Raman Spectroscopy and XRD investigation on TiO₂ sol-gel dip coating thin films synthesizes with and without solvents

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Abstract. TiO₂ coating films were prepared by sol-gel dip coating method using TTiP precursors with and without ethanol as a medium to hydrolyze the HCl catalyst. The prepared samples of titanium dioxide (TiO₂) coating were dried at 110°C for 30 minutes then heated at 500°C and 600°C for 1h and 3h respectively to study effect of annealing temperature and soaking time. The crystallinity of the TiO₂ coating were identified by using X-ray Diffraction technique and crystallite size was calculated. Raman Spectroscopy also used as the confirmation of phases formation of TiO₂ coating films. Crystallite size of TiO₂ films were obtained at 12.35 nm, 17.29 nm for anatase, 21.71 nm, 28.95 nm for rutile and ~2.19 nm for brookite. Thus, the establishment of the desired phases, crystallinity and grain size of TiO₂ thin films sol-gel can be controlled and encouraging to explore as an effort toward producing a sustainable photocatalytic..

1 Introduction

TiO₂ is an appropriate material for industrial use at present and also perhaps in the future. Besides, TiO₂ materials are play an important role in helping solve many serious environmental and pollution challenges because of has the most efficient photocatalytic activity [1,2] the highest stability [3] and the lowest cost. There are commonly known have three polymorphs of TiO₂ found in nature such as rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). TiO₂ can be prepared in the form of powder, crystals, or thin films. Liquid-phase processing or sol-gel technique is one of the many examples and the most conventional and utilized methods in synthesizing TiO₂ because it offers many advantages such as low temperature processing, easy coating of large surface, provides high surface homogeneity and most importantly has a low cost [4]

In the sol gel, there are four parameters are considered can give their effect on the structural and morphology of TiO₂ such as TiO₂ precursor, solvent, acid and water as a medium to hydrolyze of metal alkoxide as a TiO₂ precursor. In this study, solvent content in sol gel preparation is focused. Yu et al. [5] was studied about the hydrolysis of TTiP in pure water or the EtOH/H₂O mixed solution on the photocatalytic activity of nano-sized TiO₂ powders. The nature of solvent was reported can affect the rate of hydrolysis and condensation. Higher reaction rates of hydrolysis and condensation will lead to the formation of larger particles with rough surface films whereas lower reaction rate tend to form columnar particles with a smooth surface [6]. In the work of Edusi et. al [7], they

used aerosol-assisted CVD technique to deposit TiO₂ phases and found that solvents like ethanol or propanol will lead to anatase phases while rutile phase favored when methanol was used. They concluded that, the use of different solvents can have a direct effect in controlling the TiO₂ phases when deposited as a film [7].

In the other hand, mixed anatase/rutile/brookite give an attractive in photocatalytic compare to pure anatase phase. For instance, thermal treatment at ~500 - 600°C of powder precipitated with a significant excess of water will formed the mixed anatase/brookite/rutile TiO₂ powders, with potentially attractive photocatalytic has been the subject of study Dorian et. al [8]. Therefore, the phase transformation was important to gain the best photocatalytic activity with the correlation ratio of EtOH/TTiP solution. Besides, annealing temperature also play an important role toward film structure, change in some properties and chemical composition. Ahmad et al. [9] stated that annealing temperature will affected the grain size. As the annealing temperature increase the grain size also improve the electron migration [9].

However, to our knowledge, the effect of solvent content can pose serious threat to the environment. Therefore, the element of solvent and annealing temperature becomes the studied subject in promoting TiO₂ phases and crystal size in supporting green process.

2 Methodology

2.1 Preparation of TiO₂ Sol

Titanium tetra isopropoxide (C₁₂H₂₈O₄Ti), Hydrochloric acid (HCl), Deionised water (H₂O) and Ethanol

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(C₂H₅OH) were used to prepare the coating solution. All chemicals were of analytical grade and were used without further purification. Firstly, the deionised water was added with the half volume of solvent (ethanol) and stirred about 30 minutes as a first solution. Then, the HCl was added dropwise into the first solution and continue stir about 30 minutes again. Meanwhile, the second solution was prepared the precursor (TTIP) was added into another half volume of solvent (ethanol) and stirred about 30 minutes. After that, the second solution was added into the first solution as a TiO₂ sol. Stirring process was performed for about three hours. Different combinations of TiO₂ sol were prepared by altering the volume of ethanol in the TiO₂ solution for preparing TiO₂ thin films, chemical composition in volume TTIP: C₂H₅OH: H₂O: HCl shown in Table 1.

Table 1. Chemical composition used for prepared TiO₂ thin films

TTIP (ml)	EtOH (ml)	H ₂ O (ml)	HCl (ml)
2.0	0.0	32.0	0.4
2.0	16.0	32.0	0.4

2.2 Preparation of thin films coating

The TiO₂ thin films were immobilized on glass substrates. The cleaned glass substrate was dipped into the TiO₂ solution with the withdrawing rate was constant at 0.5mm/s and immersing time in 5s. After each coating TiO₂ films were dried at 110°C for 30 min. The dip-coating and drying process were repeated for ten times. The prepare film were heated at 500°C and 600°C for 1 h and 3 h at 5°C/ min respectively. The process flow of TiO₂ thin films preparation given in Figure 1.

2.3 Characterization of TiO₂ thin films

Phases of TiO₂ thin film were analyzed using X-ray diffraction technique of an X'Pert Pro model with Cu K-Alpha of 1.54060 Å and generator settings at 30 mA and 40 kV in the range of 10-90°. The grain size of TiO₂ films was calculated from XRD line broadening using Debye-Scherrer's formula given by equation:

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

Where D is the crystal size; λ is the wavelength of the X-ray radiation ($\lambda=0.15406$ nm) for CuK α ; and β is the line width at half-maximum height. Affirmation of the TiO₂ phases were confirm with UniRAM-3500 Raman spectroscopy with laser excitation wavelength, $\lambda= 532$ nm (Nd:YAG).

Fig. 1. Process flow for Preparing TiO₂ thin film.

3 Results and discussion

3.1 XRD analysis

Figure 2 show the XRD results of TiO₂ thin films from different ethanol content in TiO₂ solution after through heat treatment 500°C and 600°C for 1h and 3h at the final stage. All the films show anatase peak at $\theta=25^\circ$ as main peak has (1 0 1) orientation except in Figure 2(b) at 600°C. However, the films of TiO₂ solution with ethanol (16 ml) produced mixed phase of anatase and brookite peak at $\theta=25^\circ$ has (1 0 1, 2 1 0) orientation. At 600°C pure brookite will be observed at (2 1 0) for the 1h and 3h soaking temperature shown figure 2(b). Besides, rutile phase was growth as the brookite transformation at 600°C without the presence of ethanol. This is probably due to the fact that ethanol solvent suppresses the hydrolysis of Titanium alkoxide and rapid crystallization of the TiO₂ particles by adsorbing on the surfaces of TiO₂ thin film [10]. In the other hand, Dorian et al.[8] state that presence of brookite likely to have enhanced the formation of rutile through a higher density of phase interfaces and consequently higher interfacial energy and also act as a nucleation site for rutile formation in anatase.

Fig. 2. XRD pattern of the deposited TiO₂ thin films versus ethanol concentrations (a) 0 ml and (b) 16 ml. A=anatase, R=rutile and B=brookite.

3.2 Crystallite Size

Figure 3 and Table 2 shown the crystallite size of the of the deposited TiO₂ thin films produced against ethanol content calculated using Debye-Scherrer's equation. At, 16 ml of ethanol brookite phase will be dominant at peak $\theta = 25^\circ$ and 31° while anatase peak will be dominant without the presence of an ethanol at peak $\theta = 25^\circ$. Rutile peak at $\theta = 27^\circ$ will appeared as the annealing temperature and soaking temperature increased. In the other hand, the pattern of the phase formation was also depend on the presence of the ethanol as a solvent. As the annealing temperature increased, the crystallite size of the deposited TiO₂ film also increased. Therefore, the effect of annealing temperatures on crystallites size was significant^[12]. At 500 °C, mixed anatase-brookite and anatase at peak 25° form the crystallite size at 12.35 nm for

both soaking time. Moreover, without presenting the ethanol, crystallite size was growth at 17. 29 nm. The same pattern was observed at peak 27° at 1 hour (21.71 nm) and 3 hour (24.81 nm) respectively. At 600°C, crystallite size of rutile increased at 28.95 nm then decreased to 24.80 nm due to the nucleation of brookite phase at $\theta = 31^\circ$ with 3.66 nm. Besides, at 16 ml of ethanol mixed phase anatase-brookite were presence at peak 25° with 17.29 nm and decreased to 10.81 nm as increased the annealing temperature. Furthermore, soaking time also play an important role to increase the crystallite size and retarded the brookite phase at peak 31° . Then,rutile peak at 27° presence due to anatase to rutile phase transformation with the offset slower transformation kinetics in the absence of brookite ^[8]

Fig.3. Bar chat of crystal size between 500°C and 600°C annealing temperature for 0 ml ethanol and 16 ml ethanol

Table 2. Crystal size of the deposited TiO₂ film (Anatase=JCPDS No: 01-071-1167, Rutile= JCPDS No: 01-072-4813 and Brookite= JCPDS No: 00-029-1360)

Solvent (ml)	Temp. (°C)	Soaking Time (h)	Postion (2 Theta)	d-spacing (Å)	Crystal size (nm)
0	500	1	25.3629	3.51175	12.35
			27.4091	3.25406	21.71
		3	25.2973	3.52071	12.35
			27.4605	3.24809	24.81
	600	1	25.2597	3.52587	17.29
			27.4344	3.25111	28.95
		3	25.2845	3.52247	17.29
			27.2661	3.27081	24.8
16	500	1	25.3097	3.51901	17.29
			32.153	2.78397	2.74
		3	25.3821	3.50915	17.29
			31.0923	2.87648	3.65
	600	1	25.3741	3.51024	10.81
			30.5765	2.92382	2.19
		3	25.3497	3.51356	43.23
			27.5302	3.24002	14.48

3.3 Raman spectrum and analysis

Figure 4 shows the Raman spectrum of the deposited TiO₂ thin films. Overall, there are six characteristics of active bands for the Raman spectrum of anatase which are ($A_{1g} + 2B_{1g} + 3E_g$). Brookite has thirty-six active bands of ($9A_{1g} + 9B_{1g} + 9B_{2g} + 9B_{3g}$) and rutile have four Raman active bands of ($A_{1g} + B_{1g} + B_{2g} + E_g$)^[11]. Thus, for all deposited TiO₂ samples, Raman bands appeared at 144, 396, 514, and 636 cm⁻¹ and 142, 394, 514 and 638 cm⁻¹ are very distinctive and can be assigned to anatase phase shown in figure 4(a) and 4(b). For the 0 ml of

ethanol, the Raman bands appeared at 442 cm⁻¹ can be appointed to rutile phase but then slowly disappeared as the ethanol content was added 16 ml shown in figure 4(a) and (b) respectively. There are also others Raman bands noticeable at 248 and 319 cm⁻¹ for the 0 ml while 16 ml of ethanol Raman bands was noticeable at 240 and 322 cm⁻¹ which can be assigned to the brookite phases. As an increased the annealing temperature and soaking time rutile phase was clearly observed due to the thermal treatment^[9].

Fig. 4. Raman spectrum of the deposited TiO₂ thin films versus ethanol concentrations (a) 0 ml and (b) 16 ml. A=anatase, R=rutile and B=brookite.

4 Conclusions

TiO₂ thin films were successfully deposited on glass slide substrate from the ethanol content of 0 ml and 16 ml via sol gel dip coating technique. Anatase was the main phases appeared throughout all TiO₂ thin films without the presence of ethanol while pure brookite and mixed phase anatase-brookite will appeared in the presence of 16 ml of ethanol. Rutile phases were found to presence with the annealing temperature. The pattern of the crystal size of all phases increased as the annealing temperature increased from 500°C to 600°C. These observations lead to a conclusion that without the used of ethanol as a function of annealing temperature, desired TiO₂ thin film can be controlled and encouraging to explore as an effort toward producing a sustainable photocatalytic activity.

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