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INVESTIGATING THE NANOCRYSTALLINITY OF SOL GEL DERIVED TiO_2 NANOPARTICLES UPON ANNEALING AND POST HYDROTHERMAL TREATMENTS

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ABSTRACT

INVESTIGATING THE NANOCRYSTALLINITY OF SOL GEL DERIVED TiO_2 NANOPARTICLES UPON ANNEALING AND POST HYDROTHERMAL TREATMENTS. The present study is aimed at investigating the major factor causing the low nanocrystallinity nature of the sol gel derived TiO_2 nanoparticles. For this purpose, TiO_2 nanoparticles of different nanocrystallinity was synthesized by various hydrolysis ratio (R_w) of 0.85; 2.00 and 3.50 upon sol solution preparation, followed with subsequent drying, conventional annealing and post-hydrothermal treatments. The resulting nanoparticles were studied by dynamic light scattering, XRD and FT-IR spectroscopy which confirm that the highly amorphous state of TiO_2 is related to the fast development of stiff Ti-OH networks during hydrolysis and condensation upon sol gel process. A post hydrothermal treatment involving high-pressure water vapor has been successfully devised to enhance the nanocrystallinity of TiO_2 nanoparticles. It has been found in this study that R_w value of 2.00 was the optimum hydrolysis ratio during sol solution preparation of TiO_2 precursor to result in the most enhanced nanocrystallinity as represented with the biggest crystallite size of 12.46 nm.

Key words : TiO_2 nanoparticles, Sol gel, Nanocrystallinity, Annealing, Post hydrothermal

ABSTRAK

INVESTIGASI NANOKRISTALINITAS NANOPARTIKEL TiO_2 TERDERIVASI SOL GEL DENGAN PERLAKUAN *ANNEALING* DAN *POST HYDROTHERMAL*. Penelitian ini bertujuan untuk menginvestigasi faktor utama yang menyebabkan rendahnya nanokristalinitas struktur nanopartikel TiO_2 hasil derivasi sol gel. Untuk tujuan tersebut, telah disintesis berbagai nanokristalinitas dari nanopartikel TiO_2 dengan variasi rasio hidrolisis (R_w) 0,85, 2,00 dan 3,50 dengan preparasi larutan sol diikuti dengan pengeringan, *annealing* konvensional dan penanganan *post hydrothermal*. Nanopartikel yang dihasilkan selanjutnya dipelajari dengan *dynamic light scattering*, *XRD* dan spektroskopi *FT-IR* yang mengkonfirmasi bahwa tingkat amorf yang tinggi dari TiO_2 berhubungan dengan perkembangan *network* yang cepat dari *stiff* Ti-OH selama hidrolisis dan kondensasi dalam proses sol gel. Penanganan *post hydrothermal* menggunakan uap air bertekanan tinggi telah berhasil meningkatkan nanokristalinitas nanopartikel TiO_2. Telah diketemukan bahwa nilai R_w 2,00 adalah rasio hidrolisis optimum selama preparasi larutan sol *precursor* TiO_2 untuk menghasilkan nanokristalinitas yang paling tinggi sebagaimana ditunjukkan dengan ukuran kristalit terbesar yakni 12,46 nm.

Kata kunci : Nanopartikel TiO_2, Sol gel, Nanokristalinitas, *Annealing*, *Post hydrothermal*

INTRODUCTION

Sol gel process has been widely practiced to respond to the demand for advanced ceramics of high purity, well controlled homogeneity, and properly tailored properties as well as various nanostructured materials [1]. This is mainly due to its versatility i.e.: (i). a lowered processing temperature, (ii). high purity and (iii). feasibility of employing various post forming processes [2]. Sol gel process is basically a wet chemical route which involves the evolution of a system from a colloidal suspension (the sol) into a solid/semi solid (the gel) phase. Upon the phase evolution, two important reactions namely hydrolysis and condensation are involved. This process was developed initially as a technique to prepare pure ceramic precursors and inorganic glasses at low temperatures. For the synthesis of TiO_2 nanoparticles, however, the sol gel process has a major limitation, which is the low crystallinity in the resulting TiO_2 phase, as a consequence of the relatively

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low processing temperatures. In connection with this case, Brinker and Hurd [3] and Langlet et al. [4] proposed that the low nanocrystallinity of sol gel derived TiO_2 phase could be due to the fast development of a stiff Ti-O-Ti network, which in turn hinders the densification during post-solution treatments.

Structural changes of TiO_2 can be induced by the treatment in a high humidity environment at temperatures above 100 °C [5,6]. Furthermore, reported that exposure of sol gel derived TiO_2 films to water vapor induced rearrangement of Ti-O-Ti network leading to formation of anatase phase at 180 °C [7,8].

Therefore, it is thus of interest in the current work to investigate the factor causing the amorphous nature of sol gel derived TiO_2 nanoparticles. For this purpose, a variation in hydrolysis ratio or amount of water to inorganic precursor (R_w) of 0.85; 2.00 and 3.50 upon sol solution preparation will be performed. The resulting gel is furthermore subjected to drying, conventional annealing and post hydrothermal treatments in order to observe the nanocrystallinity of TiO_2 phase under investigation.

EXPERIMENTAL METHOD

TiO_2 nanoparticles in the current study were synthesized through a well controlled sol gel process using titanium tetra isopropoxide (TTIP) as inorganic precursor. First, TTIP was mixed carefully with ethanol in a container and stirred for 30 minutes. A mixture of deionized water and hydrochloric acid (HCl) was then added under stirring condition into the transparent solution to promote hydrolysis. The TTIP concentration in the solution was controlled at 0.4 M with the ratio of water to TTIP (R_w) was varied as 0.85, 2.00 and 3.50 while the pH value of all solution was kept to be consistent as low as ~1.30 for obtaining a stable highly transparent solution.

The solution was further stirred overnight and poured into a petri-dish to form thick film. The thick film was subjected to drying at room temperature for 1 week and 60 °C for 3 days, followed with conventional annealing in dry atmosphere at 150 °C for 24 hours and subsequent post hydrothermal treatment with highly pressurized water vapor at 150 °C for 24 hours.

For the post hydrothermal treatment, a Teflon lined stainless steel autoclave (Parr, Moline, IL) was used where a specially designed stand was placed inside the autoclave in order to prevent the samples from direct contact with liquid water. In order to confirm the effect of different treatments on the TiO_2 nanostructures, the resulting sol solution and powders were further characterized by particle size analyzer (Delsa TM Nano Submicron dynamic light scattering), X-Ray diffraction (XRD, Bruker AXS θ–2θ diffractometer) and Fourier transform infrared spectroscopy (Bio Rad QS-300 spectrometer).

RESULTS AND DISCUSSION

Figure 1 shows the result of dynamic light scattering of TiO_2 sol solution with different hydrolysis ratio, R_w. It can be seen that with the increase of hydrolysis ratio (R_w), i.e. the amount of water content added to the inorganic precursor (TTIP) upon sol gel process, the particle size has increased significantly. It should be noted, however, that the presented values here are not the real size of the solid nanocrystalline TiO_2. Instead, they still represented the size of Ti-OH and Ti-O-Ti networks as the species resulted from the hydrolysis and condensation reactions of inorganic precursor. It is highly possible that they formed clusters or particle like networks among the random and entangled chains of inorganic molecules.

In order to further analyze, the results of dynamic light scattering will be compared with the crystallite size measurement obtained through XRD on the resulting TiO_2 powders after drying, annealing and post hydrothermal treatments.

Figure 2 shows the XRD traces of the resulting TiO_2 powders derived from the sol gel process with various hydrolysis ratios after drying, conventional annealing and post hydrothermal treatment.

It can be seen that all as dried samples are not crystalline yet as indicated by a very broad hump in the 2θ range of 20°-35° in traces (a), (b) and (c). The

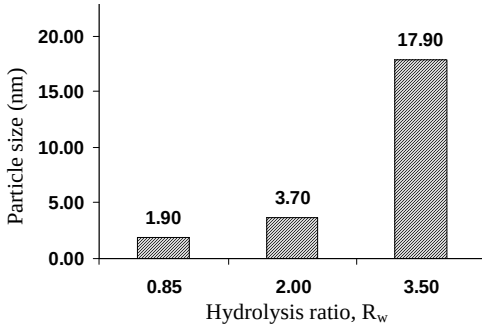

Figure 1. The result of particle size measurement by dynamic light scattering for TiO_2 sol solution with various R_w

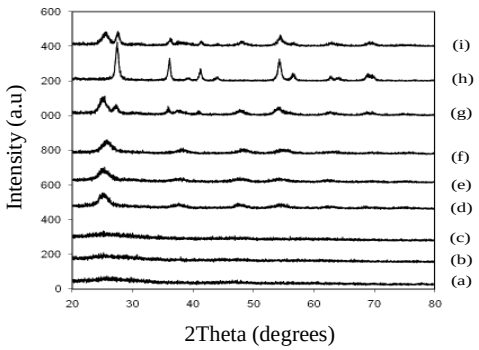

Figure 2. XRD traces of TiO_2 derived from sol-gel with hydrolysis ratio, R_w of 0.85; 2.00 and 3.50 at drying (traces (a), (b) and (c)), conventional annealing (traces (d), (e) and (f)), and post-hydrothermal (traces (g), (h) and (i)) conditions, respectively.

crystallinity enhancement started to occur when the conventional annealing were applied on all the samples. This can be seen from a slightly increase in the intensity for the diffraction peaks at 2θ angles of 25 °-26 °, 38 °, 48 ° and 54 ° in traces (d), (e) and (f). A much more significant enhancement, as demonstrated with further increase in the above mentioned peaks, was apparently shown by the post hydrothermally treated samples (traces (g), (h) and (i)). Among the post hydrothermally treated samples, the most enhanced nanocrystallinity was achieved by TiO_2 derived from the sol gel process with R_w of 2.00 (trace (h)).

In order to obtain a more quantitative data, Scherrer's formula was applied on the above XRD traces and the result of crystallite size estimation is given in Figure 3. It should be noted that throughout the use of Scherrer's formula, all the additional broadening on the XRD peaks due to non uniform strain and instrument effect has been excluded [9]. It can be seen that the increase of hydrolysis ratio from 0.85 to 2.00 has increased the crystallite size of TiO_2 nanoparticles at both annealed and post hydrothermal conditions from 3.10 and 4.84 nm to 4.07 and 12.46 nm, respectively.

However, a further R_w increase to 3.50 has adversely decreased the crystallite size down to 3.81 and 7.21 nm, although these values are still higher than those shown by R_w of 0.85. It is also apparently

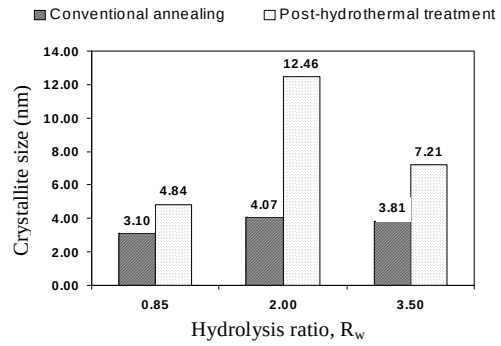

Figure 3. The result of crystallite size estimation by using Scherrer's formula for sol gel derived TiO_2 nanoparticles with R_w of 0.85; 2.00 and 3.50 at conventional annealing and post hydrothermally treatment conditions

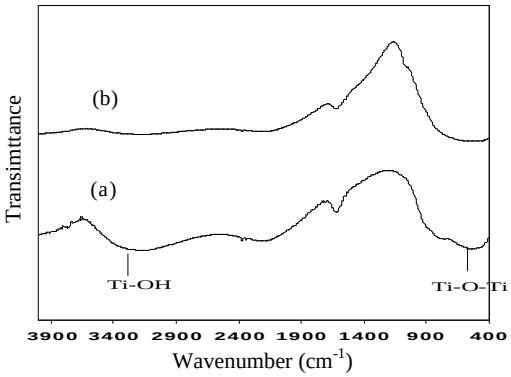

Figure 4. FT-IR spectra of (a). conventionally annealed and (b). post hydrothermally treated TiO_2 nanoparticles derived from the sol gel technique

demonstrated that the post hydrothermally treated sample with R_w of 2.00 provides a much more pronounced nanocrystallinity enhancement as represented with a significant increase in the crystallite size up to 12.46 nm.

In order to further understand the phenomenon behind the observed results, FT-IR spectroscopy was performed on both conventionally annealed and post hydrothermally treated TiO_2 nanoparticles. Figure 4 shows obviously the existence of broad absorption bands located at ~3400-3500 cm^{-1}, which is assigned to hydroxyl groups of Ti-OH [10]. In addition, there exists also an absorption band in the range of ~400-900 cm^{-1}, which is accounted for by stretching vibrations of Ti-O-Ti groups [11].

From the Figure 4, it can be apparently demonstrated that the conventionally annealed sample (spectrum (a)) provides a high intensity Ti-OH absorption band, but with a weak intensity in Ti-O-Ti absorption band. By contrast, a reverse phenomenon is resulted by the post hydrothermally treated sample (spectrum "b') where the intensity of Ti-OH absorption band is decreased significantly, accompanied with an increase in the intensity of Ti-O-Ti absorption band.

By correlating the above XRD and FT-IR analyses, it was known that the crystallinity enhancement of the sol gel derived TiO_2 phase is represented with an increase in the intensity of Ti-O-Ti absorption band and a decrease in intensity of Ti-OH absorption band. The stretching vibration of Ti-O-Ti absorption band is regarded as the characteristic peak for TiO_2 nanocrystalline [11]. Water vapor exposure in the post hydrothermal treatment can successfully enhance the nanocrystallinity of TiO_2 phase as a result of cleavage mechanism of strained Ti-OH networks by high pressure water molecules to provide much more flexible Ti-O-Ti networks which can further densify to form nanocrystalline TiO_2 [7,8].

R_w of 2.00 is the optimum hydrolysis ratio that can lead to a proper number of Ti-OH species which function as flexible nuclei for the formation of TiO_2 nanocrystalline, both at annealed and post hydrothermal conditions, while the R_w value of 3.50 caused an excessive formation of stiff Ti-OH networks which could not densify further to form TiO_2 nanocrystalline, although the cleavage mechanism has been applied on this sample through post hydrothermal treatment [3,4]. This mechanism is highly possible causing the decrease in the crystallite size of TiO_2 from 12.46 nm to 7.21 nm when the hydrolysis ratio was increased from R_w 2.00 to 3.50 upon sol solution preparation.

CONCLUSION

A systematic investigation has been conducted into TiO_2 nanoparticles derived from sol gel process, aimed at understanding the mechanisms responsible for the occurrence of the largely amorphous state in TiO_2 nanoparticles. The results confirm that the low

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nanocrystallinity of TiO_2 is shown to relate to the fast development of stiff Ti-OH networks during hydrolysis and condensation upon sol gel. A post hydrothermal treatment involving high pressure water vapor has been successfully devised to enhance the nanocrystallinity of TiO_2 nanoparticles. The nanocrystallinity enhancement is related to the cleavage of stiff Ti-O-Ti bonds by water molecules, which effectively increases the number of flexible Ti-OH groups and rearranges Ti-O-Ti bonds promoting crystallization of TiO_2. In this study, the R_w value of 2.00 has been found to be the optimum hydrolysis ratio for the sol solution preparation of TiO_2 precursor to provide the most enhanced nanocrystallinity of 12.46 nm.

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