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Study on Dispersion of TiO_2 Nanopowder in Aqueous Solution via Near Supercritical Fluids

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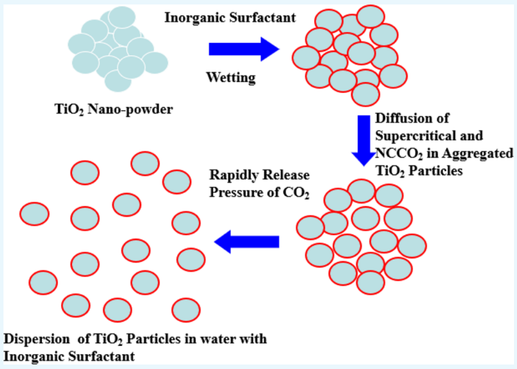
ABSTRACT: In this study, we investigated the effects of near supercritical carbon dioxide ($SCCO_2$) parameters, including pressure, temperature, and saturation time on titanium dioxide (TiO_2) nanopowder dispersion in water-containing sodium hexametaphosphate (SHMP). The stability and morphology of TiO_2 particles dispersed in an aqueous solution were examined using a zeta potential instrument, dynamic light scattering, and transmission electron microscopy. As shown in the results, of particular interest, it was found that near $SCCO_2$'s pressure and saturation time had the strongest impact on TiO_2 dispersion in water-containing SHMP. This finding indicated that TiO_2's secondary average particle size was significantly reduced with an increase in near $SCCO_2$'s pressure and saturation time. Additionally, in the presence of SHMP, the zeta potential of the as-prepared dispersion solution reached −53.7 mV because of production of the larger negative static charge repulsion force (resulting from SHMP dissociation) on the TiO_2 particle surface. The secondary average size was 127 ± 68 nm, indicating good stability of TiO_2 dispersed in water containing an inorganic dispersant.



1. INTRODUCTION

Titanium dioxide (TiO_2) has been widely used for photocatalytic coating,[1,2] cosmetic,[3] antibacterial,[4] self-cleaning,[5] and biological[6] purposes. Furthermore, TiO_2's smaller particle size has a specific surface area effect,[7] resulting in outstanding light absorption, catalytic, and magnetic qualities. However, the small particle size is easily agglomerated because of van der Waals forces,[8] decreasing the stability of the TiO_2 dispersion solution and making it difficult to detect the advantages of the small particle size.[9] Therefore, the process to reduce the secondary average particle size and enhance the stability of TiO_2 dispersion solution is a very important topic in application sectors.

Generally, the dispersion processes involve three steps: wetting, mechanical dispersion, and stability. In order to understand TiO_2 dispersion in solution, it is essential to understand the formation and properties of the solid−liquid interface. Dispersion may be defined as a two-phase system, in which one is the dispersion of the small particle phase and the other is the continued fluid phase. Following particle wetting, a mechanical process, such as ultrasonic dispersion,[10] is usually required to complete their separation. Typically, a mechanical method, such as a continuous stirring recirculating media mill,[11] is applied to disperse the wetted particles into a separating unit. Ultrasonic waves have also been proven as useful tools for dispersing nanoparticles and eliminating agglomeration in aqueous suspensions.[12] Ultrasonic irradiation generates shock waves by causing cavitation collapse, leading to interparticle collisions. The agglomerated particles thus become eroded and split by the collisions. Many studies have applied ultrasonic wave to disperse TiO_2 particles in various solutions for application in different fields.[13−18]

Supercritical fluids (SCFs) are involved in numerous industrial processes and have a potentially wide field of new applications.[19] The SCF has both liquid- and gas-like properties, so that it concurrently exhibits good diffusion and wettability. Additionally, SCFs have lower surface tensions, resulting in faster permeations than those seen with a liquid.[20] As a result, a SCF dispersion process was developed in order to separate the aggregated particles. The supercritical carbon dioxide ($SCCO_2$) dispersing method was first studied by Kamiwano et al.[20] for dispersing carbon black particles in water without dispersants. The results showed that the samples of 2 wt % carbon black were uniformly dispersed throughout the solutions after standing for 100 h and had a secondary average particle size of <5 μm. Cheng et al.[21] used $SCCO_2$ to disperse aminoanthraquinone red, green 36, and blue 15:6 organic pigments in propylene glycol monomethyl ether acetate (PGMEA) in which the organic pigment concentration was 0.001 wt % in order to obtain secondary average particle sizes of 178.5, 93.5, and 188.7, respectively, in the dispersion solution. Wu et al.[22] used $SCCO_2$

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to disperse 1 wt % violet 23 organic pigment in PGMEA. They found that under the favorable conditions of 328.2 K and 20 MPa, the secondary average particle size of pigment dispersion containing dispersants in PGMEA was as small as 175 nm. Cheng and Wu[23] studied a cyclohexanone and PGMEA mixture as a binary solvent for assisting $SCCO_2$ dispersion and stabilizing organic nanoparticles in the presence of a polyester/polyamine copolymer as a capping agent. As shown in the results, a secondary average particle sizes of 59 and 64 nm were obtained for diketopyrrolopyrrole (red 254) and copper phthalocyanine (green 36) organic pigments, respectively.

After dispersing the wetted particles into a separated unit, sufficient stability should be maintained for a long time for application purposes. Many studies have focused on the TiO_2 particle dispersion stability in water. Mou et al.[24] studied the TiO_2 dispersion solution's solubility by adding ethanol, tetrahydrofuran, polyvinylpyrrolidone (PVP), and sodium hexametaphosphate (SHMP) as dispersants. The results showed that SHMP and tetrahydrofuran as dispersants were the most stable ones. Almusallam et al.[25] explored the stability of TiO_2 particles suspended in various aqueous solutions with and without salicylic acid as an organic contaminant. They found that stable TiO_2 dispersion solution could be obtained under basic solution conditions. However, when changing the pH values of the solution from basic to acidic, it was observed that TiO_2 particles aggregated at pH values below the isoelectric point.[26] It was also shown that TiO_2 aggregation was accelerated by an increase in the concentration of particles in solution. Mahlalela et al.[27] examined the stability of the dispersion solution by using different conducting liquids (deionized water, NaCl, $CaCl_2$, and $MgCl_2$) in the various solutions with different pH values. Agglomeration and zeta potentials were influenced by ionic strength, electrolyte type, and the presence of dyestuff. Tsai et al.[28] investigated SHMP and polyacrylic acid (PAA) dispersant effects on TiO_2 dispersion stability. The results illustrated that the SHMP was more stable than PAA for facilitating TiO_2 dispersion in water. In addition, ammonium polyacrylate ($PAA-NH_4$) has been investigated and compared with respect to the dispersion stabilities of TiO_2 powders with different particle sizes and surface chemistries in aqueous suspensions containing a common water-based dispersant.[29]

According to the studies described in the literature, the present study examined the use of near $SCCO_2$ dispersing TiO_2 nanopowder in water-containing SHMP as a dispersant, which could be called as a green process because the used materials are nontoxic chemicals. The effects of near $SCCO_2$ conditions, including pressure, temperature, and saturated time, on the stability and morphology of TiO_2 particles dispersed in aqueous solution was examined by zeta potential instruments, a pH meter, dynamic light scattering (DLS), transmission electron microscopy (TEM), and ultraviolet−visible absorption spectroscopy (UV−vis) associated with high-speed centrifugation and natural sedimentation in this study.

2. RESULTS AND DISCUSSION

2.1. Ratio of the Dispersant to TiO_2 and Effect of the pH Value on TiO_2 Dispersion Solution. Figure 1 shows that the zeta potential of dispersed TiO_2 in water varied with different dispersant concentrations under specified conditions of near $SCCO_2$. As observed in the figure, when the ratio of the dispersant is two times that of TiO_2 in weight percentage, the most stable dispersion solution exists because SHMP in water has been dissociated into negatively charged phosphate ions and adsorbed on the surface of TiO_2 particles to form a perfect electrical double layer. A small amount of inorganic dispersants cannot form an effective electrical double layer on the surface of TiO_2 particles, indicating that the electrostatic repulsion force is small, which results in unstable TiO_2 dispersion in the solution; however, an excess amount of inorganic dispersants would compress the electrical double layer on the surface of TiO_2 particles leading to a low negative zeta potential. Therefore, the weight ratio of the dispersant to TiO_2 was determined as 2/1 in this study.

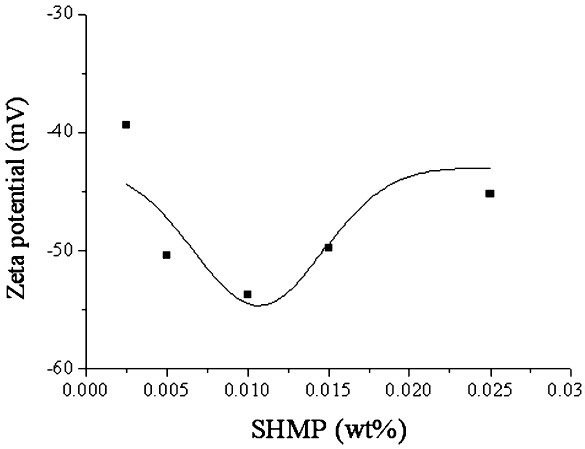


Figure 1. Zeta potential varying with concentration of the SHMP dispersant in 0.005 wt % TiO_2 solution after being dispersed via $SCCO_2$ under conditions of 35 °C, 1200 psi, and a saturation time of 30 min, in which the residual CO_2 in the TiO_2 dispersion solution was removed with a ultrasonic bath for 10 min after depressurizing.

In addition, the effect of pH values on zeta potential and the secondary average particle size estimated by DLS, for the dispersion of 0.05 wt % TiO_2 in solution with 0.1 wt % SHMP through near $SCCO_2$ under conditions of 35 °C, 1200 psi, and a saturation time of 30 min, is shown in Figure 2. As seen in the figure, it was found that the maximum negative zeta potential reached −53.7 mV at a pH of 6.25, corresponding to a minimum secondary average particle size of about 200 nm. This is because the acidic conditions cause $TiOH_2^+$ formation on the TiO_2 particles' surfaces; in the meantime, adsorption of phosphate ions occurs, resulting in a decrease in the negative charge on

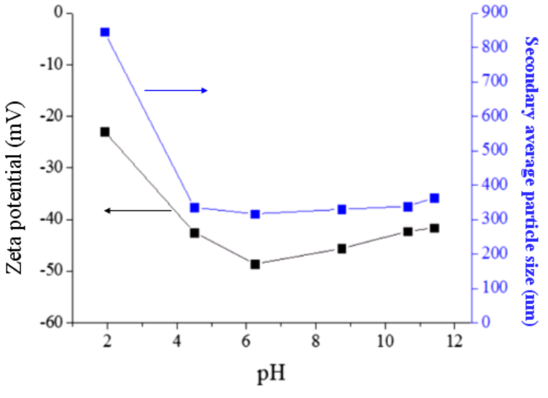


Figure 2. Zeta potential (black) and the secondary average particle size (blue) estimated by DLS of dispersed 0.005 wt % TiO_2 in water varying with the pH value of dispersion solution containing 0.01 wt % SHMP through $SCCO_2$ under the conditions of 35 °C, 1200 psi, and a saturation time of 30 min.

particles' surface. In other words, with an increase in the pH value, the TiO^- formation on the surface of TiO_2 particles would couple with the adsorbed phosphate ion to enhance negative charges on TiO_2 particles' surfaces, thus inducing dispersed solution stabilization. The Na^+ ion in the solution would also increase and absorb the negative charge on the TiO_2 surface, causing a decrease in the electrical double layer thickness and resulting in an unstable TiO_2 dispersion solution.

2.2. Effects of Near $SCCO_2$ Conditions on Dispersion of TiO_2 in Water. *2.2.1. Temperature.* In this study, we changed the $SCCO_2$ temperature in the dispersion process at a pressure of 1200 psi and the saturation time of 30 min followed by CO_2 removal in the dispersion solution using an ultrasonic bath for 10 min after depressurization. As seen in Figure 3, the temperature had a significant effect on the secondary average particle size of the dispersed TiO_2 in solution. As the temperature increased, the secondary average particle size of TiO_2 was decreased to 292 ± 4 nm at 55 °C followed by an increase in particle size to 325 ± 16 nm at 65 °C, indicating that the temperature should be optimized for TiO_2 dispersion in water through near $SCCO_2$. This process occurs because the elevated temperature can input energy and disrupt van der Waals forces between the particles followed by enhancement of particle mobility in the solution leading to formation of smaller and more uniform secondary average particle sizes; in contrast, an increase in temperature would reduce carbon dioxide solubility in water,[30] which would yield in weakening of aggregated TiO_2 particle dispersion by near $SCCO_2$.

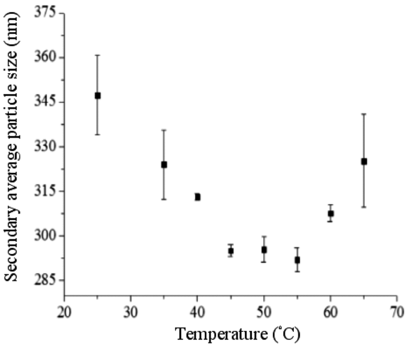


Figure 3. Secondary average particle size estimated from DLS of 0.005 wt % TiO_2 dispersion solution involving 0.01 wt % SHMP as a function of temperature of $SCCO_2$ under a pressure of 1200 psi and a saturation time of 30 min.

In order to further understand the temperature effects of near $SCCO_2$, we increased the TiO_2 concentrations in solution from 0.005 to 0.1 wt % in addition to selecting three different temperatures: (1) 25; (2) 55; and (3) 65 °C. As estimated from the TEM images shown in Figure 4, the secondary average particle sizes of dispersed TiO_2 in water by near $SCCO_2$ were 210 ± 135, 184 ± 81, and 207 ± 153 nm at the temperatures of 25, 55, and 65 °C, respectively. This suggests that applying energy to enhance separation of aggregated particles and solubility of near $SCCO_2$ in water would be traded for a smaller secondary average particle size of dispersed TiO_2 in solution.

2.2.2. Pressure. At a temperature of 55 °C and a saturation time of 30 min, we changed the pressure of near $SCCO_2$ in the dispersion process followed by CO_2 removal from the dispersion solution using an ultrasonic bath for 10 min. As shown in Figure 5, with an increase in pressure from 1200 to 4000 psi, the secondary average particle size was reduced from 292 ± 4 to 237 ± 6 nm as measured by DLS. It was indicated that higher near $SCCO_2$ pressure was favorable for the formation of smaller TiO_2 particles in solution. This process probably occurs because an elevation in pressure leads to an increase in CO_2 solubility in water, resulting in facilitating near $SCCO_2$ penetration into the pores of aggregated particles in solution. Additionally, Figure 6 shows the TEM of dispersed TiO_2 particles in solution under different near $SCCO_2$ pressures. As exhibited in the images, the secondary average particle size of thedispersed TiO_2 particle decreases with increasing near $SCCO_2$ pressure. When the pressure was increased from 2000 to 4000 psi, the secondary average particle size of dispersed TiO_2 particle was reduced from 165 ± 98 to 148 ± 68 nm. The standard deviation was decreased, indicating that the narrow particle size distribution of dispersed TiO_2 in solution could be obtained by increasing the pressure of near $SCCO_2$.

2.2.3. Saturation Time. Figure 7 illustrates the effect of near $SCCO_2$ saturation time on the secondary average particle size of dispersed TiO_2 particles in water, in which CO_2 pressure and temperature in addition to the time of CO_2 removal from the dispersion solution after ultrasonication were 4000 psi, 55 °C, and 10 min, respectively. As determined from the figure, an increase in saturation time from 0 to 120 min led to a reduction in the secondary average particle sizes of dispersed TiO_2 in solution from 418 ± 22 to 237 ± 9 nm as determined by DLS. This finding indicated that more of the near $SCCO_2$ permeated the pores in-between TiO_2 particles as the saturation time increased, resulting in full wetting of aggregated particles in solution. Meanwhile, we also found that the secondary average particle size of TiO_2 in solution would present a constant trend when the saturation time of near $SCCO_2$ reached 30 min, indicating that the agglomerated particle pores were completely filled with near $SCCO_2$. Figure 8 shows the TEM of dispersed TiO_2 in solution with near $SCCO_2$ at different saturation times. As observed from the figure, the secondary average particle size of dispersed TiO_2 in solution containing near $SCCO_2$ decreased with an increase in saturation time. When the saturation time was increased from 5 to 120 min, the average particle size of dispersed TiO_2 particles in solution through near $SCCO_2$ was reduced from 201 ± 135 to 149 ± 65 nm as estimated by TEM.

2.3. Stability of TiO_2 Dispersion Solution. The UV−vis light absorption associated with centrifugation was used to examine stability of dispersed TiO_2 in solution without and with inorganic dispersants via near $SCCO_2$ in this study. Figure 9 presents the UV−vis light absorption spectra of four samples before and after centrifugation at a rotational speed of 3000 rpm for 30 min. As observed from Figure 9d, the UV−vis light absorption value of dispersed TiO_2 in water without dispersants by only magnetic stirring for one day was the lowest because of aggregation seriously leading to particle precipitation. The UV−vis light absorption spectra of the sample dispersed by near $SCCO_2$ in the absence of dispersants is shown in Figure 9c, in which the absorption value was obviously higher than the sample without dispersion by $SCCO_2$, resulting from TiO_2 particles suspended in water stably.

We further investigated the UV−vis light absorption of TiO_2 with and without dispersion by near $SCCO_2$ in the presence of SHMP. As shown in Figure 9a,b, the absorption peak was blue-shifted[31] for the sample dispersion by near $SCCO_2$, indicating that the secondary average particle size of dispersed TiO_2 in water was reduced in order to induce an absorption peak shift to a shorter wavelength. This could be used to demonstrate that the

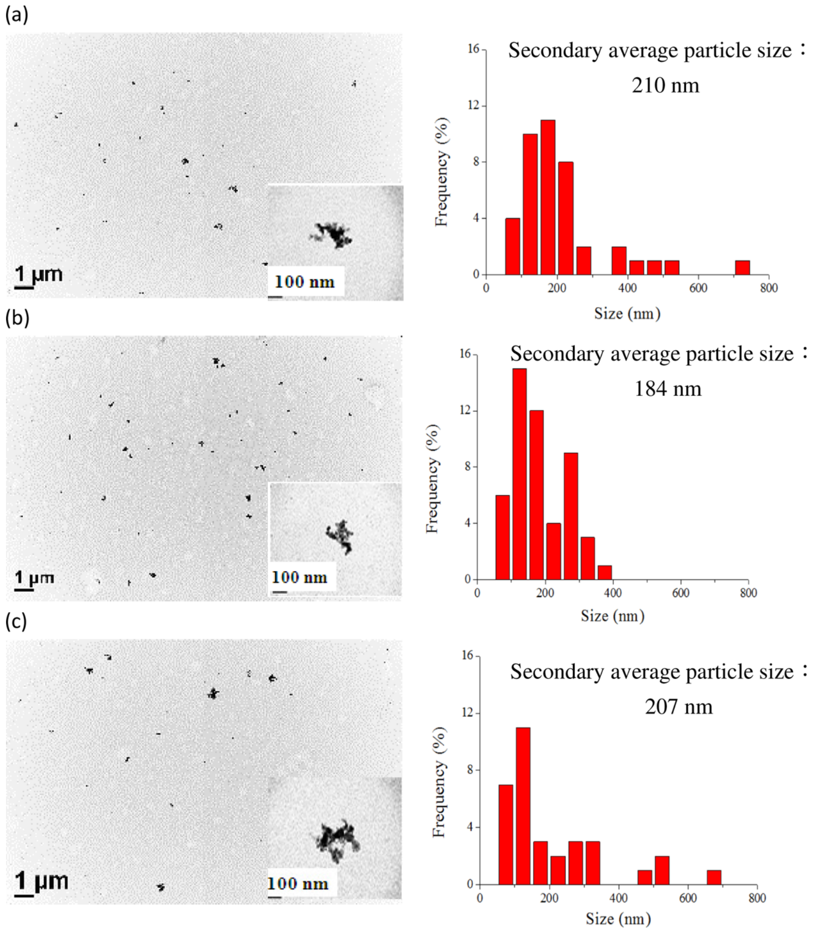


Figure 4. TEM images (1) and particle size distribution (2) calculated from TEM of dispersed 0.1 wt % TiO_2 in water containing 0.2 wt % SHMP through $SCCO_2$ under temperatures of (a) 25, (b) 55, and (c) 65 °C, respectively, as well as at a pressure of 1200 psi and a saturation time of 30 min. The inset is the morphology of aggregated TiO_2 particles in solution.

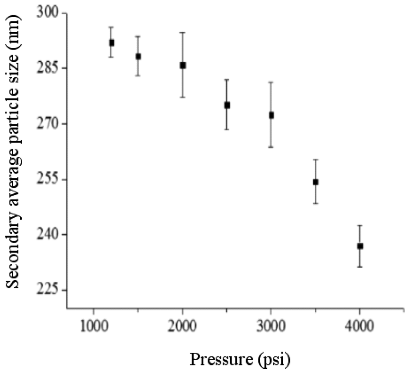


Figure 5. Secondary average particle size estimated from DLS of 0.005 wt % TiO_2 dispersion solution involving 0.01 wt % SHMP varying with pressure of $SCCO_2$ under a temperature of 55°C and a saturation time of 30 min.

near $SCCO_2$ is an effective method for TiO_2 dispersion in water with inorganic dispersants.

Figure 10 shows photographs of the natural sedimentation experiment in which sample (a) was made from 0.1 wt % TiO_2 in water; sample (b) was prepared from blending 0.1 wt % TiO_2 and 0.2 wt % SHMP in water; sample (c) was fabricated by mixing 0.1 wt %TiO_2 and 0.2 wt % SHMP and dispersed by near $SCCO_2$; and sample (d) was water for comparison, as well as the $SCCO_2$ dispersion conditions were 55 °C, 4000 psi, and 30 min saturation time. As observed from the photographs, without inorganic dispersants in water, the TiO_2 particles had completely precipitated in the bottom of the scintillation flask after dispersion for about one day; on the other hand, adding SHMP could significantly enhance dispersed TiO_2 stability in solution, which clearly indicated that the TiO_2 dispersion solution with dispersants was more stable than that without dispersants. This difference resulted from smaller secondary average particle size of dispersed TiO_2 in solution through near $SCCO_2$ in the presence of dispersants. The lifetime of dispersed TiO_2 in water-containing SHMP was over two weeks in this study.

3. CONCLUSIONS

In this study, near $SCCO_2$ was successfully employed to disperse TiO_2 particles in water involving inorganic dispersants. First, the amount of the SHMP dispersant was determined by zeta potential analysis. The effects of different temperatures, pressures, and saturation times on the dispersed TiO_2 in solution through near $SCCO_2$ were then examined by DLS and TEM. Finally, the stability of dispersed TiO_2 in solution was characterized via UV−vis light absorption associated with centrifugation and natural sedimentation method. As shown in the results, we summarize the study by highlighting several significant findings:

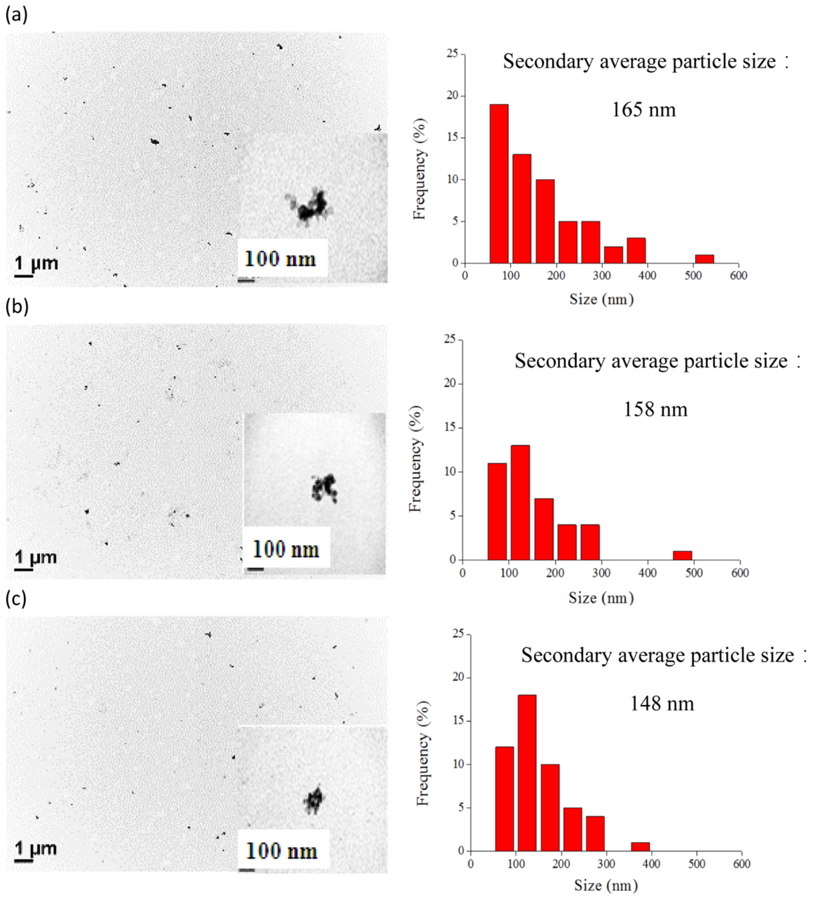


Figure 6. TEM images (1) and particle size distribution (2) calculated from TEM of dispersed 0.1 wt % TiO_2 in water containing 0.2 wt % SHMP through $SCCO_2$ under pressures of (a) 2000, (b) 3000, and (c) 4000 psi, respectively, as well as at a temperature of 55 °C and a saturation time of 30. The inset is the morphology of aggregated TiO_2 particles in solution.

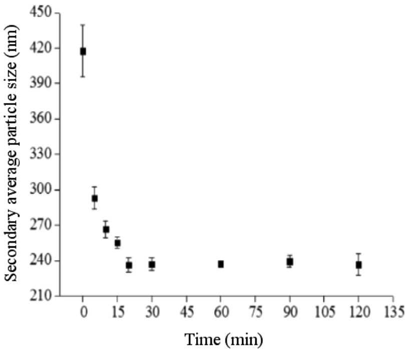


Figure 7. Secondary average particle size estimated from DLS of 0.005 wt % TiO_2 dispersion solution involving 0.01 wt % SHMP varying with saturation time of $SCCO_2$ under a temperature of 55°C and a pressure of 4000 psi.

(1) As the addition of SHMP was twice the concentration of TiO_2 in weight, the maximum zeta potential of the dispersion solution was −53.7 mV as measured by a zeta potential instrument, suggesting that the SHMP as a dispersant was well dissociated from the phosphate ions and adsorbed on the surface of the TiO_2 particles. This finding implied that TiO_2 dispersion in solution had a large negative charge from the electrostatic repulsive force and had good stability at a pH of 6.25 in order to prevent TiO_2 particle precipitation under operating conditions of near $SCCO_2$.

(2) When the concentration of TiO_2 in solution with SHMP was 0.1 wt %, the secondary average particle size was 366 ± 295 and 148 ± 68 nm as measured by TEM before and after dispersion by near $SCCO_2$, respectively, indicating that near $SCCO_2$ was validated as having penetrated the pores of aggregated particles, and then rapidly depressurized to effectively separate aggregated particles in solution.

(3) It was found that applying energy to promote separation of aggregated TiO_2 particles and solubility of CO_2 in water should be compromised, namely, the temperature of near $SCCO_2$ must be optimized in this work.

(4) Raising the pressure could increase the density of near $SCCO_2$ in order to elevate wettability of the near SCF on the surface of particles and enhance the separation of aggregated TiO_2 particles during the rapid depressurization process.

(5) As analyzed from DLS, when the concentration of TiO_2 ranged from 0.005 to 0.1 wt %, a 30 min $SCCO_2$ saturation time was enough to completely wet the surface of the aggregated particles.

(6) As measured by natural sedimentation, the storage time of the as-prepared 0.1 wt % TiO_2 dispersion solution could be over two weeks.

Hopefully, the above results promise to facilitate fabrication of colloid inorganic oxide suspension through a green process.

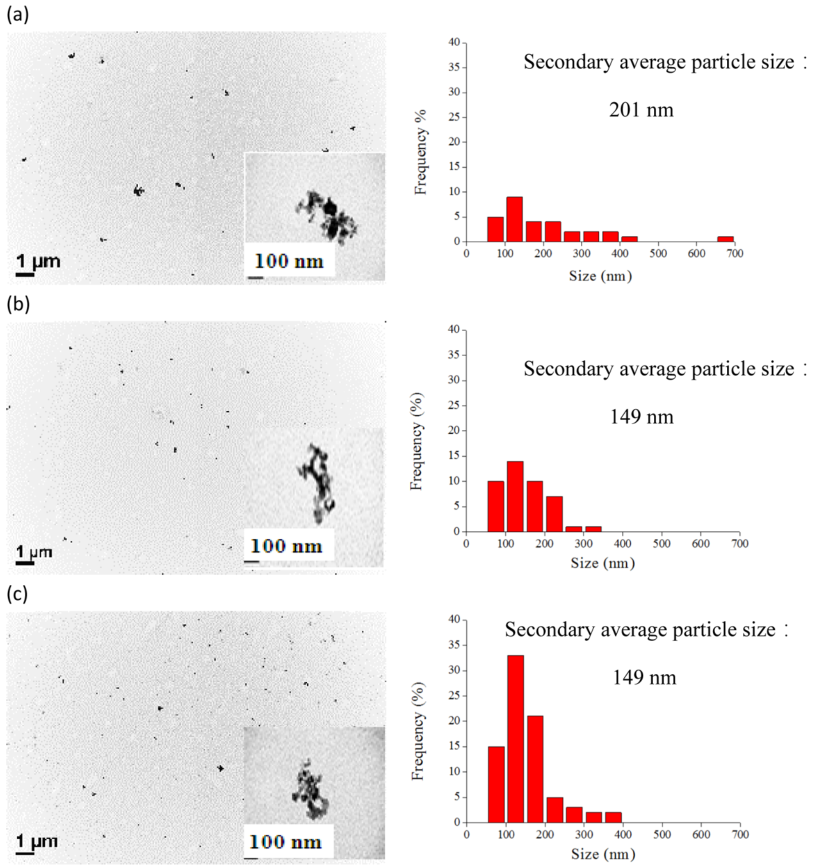


Figure 8. TEM images (1) and particle size distribution (2) calculated from TEM of dispersed 0.1 wt % TiO_2 in water containing 0.2 wt % SHMP through SCCO2 under the saturation times of (a) 5, (b) 20, and (c) 120 min, respectively, as well as at a temperature of 55 °C and a pressure of 4000 psi. The inset is the morphology of aggregated TiO_2 particles in solution.

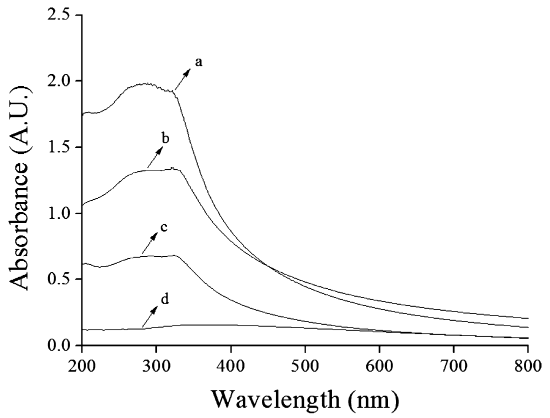


Figure 9. UV–vis light absorption spectra of 0.005 wt % TiO_2 in water (a) with both 0.01 wt % SHMP and dispersion by $SCCO_2$, (b) with 0.01 wt % SHMP but without dispersion by $SCCO_2$, (c) without SHMP but with dispersion by $SCCO_2$, and (d) without both SHMP and dispersion by $SCCO_2$. The conditions of $SCCO_2$ are a temperature of 55 °C, a pressure of 4000 psi, and a saturation time of 30 min.

4. MATERIALS AND METHOD

4.1. Chemicals. TiO_2 powder (P25) with a primary average particle size of 21 nm and a spherical shape was purchased from Degussa. SHMP (99%) was used as an inorganic surfactant (SHOWA) in order to enhance dispersion stability. Deionized water (18.1 Ω), which was mechanically filtered and processed to remove impurities, was used as a continuous phase. Hydrochloric acid (32.4%) and sodium hydroxide (96%) were obtained from Choneye Pure Chemicals and SHOWA, respectively. Both were diluted to 0.1 wt % for adjusting the pH values of the dispersion solutions.

4.2. Determination of the Ratio of the Dispersant to TiO_2 in Dispersion Solution. In order to stabilize the dispersed TiO_2 and prevent it from precipitating in water under near $SCCO_2$ operating conditions, the experiments were conducted by varying the amounts of SHMP from 0.0025 to 0.025 wt % (0.0025, 0.005, 0.01, 0.015, and 0.025 wt %) in 50 mL deionized water containing 0.005 wt % TiO_2 with continuous magnetic stirring (Ciamarec 2 Thermolyne, 950 rpm) for 24 h followed by transfering to a 300 mL supercritical vessel through a peristaltic pump (Cole-Parmer Masterflex L/S) at normal atmospheric pressure and ambient temperature. A schematic diagram of the experimental system used in this study is shown in Figure 11. For each experiment, the supercritical vessel was operated according to the following procedure; after introducing 50 mL of the dispersion solution, the supercritical vessel was closed, and the temperature was controlled at 35 °C via a circulating water bath (Deng Yang Water Bath D-606). The carbon dioxide concentration was then increased up to 1200 psi in the supercritical vessel using an air driven pump (Haskel ALG-60), followed by maintaining it at this pressure for 30 min, and then followed by rapid depressurization of the near $SCCO_2$ to disperse the TiO_2 particles in the solution. In order to remove the residual carbon dioxide in the TiO_2 dispersion solution after the near $SCCO_2$ dispersion process, an ultrasonic bath was used for 10 min before characterization. The pH of the TiO_2

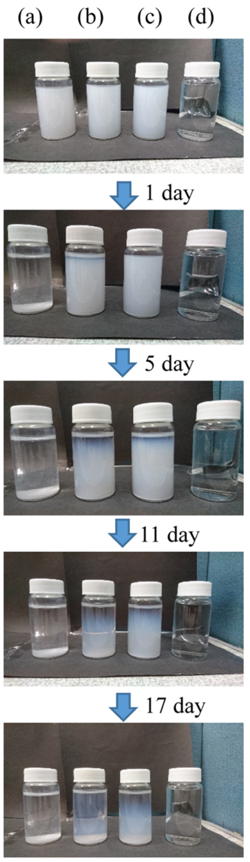
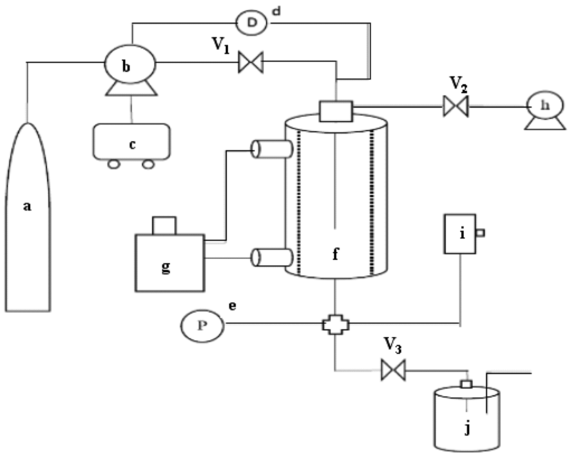


Figure 10. Photographs of the natural sedimentation experiment for the samples: (a) TiO_2 in water; (b) TiO_2 and SHMP in water; (c) TiO_2 and SHMP in water after being dispersed by $SCCO_2$; and (d) water for comparison.



Nomenclature:

a. CO_2 storage tank	b. CO_2 pump (ALG-60)	c. Air compressor
d. Digital multifunctional meter	e. Pressure meter	f. Pressure vessel
g. Water circulation bath	h. Peristaltic pump	i. Safety valve
j. Collection bottle	V_1, V_2, and V_3: Needle valve	

Figure 11. Schematic diagram of experimental apparatus in this study.

dispersion solution was varied by addition of sodium hydroxide or hydrochloric acid. In addition, a zeta potential instrument (Malvern Zetasizer Nano Series) was used for measuring the zeta potential of the TiO_2 particles in the dispersion solution after the pH was measured using a pH meter (SUNTEX SP-701).

4.3. Effects of Near SCF Conditions on TiO_2 Dispersed in Water with the SHMP Dispersant. The experimental samples were prepared by using 0.01 wt % SHMP in 50 mL deionized water, followed by adding 0.005 wt % TiO_2 with continuous magnetic stirring for 24 h. The subsequent procedure was similar to the dispersion method used in the previous experiment, but the near $SCCO_2$ dispersion temperature was varied from 25 to 65 °C, the pressure was regulated from 1200 to 4000 psi, and the saturation time was limited between 0 and 120 min. We used the same conditions and steps to disperse TiO_2 in solution in three separate experiments.

A DLS analyzer (Brookhaven 90Plus Particle Sizer) was used for measuring the secondary average particle size and dispersion solution distribution. For further validation, the dispersed TiO_2 particles in solution were characterized by TEM (JEOL JEM-1200CX). The TEM images of dispersed TiO_2 particles were analyzed with ImageJ.[31]

4.4. Stability of As-Dispersed TiO_2 in Water through Near $SCCO_2$. The stability of the dispersed TiO_2 in solutions with and without dispersants was evaluated by ultraviolet−visible absorption spectroscopy (UV-1800 SHIMADZU) together with high-speed centrifugation (CN-3302 HSIANG-TAI) in addition to natural sedimentation.

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Notes

The authors declare no competing financial interest.

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