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NON-AQUEOUS SOLVOTHERMAL ROUTE TO PREPARE MONO-DISPERSED TITANIUM DIOXIDE NANOPARTICLES SUSPENSION

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ABSTRACT

Titanium dioxide (TiO_2) has a potential application in advanced technologies such as solar cell, photo-induced self-cleaning, photoelectrochromic windows, gene therapy, catalysis, drug delivery, degradation of organic contaminants, photocatalysis, etc. Due to these wide applications, the study of TiO_2 has attracted increasing attention and a number of TiO_2 nanostructures, including nanoparticles, nanorods, nanotubes, nanowires, hollow spheres have been reported to date. In this research, for coating application, we aim to prepare the transparent suspension of titanium dioxide containing nearly mono-dispersed nanoparticles. Non-aqueous solvothermal method is chosen to obtain high crystalline of TiO_2 at low temperature. The solvothermal reactions are carried out in a sealed autoclave that provides suitable conditions for hydrolysis, polycondensation reactions and formation of nanoparticles.

The suspension was prepared by stirring ammonium bicarbonate, triethylamine, ethyl acetate and linoleic acid in a flask. Titanium tetra-*t*-butoxide was added dropwise into the solution and stirred for 5 minutes. Different volume of linoleic acid was added. Then the solution was transferred and sealed in a stainless autoclave and heated at different temperatures for 24 hours without stirring. The collected products of TiO_2 were characterized using X-ray diffractions (XRD), Zetasizer and TEM (Transmission Electron Microscopy).

The results showed that the increase of temperature from 130 to 180°C and linoleic acid from 7 to 25 mL promote the colour of the suspensions are darker. Since ester $\text{C}_{17}\text{H}_{31}\text{COOC}_4\text{H}_9$ was formed, the average particle size is increased with the volume of linoleic acid. The amount of catalyst promotes the nanoparticles reactions. A better suspension is obtained by adding triethylamine as catalyst. The suspension color is transparent and the particle size is between 21 and 27 nm. XRD patterns showed that this nanoparticles have a good structure, i.e. anatase. The stable and transparent suspension was obtained by non-aqueous route at 150°C. This suspension can be applied for coating purpose.

Keywords: titanium dioxide, suspension, coating, non aqueous, solvothermal

I. INTRODUCTION

Titanium dioxide (TiO_2) is a promising metal oxide that has a potential application in advanced technologies such as solar cell, photo-induced self-cleaning (hydrophilicity property), photoelectrochromic windows, gene therapy, catalysis, drug delivery, degradation of organic contaminants, and photocatalysis [1]–[5]. Due to these applications, the study of TiO_2 has attracted increasing attention and a number of TiO_2 nanostructures, including nanoparticles, nanorods, nanotubes, nanowires, hollow spheres have been reported to date [6]–[7].

Currently, developed synthetic routes for producing metal oxide nanoparticles are sol-gel process [8]–[9], microemulsion-assisted process [3] and non-aqueous solvothermal methods [6],[11]. The requirement of high crystallinity of metal oxide nanoparticles is a major problem in their synthesis. Sol-gel methods, included both hydrolytic and non hydrolytic [3] and microemulsions provide amorphous metal oxide. Calcination of gels is required to induce crystallization that leading to grain growth and loss of surface area. Hydrothermal synthesis solves the problems encountered during sol-gel process, but the product nanocrystals are rather agglomerate after a long (3 days) or short (from 5 minutes to a few hours) aging at moderate (110–140°C) or high temperatures (250–300°C) [7]. Commonly, some binders are added to form a stable colloidal solution. The binders are easily lumped with the TiO_2 colloidal particle. After calcination step, the remained binders will form byproduct in VOC decomposition [12]. Non-aqueous solvothermal is the best method to get high quality of nanoparticles. In a sealed vessel, solvent is heated to temperature higher than its boiling point by increasing pressures in heating process [10]. The solvothermal

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treatment can be used to control the particle size, particle's morphology, and crystalline phase by varying the composition, temperature, solvents and aging time [11]. The solvothermal method is chosen to obtain highly crystalline TiO₂ at low temperature. The solvothermal reactions are carried out in a sealed autoclave that provides suitable conditions for hydrolysis, polycondensation reactions and formation of nanoparticles [6].

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Some kinds of nanoparticles are already available commercially in powders or liquid dispersions. The latter is obtained by combining nanoparticles with an aqueous or organic liquid to form a suspension or paste. It may be necessary to use chemical additives (surfactants, dispersants) to obtain a uniform and stable dispersion of particles. Further processing steps, nanostructured powders and dispersions can be used to fabricate coatings and paints. Reference [6] synthesized crystalline, nearly mono-dispersed and transparent solution of TiO₂ in cyclohexane using solvothermal method.

In this research, for coating application, we aim to prepare the transparent suspensions of titanium dioxides containing nearly mono-dispersed nanoparticles by employing a non-aqueous solvothermal method. Based on the environment effect and healthy [13], ethyl acetate is chosen as solvent in this coating suspension preparation.

II. METHODOLOGY

Reagents used for preparing TiO₂ suspension were as follows: titanium tetra-t-butoxide (Aldrich 24,411-2), linoleic acid (Sigma L1626), ammonium bicarbonate (Sigma A6141), triethylamine (Merck M.8.08352) and ethyl acetate (Lab-Scan M.8.08352). All chemicals were used without any further purification.

The suspension was prepared by stirring ammonium bicarbonate, triethylamine, ethyl acetate and linoleic acid in a flask. Titanium tetra-t-butoxide was added dropwise into the mixed solution and stirred for 5 minutes. Then the solution was transferred and sealed in a stainless autoclave and heated at some different temperatures for 24 hours without stirring. The collected products of TiO₂ were characterized using X-ray diffractions (XRD), Zetasizer and Transmission Electron Microscopy (TEM). The XRD pattern was recorded in the 2θ range from 20 to 70° with a Rigaku-MiniFlex at a scan speed of 2 degree per minute. Zetasizer (Malvern, nano ZS) has been used to get the particles size distribution and the micrograph of nanoparticles obtained using TEM (JEOL, JEM-1011).

III. RESULTS AND DISCUSSION

The volume of linoleic acid (LA) as surfactants and temperatures were varied to study the effect of these variables on TiO₂. The obtained suspensions are shown in Fig. 1.

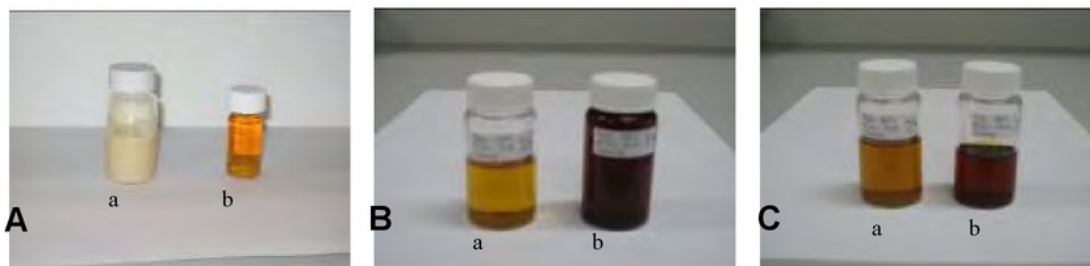


Fig. 1 TiO₂ suspensions at different volume of LA (mL): (a) 7; (b) 25 and temperatures (°C): (A) 130; (B) 150 and (C) 180

As can be seen from Fig. 1 that the increase of LA from 7 to 25 mL cause the suspensions were darker. LA, C₁₇H₃₃COOH, is one of polyunsaturated fatty acids. As a result, the heating process cause the fatty acid is unstable and the oxidation reaction promotes the suspension colors were darker. The oxidation process enhanced strongly with the increase of temperatures. The more LA added to the solution, the darker the suspension obtained.

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particle size distribution of TiO₂ synthesized by solvothermal route at different volume of LA and temperatures are shown in Fig. 2 and 3. The average size of nanoparticles and suspension colors are shown in Table 1. Figure 2 and 3 show distributions of particles size obtained from Zetasizer at LA addition of 7 and 25 mL, respectively. The narrow particle size distribution was obtained at 7 mL of LA. As shown in Table 1, the average particle size at 7 mL LA was smaller than 25 mL and the particle size was increased with temperature, except data at 130°C – 7 mL LA. The morphology of nanoparticles did not affected by the volume of LA. At high temperature, ammonium bicarbonate will be decomposed to water, carbon dioxide and ammonia. Titanium precursor was hydrolyzed and promotes the TiO₂ formation. LA will disperse TiO₂ particles well. TiO₂ precursor also reacts with LA and water to form TiO₂ and C₄H₉OH. Since the volume of LA was increased, C₄H₉OH reacted with LA to form esters C₁₇H₃₃COOC₄H₉ [6]. As a consequence, the average of particle size was increased with the volume of LA. The rate of chemical reaction is highly dependent upon temperature. Increasing the temperature from 130 to 150°C promote the TiO₂ formation reactions. For temperature over 150°C, the formation of TiO₂ and ester C₁₇H₃₃COOC₄H₉ are faster so the average particle sizes were bigger as shown in Table 1. There was no good TiO₂ suspensions produced from these synthesizes because large particles allowed the precipitation.

The increase of particle size can be seen clearly from the TiO₂ suspension colors as shown in Table 1. The changes of color from transparent to yellow colloidal showed that the particle size was increased. The yellow colloidal also indicated that the reactions were not completely at low LA and temperature. Extra time was needed to complete the reactions [11].

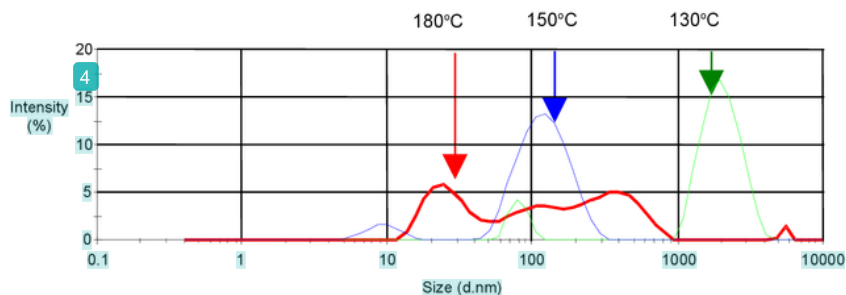


Fig. 2 Particle size distributions of TiO₂ at addition of 7 mL LA with different temperature

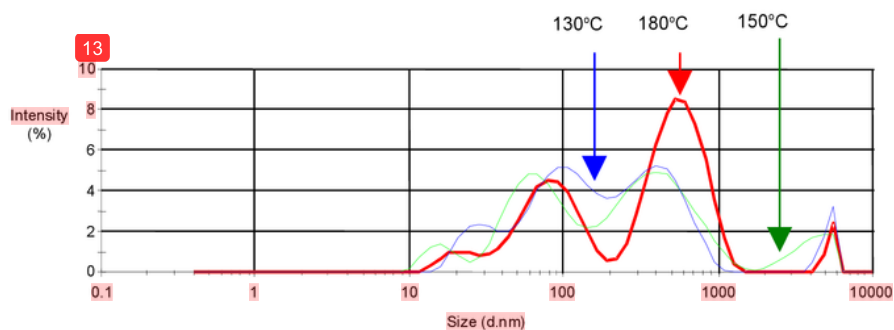


Fig. 3 Particle size distributions of TiO₂ at addition of 25 mL LA with different temperature

Table 1 TiO₂ particle size and suspension colors at different volume of LA and temperature

LA (mL)	Temperature (°C)	Particle size (nm)	Suspension
7	130	1,069	Yellow colloidal
	150	79	Brown*, transparent, precipitate
	180	110	Brown**, precipitate
25	130	135	Brown, transparent, precipitate
	150	113	Brown***, transparent, precipitate
	180	180	Brown***, precipitate

Note: the increase of * shows the colour was darker

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X-ray diffraction pattern of nanoparticles produced at 180°C and different volume of LA are shown in Fig. 4.

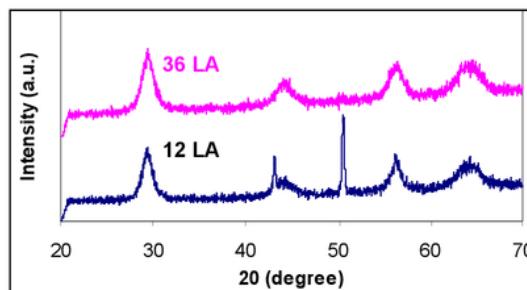


Fig. 4 TiO₂ X-ray diffraction pattern at different volume of LA (mL)

The reflection peaks as shown in Fig. 4 show that the nanoparticles had a sharp peak in the range 2 θ between 28° and 30°. This obviously indicate the presence of crystalline phase of TiO₂. The crystalline phase was identified as the anatase phase. TiO₂ nanoparticles synthesized with 36 mL of LA had a slightly sharp peak than the other. This indicate that the nanoparticles had a high crystallinity. The mechanical property of particles is affected by crystallinity degree. Besides as a surfactant, LA also improved the crystallinity of nanoparticles. This result is consistent with the previous study [6].

Based on the previous discussion, the best temperature for TiO₂ nanoparticles formation was at 150°C. This temperature will be used for further research and the volume of LA still be varied to get a better suspension. The volume of LA was varied in the range between 12 and 24 mL. TiO₂ suspensions produced at 150°C and different volume of LA are shown in Fig. 5.

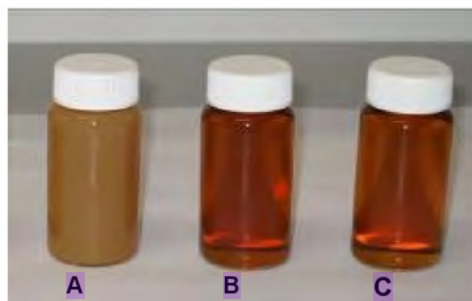


Fig. 5 TiO₂ suspensions with different volume of LA: (A) 12; (B) 18 and (C) 24 mL

Fig. 5 shows that the increases of LA promote the nanoparticles reactions that affect the suspension colors. The effect of the volume of LA to particle size has discussed well. The particle size distributions of TiO₂ are shown in Fig. 6. The average particle size and suspensions produced from these experiments are shown in Table 2.

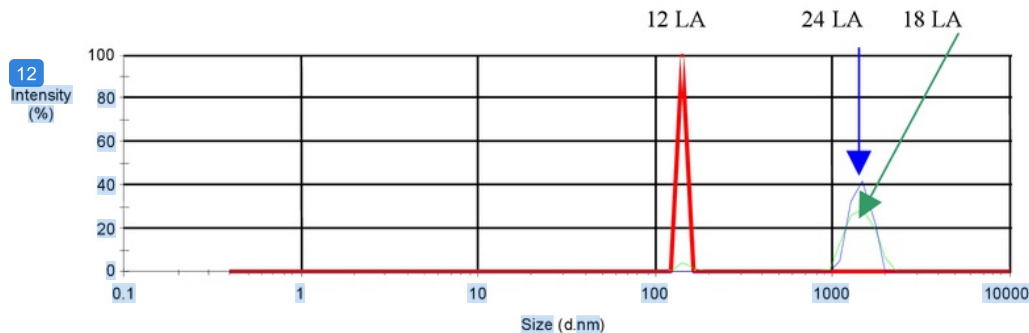


Fig. 6 Particle size distribution prepared from different volume of LA (mL)

Table 2 TiO₂ particle size and colors obtained at 150°C and different volume of LA

LA (mL)	Particle size (nm)	Suspension
12	2,210	Brown colloidal
18	1,370	Brown*, transparent, precipitate
24	2,030	Brown*, transparent, precipitate

As can be seen from Table 2 that the average particles in suspensions were quite big that allows precipitation. The addition of 12 mL of LA might cause the reactions were not completely. As a consequence, the colloidal particles were produced. A better suspension was obtained from 18 and 24 mL of LA, despite there were some precipitate in suspensions. The smallest particle size was obtained by adding 18 mL of LA to the solution.

XRD pattern of TiO₂ nanoparticles produced at 150°C in ethyl acetate solution at different volume of LA is shown in Fig. 7. A sharp peak was obtained by adding 18 mL of LA, this indicated that particles have a high crystallinity.

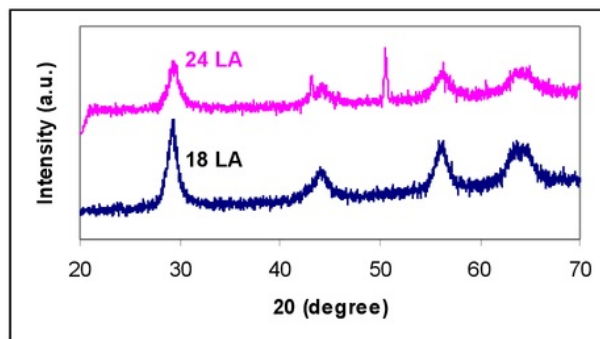


Fig. 7 XRD pattern of TiO_2 nanoparticles at 150°C and different volume of LA (mL)

Based on the information in terms of average particle size, suspension color and XRD pattern, the optimum volume of LA in ethyl acetate solution was 18 mL. Compared with the previous results, the addition of more solvent in solution had not improved the suspension quality well. Another way that can be used to improve the process was by adding the volume of triethylamine (TEA) as catalyst. The increase of the catalyst amount might promote the nanoparticles reactions were better. In these experiments, the volume of TEA was doubled. The results are shown in Fig. 8.



Fig. 8 TiO_2 suspensions with 10 mL of TEA and different volume of LA: (A) 18 and (B) 24 mL

The solutions were transparent but there was a little precipitates in the last one. It can be summarized that the best TiO_2 suspension was obtained by adding 18 mL of LA and 10 mL of TEA into ethyl acetate solution. The average particle size is between 21 and 27 nm. All the nanoparticles dispersed well. The TEM image of these nanoparticles is shown in Fig. 9.

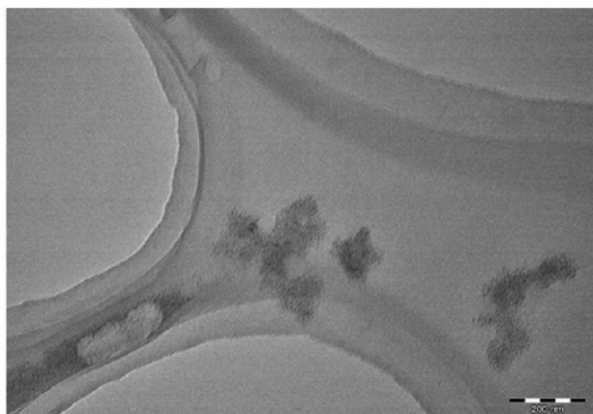


Fig. 9 TEM micrograph of TiO_2 nanoparticles with magnification $\times 100,000$

IV. CONCLUSIONS

In summary, the stable and transparent suspension was synthesized by non-aqueous solvothermal route at 150°C. TiO₂ suspension color was brown. The surfactant plays a key role in both color and nanoparticle size. TiO₂ nanoparticles obtained from this synthesis have anatase structure and the average particle sizes are between 21 and 27 nm.

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