Preparation and Characterization of Nano-TiO_2 Thin Films by Sol-gel Dip-coating Method

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ABSTRACT

Anatase nanocrystalline titania (nano-TiO_2) thin films were deposited on glass slide substrates by a sol-gel dip-coating method. The sol-gel of nano TiO_2 was prepared in a home-made nitrogen dry box and titanium tetraisopropoxide $Ti[OCH(CH_3)_2]_4$ was used as a precursor. The effects of calcination temperatures on the thin films were discussed. The films were characterized by X-ray diffraction, UV-Vis spectrometry and Scanning Electron microscopy. The calcined samples show crystallinity with (101) preferred orientation which the higher crystallinity shows the better transmittance. The optical measurement shows the indirect bandgap of 3.3 eV to 3.5 eV corresponding with crystallite sizes from 8.1 nm to 2.7 nm and the transmittance of 80%.

Key words: Titania (TiO_2), Thin Films, Nanocrystalline, Sol-gel dip-coating Method

INTRODUCTION

Nanocrystalline titanium dioxide or titania (nano-TiO_2) has gained considerable attention due to its important roles in many applications such as photocatalysis (Fujishima et al., 2000), photo-induced water splitting for hydrogen production (Nowotny et al., 2005), dye-sensitized solar cells (Gratzel, 2003) and environmental purification (Zhao and Zang, 2003). Titania occurs in three crystalline forms: rutile, anatase, and brookite. Excellent review on TiO_2 was given by Diebold (2003). Among these forms, anatase-type TiO_2 exhibits superior photocatalytic properties and when compared to any other form of titania. It has been shown that the properties of titania depend on size, morphology and crystalline forms and these characters also rely on processing conditions. Recently, many researches have emphasized on the preparation and characterization of TiO_2 anoparticles, nanostructured thin films, and nanocrystalline powders (Ni et al., 2007) as well as TiO_2 nanotubes (Mor et al., 2007). One of beneficial characters of nanosized TiO_2 as a photocatalyst is its high surface-to-volume ratio providing more reactive sites at surface for photocatalytic reaction.

Good photocatalytic activities of the TiO_2 films should have abilities to generate photo-induced electron-hole pairs efficiently and to prevent electron-hole recombination, which requires in turn preparations of well-crystalline TiO_2 films, preferably in the anatase crystalline form. Many papers have published on synthesis of nano-TiO_2 films to prepare nano-TiO_2 films. The methods include sputtering (Wong et al., 2006), chemical vapor deposition (CVD) and metallorganic CVD (Lee et al., 1994), etc. These methods require a large amount of energy and expensive tools. However, some methods, namely chemical routes such as sol-gel dip-coating (Sreemany et al., 2007), sol-gel spin-coating (Mishra et al., 2003) consume less energy and do not require expensive equipment. Among these sol-gel method using titanium tetraisopropoxide $Ti[OCH(CH_3)_2]_4$ as a starting material is of great interest because its commercial viability and low cost. Many research groups have demonstrated that nano-TiO_2 films prepared from sol-gel method can make good photoanodes of dye-sensitized solar cells (Jiu et al., 2007) and photoelectrocatalytic hydrogen production devices (Mishra et al., 2003). Inagaki et al., (2001) have prepared stable anatase- TiO_2 by sol-gel method using $TiOSO_4$ as a starting material and followed by calcination at 700°C to 1100°C and found that anatase-TiO_2 fine powder was stable up to 800°C. Ge et al. (2006) have synthesized nano-TiO_2 thin films on glass slide substrates by sol-gel dip-coating method using titanyl sulfate ($TiOSO_4 \bullet nH_2O$, 23.2% TiO_2) followed by drying in air oven from 100°C to 300°C, relatively low temperature. In this work, we demonstrate the fabrication of anatase nano-TiO_2 thin films by sol-gel dip-coating method using titanium tetraisopropoxide as a starting material and discuss the effects of calcination temperatures on the structure and properties of the nanocrystalline TiO_2 thin films.

MATERIALS AND METHODS

All chemicals obtained from Fluka (Swtzerland) were analytical research grades and were used without further purification. Nano-TiO_2 thin flims were deposited through sol-gel dip-coating route. The synthesis procedure for the sol-gel was prepared in the following way: Titanium tetraisopropoxide solution was added slowly to 0.1 M nitric acid solution drop-wise under vigorous stirring condition in a nitrogen dry box (atmosphere). During the addition, a white precipitate was formed. The solution was then heated at 70°C for 10 h for peptization. In this way, white nanoparticles of TiO_2 colloids were obtained as indicated by the appearance of turbidity. Finally, Carbowax M-20000, aqueous polyethylene glycol with molecular weight of 20,000 solution, with 40% by weight of TiO_2 was added to get the viscous dispersion of TiO_2 colloidal solution.

Microscopic glass slides were used as substrates. Prior to coating, the substrates were cleaned thoroughly. First, the substrates were cleaned in water with liquid detergent. Then, they were ultrasonically cleaned in acetone and ethanol for 10 min, respectively. Finally, they were thoroughly rinsed with deionized water. TiO_2 thin films were deposited on the substrates by a dip-coating method at room temperature with the withdrawing speed of a dip-coater about 6 cm/min. To coat single side on the substrate, we immediately wiped off an undesired side using isopropyl alcohol. The films were dried in air and then were calcined in air at 100-500°C for 2 h. The dip-coating technique is relatively cheap and easy. Another aspect of this technique is that one can deposit thin films layer by layer.

Several techniques were employed to characterize of the resultant films. X-ray diffraction technique (XRD) with X'Pert-MPD System with CuKα radiation source (λ = 1.45 Å) was used to identify the crystal phase and estimate the crystallite size. UV-vis spectroscopy was used to study optical property. Field emission Scanning Electron Microscope (SEM) was used to probe the particle size and morphology of the films.

RESULTS AND DISCUSSION

The crystalline phase of synthesized nano-TiO_2 films was analyzed by XRD and their XRD patterns are shown in Figure 1. The polycrystalline anatase phase was confirmed by (101), (004), (200), (211), and (204) diffraction peaks. These peaks are marked by the letter A in Figure 1. The patterns reveal that the effects of calcination temperatures on the phase change of nano-TiO_2. It is observed that the samples calcined lower 200°C show the amorphous structure and exhibit pure anatase when calcined between 350°C and 450°C. However, the XRD patterns of the samples were calcined at 500°C and higher temperatures show partial formation of rutile phase. The XRD diffraction data also show that the increase of the calcination temperatures, the peak intensities of anatase increase and the width of (101) plane of nano-TiO_2 films become narrow resulting in the increase of the crystallinity. The average crystallite size of the particles was calculated from XRD (101) peaks of anatase TiO_2 by applying Scherrer's formula (Cullity and Stock, 2001),

$$D = \frac{0.9\lambda}{\beta \cos\theta} , \qquad (1)$$

where is the average crystallite size, is the X-ray wavelength, is the broadening of the diffraction line measured as the full width at half maximum intensity (FWHM), and is the corresponding diffraction angle. The crystallite size of anatase TiO_2 is found to be from 2.7 nm to 8.1 nm in diameter when calcination temperature is from 200°C to 500°C, respectively.

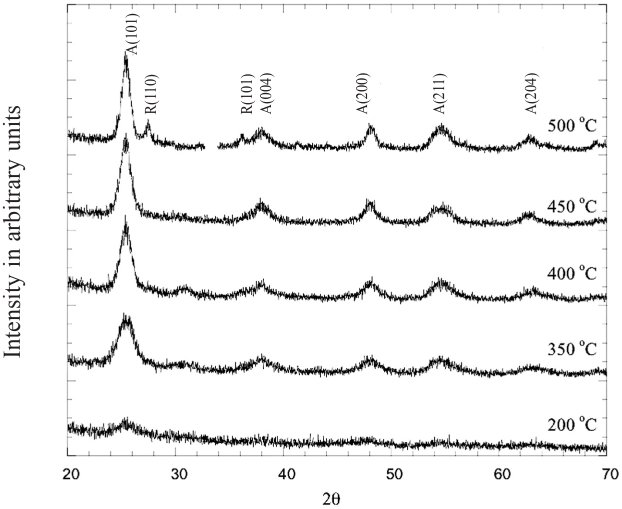

Figure 1. XRD patterns of the nano-TiO_2 films at different calcination temperatures.

The effect of calcination temperatures on crystallite sizes are shown in Figure 2. The crystallite size of anatase TiO_2 is increase slightly when calcination temperature is elevated between 200°C and 300°C, but increase rapidly when calcination temperature is elevated from 450°C to 500°C. The crystallite growth may be the contribution of thermal promotion.

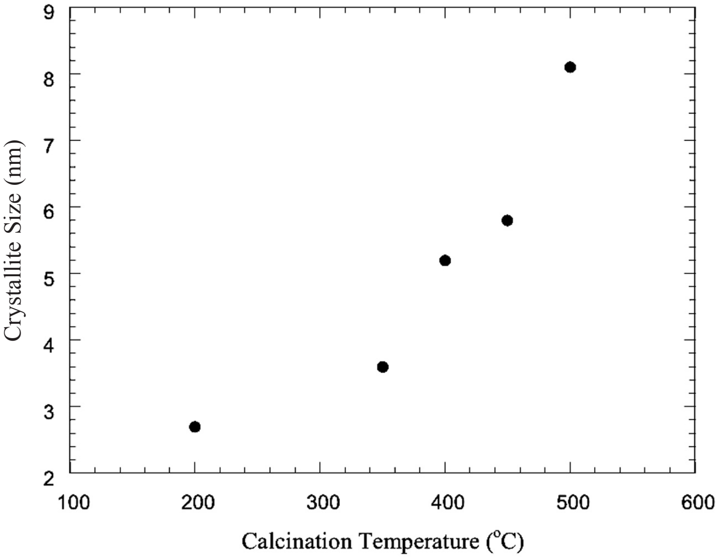

Figure 2. The crystallite size of anatase TiO_2 as a function of calcination temperatures.

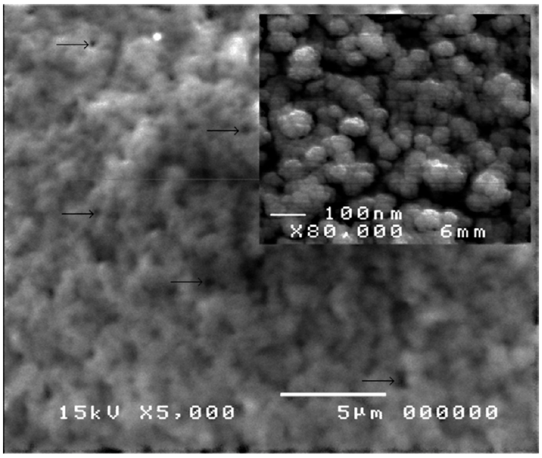

Figure 3. SEM image of nano- TiO_2 film calcined at 500°C. The inset shows a high resolution SEM image of the film. The arrows point the porous structure of the film.

The SEM image of nano- TiO_2 film calcined at 500°C is shown in Figure 3. The inset in Figure 3 shows that the particle morphology is spherical. The crystallite sizes of TiO_2 obtained from SEM image are between 10 nm and 100 nm bigger than those of estimation from XRD data. The spheres consist of many small spherical crystals of TiO_2 crystals due to agglomeration. The SEM image also reveals a porous structure of the film. The pore size ranges form 20 nm to 100 nm in diameter. The porosity may occur when aqueous polyethylene glycol which is used as a binder leaves the surface of the substrate at high calcination temperature.

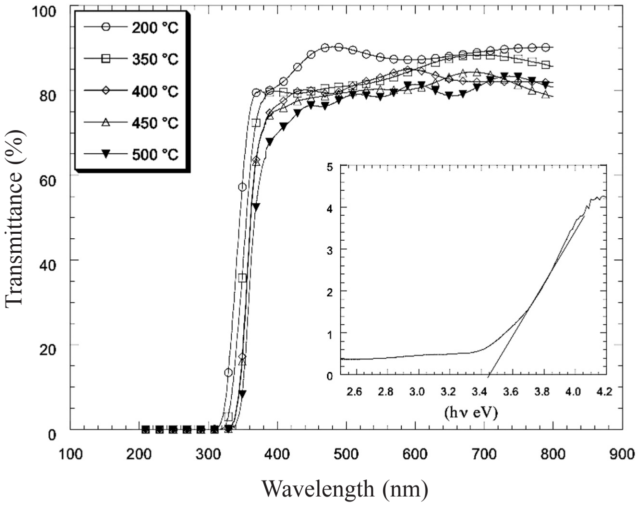

Figure 4. Transmittance spectra of the nano- TiO_2 thin films calcined at different temperatures. The inset shows the plot of variation of $(\alpha h\upsilon)^{1/2}$ vs. $h\upsilon$ of the TiO_2 film calcined at 450°C.

The UV-vis spectra of the TiO_2 films are shown in Figure 4. The transmissions of about 80 % were obtained in the visible region of solar spectrum. It is evident from Figure 4 that transmission coefficients of the films calcined at low temperatures which have bigger crystallite sizes are slightly larger than those of the films calcined at high temperatures having smaller crystallite sizes. To obtain bandgap (E_g) of nano- TiO_2 thin films, we process the UV-vis spectra from the expression (Tauc,1974) corresponding to indirect gap semiconductors

$$(\alpha h\upsilon)^{1/2} = \mathrm{A}(h\upsilon - E_g) \ , \tag{2}$$

where α is the absorption coefficient (cm^{-1}), A is a constant which is independent of photon energy, and $h\upsilon$ (*eV*) is the energy of excitation. The calculation of the bandgap can be performed by plotting $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$ and extrapolating of the absorption edge to zero as shown in the inset of Figure 4. The values of the bandgap are from 3.3 eV to 3.5 eV corresponding with crystallite sizes from 8.1 nm to 2.7 nm, respectively. The smaller crystallite sizes have higher bandgap may be caused by the quantum size effects. Our samples have higher bandgap than others (Sagkapal et al., 2005; Ge et al., 2006) because we have smaller crystallite sizes of nano-TiO_2 thin films.

CONCLUSION

We have synthesized anatase nano-TiO_2 thin films by sol-gel dip-coating method. Titanium tetraisopropoxide was used as a starting material. The sol-gel processing was prepared in nitrogen atmosphere. Carbowax M-20000, aqueous polyethylene glycol with molecular weight of 20,000 solution, was added to the sol-gel and served as a binder between the nano-TiO_2 particles and the glass substrates. XRD data analysis shows that the crystallite sizes of nano-TiO_2 are between 2.7 nm and 8.1 nm in diameter. SEM images reveal that the particles making of the films form a cluster of nanocrystalline TiO_2 due to agglomeration. The films also have a porous structure. The porosity may result from the evaporation of the aqueous polyethylene glycol when calcined at high temperatures. The optical measurement yields energy bandgab. The bandgap vary from 3.3 eV to 3.5 eV when crystallite size changes from 8.1 nm to 2.7 nm, respectively. The smaller crystallite size of nanocrystalline TiO_2 gives larger the bandgap due to the quantum size effects. The nano-TiO_2 thin films may serve as photoanodes for photoelectrochemical devices and dye-sensitized solar cells.

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