Effect of Nanoplatelet Size on the Colloidal Stability of Coupled Nanocomposite of TiO₂ and Zirconium Phosphate Nanoplatelets

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The aggregation and sedimentation of nanoparticles affect the dispersion stability and application of nanosuspension. TiO₂ nanoparticles were coupled on zirconium phosphate (ZrP) disks with different diameters to study the effect of ZrP size on the dispersion stability of nanocomposite suspensions. Four suspensions, namely, TiO₂ nanosuspensions and three exfoliated TiO₂–ZrP nanocomposite suspensions with diameters of 729.6, 1004.5 and 1168.5 nm were prepared. Dispersion stability was compared among the suspensions. The zeta potential, viscosity, particle morphology and particle size distribution of the suspensions were also tested to analyze the stability mechanism of the nanocomposite suspensions. Results of the stability tests within 100 days show that the TiO₂–ZrP nanocomposite suspensions exhibited slower sedimentation, higher ultraviolet-visible absorbance, smaller light transmission and backscattering variation and lower Turbiscan Stability Index than those of the pure TiO₂ suspension. Among the samples, the smallest TiO₂–ZrP nanocomposites exhibited improved stability. The absolute zeta potential and viscosity of each nanocomposite suspension were comparable with one another, but higher than those of the TiO₂ suspension. The transmission electron microscope images and particle size distribution suggest that TiO₂–ZrP can better control the aggregation of small TiO₂ nanoparticle clusters.

Keywords: colloidal stability, nanocomposite, TiO₂, zirconium phosphate, size, aggregation.

1. INTRODUCTION

Extensive research on nanoparticles has been conducted in recent years as they have many potential applications. For example, TiO₂ nanoparticles have several advantages such as high chemical stability, high catalytic activity and nontoxicity; as such these particles exhibit potential for applications in photocatalysts [1, 2], solar cells [3], pollutant removal [4, 5] and cold thermal energy storage (TES) [6–11].

However, suspended nanoparticles tend to aggregate because of their high specific surface area and high surface energy, restricting their development for potential application. Thus, nanoparticles should be uniformly dispersed in the base fluids and maintained as stable in the suspensions. Most studies have focused on using surfactants and polymers as dispersants to stabilize nanoparticle suspensions against aggregation [12–20]. For TiO₂ nanoparticles, several types of surfactants have been used to improve the stability of nanosuspensions in previous studies, such as sodium dodecyl benzene sulfonate (SDBS) [21–23], sodium dodecyl sulfate (SDS) [24–26], cetyltrimethylammonium bromide (CTAB) [24, 27, 28] and polyvinylpyrrolidone (PVP) [29, 30]. The ionic surfactants, including SDBS, SDS and CTAB, lead to electrostatic repulsion between particles, which significantly reduced the particle agglomeration owing to van der Waals forces of attraction. Nonionic surfactants, such as PVP, caused a hindrance between the particles, which can inhibit the nanoparticle aggregation to maintain good suspension stability.

Our preliminary experimental studies indicate that the size of TiO₂ nanoparticle aggregation would decrease through the hindrance effect caused by zirconium phosphate (ZrP) nanoplatelets without the use of surfactants [31]. We previously proposed a new method to improve TiO₂ suspension stability by coupling TiO₂ nanoparticles on ZrP nanoplatelets [32]. Particle size affects dispersion stability [33, 34]. However, the effect of nanoplatelet size on dispersion stability remains unknown and the mechanism for stability improvement is still unclear.

In this study, the dispersion stability of TiO₂–ZrP nanoparticle suspensions with different diameters is investigated and compared with that of TiO₂ suspension. The effects of nanoplatelet size and dispersion mechanism of TiO₂–ZrP nanosuspensions were analyzed.

2. EXPERIMENTAL DETAILS

2.1. Synthesis of ZrP disks

The hydrothermal method was used to synthesize ZrP disks. Phosphoric acid (H₃PO₄, analytical reagent, Guangzhou Chemical Reagent Factory, China) and zirconium oxychloride octahydrate (ZrOCl₂·8H₂O, analytical reagent, Tianjin Fu Chen Chemical Reagent Factory, China) were the main reactants. ZrP disks of different diameters can be synthesized by controlling the
reaction duration time and temperature [35]. A sample of 10.0 g ZrOCl₂·8H₂O was mixed with 100 ml of H₃PO₄ sealed into the Teflon pressure vessel and heated at 200 °C for 10, 15 and 24 h to prepare ZrP of different sizes. After the reaction, the final products were identified as ZrP (10 h), ZrP (15 h) and ZrP (24 h) (Fig. 1). A scanning electron microscope (SEM, S3400N, Hitachi, Japan) was used to observe the shape and the approximate particle size of ZrP disks. The average diameters of the disks were different.

![SEM images: a – ZrP (10 h); b – ZrP (15 h); c – ZrP (24 h)](image)

The size distribution (Fig. 2), average diameter and polydispersity (Table 1) of the exfoliated platelets were measured by using a dynamic light scattering (DLS) instrument (Delsa Nano C, Beckman Coulter Instruments Corporation, Fullerton, California) [36]. The results show that the ZrP disks have different sizes but similar size distributions and polydispersities. The small polydispersity and narrow size distribution indicated that these three kinds of ZrP disks have good uniformity [37].

![Size distribution of ZrP nanoplatelets](image)

**Fig. 1.** SEM images: a – ZrP (10 h); b – ZrP (15 h); c – ZrP (24 h)

**Fig. 2.** Size distribution of ZrP nanoplatelets

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average size</th>
<th>Polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrP (10 h)</td>
<td>729.6 nm</td>
<td>24.7 %</td>
</tr>
<tr>
<td>ZrP (15 h)</td>
<td>1004.5 nm</td>
<td>27 %</td>
</tr>
<tr>
<td>ZrP (24 h)</td>
<td>1168.5 nm</td>
<td>28.7 %</td>
</tr>
</tbody>
</table>

**Table 1.** Size characterization of ZrP nanoplatelets

2.2. Coupling TiO₂ on ZrP disks

The ZrP loading TiO₂ (TiO₂ – ZrP) was synthesized using a three-step approach [19]. 3-(Triethoxysilyl) propyl isocyanate (IPTS, C₁₀H₂₁NO₃Si, AR, Alfa Aesar), a silane coupling agent, was used to combine TiO₂ and ZrP. Dimethyl sulfoxide (DMSO, C₅H₄OS, AR, Tianjin Damao Chemical Reagent Factory, China) was utilized as the solvent. The morphology of TiO₂–ZrP was observed using a JEOL-2100 transmission electron microscope (TEM), as shown in Fig. 3 a, b and c. The average diameter of anatase TiO₂ (Alfa Aesar) was 32 nm, as illustrated in Fig. 3 d.

![SEM images: a – TiO₂ – ZrP (729.6 nm); b – TiO₂ – ZrP (1004.5 nm); c – TiO₂ – ZrP (1168.5 nm); d – the TEM image of TiO₂](image)

**Fig. 3.** The SEM images: a – TiO₂ – ZrP (729.6 nm); b – TiO₂ – ZrP (1004.5 nm); c – TiO₂ – ZrP (1168.5 nm); d – the TEM image of TiO₂

2.3. Preparation of TiO₂–ZrP nanosuspensions

Two kinds of samples, namely, TiO₂ nanosuspension and exfoliated TiO₂–ZrP nanosuspension, were prepared for the experiments. TiO₂ nanosuspension was prepared by adding 1 g of TiO₂ into 100 ml of deionized water. TiO₂–ZrP suspension was prepared by adding 3 g TiO₂–ZrP (mass ratio of 1:2) into 100 ml of DI water. TiO₂–ZrP was then exfoliated into nanoplatelets in the suspensions. The mass ratio of the TiO₂ nanoparticles of all the samples was 1 wt.%, and the mass ratio of ZrP was 2 wt.%

3. RESULTS AND DISCUSSION

3.1. Stability experiment

Fig. 4 shows the sedimentation image of samples and UV-vis absorption spectra after 100 days. The height of the suspension decreases in the sequence of TiO₂–ZrP (729.6 nm), TiO₂–ZrP (1004.5 nm), TiO₂–ZrP (1168.5 nm) and TiO₂, with the height of TiO₂–ZrP (729.6 nm) remaining almost unchanged on the 100 th day. Ultraviolet-visible (UV-vis) absorption spectra (Fig. 4 b) were used to quantitatively evaluate the stability of the samples. The TiO₂–ZrP suspension had higher absorbance compared with the TiO₂ suspension. The absorbance of TiO₂–ZrP (729.6 nm) was approximately 6.67 % higher than that of the TiO₂–ZrP (1004.5 nm) suspension, and the
The absorption of TiO$_2$–ZrP (1004.5 nm) was 25% higher than that of the TiO$_2$–ZrP (1168.5 nm) suspension. The result shows that TiO$_2$–ZrP (729.6 nm) suspensions exhibited the optimal stability, and the decreasing sequence of suspensions is TiO$_2$–ZrP (729.6 nm), TiO$_2$–ZrP (1004.5 nm), TiO$_2$–ZrP (1168.5 nm) and TiO$_2$.

![Absorbance spectra](image)

**Fig. 4. a—sedimentation image of the samples; b—UV-vis absorption spectra**

A novel optical analyzer, Turbiscan Lab (Formulation, France) equipment, which can measure the dispersion state through multiple light scattering data, was used to analyze the sedimentation phenomenon [38]. In the test, the particle suspensions were transferred to a glass cylindrical cell (70 mm height and 27.5 mm external diameter) and analyzed using a light beam, which periodically scanned the sample from the bottom to the top. The transmission (T) and backscattering (BS) optical sensors received the light that goes across the sample and scattered backward synchronously. When sedimentation took place, the T profiles varied with the cell height over time. Fig. 5 shows the T and BS profiles obtained from Turbiscan Lab, which indicate the light percentage transmitted though and scattered by the sample versus the sample cell height for TiO$_2$–ZrP and TiO$_2$ suspensions. The x and y axes in the T diagram represent the sample cell height and the variation of transmitted light and backscattering throughout the sample cell. Obviously, TiO$_2$ (Fig. 5 d) exhibited high transmission at about 42 mm sample cell height, which indicates that TiO$_2$ showed rapid aggregation. On the contrary, TiO$_2$–ZrP maintained moderate and low transmission, suggesting its higher stability than TiO$_2$.

A quantitative analysis was conducted using the Turbiscan Stability Index (TSI) to estimate the suspension stability. This parameter is a statistical factor and its values are obtained as the sum of all processes taking place in the studied probe. The TSI values were calculated with the special computer program using the following equation [39]:

\[
\text{TSI} = \sqrt{\frac{\sum_{i=1}^{n}(x_i - x_{BS})^2}{n-1}},
\]

where $x_i$ is the mean backscattering for each minute of measurement, $x_{BS}$ is the mean $x_i$, and $n$ is the number of scans.

Fig. 6 shows the TSI values. Small TSI value represents better stability [39]. As the diameter of ZrP nanoplatelets decreased, the TSI value also decreased, indicating enhanced dispersion stability.

### 3.2. Zeta potential analysis

The possible reason for the stability difference is zeta potential. The relationship between suspension stability and zeta potential arises from the mutual repulsion that occurs between charged particles. For this reason, particles with high surface charge tend not to aggregate. Table 2 and Table 3 show the zeta potential values of the suspensions and the typically accepted corresponding relationship between zeta potential values and stability [40], respectively. As shown, the absolute zeta potential value of TiO$_2$ was in the unstable range (0, 15). The absolute zeta potential values of ZrP nanoplatelets (53.11 mV, 57.13 mV and 57.6 mV) were within the range (45, 60). After coupling TiO$_2$ on ZrP, the absolute zeta potential values of TiO$_2$–ZrP (49.12 mV, 50.14 mV and 55.9 mV) decreased slightly compared with ZrP but were still in the good stable range (45, 60). The results indicated that TiO$_2$–ZrP with a high surface charge is more difficult to aggregate and has better stability compared with TiO$_2$.

### 3.3. Aggregation size analysis

The viscosity and the aggregation size are important parameters that influence the particle sedimentation rate [41]. Fig. 7 shows the viscosity properties of the samples. The shear rate ranged from 1 s$^{-1}$ to 10$^{3}$ s$^{-1}$. The viscosity curve of TiO$_2$–ZrP slowly declined along with the shear rate increase. The viscosity of TiO$_2$ was much lower than that of the TiO$_2$–ZrP suspensions. In general, the aggregation sedimentation rate decreased along with the suspension viscosity increase [41]. Thus, TiO$_2$–ZrP suspension has better stability than TiO$_2$. However, the viscosity is not enough to explain the results of sedimentation experiment because the viscosities of TiO$_2$–ZrP (729.6 nm), TiO$_2$–ZrP (1004.5 nm) and TiO$_2$–ZrP (1168.5 nm) are almost the same, but their stabilities are different. Thus, aggregation size is another important factor that can affect the stability of the suspensions.

### Table 2. Zeta potential of TiO$_2$, TiO$_2$–ZrP and ZrP suspensions

<table>
<thead>
<tr>
<th>Samples</th>
<th>TiO$_2$ (729.6 nm)</th>
<th>TiO$_2$–ZrP (1004.5 nm)</th>
<th>TiO$_2$–ZrP (1168.5 nm)</th>
<th>ZrP (729.6 nm)</th>
<th>ZrP (1004.5 nm)</th>
<th>ZrP (1168.5 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z potential, mV</td>
<td>–14.92</td>
<td>–49.12</td>
<td>–50.14</td>
<td>–55.9</td>
<td>–53.11</td>
<td>–57.13</td>
</tr>
</tbody>
</table>
Fig. 5. T and BS versus sample height for: a – TiO$_2$ – ZrP (729.6 nm); b – TiO$_2$ – ZrP (1004.5 nm); c – TiO$_2$ – ZrP (1168.5 nm); d – TiO$_2$

Table 3. Zeta potential and associated suspension stability

<table>
<thead>
<tr>
<th>Z potential (absolute value, mv)</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Little or no stability</td>
</tr>
<tr>
<td>15</td>
<td>Some stability but settling lightly</td>
</tr>
<tr>
<td>30</td>
<td>Moderate stability</td>
</tr>
<tr>
<td>45</td>
<td>Good stability, possible settling</td>
</tr>
<tr>
<td>60</td>
<td>Very good stability, little settling likely</td>
</tr>
</tbody>
</table>

The TEM images of TiO$_2$–ZrP and TiO$_2$ were recorded on the 100th day to get a better look at the aggregation of the samples. As shown in Fig. 8, TiO$_2$ became large aggregations. In contrast, the TiO$_2$ aggregations distributed on the ZrP platelets was smaller because TiO$_2$ nanoparticles are fixed on the surface of the ZrP nanoplatelets, making them unable to aggregate into large particles.

Dynamic light scattering analysis is a common method used to measure the particle size distribution. Fig. 9 shows the particle size distribution of the TiO$_2$–ZrP and TiO$_2$ samples on the 0th and 100th day. The results show that aggregation appeared in TiO$_2$ and TiO$_2$–ZrP suspensions. Given that the primary size of the single TiO$_2$ particle is 30–60 nm, the particles in the pure TiO$_2$ suspension...
aggregated considerably to about 10 nm on the 0th day. The TiO$_2$–ZrP aggregation size was evidently smaller compared with that of TiO$_2$ aggregation as TiO$_2$ loaded on the ZrP nanosheets.

![Graph](image)

**Fig. 6. TSI values of TiO$_2$ and TiO$_2$–ZrP suspensions**

![Graph](image)

**Fig. 7. Viscosity of TiO$_2$–ZrP and TiO$_2$**

Table 4 shows that TiO$_2$ has more size distribution peaks and bigger aggregation size compared to TiO$_2$–ZrP on the 100th day. The aggregation sizes of TiO$_2$–ZrP (1168.5 nm), TiO$_2$–ZrP (1004.5 nm) and TiO$_2$–ZrP (729.6 nm) were 11368.5, 7240.1 and 5642.6 nm, respectively. The aggregation size decreased along with the diameter. Owing to the viscosity increment and aggregation size decrease, the sedimentation rate of TiO$_2$–ZrP slowed down compared with TiO$_2$. In addition, the sedimentation of smaller TiO$_2$–ZrP is even slower.

![TEM Images](image)

**Fig. 8. TEM images: a–TiO$_2$–ZrP (729.6 nm); b–TiO$_2$–ZrP (1004.5 nm); c–TiO$_2$–ZrP (1168.5 nm); d–TiO$_2$**

![Graph](image)

**Fig. 9. Particles size distributions: a–TiO$_2$–ZrP (729.6 nm); b–TiO$_2$–ZrP (1004.5 nm); c–TiO$_2$–ZrP (1168.5 nm); d–TiO$_2$ on the 0th and 100th day**

The experimental results of stability improvement achieved through coupling ZrP of different sizes can be explained by the effect of ZrP on controlling aggregation, and Brownian motion of particles. For the pure TiO$_2$ suspension, the zeta potential is low. Thus, the interparticle electrostatic repulsion cannot balance the van der Waals attraction, causing the particles to aggregate (Fig. 8 and Fig. 9) because they continually collide with each other owing to Brownian motion.
Consequently, the TiO$_2$ particle aggregations were large enough and settled down (Fig. 4) because gravity became significant. On the other hand, the well dispersion of particle aggregations may be maintained because of Brownian motion if they can be controlled to be small enough [34]. The ratio of gravitational to Brownian forces can be determined as follows

$$R_g = a^3 \Delta \rho g/(k_B T),$$

where $a$ is the radius of particles, $\Delta \rho$ is the density difference between the particles and the base fluid, $g$ is the gravitational acceleration, $k_B$ is the Boltzmann constant and $T$ is the temperature. The dispersion stability of suspension can be predicted using Eq. 2. If $R_g > 1$, particle (or aggregation) sedimentation can be expected, otherwise, the suspension is likely to be stable. Fig. 10 shows the plot of $R_g$ determined based on Eq. 2.

If the aggregation size is larger than 1430 nm, which is the case of pure TiO$_2$ suspension even at the first day (Table 4), then $R_g > 1$ and the aggregation will settle down because of gravity, as shown in Fig. 4. As for TiO$_2$–ZrP nanoplatelets, TiO$_2$ nanoparticles were fixed with ZrP, and the surface charge prevented the nanoplatelets to aggregate. The TiO$_2$–ZrP suspension stability were much better than that of TiO$_2$ suspension because the sizes of the three types of TiO$_2$–ZrP nanoplatelet were all smaller than 1002 nm even at day 100 (Table 4).

Moreover, smaller ZrP resulted to smaller particle aggregation of TiO$_2$–ZrP, thus indicating better dispersion stability (Fig. 10). There are two reasons, one is that the TiO$_2$ nanoparticles are fixed on ZrP and their aggregation is better controlled by smaller ZrP nanoplatelets, and the other is attributed to the steric stabilization effect of the ZrP nanoplatelets [31]. The number concentration of the smaller ZrP nanoplatelets is higher than that of larger ZrP nanoplatelets at the same ZrP mass concentration. Therefore, the smaller ZrP nanoplatelets better separated the particle aggregations and better control further aggregation at the same ZrP mass concentration.

2. The dispersion stability of TiO$_2$–ZrP suspensions increased along with the decreased in ZrP diameter because their aggregation is better controlled by smaller ZrP nanoplatelets. The first reason is that the TiO$_2$ nanoparticles are fixed on smaller ZrP nanoplatelets and the other reason is that there are more ZrP nanoplatelets for smaller ZrP nanoplatelets at the same ZrP mass concentration to separate the TiO$_2$ nanoparticles.

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![Fig. 10. Ratio of gravitational to Brownian forces versus particle size](image)

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