Electrostatic and Sterical Stabilization of CuO Nanofluid Prepared by Vacuum Arc Spray Nanofluid Synthesis System (ASNSS)

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1. Introduction

In colloidal science, the interactions between particles in a suspension fluid include van der Waals force, electrical double layer action and sterical action. These interactions lead to the dispersion of colloids, maintain the suspension and dispersion for a long time, and do not flocculate sediments.¹,² If nanoparticles can stay suspended in fluid stably, they can be applied in many industries to exert special effects of nanomaterials. The most common method for particles to maintain good dispersion and stable suspension in fluid has been ultrasonic vibration, a physical method. Many related research papers have reported the use of ultrasonic vibration to disperse and suspend nanoparticles in fluid, and investigated the influence of particle size and surface potential on suspension and dispersion.³ But currently most of the physical dispersion methods are being replaced by chemical methods, mainly because the addition of chemicals can more evenly disperse the particles in suspension fluid, and can maintain the suspension stability over a longer time. Therefore, many studies have investigated the addition of different acidic and saltic materials in nanofluids to enhance the suspension stability.⁴–⁶

The study uses a self-developed arc spray nanofluid synthesis system (ASNSS) to prepare a CuO nanofluid with high suspension stability.⁷ This good suspension stability does not depend on a physical or chemical method, but it can keep CuO nanoparticles stably suspended for an extended period. This study investigates the influence of the various forces in the prepared suspension fluid, observes the suspension properties of CuO nanofluid as well as the morphological and surface potential changes of CuO nanofluid over an extended period of time, and explores the influence of electrostatic repulsion force, sterice stabilization force and van der Waals attraction force in the suspension fluid. Finally, employing DLVO theory to calculate the total interacting energy \( V_{\text{total}} \) produced by double-layer repulsion force and van der Waals attraction force, the study investigates the relationship between potential energy and stability of CuO nanofluid.

2. Theory Analysis

The model used to describe the ion distribution function and potential in the region near the charged interface was developed independently by Gouy and Chapman by combining the Poisson equation for the second derivative of the electric potential as a function of charge density with the Boltzmann equation for the charge density as a function of potential.⁸–¹⁰ The net volume charge density \( \rho \) at the points where the potential is \( \psi \) is thus expressed as:

\[
\rho = -2\varepsilon \kappa n_0 \sinh \frac{2e\psi}{\kappa T} \quad (1)
\]

\( \rho \) is related to \( \psi \) in Possion’s equation, which for a flat double layer takes the form as follows:

\[
\frac{d^2\psi}{dx^2} = -\frac{\rho}{\varepsilon} \quad (2)
\]

where \( \varepsilon \) is the permittivity.

The combination of eqs. (1) and (2) is expressed as:

\[
\frac{d^2\psi}{dx^2} = \frac{2\varepsilon n_0}{\varepsilon} \sinh \frac{2e\psi}{\kappa T} \quad (3)
\]

The solution of this expression, with the boundary conditions \( \psi = \psi_0 \text{ when } x = 0; \text{ and } \psi = 0, d\psi/dx = 0 \text{ when } x = \infty \) taken into account, can be written as:

\[
\psi = \frac{2kT}{\varepsilon} \ln \left( \frac{1 + \gamma \exp[-\kappa x]}{1 - \gamma \exp[-\kappa x]} \right) \quad (4)
\]

where

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\[ \gamma = \frac{\exp[ze\psi_0/2kT] - 1}{\exp[ze\psi_0/2kT] + 1} \]  
(5)

and

\[ \kappa = \left( \frac{8\pi e^2 N_A}{1000e kT} \right)^{\frac{1}{2}} \]  
(6)

where \( N_A \) is Avogadro’s constant, \( I \) is the ionic strength, \( c \) is the concentration of electrolyte, \( n_0 \) is the corresponding bulk concentration of each ionic species, \( z \) is the valence, \( e \) is the charge on electron (1.602 x 10^{-19} C), \( F \) is the force between two charges, \( R \) is the molar gas constant, and \( k \) is Boltzmann’s constant. In the above equation, \( \kappa \) denotes the Debye-Huckel reciprocal length parameter and has the unit of (length)^{-1}, 1/\( \kappa \) is the distance at which the potential \( \psi \) drops to 1/e of its value at the Stern plane, and this distance is called the double layer thickness or Debye length.

\[ V_{\text{van der Waals}} = -\frac{A}{12} \left[ \frac{y}{x^2 + xy + x} + \frac{y}{x^2 + xy + x + y} + 2 \ln \left( \frac{x^2 + xy + x + y}{x^2 + xy + x} \right) \right] \]  
(7)

In the equation, \( A \) denotes the Hamaker constant, \( x \) denotes \( H_0/2a_1 \), \( y \) denotes the \( a_2/a_1 \), \( a_1 \) and \( a_2 \) denote the particle radius, and \( H_0 \) denotes the distance separating the surfaces.

When two different kinds of particles are in a solution, the solution’s double-layer action equation is expressed as follows:

\[ V_{\text{double layer}} = \frac{e}{4} g_{12}(\psi_{01}^2 + \psi_{02}^2) \times \left( \frac{2R}{1 + R^2} \right) \times \ln \left[ 1 + \exp(-kH_0) \right] \]  
(8)

where \( g_{12} = (a_1^{-1} + a_2^{-1})^{-1} \) and \( R = \psi_{02}/\psi_{01} \).

The term \( g_{12} \) is a geometry factor dependent upon the radii, \( a_1 \) and \( a_2 \), of the two particles under consideration. \( \psi_{01} \) and \( \psi_{02} \) are the surface potentials of the two particles at infinite separation, and \( e \) is the dielectric constant of the solution.

Suppose that there is only a single kind of particles in solution, then eqs. (7) and (8) can be simplified as:

\[ V_{\text{van der Waals}} = -\frac{Aa}{12H_0^2} \]  
(9)

\[ V_{\text{double layer}} = \frac{e\psi_0^2}{2} \ln[1 + \exp(-kH_0)] \]  
(10)

Finally, the summing of the two kinds of energy yields the total energy for the dispersion stability of particles in solution, as shown in the following equation:

\[ \Delta V = \Delta V^{\text{vdw}} + \Delta V^{\text{elstat}} \]  
(11)

\[ = -\frac{Aa}{12H_0^2} + \frac{e\psi_0^2}{2} \ln[1 + \exp(-kH_0)] \]

From this equation, the relationship among the total action force \( \Delta V \), van der Waals attraction force \( \Delta V^{\text{vdw}} \) and electrostatic repulsion force \( \Delta V^{\text{elstat}} \) can be seen. Besides, as known from Lambert-Beer theory, the absorption of solution is positively proportional to the concentration of solution and the length of beam going through. Therefore, if the lengths of beams going through the nanofluid are the same, and the analyzed materials are also the same, then the concentration of this solution will be positively proportional to the absorption. Hence, we can judge the suspension stability from the concentration change.

3. Experimental

Using the basic principles of the gas condensation method, this study has developed the vacuum arc spray nanofluid synthesis system (ASNSS) combined with ultrasonic vibration.\(^{14,15}\) The experimental devices are mainly comprised of an electrical power utility, a servo-positioning system, a vacuum chamber, a vacuum pump, a heating source, a cooling system, and a pressure control unit. The ultrasonic system allows different settings of frequency and amplitude. With the help of ultrasonic vibration, the disturbance of the dielectric liquid can be increased and the nanoparticles thus produced can quickly come out of the fusion zone. In the meantime, the gasified metal can be quickly cooled down. Ultrasonic vibration can effectively improve the state of dispersion of nanofluids and obtain smaller nanoparticles.

After the analysis of the results of multiple experiments, a CuO nanofluid with high suspension stability is prepared. The main process parameters are peak current 4A, on-time pulse duration 50 \( \mu \)s, and off-time pulse duration 50 \( \mu \)s. The weight concentration of the prepared CuO nanofluid is 0.01%. For observation of different lengths of settling time, CuO nanofluids allowed to rest for 7 days, 30 days, 90 days and 180 days are taken out to test the average particle diameter, Zeta potential and pH value of the nanofluid. The
CuO nanofluid prepared by the study is preserved by pouring the newly prepared nanofluid immediately into a glass bottle with cap. Then the bottle is placed at rest under room temperature for 180 days. From the SEM image, the morphological change of particles can be observed. In addition, UV-Vis spectrophotometer and viscosity analyzer are used to test the absorption intensity and rheology of the nanofluids of different concentrations produced at different process durations. Finally, DLVO theory is employed to prove the suspension stability of CuO nanofluid. The particle size and morphology of the prepared nanoparticle was examined by transmission electron microscopy (TEM) and field emission scanning electron microscope (FESEM). The crystal structural of nanoparticle was determined by X-ray diffraction (XRD). The zeta potential of the nanoparticle suspension was measured using zeta potential analyzer. In addition, a Ultraviolet-Visible (UV-Vis) spectrophotometer is used to measure the optical property of the nanofluids. The Calibration Curve can also be used to calculate the concentration of nanofluid.

4. Results and Discussion

4.1 Influence of settle times on the morphology of particle

Figure 1(a) shows the morphology of the newly prepared Cu particles, which are in narrow strips. The length of long axis is around 200 nm, and the length of short axis is around 50 nm. Seven days later, their morphology is shown in Fig. 1(b), appearing to be in the shape of a bamboo leaf; and their particle size is around 60 nm. Furthermore, the test results of XRD show that after 7 days, the Cu particles are oxidized to become CuO. Figure 1(c) shows the SEM image of a CuO nanoparticle after resting for 180 days. The particle size of the CuO nanoparticle shown in this figure is around 70 nm, with particles well dispersed. Comparing Figs. 1(b) and (c), it is known that after the CuO nanoparticles prepared by the study have remained at rest for 180 days, the morphology of the particles changes from the original bamboo leaf shape to be irregular polygon shape, but no obvious change in particle size is found in average. Therefore, it is demonstrated that the CuO nanofluid prepared by this study can maintain particle dispersion for an extended period of time, and have a good consistency in the CuO nanoparticle dimensions.

4.2 Influence of settling time on the Zeta potential of nanofluid

Figure 2(a) shows the change in Zeta potential of CuO nanofluid at different process durations after different lengths of settling time. The figure shows that the Zeta potential of CuO nanofluid at a process duration of 10 min falls from 45.3 mV when newly prepared, to 34 mV after it has been rested for 6 months. As for the CuO nanofluids with process duration of 5 min and 15 min, after they remain at rest for 180 days, their Zeta potentials fall from the original 39 mV to 30 mV and from 44.1 mV to 31 mV respectively. As shown in Fig. 2(a), before the prepared CuO nanofluid is oxidized to be CuO, its Zeta potential falls rapidly. In addition, with the increase of settling time, the Zeta potential of the prepared CuO nanofluid tends to decrease gradually. Furthermore, the concentration of CuO nanoparticles in CuO nanofluid would affect the Zeta potential of nanofluid. The study finds that the CuO nanofluid with process duration of 10 min has the best suspension stability. It is also known from the literature that when the Zeta potential of a fluid is greater than 30 mV, the nanofluid can maintain its suspension stability. The nanoparticles in a fluid achieve a stable situation through the electrostatic repulsion force. Thus, as seen from Fig. 2(a), the CuO nanofluid prepared by this study can keep its suspension stability at least for six months. Furthermore, the newly
prepared nanofluid with process duration of 10 min is immediately blended with 0.05 M of HCl or NaOH to produce solutions with different pH values. The Zeta potential change of the prepared nanofluids with different pH values is tested, as shown in Fig. 2(b). As observed from Fig. 2(b), the pH value of nanofluid at the isoelectric point is 9.2. The pH value of the CuO nanofluid prepared by this study is about 6, which is much smaller than 9.2. Therefore, it is proved that the CuO nanofluid prepared by this study meets the basic condition of suspension stability.

4.3 Influence of process duration of CuO nanofluid on absorption intensity

The Uv-Vis absorption spectra of CuO nanofluid with different process durations was tested, as shown in Figs. 3(a) and (b). Figure 3(a) shows that the absorption intensity of CuO nanofluid with process duration of 15 min is less than that with process duration of 10 min. This is because when the process duration is over 10 min, the particles of the prepared nanofluid begin to agglutinate and sediment for being saturated, thus leading to the low suspension dispersion. Therefore, the process duration for better suspension and dispersion stability of CuO nanofluid is 10 min. Moreover, the absorbance value of CuO nanofluid reduces with the increase of settling time because the particles begin to flocculate slightly. Thus, when the Zeta potential gradually reduces with the increase of settling time, leading to the flocculation and sedimentation of particles, and reducing suspended particles in the fluid. As a result, the absorbance value is reduced. Figure 3(b) shows the Uv-Vis absorption spectra of CuO nanofluid after static placement for 180 days. It can be seen that the prepared CuO nanofluids with process durations of 5 min and 15 min after being settling times of 180 days, their absorbance values are almost equal. Comparing Figs. 3(a) and (b), after the CuO nanofluid with process duration of 10 min have remained at rest for 180 days, its absorbance value falls from the original 2.4 to 1.43, with a falling rate of 40.4%. And after the CuO nanofluids with process durations of 5 min and 15 min have remained at rest for 180 days, their absorbance value falls from the original 1.55 to 1.28 and from 2.3 to 1.3, with falling rates of 17.4% and 43.5% respectively. In order to further confirm that the falling absorbance value of CuO nanofluid is related to the concentration of CuO nanoparticles in fluid, the study inspects the concentration change of the CuO nanofluids with process durations of 5 min and 15 min have remained at rest for 180 days, their absorbance value falls from the original 2.4 to 1.43, with a falling rate of 40.4%. And after the CuO nanofluids with process durations of 5 min and 15 min have remained at rest for 180 days, their absorbance value falls from the original 1.55 to 1.28 and from 2.3 to 1.3, with falling rates of 17.4% and 43.5% respectively. In order to further confirm that the falling absorbance value of CuO nanofluid is related to the concentration of CuO nanoparticles in fluid, the study inspects the concentration change of the CuO nanofluids with process durations of 5 min and 15 min have remained at rest for 180 days, their absorbance value falls from the original 2.4 to 1.43, with a falling rate of 40.4%. And after the CuO nanofluids with process durations of 5 min and 15 min have remained at rest for 180 days, their absorbance value falls from the original 1.55 to 1.28 and from 2.3 to 1.3, with falling rates of 17.4% and 43.5% respectively. In order to further confirm that the falling absorbance value of CuO nanofluid is related to the concentration of CuO nanoparticles in fluid, the study inspects the concentration change of the CuO nanofluids with process durations of 5 min and 15 min have remained at rest for 180 days, their absorbance value falls from the original 2.4 to 1.43, with a falling rate of 40.4%. And after the CuO nanofluids with process durations of 5 min and 15 min have remained at rest for 180 days, their absorbance value falls from the original 1.55 to 1.28 and from 2.3 to 1.3, with falling rates of 17.4% and 43.5% respectively. In order to further confirm that the falling absorbance value of CuO nanofluid is related to the concentration of CuO nanoparticles in fluid, the study inspects the concentration change of the CuO nanofluids with process durations of 5 min and 15 min have remained at rest for 180 days, their absorbance value falls from the original 2.4 to 1.43, with a falling rate of 40.4%. And after the CuO nanofluids with process durations of 5 min and 15 min have remained at rest for 180 days, their absorbance value falls from the original 1.55 to 1.28 and from 2.3 to 1.3, with falling rates of 17.4% and 43.5% respectively.
4.4 Analysis of rheology

Figure 5(a) shows how different process durations of CuO nanofluids are related to the shear rate and shear stress of deionized water, indicating that CuO nanofluids appear to have the properties of a dilatant fluid. The fluid prepared over a longer period of time is found to have saturated particles, so a slight flocculation is caused, and its shear stress is greater than that of the CuO nanofluid prepared in a shorter period of time. The main reason for this is that when particles in the fluid start to flocculate, their flowability is reduced. Hence, a shear stress should be applied to produce the strain rate. With the CuO nanofluid prepared in a shorter period of time, since its particles are more dispersed, it is more similar to a Newtonian fluid. Figure 5(b) shows how different process durations of CuO nanofluids are related to the shear rate and viscosity of deionized water. This figure shows a fluid prepared over a longer period of time has higher viscosity. This is because after the process exceeds 10 min, the concentration of the fluid is saturated, and the particles then start to flocculate, producing larger particles. This enhances the nanofluid viscosity and its flowability is reduced. Therefore, in addition to the original viscosity of the carrier fluid, the particle size and dispersion are actually the factors most influencing the viscosity of fluid.

4.5 Interacting forces in CuO nanofluid

The Hamaker constant of CuO nanofluid (A_{131}) is 9.219 \times 10^{-20} \text{J}.^{16-18} Having substituted this numerical value in eq. (9), the potential energy curve for the van der Waals attraction force of CuO particles in solution can be acquired. Furthermore, the Debye length \kappa is 11651995.94 (1/m) after calculation of eq. (6). After the parameters are sequentially substituted in eq. (10), the potential energy curve for the double-layer repulsion force of CuO particles can be acquired. Synthesizing the above two interaction energies among the particles of fluid, total interaction energy curves can be acquired. When interaction energy curves are being drawn, the x-coordinates represents the distance between particles, with a range of 0–10 nm and the interval between each points being 0.2 nm. Figure 6(a) shows the potential energy curve (V_T = V_A + V_{double layer}) of CuO nanofluid after being prepared in 7 days. As the minimum separation between the particles increases to the range of double-layer thickness, the double-layer repulsion force is greater than van der Waals attraction force. Therefore, a potential energy barrier is caused between two particles to prevent the flocculation of particles. As found from Fig. 6(a), the potential energy of the entire dispersion system is 18.92 kT, which is greater than the potential energy (15 kT) required for the stability of dispersion system. Therefore, it is confirmed that the dispersion mechanism of the prepared CuO nanofluid makes use of double-layer repulsion force to maintain the dispersion stability. After that, the change of potential energy with the increase of settle times of CuO nanofluid is tested. Since the Zeta potential of CuO nanofluid is slightly reduced and the particles are slightly enlarged with the increase of settling time, the potential energy tends to fall. After CuO nanofluid is allowed to rest for 1 month, its...
potential energy barrier is reduced to 15.2 kT, and after six months its potential energy barrier is 11.18 kT (Fig. 6(b)). As seen from the experimental results, as the settling time lengthens, and when the Zeta potential of CuO nanofluid is reduced, this causes a slight flocculation of the particles in fluid, and the influence of van der Waals attraction force of CuO nanofluid is created, thus leading to the reduction of potential energy.

5. Conclusion

The study investigates the dispersion stability of the particles of CuO nanofluid prepared by the self-developed arc spray nanofluid synthesis system (ASNSS). After observing the solution over a long time, the study uses DLVO theory to verify the suspension and dispersion stability of CuO nanofluid, with the following conclusions:

(1) The prepared CuO nanofluid has 39 mV of Zeta potential. Hence, without the addition of any dispersant, a stable suspension can be maintained, and an extremely good effect of sterical stabilization can be achieved. After observation for a long time, its Zeta potential can still remain above 30 mV. Therefore, the dispersion stability of the fluid is quite good.

(2) After 7 days of preparation, the structure of Cu particles is oxidized to become CuO, with particle size being around 60 nm. After CuO allowed to rest for 180 days, the particle size of CuO nanoparticle is around 70 nm, and the dispersion of particles is good.

(3) The CuO nanofluid with better suspension and dispersion stability needs a process duration of 10 min. Furthermore, the absorbance value of CuO nanofluid is slightly reduced with the increase of settling time.

(4) CuO nanofluid appears to have the properties of a dilatant fluid. Besides, the shear stress of the fluid prepared over a longer period of time is greater than that prepared in a shorter period of time. The viscosity of the fluid prepared in a longer period of time is greater.

(5) According to DLVO theory, this study investigates the dispersion stability mechanism of CuO nanofluid, and calculates the potential energy curve of CuO fluid. The potential energy barrier between CuO nanofluid is 18.92 kT, which can effectively prevent the flocculation of particles, and maintain their dispersion stability.

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