 °C and 350 °C can be attributed to the removal of chemisorbed water and the release of organic residues. The last weight loss from 380 °C to 600 °C is due to the removal of -OH groups. The wide range of temperature is associated with terminal Ti-OH and bridge Ti-OH-Ti. This is because dissociation temperature of these surface

Fig. 3. DTA curves of (a) TiO₂, (b) 0.09wt% Ce-TiO₂, and (c) 0.44wt% Ce-TiO₂ powders synthesized by sol-gel process.

Fig. 4. TGA curves of (a) TiO₂, (b) 0.09wt% Ce-TiO₂, and (c) 0.44wt% Ce-TiO₂ powders synthesized by sol-gel process.

-OH groups differs from each other depending upon the chemical surroundings. The last weight loss and a sharp exothermic peak are observed at about 300 °C in all sample and correspond to the crystallization of TiO₂ phase. Total weight loss is approximately 20 %.

The FE-SEM images of TiO₂ and Ce-TiO₂ powder shown in Fig. 5 (and Fig. 6), illustrate that the addition of cerium led to a change in the morphology and spherical clusters of agglomerate structures were observed. The particle size decreases with increasing cerium contents. Yan et al¹⁹, doping CeO into TiO₂ not only suppressed the crystal growth of TiO₂ but also prevented phase transition of anatase to rutile. Also, this can be attributed to the presence of Ce-O-Ti bonds.¹¹ The morphology of TiO₂ and Ce-TiO₂ powders were consistent with the calculated crystallite size of XRD result.

The UV-vis spectra of pure TiO₂ and Ce-TiO₂ powder shown in Fig. 7. There is a strong absorption at 200 nm up to 380 nm for pure TiO₂ powder which can be attributed to the band gap excitation of anatase (3.2 eV).² However, Ce-TiO₂ powder show absorption shifts towards longer wavelengths, thus extending absorption into the visible range.^{10,17} Yan et al¹⁹ suggested that photon penetration into TiO₂ particles is a more likely explanation for the observed dependence of the optical absorption property

Fig. 5. FE-SEM micrographs of (a) TiO₂, (b) 0.09wt% Ce-TiO₂, and (c) 0.44wt% Ce-TiO₂ powder calcined at 550 °C.

Fig. 6. Agglomeration of Ce-TiO₂ particles calcined at 550 °C.

Fig. 7. UV/Vis spectra of (a) TiO₂, (b) 0.09wt%Ce-TiO₂, and (c) 0.44 wt%Ce-TiO₂ powder calcined at 550 °C.

on the dopant content.

4. Conclusion

The preparation of TiO₂ and Ce-TiO₂ powder by sol-gel process was systematically investigated. This study have shown that anatase type of TiO₂ was obtained in as prepared TiO₂ and Ce-TiO₂ powder. The addition of cerium into TiO₂ leads to the reduction of crystallite size, which may be ascribed to the segregation of the dopant cations at the grain boundary, and preventing the growth of crystals and also this is explained by possible monolayer coverage of ceria over TiO₂. The crystallization temperature decreased with increasing cerium contents. The crystallite size of TiO₂ particles decreased from 55 nm to 25 nm and the particle size decreased with increasing cerium contents. Furthermore cerium doped TiO₂ exhibit obviously enhanced absorbance in the visible light region compared to undoped TiO₂.

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