Composite Dispersion of Nanosized AlOOH in Liquid Phase

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TEM, SEM and laser particle size analysis were used to study hydrothermal crystallization and a charging composite dispersion of nanosized AlOOH, using a self-dispersed nanosized AlOOH crystal powder prepared by sol-hydrothermal method. The results show that the composite method can improve particle dispersion and stability in liquid. The improvement in the dispersion effect is attained by weakening the van der Waals force, reducing the particle surface energy through hydrothermal crystallization, and increasing the charge by partly dissolving the anions or cations at the crystal lattice surface. Based on these results, a mechanism for hydrothermal crystallization and a charging composite dispersion of nanosized AlOOH is proposed. The preparation of nanometer TiO2 and nanometer Al2O3 have been preliminarily studied using the composite dispersion method. [doi:10.2320/matertrans.MRA2008004]

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1. Introduction

The nanometer AlOOH powder, as an important inorganic functional power material, has wide potential application value. Its main application fields can be generalized as followings: nanometer aluminum oxide, fine ceramics, biological ceramics, high performance porous ceramic support, high performance non-toxic special flame retardant for polymer and so on.1) At present, the nanometer AlOOH powder was prepared by calcining Al(OH)3 or AlOOH gel which was obtained by controlled hydrolysis of inorganic salt and organic alkoxide of aluminum. But this method has a fatal shortcoming, which is the same with other precipitation method on preparing nanometer powders. Namely, aggregation phenomenon of nanoparticles occurred easily and results in increase of particle size. The composite dispersion method for preparation of metal oxide nanoparticles is an effective method for solving the question on nanoparticles dispersion.

The composite dispersion is a highly effective dispersing method that combines two or more advantages of other dispersion methods.2) The composite dispersion method commonly includes composites of:1) a mechanical dispersion and surface chemical modification dispersion, an ultrasonic dispersion and a surface chemical dispersion, high-energy treatment (corona charging) dispersion and a surface chemical dispersion, and so on. These composite methods are all used to overcome the physical dispersion problem associated with surface chemical dispersion, i.e., the re-agglomeration of nanoparticles that can easily occur once an external force is removed. However, surface chemical modification causes the nanoparticles to lose their original properties, which has a notable effect on their applications and may even produce extremely large negative effects at times. A surface modification and electrostatic composite dispersion can be used to increase the dispersion index of calcium carbonate and ultrafine talcum powder from 1 to 1.531–1.564 and 1.543–1.682, respectively, in air.3,4) However, this composite dispersion method only suits dispersions of nanoparticles in air. The hydrothermal techniques which surface modification and preparation of nanoparticles take place at the same time were employed to prepare the well-dispersed nanosized barium titanate powders. This technology uses hydrothermal crystallization to reduce the surface energy of the nanoparticles, thereby benefiting the dispersion of the particles.5,6) In addition, the hydrothermal crystallization technique uses simultaneous surface modification methods to further improve the particle dispersion. However, only a small volume of literature that reports on dry nanosized powders which are obtained by drying metal oxide nanoparticles containing hydroxyls from aqueous solution, and can self disperse in liquids without any surface modifying agents, dispersants, additives or other special conditions (e.g., ultrasonic wave dispersion, ball-mill dispersion); In this paper, self-dispersed nanosized AlOOH crystal powders were prepared by hydrothermal crystallization and by a charging process under different conditions. The particle size, morphology and dispersion properties of the final products were studied by means of TEM, SEM and laser particle size analysis, and the mechanism of the composite dispersion comprising both the hydrothermal crystallization and charging processes was discussed. The preparation of nanometer TiO2 and nanometer Al2O3 using the composite dispersion method have been preliminarily studied, which provides theory guide for preparation of other metal oxide nanoparticles using the composite dispersion method.

2. Experimental

2.1 Evaluation of dispersion property

2.1.1 Determination of light transmittance ratio of suspensions or sols

Samples of suspensions or sols with identical concentrations were prepared by directly adding a determined amount of sample into distilled water without any surface modifying
agent, dispersant or special conditions (e.g., ultrasonic wave dispersing, ball-mill dispersing). After a definite span of interval time, the light transmittance was determined for all samples (using a 916 type ultraviolet-visible light spectrometer, GBC Co., Australia, illumination wavelength 810 nm). The light transmittance ratio \( D \) of the samples was calculated from the initial light transmittance \( T_0 \) and the light transmittance after a certain time interval \( T_n \) (\( D = T_0/T_n \times 100 \)). In general, the greater the value of \( D \) became, and the smaller the change in light transmittance is, the better the particle dispersion turn to be.

### 2.2 Hydrothermal crystallization and charging process

#### 2.2.1 Preparation of precursor

Industrial grade hydrogen alumina and NaOH were placed in a high pressure reaction kettle at a definite mass ratio of \( \text{Na}_2\text{O}/\text{Al}_2\text{O}_3 \), where they were heated together at 150°C for 1 h and then filtered. Then, acid was added to neutralize the filtrate, and the precipitate was washed and dissolved in acid and mixed so that an aluminium salt solution of definite concentration was obtained. Ammonium acid carbonate solution was then added to the solution obtained by acid-dissolution under stirring, and the resulting precipitate obtained using a plate-and-frame type filter press was washed with deionized water to form an amorphous AlOOH precursor. The reaction process was as follows:

\[
3\text{NH}_3\text{HCO}_3 + \text{Al(NO}_3)_3 \rightarrow \text{AlOOH} + 3\text{CO}_2 + 3\text{NH}_4\text{NO}_3 + \text{H}_2\text{O}
\]

#### 2.2.2 Principles of hydrothermal crystallization and charging treatment of precursor

The precursor is divided into two parts and one is added to a high-pressure reactor. The hydrothermal treatments were then carried out under definite hydrothermal temperature, hydrothermal time, additive (non-surface modifiers) concentration and precursor concentration conditions. The reaction mixture was then filtered and washed with deionized water, and the resulting filter cake was mixed to turn it into a slurry, where it was then spray-dried (inlet temperature 190°C, outlet temperature 100°C). Nanosized \( \gamma \)-AlOOH crystal powders were obtained, which is called powder A. Another part of the precursor is added to a kettle. Peptizing agents and dispersants were added to the precursor. Peptizing and dispersing process were then carried out at 80°C for 2 h and it was then spray-dried according to above-mentioned methods and conditions. The powder obtained is called powder B.

In general, nanoparticles prepared by the sol–gel method tend to agglomerate when it was without surface modification treatment or the modification was in a poor way. This is probably because of: (1) exposure of higher index crystal faces with a very high specific surface energy on the crystal grain; (2) bonding between many dangling bonds of OH functional groups on the particles; (3) defects inside the crystal grains which cause the surface energy of the particles to increase greatly.\(^\text{5}\) The chemical bonding between the dangling bonds of OH functional groups can be mostly eliminated by using a suitable alcohol. Crystal defects have a much greater influence on increases in the grain surface energy of nanometer-sized grains than the high index crystal surface. A general hydrothermal process can achieve fuller crystal grains and a reduction in the number of defects inside the crystal lattice. However, this type of process cannot achieve a completely stable dispersion of nanoparticles in solution. In a hydrothermal process, controlling the hydrothermal conditions cause AlOOH to become charged, produce a strong electrostatic repulsive force between particles, and then greatly improve the dispersion stability of the nanoparticles. The reaction process is as follows: crystallization process

\[
\gamma\text{-AlOOH (amorphous)} \rightarrow \gamma\text{-AlOOH (more perfect crystal)}
\]

charging process

\[
m\text{AlOOH} + (m - n)\text{H}_2\text{O} \rightarrow [(\text{AlOOH})_n(m - n)\text{AlO}^+\text{OH}^- + (m - n)\text{OH}^-]
\]

However, there is a contradiction between the full growth of particles and the control of the particle size in the crystallization process of AlOOH. The charging process is propitious for controlling the grain diameter, but not for achieving full growth of the particle (especially the particle surface). To solve this problem, the two step method and the synchronization method can be employed. The two step method is as follows. First, hydrothermal process conditions which are suitable for crystallization and growth of the AlOOH particles are selected for good particle development and reduction of the surface energy of the AlOOH particle. Then, to create a charge on the particle and make the particle grow while controlling the size so that the particle retains its nanometer dimensions, the conditions of the hydrothermal process (e.g., the hydrothermal system, the reaction temperature, properties of the medium, use of additives, reactant concentrations, etc.) are changed. In the synchronization method, the crystallization and growth, and the charging and control of the grain size, are carried out simultaneously by using processing conditions which are suitable not only for the crystallization, charging and growth of the particles, but also for maintaining the nano-sized scope. The latter method was used in this paper.

### 2.3 Determination of wetting contact angle, crystallinity and charging of nanoparticles

The wetting contact angle of the samples was determined by Washburn’s dynamic method.\(^\text{8,9}\) An X-ray diffractometer (D/MAX2500PC type) was used to determine the crystallinity of the samples. A laser particle size and Zeta potential
and other special conditions (e.g., ultrasonic wave dispersion, ball-mill dispersion), definite amounts of powder A and powder B samples were added respectively into distilled water, to prepare sols or suspensions of identical concentrations. A high-resolution transmission electron microscope (JEM-2010F type, JEOL Co., Japan) and laser particle size analyzer (Nano-ZS90 type, MALVERN Co., England) were used to determine the particle morphology, particle diameter distribution and dispersion/agglomeration states.

2.4 Observation and testing of dispersion/aggregation states of nanoparticles

2.4.1 Particle size distribution and TEM analysis (in water)

Without any surface modifying agent, dispersant, additives and other special conditions (e.g., ultrasonic wave dispersion, ball-mill dispersion), definite amounts of powder A and powder B samples were added respectively into distilled water, to prepare sols or suspensions of identical concentrations. A high-resolution transmission electron microscope (JEM-2010F type, JEOL Co., Japan) and laser particle size and Zeta potential analyzer (Nano-ZS90 type, MALVERN Co., England) were used to determine the particle morphology, particle diameter distribution and dispersion/agglomeration states.

2.4.2 Particle diameter distribution in the organic phase and SEM analysis of particles in a polymer

Without any surface modifying agent, dispersant, additives or other additional treatments (ultrasonic wave treatment, ball-mill treatment), definite amounts of powder A samples were added directly into a variety of frequently used organic solvents or mixed solvents, stirred to homogeneity, and then heated in a water bath at 60°C for 0.5 h. The particle diameter distribution in the organic phase of each sample was then measured by the laser particle size analyzer.

The organic or mixed solvents in which the nanocrystalline powders were well dispersed were chosen as the dispersing media for the nanoparticle sols for preparing polymer/inorganic nanocomposite materials, and the appropriate organic sol concentrations of the nanoparticles for the experiments were prepared by using these solvents. The sol was then added directly into the organic solvent containing the polymer, and these mixtures were dispersed to a translucent sol in a water bath at 70°C, and then cooled in preheated moulds of the requisite size, and dried in a vacuum drying oven at 80°C, and then cooled.

Table 1 Optimizing of the composite dispersion technology terms and light transmittance ratio.

<table>
<thead>
<tr>
<th>Samples No.</th>
<th>hydrothermal temperature (°C)</th>
<th>hydrothermal time (min)</th>
<th>additive (mass percent)</th>
<th>precursor (mol/dm³)</th>
<th>D (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>D₁</td>
</tr>
<tr>
<td>1</td>
<td>110</td>
<td>5</td>
<td>0.3</td>
<td>0.7</td>
<td>88.3</td>
</tr>
<tr>
<td>2</td>
<td>130</td>
<td>5</td>
<td>0.3</td>
<td>0.7</td>
<td>90.4</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>5</td>
<td>0.3</td>
<td>0.7</td>
<td>98.4</td>
</tr>
<tr>
<td>4</td>
<td>150</td>
<td>7</td>
<td>0.3</td>
<td>0.7</td>
<td>98.7</td>
</tr>
<tr>
<td>5</td>
<td>150</td>
<td>3</td>
<td>0.3</td>
<td>0.7</td>
<td>89.5</td>
</tr>
<tr>
<td>6</td>
<td>150</td>
<td>5</td>
<td>0.1</td>
<td>0.7</td>
<td>78.5</td>
</tr>
<tr>
<td>7</td>
<td>150</td>
<td>5</td>
<td>0.5</td>
<td>0.7</td>
<td>84.6</td>
</tr>
<tr>
<td>8</td>
<td>150</td>
<td>5</td>
<td>0.3</td>
<td>0.5</td>
<td>85.5</td>
</tr>
<tr>
<td>9</td>
<td>150</td>
<td>5</td>
<td>0.3</td>
<td>0.9</td>
<td>86.3</td>
</tr>
<tr>
<td>10</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.7</td>
<td>73.7</td>
</tr>
</tbody>
</table>

Notes: (1) D₁, D₅₀ and D₉₀ are the ratio (percentage) of initial light transmittance to the light transmittance after 1d, 10d and 30d, respectively, when the samples were dispersed in distilled water and their concentration is 0.1 mass%; (2) 1–9 are powder A sample and 10 is powder B sample.

3. Results and Discussion

3.1 Optimization of composite dispersion technology conditions

The light transmittance ratios D of the powder A sample prepared by hydrothermal crystallization and charging composite dispersion under different composite dispersion technology conditions are shown in Table 1. For comparison, the D value of powder B was also listed in the table.

From Table 1, it can be seen that the temperature raising or the time increasing is beneficial for dispersion of nanosized AIOOH grain in water when other conditions remain constant. This may be thought to be beneficial for speeding the crystallization of the grains and decreasing surface energy. Also, it can be seen that nanosized AIOOH grain disperses better in water when the ratio of non-surface modifiers mass percentage to precursor concentration is 3/7. It is reasonable to believe that, as the non-surface modifiers is a particle charging promoter, the excessive amount of it is unfavorable to crystallization of grains and the insufficient amount is unfavorable to particle charging. From the light transmittance ratio D of powder B in water, it can be seen that, when the precursor was without surface modification treatment, its product has poor dispersion.

3.2 Effect of composite dispersion

3.2.1 Particle diameter distribution

Figure 1 shows the particle diameter distribution graph which is obtained when the powder A No. 3 sample is dispersed directly into distilled water or N,N-dimethylformamide. When there is no dispersant or additive present, the unmodified AIOOH shows a narrow particle diameter distribution and smaller average particle diameters of 66.52 nm and 56.47 nm in water and organic solvent, respectively, as seen from Fig. 1.

3.2.2 TEM analysis

Figure 2 shows the TEM image obtained after adding the

The light transmittance ratios D of the nanoparticles in the nanocomposite materials were observed by using scanning electron microscopy (S-3400N type, Hitachi Ltd., Japan).
unmodified No. 3 powder A directly into distilled water without the need for any surface modification, dispersant or additives and becoming automatically dispersed into a transparent colloid. From Fig. 2, it can be seen that the AlOOH is dispersed evenly in the water, and shows a single dispersion state with no agglomeration. Figure 3 shows the TEM image obtained after adding the powder B directly into distilled water and making ultrasonic treatment for 30 min without the need for any surface modification, dispersant or additives. From Fig. 3, it can be seen that the powder B sample are agglomerated greatly and its dispersion is very poor. The results show that the agglomeration between AlOOH particles isn’t effectively controlled and the agglomeration is very serious when the precursor of AlOOH was without any treatment on hydrothermal crystallization and charging composite dispersion.

### 3.2.3 Dispersion in polymer

Figure 4 shows the SEM image of a polyvinyl chloride/AlOOH nanocomposite films (77 mass% AlOOH powder A, and a surface etched lightly by solvent) prepared by blending a composite of polyvinyl chloride with AlOOH in N,N-dimethylformamide. Here, it should be noted that the AlOOH powder were not modified and directly added into the N,N-dimethylformamide solution of polyvinyl chloride, and they
could be dispersed without surface modification, dispersant or additives. As seen from Fig. 4, the AOOOH is well dispersed in the polymer. That is, it dispersed evenly in the polymer matrix in a single particle state. The average length-diameter ratio is 100 nm: 10 nm, which is almost the same as that in water, thereby achieving nano-scale dispersion.

### 3.2.4 Characteristics of self-dispersion

From Figs. 1, 2 and 4, it can be concluded that the nanosized AOOOH crystal powder prepared by hydrothermal crystallization and charging composite dispersion technology can automatically disperse into a stable single-dispersion state in both water and N,N-dimethylformamide with no agglomeration. From these results, we consider this to be a self-dispersion phenomena and propose that the self-dispersion characteristics of the nanopowders can be described as follows: the unmodified nanopowders can automatically disperse into a stable single-dispersion state with no agglomeration in water or some organic solvents without any surface modifying agents, dispersants, additives or other special conditions (e.g., ultrasonic wave dispersion, ball-mill dispersion), and the average grain diameter is smaller than 100 nm.

### 3.3 Self-dispersing mechanism of AOOOH

The stable dispersion process of the nanoparticles in the liquid phase involves three steps: 10–12) wetting, mechanical dispersion and dispersion stabilization. In the dispersion stabilization step, the Van der Waals force is shielded and the re-aggregation of particles is prevented by subjecting the primary particles or minor agglomerates to electrostatic repulsive forces and steric hindrance repulsion. Therefore, two basic principles of stable nanoparticle dispersion are as follows: (1) Wetting principle (polar similarity principle). Nanoparticles must be wetted by a liquid medium, so that they can be well immersed in the liquid medium; (2) Surface acting force principle. The total interaction forces between the nanoparticles must have a large enough positive value, so that agglomeration due to direct contact and adherence between the nanoparticles is prevented. Based on the DLVO theory, the total interaction force between nanoparticles can be represented as: 13)

\[
F_T = F_A + F_{ER}
\]

In this formula, \( F_T \) is the total interaction force between the nanoparticles, \( F_A \) is the Van der Waals force, and \( F_{ER} \) is the repulsion force of the double electrical layer.

In air, the Van der Waals force between two particles with the same mass and diameter can be presented as: 14)

\[
F_A = -A_d/24H^2
\]

of which 15,16)

\[
A_{11} = 4\pi\gamma S^2 H^2/1.2
\]

\[
A_{131} \approx [(A_{11})^{1/2} - (A_{133})^{1/2}]
\]

Here, \( A_{11} \) is the Hamaker constant of the interaction between particles in a vacuum, \( A_{131} \) is the Hamaker constant of the interaction between media, \( A_{133} \) is the Hamaker constant of particle 1 in media, \( d \) is the average diameter of the particles, \( H \) is the separation distance between two particles, and \( \gamma S \) is the non-polar heft of the surface free energy of particles.

Based on the surface energy calculation method for high-energy particles put forward by Kacibl: 17)

\[
(1 + \cos \theta)\gamma L = 2[(\gamma S \cdot \gamma L)^{1/2} + (\gamma R \cdot \gamma L)^{1/2}]
\]

and

\[
\gamma_{SAB} = 2(\gamma R^L \cdot \gamma L)^{1/2}
\]

\[
\gamma S = \gamma L + \gamma S_{AB}
\]

We can obtain the surface free energy of a solid, \( \gamma S \). Here, \( \theta \) is the wetting contact angle at the interface between the solid and the liquid, \( \gamma L \) and \( \gamma R \) are the surface free energies of the liquid and its non-polar heft, \( \gamma R^L \) are the electron accepting portion and electron donating portion of the polar heft of the surface free energy of the liquid, \( \gamma L S \) is the non-polar heft of the surface free energy of the solid, \( \gamma L^R \) are the electron accepting portion and electron donating portion in the polar heft of the surface free energy of the solid, and \( \gamma S_{AB} \) is the polar heft of the surface free energy of the solid.

The \( \gamma L \), \( \gamma R^L \), \( \gamma L^R \) of three kinds of liquids with different polarities are known and their wetting contact angles \( \theta \) at the interface between water and solid for four kinds of powder A samples are listed in Table 2.

The electrostatic repulsive force of the double electrical layer between two particles with the same mass and diameter can be presented as: 18,19)

\[
F_{ER} = 64\pi a C L R T \gamma^2 e^{l H S}/H e^2
\]

Where

\[
\exp\left(\frac{ze\psi}{2BT}\right) - 1
\]

\[
\exp\left(\frac{ze\psi}{2BT}\right) + 1
\]

\[
\kappa \text{ of a symmetrical electrolyte in aqueous solution at 298 K is presented as:}
\]

\[
\kappa = 1.039 \times 10^6 (c^2)^{1/2}
\]
where \( n \) is the electrolyte concentration, the number of ions/m\(^3\); \( R \) is the radius of the particles, m; \( \varepsilon \) is the dielectric constant of the medium; \( B \) is the Boltzmann constant, J/K; \( e \) is the elementary charge, C; \( \kappa \) is the reciprocal value of the thickness of the double electrical layer, 1/m; \( c \) is the molar concentration, mol/m\(^3\); \( z \) is the charge number of the ions; and \( \varphi \) is the surface potential of the particles, mV.

If the data in Table 2 is substituted into eq. (5), \( \gamma^S, \gamma^-S \) and \( \gamma^S \) can be worked out by a simple three-dimensional equation. Then, the different interaction forces between the AlOOH grain in the four kinds of powder A samples can be worked out by other equations (the original data for the AlOOH grain in the four kinds of powder A samples can be calculated according to the equation. Then, the different interaction forces between the particles, and the Van der Waals force is accordingly weakened during the process. At the same time, in the hydrothermal process, the preferential dissolution of part of the OH\(^-\) ions structured AlOOH crystal lattice is promoted under appropriate experimental design and control conditions. This forms an excess of cationic AIO\(^+\) ions and a positive charge over the surface of the crystal lattice (from Fig. 6, it can be seen that the electric potential value of the AlOOH particles treated by crystallization and charging at 150°C in water reaches to 49.63 mV). This process can be called the “hydrothermal crystallization and charging composite dispersion method” and can be considered an effective “wetting composite dispersion method”. With appropriate experimental design and under control conditions, increasing the hydrothermal temperature can synchronously promote crystallization and charging of the AlOOH particles.

From Table 3, it can be seen that the total interaction forces between the AlOOH particles treated by crystallization and charging at 150°C are 3.2 times higher than those at 120°C. From Table 3, it can also be seen that a necessary condition for the self dispersion of nanosized AlOOH particles is an \( F_T/d \) ratio of over 7.27 \( \times \) \( 10^{-12} \) N/nm (0.08 \( \times \) \( 10^{-8} \)/110).

### Table 3 Different interaction forces (\( \times 10^{-8} \) N) between AlOOH grain in four kinds of powder A samples and some related data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( d ) (nm)</th>
<th>( f ) (mV)</th>
<th>( \gamma^- ) (J/m(^2))</th>
<th>( A_{131} ) (J/( 10^{-20} ))</th>
<th>( F_\text{A} ) (N/( 10^{-2} ))</th>
<th>( F_\text{ER} ) (N/( 10^{-2} ))</th>
<th>( F_T ) (N/( 10^{-2} ))</th>
<th>( D ) (%)</th>
<th>Dispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>140</td>
<td>18.56</td>
<td>0.1786</td>
<td>1.39</td>
<td>-5.08</td>
<td>2.77</td>
<td>-0.231</td>
<td>88.3</td>
<td>no</td>
</tr>
<tr>
<td>2</td>
<td>116</td>
<td>30.34</td>
<td>0.2872</td>
<td>0.72</td>
<td>-2.18</td>
<td>5.93</td>
<td>0.375</td>
<td>90.4</td>
<td>not good</td>
</tr>
<tr>
<td>3</td>
<td>110</td>
<td>40.12</td>
<td>0.3721</td>
<td>0.17</td>
<td>-0.50</td>
<td>9.44</td>
<td>0.894</td>
<td>98.4</td>
<td>good</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>49.63</td>
<td>0.4490</td>
<td>0.13</td>
<td>-0.34</td>
<td>12.50</td>
<td>1.216</td>
<td>98.7</td>
<td>good</td>
</tr>
</tbody>
</table>

Notes: (1) Where \( A_{131} \) is the Hamaker constant of AlOOH grain in water. (2) Diameter of AlOOH particles is an approximate value calculated for a spherical pellet.
3.4 Preliminary research on preparation of nanometer TiO$_2$ and nanometer Al$_2$O$_3$ using composite dispersion method

Figure 7 shows the particle diameter distribution graph which was obtained when the unmodified α-Al$_2$O$_3$ and R–TiO$_2$ samples are dispersed directly into distilled water. The nanometer AlOOH and Ti(OH)$_4$ sols, as precursors, are used to prepare the α–Al$_2$O$_3$ and R–TiO$_2$ by hydrothermal crystallization and charging composite dispersion method. Prepared conditions of the α–Al$_2$O$_3$ and R–TiO$_2$ were as follow: HNO$_3$/precursor mole ratio respectively 0.18 and 1.5, hydrothermal temperature respectively 180°C and 190°C, calcination temperature respectively 600°C and 1150°C, hydrothermal time 5 h. From figure, it can be seen that the particle diameter distribution of nanometer Al$_2$O$_3$ and TiO$_2$ in the water are narrow and their average grain diameter are small, respectively 69.53 nm and 143 nm.

4. Conclusions

The hydrothermal crystallization and charging composite dispersion method is an effective method for the dispersion of nanoparticles in a liquid phase, especially for metal oxides and their hydrates. This composite method combines the advantage of crystallization dispersion treatment (which decreases the particle surface energy to accomplish surface modification) with the advantage of charging dispersion treatment. Thus, since the hydrothermal crystallization and charging composite dispersion method causes the nanoparticles to self-disperse, this method prevents the nanoparticles from losing their beneficial properties for surface modification.

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REFERENCES