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Synthesis of TiO_2 Nanoparticles by Sol-Gel and Sonochemical Combination

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***Abstract*—**Nanocrystalline TiO_2 particles were successfully synthesized via sol-gel and sonochemical combination using titanium tetraisopropoxide as a precursor at lower temperature for a short time. The effect of the reaction parameters (hydrolysis media, acid media, and reaction temperatures) on the synthesis of TiO_2 particles were investigated in the present study. Characterizations of synthesized samples were prepared by X-ray diffraction (XRD) analysis. It was shown that the reaction parameters played a significant role in the synthesis of TiO_2 particles.

***Keywords*—**Crystalline TiO_2, sonochemical mechanism, sol-gel reaction.

I. Introduction

OVER the past two decades, oxide semiconductor mediated photocatalysts have attracted a great deal of attention in the purification of environmental contaminants [1]. Among the various oxide semiconductor photocatalysts, TiO_2 has proven to be the most suitable material for its long-term chemical stability, powerful oxidation strength, non-toxicity and low cost [2]. Thus, an alternative particle preparation method for crystalline TiO_2 was sought in which the heat treatment step was not required. As a competitive alternative, the sonochemical method has been extensively used to generate novel materials with improved or unusual properties. The physicochemical effects of ultrasound arise from acoustic cavitation, i.e. the formation, growth, and implosive collapse of bubbles in a liquid [3], [4]. The collapse of bubbles generates localized hot spots with transient temperatures of 5000 K and cooling rates in excess of 1010 K/s. These extreme conditions during sonication lead to enhanced medium mixing and in addition the particle size of the solid present in the reaction medium decreases and the reactive surface area increases [5]. However, reports on the coating of crystalline material directly onto magnetic core particles via sonochemistry method are very scarce so far.

In this study, a sol-gel and sonochemical combination to directly prepare anatase nanocrystalline TiO_2 has been established. TiO_2 nanoparticles were synthesized by the hydrolysis of titanium isopropoxide in the presence of water and iso-propyl alcohol under ultrasonic irradiation (35 KHz) at 70 ºC for 4 h. The product structure was dependent upon the molar ratio of $[H_2O]$/[Alkoxide] (Rw), molar ratio of [Acid]/[Alkoxide] and reaction temperature. The synthesized samples were characterized by XRD XRD analysis.

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II. Experimental

A. Materials and Characterization

All chemicals used in the synthesis of TiO_2 particles were higher grade. An ultrasonic bath (Bandelin Sonorex Super RK 255H, frequency of irradiation of 35 kHz) was used as the source of ultrasonic irradiation to perform the synthesis reaction of TiO_2 particles.

XRD patterns of F_O and F_T were recorded using a Philips PANanalytical X'Pert-Pro diffractometer using CuKα radiation (γ=1.540 Å) at operating parameters of 40 mA and 45 kV with step size 0.02° (Fig. 1).

Fig. 1 XRD equipment

B. Synthesis of TiO_2 Particles

In the synthesis of TiO_2 nanoparticles, firstly titanium (IV) isopropoxide was dissolved in 2-propanol. This solution called precursor solution. After stirring vigorously for 5 min, a mixture of HCl and propanol was added drop wise to the above solution with a burette under stirring. The mixture was stirred for 30 min. After stirring, a mixture of water and propanol which called hydrolysis solution was added to alkoxide solution. After adding the hydrolysis solution, the mixture was stirred for about 4 h in ultrasonic bath and a gel

product was obtained. The gel product was separated by centrifuging and dried at 110 ºC for a night. The dried product was then heat-treated at 450 ºC for 2 h [6]. A schematic flow diagram of synthesis of TiO_2 particles was presented in Fig. 2.

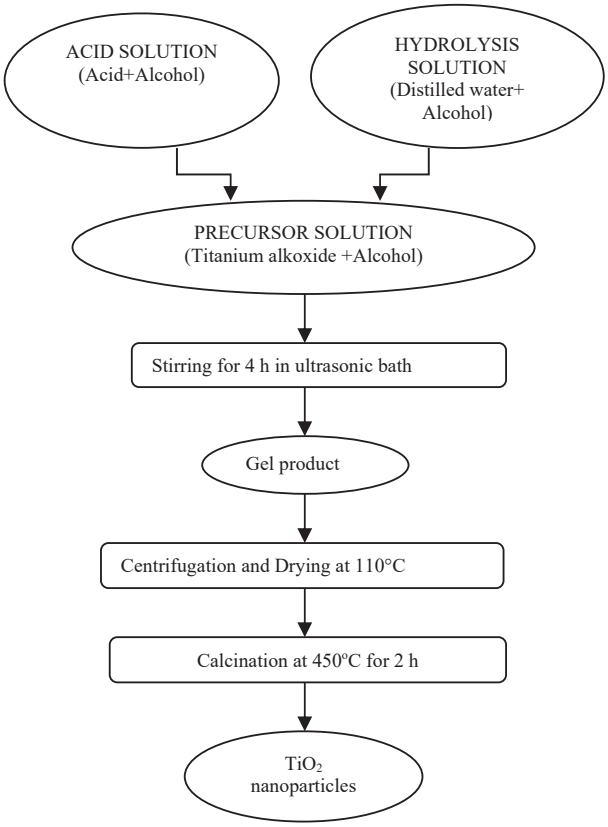

Fig. 2 Flow chart of TiO_2 synthesis

III. Result and Discussion

A. The Effect of Molar Ratio of [H_2O]/[Alkoxide] (Rw)

Fig. 3 shows XRD pattern of sol-gel and sonochemical combination synthesized TiO_2 with different molar ratio of H_2O/alkoxides (Rw) at 70ºC for 4 h. As seen in the figure, distinct peaks were noted in the XRD patterns at 25.4° of anatase TiO_2.

The hydrolysis between alkoxides and H_2O is incomplete and the condensation reaction occurs between the monomers of $(OH)_x$-$Ti(OR)_{4-x}$ when Rw is less than the required stoichiometric ratio. Increasing Rw causes a stronger nucleophilic reaction between H_2O and alkoxide molecules and more alkoxyl groups in the alkoxide will be substituted by hydroxyl groups of H_2O. The monomers, $(OH)_x$-$M(OR)_{4-x}$ so obtained interact with each other to establish a three dimensional network structure via condensation and form solids with textures like fragments of monolith (in Figs. 3 (a)-(d)).

By comparison of the XRD pattern of the obtained products, the synthesized sample in Rw=4 had the highest intensity of TiO_2 diffraction peaks. Thus, the optimal molar ratio of [H_2O]/[Alkoxide] was found as 4.

B. The Effect of Molar Ratio of [Acid]/[Alkoxide]

The acid catalyst can influence both the hydrolysis and condensation rates and the structure of the condensed product. Acid serves to protonate negatively charged alkoxide groups, enhancing the reaction kinetics by producing easily removable groups.

Fig. 4 shows the XRD patterns of TiO_2 nano particles from the sol-gel-sonochemical combination synthesized at different acid/alkoxide values. The finding indicates that the crystallinity of the obtained anatase particles increased as the molar ratio of acid/alkoxide were between 2 and 3. It was seen that the synthesized samples from the molar ratio of acid/alkoxide 1 and 4 have an amorphous phase. Therefore, based on this study, it is believed that the determination of resulting crystal structure is affected by molar ratio of acid/alkoxide values. The higher acidity or the lower acidity promotes amorphous formation. The optimum molar ratio of [Acid]/[Alkoxide] was found as 3.

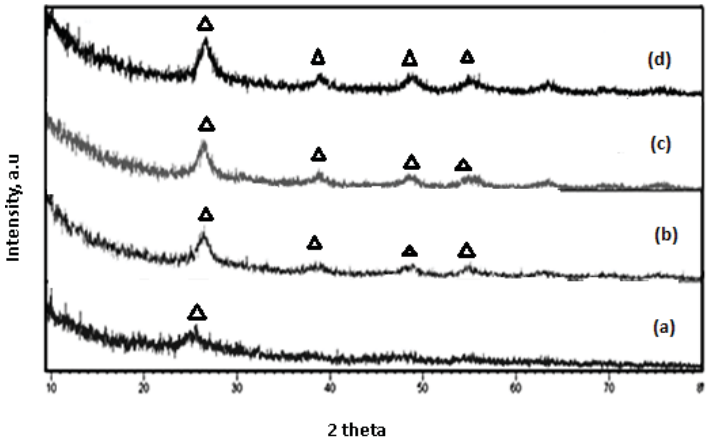

Fig. 3 The effect of molar ratio of [H_2O]/[Alkoxide] (Rw): (a) Rw=1, (b) Rw=2, (c) Rw=3 and (d) Rw=4

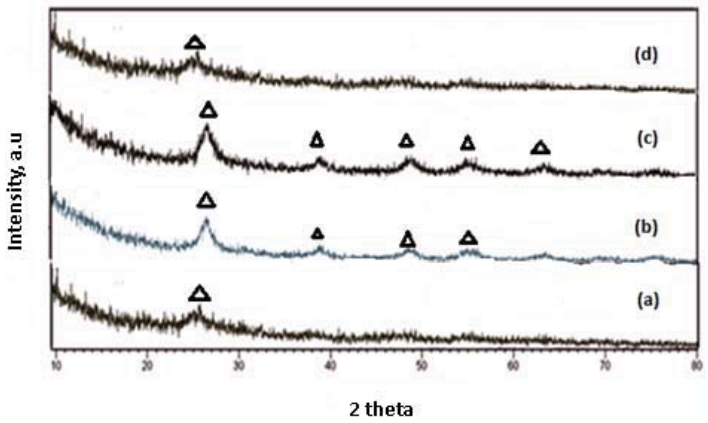

Fig. 4 The effect of molar ratio of [Acid]/[Alkoxide]: (a) $[Acid]_{mole}/[Alkoxide]_{mole}$=1, (b) $[Acid]_{mole}/[Alkoxide]_{mole}$=2, (c) $[Acid]_{mole}/[Alkoxide]_{mole}$=3 and (d) $[Acid]_{mole}/[Alkoxide]_{mole}$ =4

C. The Effect of Reaction Temperature

Fig. 5 presents the XRD patterns of TiO_2 prepared by ultrasound irradiation at various temperatures (25, 50 and 70°C). The XRD analysis of the products obtained at 25°C and 50°C (Figs. 5 (a) and (b)) does not show any sharp diffraction patterns with characteristics of crystalline phases. When the reaction temperature increase to 70°C, peaks characteristic of anatase started to appear (Fig. 5 (c)), and the pattern clearly shows that the nanoparticles have a pure anatase structure. These peaks become narrow and sharp in the XRD of the sample. The sample synthesized at 70°C calcined at 450°C for 2 h (Fig. 5 (d)). However, no new peak appears in the XRD spectra after treatment at 450°C.

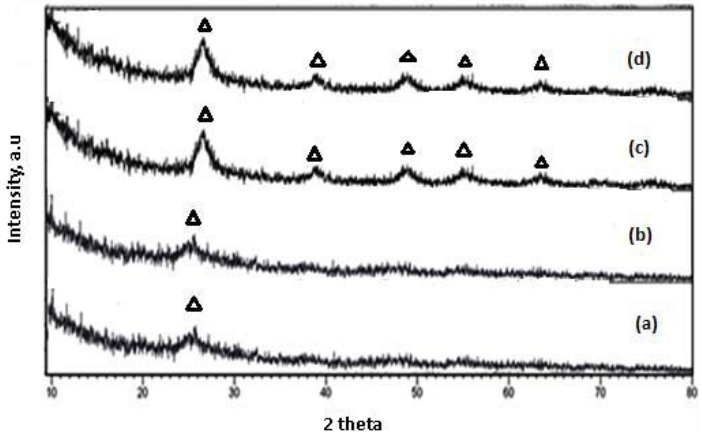

Fig. 5 The effect of reaction temperature: (a) 25°C, (b) 50°C, (c) 70°C and (d) treatment at 450°C for 2 h

IV. Conclusions

A sol-gel and sonochemical combination method for the preparation of nanocrystalline TiO_2 for 4 h has been described. The molar ratio of H_2O/alkoxides and the acid media used in the sol-gel process is the major factors that govern the characteristics of oxides. There is a critical value for the molar ratio of H_2O to alkoxides used in the process to prepare the required oxides. Another important controlling factor for the sol-gel process that was once mentioned in the previous literature is the acid media. The higher acidity or the lower acidity promotes amorphous formation.

In this study, high crystalline TiO_2 nanoparticles were prepared via a sol-gel and sonochemical combination by using the molar ratio of [Acid]/[Alkoxide] = 3 and molar ratio of $[H_2O]/[Alkoxide]$=4 at 70°C. In addition, nanocrystalline products were obtained when the system temperature was above 50°C, otherwise the products were amorphous.

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