Research Article

Dispersion and Stabilization of Photocatalytic TiO₂ Nanoparticles in Aqueous Suspension for Coatings Applications

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To produce titanium dioxide (TiO₂) nanoparticle coatings, it is desirable that the nanoparticles are dispersed into a liquid solution and remain stable for a certain period of time. Controlling the dispersion and aggregation of the nanoparticles is crucial to exploit the advantages of the nanometer-sized TiO₂ particles. In this work, TiO₂ nanoparticles were dispersed and stabilized in aqueous suspensions using two common dispersants which were polyacrylic acid (PAA) and ammonium polymethacrylate (Darvan C). The effect of parameters such as ultrasonication amplitude and type and amount of dispersants on the dispersibility and stability of the TiO₂ aqueous suspensions were examined. Rupture followed by erosion was determined to be the main break up mechanisms when ultrasonication was employed. The addition of dispersant was found to produce more dispersed and more stabilized aqueous suspension. 3 wt.% of PAA with average molecular weight (M_w) of 2000 g/mol (PAA 2000) was determined to produce the best and most stable dispersion. The suspensions were then coated on quartz glass, whereby the photocatalytic activity of the coatings was studied via the degradation of formaldehyde gas under UV light. The coatings were demonstrated to be photocatalytically active.

1. Introduction

TiO₂ nanoparticles can be used for a variety of applications including self-cleaning [1], water treatment [2], antibacterial [3], and air purification [4] due to their effective photocatalytic activity. For such applications, TiO₂ nanoparticles are generally coated on suitable substrates. TiO₂ coatings can be prepared by various ways including chemical vapour deposition (CVD), physical vapour deposition, sol-gel, as well as spraying. Among them, the coating process using TiO₂ suspensions by spraying is the most cost effective method besides being compatible for large areas. Producing TiO₂ suspensions necessitates the incorporation of TiO₂ nanoparticles in the liquid phase, the break up and dispersion of nanoparticle clusters, and subsequently stabilization.

To achieve uniform coatings, the degree of particle agglomeration should be minimized especially when working with nanoparticles. Nanoparticles have strong tendency to agglomerate compared to submicrometer particles due to their large surface area. The agglomeration is generally due to the Van der Waals attraction forces between nanoparticles which can be counterbalanced by electrostatic and steric stabilization. Electrostatic stabilization can be achieved by the addition of charge to the nanoparticles so that they can repel one another especially under the influence of the pH. Steric stabilization can be achieved by the adsorption of a thin layer of polymer onto the nanoparticle surface to physically prevent the nanoparticles from coming close enough to each other and cause agglomeration [5]. Generally, the combination of both electrostatic and steric stabilization

is termed electrosteric stabilization and can be achieved using polyelectrolytes. A polyelectrolyte is a polymer chain with numerous dissociable groups. Polyacrylic acid (PAA) is one example of polyelectrolyte dispersants, which is fully dissociated at pH 8.5 to 9 [5, 6].

Ultrasonication has been proven as a useful tool to disperse nanoparticles and to eliminate agglomeration in aqueous suspensions [7]. Shock waves caused by collapsing cavitations under ultrasonic irradiation will lead to collisions among particles, whereby the agglomerated particles are eroded and split apart by the collisions [7, 8]. Basically, there are three different mechanisms of nanoparticle cluster break up which are rupture, erosion, and shattering. Rupture occurs when large agglomerate is broken up into numerous agglomerates of either the same or different size which can be subsequently broken up further. Erosion, on the other hand, occurs when small fragments are gradually sheared off and detached from the outer surface of large agglomerates. The smaller fragments are either primary particles or aggregates that cannot be broken up further under the effect of hydrodynamic stresses. Finally, shattering occurs when the energy level provided is very high, in which the agglomerate disintegrate into numerous small fragments of either aggregates or primary particles in a single event. The details of the break up modes are reported in the work by Özcan-Taşkın et al. [9].

Although there are numerous studies incorporating TiO₂ nanoparticles into thin films [10] or polymer composites [11], the dispersion and stabilization of photocatalytic TiO₂ nanoparticles for coatings application have not been studied extensively. Greenwood and Kendall [5] studied the effect of adding various commercially available polyelectrolyte dispersants into micron-sized TiO₂ powder aqueous suspensions. Ran et al. [12] examined the effects of their synthesized PAA on rheological and dispersion properties of also micron-sized aqueous TiO₂ suspensions. Liufu et al. [13] investigated the adsorption of PAA in aqueous suspension onto the surface of TiO₂ nanoparticles and discussed the major factors influencing the adsorption of PAA. Sato et al. [7] focused on the effects of ultrasonic irradiation on slurry viscosity and aggregate size of commercial nanocrystalline TiO₂ aqueous suspensions containing polyelectrolyte dispersants and compared the results with those obtained via ball milling and bead milling. Both Liufu et al. [13] and Sato et al. [7] studied high-concentration TiO₂ aqueous suspensions. Fazio et al. [14], on the other hand, studied the effect of dispersant nature, concentration, and the effect of ultrasonication time on colloidal behaviour of dilute commercial and synthesized (sol-gel)-nanosized TiO₂ powder aqueous suspensions.

To the best of our knowledge, no study has been done on the dispersion and stability of TiO₂ nanoparticles produced via metal organic chemical vapour deposition (MOCVD) technique. Besides, no report has yet been published on the effect of ultrasonication amplitude towards the dispersion and stability of TiO₂ nanoparticle aqueous suspension although amplitude is one of the important parameters of the ultrasonic equipment. In addition, all of these studies mainly focused on preparing disperse and stable TiO₂ aqueous suspensions. There is very inadequate information about the

photocatalytic application of the TiO₂ aqueous suspensions prepared. The knowledge on the dispersion and stabilization of photocatalytic TiO₂ nanoparticles for coatings application is much needed since a more thorough understanding could bring improvement to its industrial applications.

The aim of this study was to investigate the effect of ultrasonication amplitude (0–40%), type of polyelectrolyte dispersants (PAA with average molecular weight (M_w) of 2000 (PAA 2000) and 5000 g/mol (PAA 5000), and Darvan C with M_w of 13 000 g/mol), and amount of dispersant (0–3 wt.%) on the dispersion and stability of photocatalytic TiO₂ nanoparticle aqueous suspensions. The dispersion and stability of the aqueous suspensions were characterized using particle size analyzer, zeta potential, and transmission electron microscope (TEM), and stability test. The fourier transform-infrared (FTIR) analysis was carried out to confirm the adsorption of dispersant onto the TiO₂ nanoparticles' surface. To demonstrate that the TiO₂ nanoparticle suspensions can be used for coatings application, the suspensions were then coated on quartz glass. The energy dispersive X-ray (EDX) analysis was done on the surface of the coatings to study the uniformity of the elemental distribution. Finally, the photocatalytic activity of the coatings was determined via the degradation of formaldehyde gas under UV light.

2. Experimental

2.1. Preparation and Characterization of TiO₂ Nanoparticles. TiO₂ nanoparticles were synthesized via a custom-built metal organic chemical vapour deposition (MOCVD) reactor. The dimensions of the custom-built MOCVD system and the method used to produce TiO₂ nanoparticles have been described in detail elsewhere [15]. However, in this work, oxygen feed (100 mL/min) was introduced inside the reactor along with the nitrogen carrier gas that carried the precursor. This was done to reduce carbon impurities that might originate from the precursor, and thus postdeposition heat treatment was not performed for this work. The deposition temperature was set at a fixed temperature of 700°C.

The size and morphology of the TiO₂ nanoparticles were studied by TEM (Hitachi H7100). The surface areas were determined by the N₂ adsorption using Brunauer-Emmett-Teller (BET) method (Bel Japan Inc., Belsorp II). Before any measurement, all the samples were exposed to vacuum condition at 150°C overnight to remove any remaining moisture. The mean particle size can be calculated from the BET data by applying the following equation [16]:

$$D = \left(\frac{6}{SA \times \rho} \right) \times 1000, \quad (1)$$

where D is the mean particle size, SA is the surface area from BET data, and ρ is the density. Finally, the crystalline phase of the sample was determined using X-ray diffraction (XRD, Philips X'pert Pro PW3040) with a Cu K_α radiation source ($\lambda = 0.15406$ nm) operated at 40 kV and 30 mA. The isoelectric point (iep) of the TiO₂ nanoparticles was found to be at pH 5.2.

2.2. Preparation and Characterization of Aqueous Suspensions. All the suspensions were ultrasonically irradiated using an ultrasonic homogenizer equipped with temperature controller (Cole-Parmer; frequency = 20 kHz; Power = 500 Watt with amplitude range; probe diameter = 13 mm). The ultrasonic irradiation period was set to 30 minutes because large aggregates were dispersed almost completely by ultrasonic irradiation for 30 minutes [7]. The suspensions were irradiated with a 10-second pulse with every 10 seconds of irradiation period to prevent undesirable increase in the suspension temperatures. Note that all the prepared suspensions were aged overnight at room temperature using an orbital shaker to ensure that the nanoparticles were kept dispersed in the suspensions as well as to maintain the homogeneity of the suspensions. The pH of the suspensions was adjusted and fixed at pH 8.5 using ammonia solution because PAA and Darvan C (a type of PAA) is fully associated at this pH value. Ammonia solution was chosen to adjust the pH because it has a buffering effect in which the pH of the suspensions can be kept at nearly constant value for a wide variety of chemical applications.

To study the effect of ultrasonication, 0.05 g TiO_2 nanoparticle suspensions were prepared in 100 mL of distilled water (pH adjusted to pH of 8.5) without and with ultrasonication. Based on initial preliminary studies, 0.05 g was chosen as an ideal amount of loading for further dispersion and application studies because it produced glass coatings with an optimum value of around 80% light transmittance. For the suspensions prepared with ultrasonication, the amplitude was varied from 0 to 40%. Ultrasonication amplitude is one of the important sonication parameters. It indicates the amplitude of vibration at the probe tip and directly represents the output power of ultrasonic equipment. Greater amplification creates more intense and greater disruption.

To study the effect of type and amount of dispersant on the suspensions, two types of PAA with M_w of 2000 and 5000 g/mol (Acros Organics) along with Darvan C (R.T. Vanderbilt Company, Inc.) with M_w of 13000 g/mol were used as dispersants. 0.05 g TiO_2 nanoparticles were mixed with 100 mL of distilled water (pH adjusted to pH 8.5), and the required amount of dispersant (0 to 3 % based on the TiO_2 weight (wt.%)) was added followed by ultrasonication at 40% amplitude.

The particle size distribution of the suspensions was characterized using a particle size analyzer (Zetasizer Nano S, Malvern Instruments). The potential stability of the suspensions was studied using a zeta potential analyzer (Zetasizer Nano Z, Malvern Instruments), around 24 hours after ultrasonication. Moreover, a stability test was performed to determine the ability of the TiO_2 nanoparticle suspensions to remain dispersed over a period of time. Photos of the suspensions prepared under various experiment conditions inside clear glass containers were captured at certain intervals over the course of 8 weeks. To study the effect of ultrasonication and dispersant addition on the morphology of the TiO_2 nanoparticles, TEM images of nanoparticles extracted from all suspension samples were captured and compared.

2.3. FTIR Analysis. The FTIR (Nicolet, UK) analysis was carried out to confirm the adsorption of dispersant onto the TiO_2 nanoparticles' surface. The FTIR spectrum of the dispersant was taken in liquid state. The FTIR spectrums of TiO_2 nanoparticles before adsorption of dispersant were taken in solid state after they had been dried overnight at 60°C to remove any moisture. For the FTIR spectrums of the TiO_2 nanoparticles after adsorption, the nanoparticles were prepared by centrifuging the TiO_2 suspensions with optimum dispersant. The nanoparticles were then collected, washed with deionized water, and dried overnight at 60°C to remove any moisture.

2.4. Preparation and Characterization of Glass Coatings. The suspensions were coated on both sides of 8 cm × 8 cm quartz glass using an air brush (AB931, Ingersoll Rand). The EDX (NORAN System SIX, Thermo Scientific) spectrum imaging was performed on the coated glass to characterize the elemental uniformity of the coating.

2.5. Photocatalytic Study. The photocatalytic activity of the coatings was determined using a simple qualitative analysis via the degradation of formaldehyde gas under UV light. A coated glass slide was positioned inside a 1-litre glass-beaker. Then, the beaker was sealed with a parafilm. A known amount of formaldehyde liquid was introduced inside the beaker using a pipette. The initial concentration of formaldehyde was kept at 2 ppm (short-term exposure limit (STEL) of formaldehyde gas is 2 ppm in 15 minutes average) for all experiments. Then, the beaker was quickly and carefully sealed with 2 layers of parafilm and aluminium foil to prevent any gas leakage. The beaker was placed inside a dark box overnight to allow the formaldehyde liquid to completely evaporate and reach equilibrium. After that, the photocatalytic degradation of formaldehyde gas was carried out under the illumination of an 8 W UV light (365 nm peak wavelength) for a designated period of time.

The final concentration of the gas was then estimated using a colorimetric method [17] where a known amount of gas inside the beaker was withdrawn using a syringe and mixed with a mixture of 2 M ammonium acetate, 0.05 M acetic acid, and 0.02 M acetylacetone. Then the solution was heated for 30 minutes in a water bath at around 40°C to complete the reaction. A yellow colour gradually developed owing to the formation of diacetyldihydrolutidine (DDL). A UV-vis spectrophotometer (Shimadzu UV-1650 PC) was used to determine the absorbance value at 413 nm (absorbance peak of DDL). The percentage degradation of formaldehyde gas at a certain period of time was estimated based on the absorbance value obtained from UV-vis spectrophotometer reading before and after the coatings were irradiated with UV light. All experimental runs were repeated three times.

3. Results and Discussion

3.1. Characterization of TiO_2 Nanoparticles. Figure 1(a) depicts the TEM micrographs of TiO_2 nanoparticles, while

FIGURE 1: (a) TEM micrograph and (b) XRD pattern of TiO_2 nanoparticles synthesized via MOCVD method.

Figure 1(b) illustrates the XRD pattern of the sample. The micrograph shows that the nominal size of the nanoparticles was less than 50 nm and that the nanoparticles appeared to be relatively homogeneous and uniform in size albeit fairly agglomerated.

The BET surface area of the sample was determined to be $86.9 \text{ m}^2/\text{g}$. The mean particle size calculated from the BET data was found to be 17.7 nm. Meanwhile, the XRD pattern for TiO_2 nanoparticles in Figure 1(b) shows peaks at 2θ values of 25.3, 37.8, 48.0, 53.8, and 54.9, corresponding to the diffractions of the (1 0 1), (0 0 4), (2 0 0), (1 0 5), and (2 1 1) planes of anatase, respectively [18, 19]. There were no other detectable peaks corresponding to the rutile crystal structure. These findings confirmed that the TiO_2 nanoparticles were in the pure anatase crystal structure.

3.2. Aqueous Suspensions

3.2.1. Effect of Ultrasonication. Figures 2(a) and 2(b), respectively show the particle size distribution and zeta potential of the TiO_2 suspensions with respect to ultrasonication amplitude. The average cluster size in each suspension is shown inset in Figure 2(a). From Figure 2(a), it can be seen that the particle size distribution of the TiO_2 nanoparticle suspension prepared without ultrasonication shows a bimodal curve indicating that the nanoparticles

agglomerate in two size ranges of approximately 531–3580 nm and 3580–5560 nm. When ultrasonication with an amplitude of 20% was applied, the particle size distribution curve still appeared as a bimodal shape. However, the first curve (left curve) was shifted to the left indicating that the average cluster size was decreased. The height of the second curve (right curve) was decreased indicating that the volume of large agglomerates was reduced. This implied that large agglomerates, though not all, were broken up into smaller agglomerates, suggesting that the break up process was a result of a rupture mechanism.

As the amplitude was further increased to 30%, the particle size distribution curve became unimodal and narrower with a decreased particle size distribution range of 190–1281 nm. The curve shifted slightly to the left indicating that the average cluster size was decreased. This implied that smaller fragments were sheared off from large agglomerates, and as a result, the volume of smaller cluster increased. Thus, the main break up mechanism was most likely to be erosion. As the amplitude was further increased to 40%, the curve became bimodal again. The particle size range was additionally shifted to the left, indicating that the agglomerates were further eroded to smaller size. Again, this implied that the break up mechanism was erosion and that increasing the ultrasonication amplitude improved the efficiency of the deagglomeration process. From Figure 2(a), it can be

FIGURE 2: (a) Particle size distribution and (b) zeta potential plot for different ultrasonication amplitude values.

deduced that the break up mode through ultrasonication predominantly occurs by rupture followed by erosion.

The stability of the suspensions was studied in more detail with measurements of zeta potential. Zeta potential gives an indication of the potential stability of the suspension and indicates the degree of repulsion between adjacent, similarly charged particles in the suspension. It is also an aid in predicting long-term stability. The higher the magnitude of the zeta potential, the more stable the suspensions can be. Figure 2(b) shows the effect of ultrasonication amplitude on the zeta potential of each suspension. The zeta potential increased from -35.0 to -50.3 mV as the ultrasonication amplitude was increased indicating the improvement in the suspensions potential stability, the amplitude was increased. Thus, it can be deduced that high ultrasonication amplitude did not only enhance the efficiency of the deagglomeration process but also the potential stability of the suspension.

3.2.2. Effect of Type and Amount of Dispersant. Figure 3 illustrates the effect of type and amount of dispersant on the average cluster size of the TiO_2 suspensions. The inset in Figure 3 shows, the average cluster size of the TiO_2 nanoparticles as the amount of dispersant was varied from 1 to 5% in smaller scale. From this figure, it can be seen that PAA 2000 produced TiO_2 suspensions with smallest average cluster size followed by PAA 5000 and Darvan C. This finding suggests that the lower molecular weight dispersant produced suspensions with smaller average cluster size compared to the larger one. This is most likely due to the fact that polymers of high molecular weight have longer carbon chain that can adsorb onto the surfaces of many nanoparticles and bond them with each other [13], resulting in a larger average cluster size.

The amount of dispersant required to produce the smallest average cluster size for all types of dispersants was found to be 3 wt.%. It can be seen from Figure 3 that below 3 wt.%, the average cluster sizes were relatively large most likely due to lack of dispersant to prevent the nanoparticles from being agglomerated. The average cluster sizes reduced as the amount of dispersant was increased to 3 wt.%, where the optimum average cluster size was achieved. However, as the amount of dispersant was further increased

FIGURE 3: Effect of type of dispersant and amount of dispersant on the average cluster size of TiO_2 suspensions.

to above 3 wt.%, excess of dispersant led to an increase in average cluster sizes probably due to agglomeration caused by polymeric bridging of free polyelectrolytes [14].

Figure 4 shows the effect of 3 wt.% of PAA 2000 addition on the particle size distribution. The addition of the dispersant caused the particle size distribution of TiO_2 nanoparticles suspension to become unimodal, generating monodisperse suspension of TiO_2 nanoparticles. The curve was shifted to the left indicating that the average cluster size was decreased. This implied that large agglomerates were eroded to aggregates that could not be broken up further and that the deagglomeration process was almost complete. The particle size range was greatly reduced to 21–295 nm. The average cluster size was significantly decreased from 425 to 118 nm. Hence, it can be deduced from Figures 3 and 4 that the addition of dispersant with the aid of ultrasonication contributed towards substantial enhancement of the deagglomeration process by improving the separation between nanoparticles and hindering agglomeration.

Furthermore, Figure 5 demonstrates the effect of type and amount of dispersant on the zeta potential of TiO_2

FIGURE 4: Effect of optimum dispersant addition on the particle size distribution of TiO_2 suspensions.

FIGURE 5: Effect of type of dispersant and amount of dispersant on the zeta potential of TiO_2 suspensions.

suspensions. It can be seen that PAA 2000 provides better potential stability of the TiO_2 suspensions followed by PAA 5000 and Darvan C. This suggests that the most ideal dispersant to stabilize suspension with small particles (nanometer sized particle) is low-molecular-weight dispersant that has shorter carbon chain. Polymers of high molecular weight, on the other hand, have longer carbon chains that can adsorb onto the surfaces of many particles and bond them with each other causing flocculation that results in destabilization of the suspensions [13]. The same is true for excess amounts of dispersants.

The amount of dispersant that gives the highest zeta potential and hence highest potential stability was 3 wt.% for all types of dispersant. Below 3 wt.%, the suspensions have low zeta potential and therefore the nanoparticles were expected to easily flocculate. This is probably due to inadequate repulsive force to overcome the Van der Waals attraction between nanoparticles [5]. However, the zeta

potential started to increase as the amount of dispersant was increased until it reached 3 wt.%, where the optimum potential stability was achieved. This is consistent with the fact that PAA is a polyelectrolyte that provides electrosteric stabilization when it is adsorbed onto the particles' surface [5]. Meanwhile, as the amount of dispersant was further increased, excess of dispersant led to agglomeration and destabilization as was discussed earlier. Therefore, the zeta potential decreased, indicating reduction in the potential stability of the suspensions.

The amount and type of dispersant that provides optimum potential stability (Figure 5) is similar to the amount and type of dispersant that produces the smallest average cluster size (Figure 3). In fact, the potential stability is at its maximum when the average cluster size is minimum. Thus, it can be deduced that 3 wt.% of PAA 2000 is the optimum amount and type of dispersant to disperse and stabilize TiO_2 suspensions. Finding the optimum dispersant is important not only to improve the efficiency of the deagglomeration process but also to improve the potential stability of the suspension.

TEM was used to study the morphology of the TiO_2 nanoparticles extracted from the suspensions as illustrated in Figures 6(a)–6(c). It can be clearly seen from Figure 6(a) that without ultrasonication, the nanoparticles are highly agglomerated, with the agglomerates being relatively large, more than 500 nm size structures. In contrast, Figure 6(b) shows that ultrasonication caused a considerable reduction on the agglomerate size and that the agglomeration of the nanoparticles had been greatly reduced.

However, Figure 6(c) shows that the addition of the dispersant had further reduced the size of the agglomerates to approximately 100 nm size structures. The TEM images support the findings that the addition of dispersant improves the ultrasonication break up process of the nanoparticles preventing the agglomeration of the nanoparticle aggregates and/or agglomerates as was discussed earlier.

Furthermore, a stability test was done to determine the ability of the TiO_2 nanoparticle suspensions to remain suspended over a period of time. The results are shown in Figure 7. Since zeta potential only gives an indication of the potential stability of the suspension, a stability test was conducted to determine the long-term stability of the suspension. The preparation of stable suspension is crucial in determining the quality of the coatings.

Figure 7 shows that without ultrasonication, the stability of the suspension was fairly low. The nanoparticles completely settled down at the bottom of the container after around 3-week time. Nonetheless, with ultrasonication, the stability of the suspension was fairly improved. The nanoparticles in the suspension started to settle down at around 1 week and were completely settled down upon reaching week 5.

Moreover, it can be seen that with ultrasonication and the addition of dispersant, the stability of the suspensions was greatly enhanced. The nanoparticles remain suspended up to 4 weeks. After 5 weeks, the suspensions prepared with the addition of PAA 5000 and Darvan C started to settle down with Darvan C being relatively faster compared to

FIGURE 6: TEM micrographs of TiO_2 nanoparticles extracted from the suspensions prepared (a) without ultrasonication, (b) with 40% amplitude ultrasonication, and (c) with addition of 3 wt.% dispersant.

FIGURE 7: Photos of TiO_2 nanoparticle suspensions on (a) day 1, (b) week 1, (c) week 2, (d) week 3, (e) week 4, (f) week 5, (g) week 6, and (h) week 8.

FIGURE 8: FTIR spectra of TiO_2 nanoparticles before and after adsorption of PAA2000.

PAA 5000. This is due to the longer carbon chain (higher molecular weight) of Darvan C compared to PAA 5000. As discussed earlier, longer carbon chain dispersant can adsorb onto the surfaces of many particles and bond them with each other causing flocculation and destabilization of the suspensions. The addition of the PAA 2000 dispersant was found to produce TiO_2 suspension with the best stability, thus supporting previous potential stability findings (Figure 5). The suspension remained stable for more than 2 months.

3.2.3. FTIR Analysis. FTIR analysis was done on PAA 2000 as well as TiO_2 nanoparticles before and after adsorption of 3 wt.% PAA 2000 as can be seen from Figure 8. The assignments of various bands and peaks made in this study are in reasonable agreement with those reported in the literature for similar functional groups [12, 13, 20]. The FTIR spectrum of PAA 2000 shows a strong absorption band at 1650 cm^{-1} indicates $\text{C}=\text{O}$ stretching vibration for carboxylic acids. The band at 1377 cm^{-1} is due to the $\text{C}-\text{O}$ stretching vibration. The broad peak at 3420 cm^{-1} is attributed to the hydroxyl group ($\text{O}-\text{H}$) due to water. Note that the FTIR spectrum of PAA 2000 was taken in liquid form.

Meanwhile, the FTIR spectrum of TiO_2 nanoparticles shows intense broadband in the vicinity of 400 to 800 cm^{-1} attributed to the stretching vibration of $\text{Ti}-\text{O}-\text{Ti}$ as expected for TiO_2 samples. The spectrum does not show peak attributed to $\text{O}-\text{H}$ group because the nanoparticles were in solid form and that they have been dried overnight to remove the moisture.

In contrast to TiO_2 spectrum before adsorption, the TiO_2 spectrum after adsorption of PAA 2000 shows new absorption peaks at around 1690 and 1390 cm^{-1} indicating $\text{C}=\text{O}$ and $\text{C}-\text{O}$ stretching vibrations, respectively. These findings proved that PAA was adsorbed onto the surface of the nanoparticles. Moreover, there is also absorption peak attributed to stretching vibration of $\text{O}-\text{H}$ at around 3350 cm^{-1} which may originate from the adsorbed PAA 2000.

3.3. Coatings

3.3.1. Uniformity of the Coatings. An EDX spectrum imaging was performed on the coated glass to characterize the uniformity of TiO_2 coatings prepared without and with dispersant. Figure 9 shows the titanium (Ti) elemental distribution on the surface of the coatings. It can be clearly seen that the addition of the dispersant addition results in a higher surface concentration of Ti and more uniform Ti distribution. These findings indicate that the dispersant facilitated the TiO_2 nanoparticles to distribute evenly in the suspensions and hence produced better coatings.

3.3.2. Photocatalytic Activity. TiO_2 suspensions without and with dispersant were coated on quartz glass using an air brush, and the coatings were tested for degradation of formaldehyde gas under UV light irradiation. The degradation percentage of formaldehyde gas at a certain period of time was estimated and plotted in Figure 10.

It can be seen from Figure 10 that all the coatings were photocatalytically active because the formaldehyde was able to be degraded after a certain period of time. The degradation percentage of formaldehyde increased as the irradiation time of the coatings was increased. The degradation percentage almost reached a plateau after the coatings were irradiated under UV light for 20 minutes demonstrating that the formaldehyde degradation was almost completed within that time. The degradation of formaldehyde from both types of coatings was almost comparable with each other indicating that the addition of dispersant does not affect the photocatalytic activity of the coatings. Nonetheless, it is believed that the TiO_2 coatings prepared with the addition of dispersant have better adhesion to the glass compared to that prepared without dispersant owing to the fact that PAA is a polymer adhesive that can adhere or bond the coating onto the glass.

4. Conclusion

PAA and Darvan C were employed to disperse and stabilize TiO_2 nanoparticles produced using MOCVD method in aqueous suspensions. The use of ultrasonication was found to assist the agglomerates to break down to smaller agglomerates and aggregates. Rupture followed by erosion were found to be the main break up mechanisms when ultrasonication was employed. The deagglomeration process and the stability of the suspensions were improved by increasing the ultrasonication amplitude.

Moreover, the addition of dispersant was found to improve the deagglomeration process via ultrasonication by enhancing the separation between nanoparticles and hindering the agglomeration of the nanoparticles. Low-molecular-weight dispersant, PAA 2000, produced the most stable suspension with the smallest average cluster size. The optimum amount of dispersant to disperse and stabilize the TiO_2 aqueous suspensions was found to be 3 wt.%.

The TiO_2 coatings produced from suspension prepared with optimum dispersant result in a higher surface concentration of Ti and more uniform Ti elemental

FIGURE 9: EDX spectra of TiO_2 coating (a) without dispersant and (b) with PAA 2000 dispersant.

FIGURE 10: Degradation percentage of formaldehyde for TiO_2 coatings produced from the suspensions prepared without and with dispersant suspensions under UV light irradiation.

distribution. The degradation of formaldehyde for TiO_2 coatings produced from the suspensions prepared without and with dispersant was almost comparable with each other, indicating that the addition of dispersant does not affect the photocatalytic activity of the coatings.

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