Process Development and Material Property of ZnO Nanoparticle Suspension by High Frequency Induction∗

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The main purpose of this study is to develop a high frequency induction process that is capable of producing the nanoparticle suspension, as well as the investigation into the properties of nanoparticle suspension. Also the effects of the process parameters, such as cooling temperature, vacuum pressure and inert gas on the rheology of nanoparticles are investigated. Experimental results indicate that under lower vacuum pressure, the nanoparticle suspension performs a larger rheological change and produces smaller nanoparticles, whereas under lower cooling temperature, it can produce finer ones. Besides, by adding inert gas during the process, the rheology of nanoparticle suspension would change. Furthermore, by adjusting the pH value of nanoparticle suspension below 7, its surface electric potential can also be increased and subsequently acquires smaller suspension particles. Besides, the nanoparticle suspension produced by this study has a good capability of absorbing UV light.

Key Words: ZnO, Nanoparticle Suspension, High Frequency Induction

1. Introduction

A nanomaterial composes of their particle sizes between 1 – 100 nm. Since the nanomaterials carries multiple effects such as quantum size, small size, surface and macroscopic quantum tunneling, so they display many specific natures(1) – (3). Carrying the properties of ideal reduction and oxidation capabilities, high chemical stability, environmental harmless and low cost, especially ZnO nanoparticle can be made into a brand-new type of photocatalyst(4), applying to the areas of anti-bacteria and mold prevention, air-ventilation and purification, water purification, self-cleaning and photosynthesis etc. Thus, it is highly prospective that the research, development and production of ZnO nanoparticle suspension would prosper in the near future.

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2. Experimental Theory

Induction heating method, which has been widely applied in the making of transformers, is a metallic heating technique by means of electromagnetic induction discovered by Farady in 1831. The input side and output side of the transformer carry a set of coil accordingly. When ac voltage is charged into the input side, the primary coil would produce a magnetic field having an alternate change of positive and negative currents. This would further couple with secondary coil that would then produce induction voltage. Besides, the output side would connect to the load circuit, supplying the load current. Induction heating uses the hysteresis loss that occurs at the ruthlessness, as well as the eddy current loss caused by the induction current to heighten the temperature of materials. Since metals carry the property of electric conduction, a non-contacted electromagnetic induction method is adopted herein to act as the heating treatment. Figure 1 shows the center of few rolls of coil plugging into a metal rod, and the both ends of coil are connected with alternating current $i_1$. Right at this moment, hysteresis phenomenon would occur when the metal rod creates magnetic flux, magnetic field strength in direct proportion with the electric current $i_1$, and the change of magnetic flux density falls far behind than that of the magnetic field strength. When this phenomenon happens, the permeable material would generate heat and cause the temperature increase. Such kind of energy loss is called the hysteresis loss\(^{(7),(8)}\).

The study adopts the high frequency induction method of gas condensation to produce nanoparticles and the experiment is proceeded under a vacuum environment, instilling inert gases such as He and Ar etc. into the vacuum chamber. First of all, place the pure Zn Bulk into the crucible, which would gasify after the heating of high frequency induction. Because of the convection effect created by the instilled gases, the gasified Zn metal would float to the water curtain collector having circulation of condensation, making the gasified metals condense into particles. During the process of metallic evaporation, the evaporated Zn atom collide with the inert gas atom. This would reduce the energy of the Zn atom, enabling it to condense speedily. Such effective condensation process would create a very high regional supersaturation phenomenon inside the vapor of the Zn metal, ensuring the gasified metal to perform an evenly distributed nucleation. Besides, because of the cooling effect of the water curtain collector, the process can prevent the growth of particles, and eventually develop the nanoparticle suspension that is evenly distributed in the deionized water.

When the surface atoms of the material break away from their surface because of the heating and evaporation, nucleation would occur upon the supersaturated condition. The speed of nucleation $J$ can be indicated in the following equation\(^{(9)}\):

$$J = k \exp \left( - \frac{16\pi\sigma^3 M^2}{3R_g T^3 \rho^3 \ln \left( \frac{P}{P_s} \right)} \right)$$  \hspace{1cm} (1)

where, $k$ is the Boltzmann’s constant, $\sigma$ is the surface tension of the material, $\rho$ is the density of the material, $M$ is the molecular weight, $R$ is the gas constant, $T$ is the absolute temperature, $P$ is the actual vapor pressure when the temperature is $T$, and $P_s$ is the supersaturated vapor pressure when the temperature is $T$. Also, $P/P_s$ is called the ratio of supersaturation (RS). When $RS = 1$, nucleation would occur. The \(16\pi\sigma^3 M^2/3R_g T^3 \rho^3\) of the exponential in Eq. (1) within the room temperature is a relatively high value, so the nucleation speed $J$ is very sensitive to the change of supersaturation ratio ($P/P_s$). Within a certain level of supersaturation, the particles of nucleation remain in a highly energetic condition, and the smallest particle radius that can steadily exist is called critical radius $r_c$. The relationship can be indicated in the following equation\(^{(9)}\):

$$r_c = \frac{2\sigma M}{R_g T \ln \left( \frac{P}{P_s} \right)}$$  \hspace{1cm} (2)

from Eq. (2), it is known that the major factors affecting the size of the critical particle radius are temperature and degree of supersaturated.

The growth of nucleus determines the desired size of nanoparticles. The growth rate of nucleus is controlled primarily by the concentration of the vaporized metal and the temperature of deionized water\(^{(10)}\). The temperature has a more critical influence on the size of nanoparticles since the growth rate of nucleus is significantly affected by the metal transfer frequency from gaseous state ($\beta$) to solid state ($\alpha$) on the interface. The relationship of these parameters is shown in Eq. (3).

$$f_{\beta \rightarrow \alpha} = \nu \exp \left( \frac{\Delta G}{kT} \right)$$  \hspace{1cm} (3)

where $\nu$ is the vibration frequency of atom, and $\Delta G$ is the activation energy of diffusion. Equation (3) indicates that
the growth rate of crystal nucleus will decrease rapidly when temperature drops. So, the most effective way to check the growth of particles and acquire tiny nanoparticles is a quick cooling.

The nature of rheology refers to the flowing or transforming behavior of substances in light of external forces. Affecting by the action of shear stress, the internal of fluid would create a velocity gradient, and the relationship between the two is indicated as the following equation:

$$\tau = A\dot{\gamma}^n$$

(4)

In the above equation, $\tau$ is the shear stress, and $\dot{\gamma}$ is the velocity gradient or shear rate. If $A$ is a constant and $n = 1$, then such kind of fluid can also be known as Newtonian Fluid. Besides, the proportional constant $A$ is called the viscosity of fluid, which can be viewed as a resistance against the fluid owing to the friction occurred between the inner particles. Suppose the relationship between $\tau$ and $\dot{\gamma}$ is a non-linear one, such kind of the fluid is a non-Newtonian Fluid, which can be subdivided into the pseudoplastic fluid ($n < 1$) and dilant fluid ($n > 1$). The $A$ value of pseudoplastic fluid would decrease along with the increase of shear rate, whereas that of the dilant fluid would increase along with the increase of shear rate$^{(11),(12)}$. If the fluid can begin to flow only when the exerting shear stress has exceeded a certain value, such shear stress value is called the yield stress of fluid. The relationship between the shear stress and shear rate of fluid can also be further sub-divided into linear (Bingham fluid) and non-linear (pseudoplastic and dilant) ones. By means of the experimental result, this study investigates into the effect of important process parameters on the nanoparticle suspension in the aspect of rheology, including the temperature of cooling fluid, vacuum pressure and the type of inert gas etc. Besides, Eq. (4) is applied to formulate the relationship between the shear stress and shear rate, so as to fit the experimental data of rheology of the nanoparticle suspension acquired by different process parameters. Subsequently, we acquire the values of $A$ and $n$ in Eq. (4) which demonstrate the rheological curves.

The stability of the nanoparticles would affect the applicability of the produced nanoparticle suspension. If the particle surface carries electron charge, the agglomeration phenomenon between the particles would lessen, enabling the particles inside the nanoparticle suspension to maintain a stable state. Through the surface electric potential of the nanoparticle suspension under different pH values, the range of pH value that is capable of maintaining a stable suspension condition can be acquired.

3. Experimental

During the experiment, the high frequency induction nanoparticle condensation system developed herein would extract the vacuum chamber to the required pressure, set the high frequency current at 250 A, and further heat the metal by means of electromagnetic inductive action. When it is heated into fusion temperature, inert gas of He or Ar is induced, so that when it reaches the gasified temperature of Zn, the Zn set inside the crucible would start to gasify. A curtain is placed on top of the crucible, where a pump is used to lead the deionized water flowing evenly and downwardly along the surface of the curtain to its bottom. When the gasified metal is affected by the condensation action of the cooling fluid on the curtain, it would solidify into particles and flow along the curtain into the collector together with the deionized water, thus becoming the nanoparticle suspension. The installation and schematic diagram of the whole experiment is shown in Fig. 2, where the major experimental devices are heating installation, pressure balancing system, temperature control system and collection system. The heating installation provides the induction heating source, as well as the setting of the required induced current, heating speed and rising temperature. The pressure control system is used to maintain an appropriate vacuum pressure inside the vacuum chamber. The particle collection system collects the liquid from the curtain, using the deionized water as the collecting and cooling fluid. The temperature control system can maintain the cooling fluid in a steady and low temperature condition so as to ensure the grain nucleation and at the same time, control its growth and obtain the smaller nanoparticles.

The parameters set by the experiment include temperature of the cooling fluid, vacuum pressure and the type of inert gas etc. In order to compare the experimental conditions, temperature of the cooling fluid is set at 2°C and 20°C, vacuum pressure is set at 40 Torr and 100 Torr, and inert gas of Ar and He are selected.

4. Results and Discussion

First of all, proceed with XRD inspection towards the lattice structure of the produced nanoparticles. The result shown in Fig. 3 reveals that the produced nanoparticles is ZnO. In order to confirm the composition of a single nanoparticles, EDX pattern analysis is employed. It is
known from Fig. 4 that the produced nanoparticles contain the elements of Zn, O and C, in which the origin of element C is carbon tape, thereby confirming the composed elements of nanoparticles are Zn and O.

Figure 5 shows the effect of two different cooling temperatures of 2°C and 20°C on the rheology of nanoparticle suspension. When the pressure is 40 Torr and the cooling temperature is 2°C, the shear rate of nanoparticle suspension would have a larger shear stress at 9 s⁻¹, 11 s⁻¹ and 19 s⁻¹, and their shear stress would range from 0.1 – 6.4 Pa, resulting from a pseudoplastic fluid. Besides, by using the Eq. (4) to fit the experimental data, the values of A and n are 0.9776 and 0.6948, respectively. When the cooling temperature is 20°C, the shear stress range would lie within 5.3 – 10 Pa, and the shear rate would have a larger shear stress at 13 s⁻¹. Such kind of nanoparticle suspension can be regarded as pseudoplastic fluid having a yield stress. Besides, by using the Eq. (4) to fit the experimental data, the values of A and n are 5.1685 and 0.1991, respectively. When the pressure is 40 Torr, the shear rate of nanoparticle suspension would have a larger shear stress at 9 s⁻¹, 11 s⁻¹ and 19 s⁻¹, resulting from a kind of fluid similar to the pseudoplastic fluid. Besides, by using the Eq. (4) to fit the experimental data, the values of A and n are 0.9776 and 0.6948, respectively. When the pressure is 100 Torr, there is no big change to the shear stress of nanofluid, which lies within the range of 3.5 – 10 Pa, and reaches its largest value of 10 Pa when the shear rate is 11 s⁻¹, and somewhat looks like the pseudoplastic fluid having a yield stress. Besides, by using the Eq. (4) to fit the experimental data, the values of A and n are 5.1685 and 0.1991, respectively. When the pressure is 40 Torr, the shear rate of nanoparticle suspension would have a larger shear stress at 9 s⁻¹, 11 s⁻¹ and 19 s⁻¹, resulting from a kind of fluid similar to the pseudoplastic fluid. Besides, by using the Eq. (4) to fit the experimental data, the values of A and n are 6.059 and 0.1376, respectively. Figure 8 is the TEM image of nanoparticles under the cooling temperature of 20°C and 100 Torr pressure. In the Fig. 8, all the particles are irregular in shape and their sizes are around 150 nm. By comparing Figs. 6 and 8, it is known that when the cooling fluid possesses a higher temperature, coarser particles would occur because it can not restrain the growth of particles effectively. However, when the pressure is lower, the produced particles would also be smaller.

Figure 9 shows the rheology of nanoparticle suspension when the inert gas of He and Ar is added respectively. By adding the inert gas of He, larger shear stress would occur at the shear rate of 5 s⁻¹, 11 s⁻¹ and 17 s⁻¹, in which its variation range lies within 2.3 – 9.9 Pa, result-
Fig. 6 TEM image of produced nanoparticles at the pressure of 40 Torr with cooling temperature (a) 2°C and (b) 20°C

Fig. 7 Effect of pressure on the rheology at the cooling temperature of 2°C

Fig. 8 Particles prepared by the cooling temperature of 20°C and pressure of 100 Torr

From the above experimental result, it is found that the ad-

dition of inert gas would change the rheology of nanopar-
ticle suspension, and the effect of Ar on the shear stress of nanoparticle suspension is particularly strong. Figure 10 shows the particle size distributions of nanoparticle sus-
pensions under the pressure of 40 Torr and 100 Torr, re-
spectively, and after the adding of Ar. When the pres-
sure is 40 Torr, the average size of particles is 172 nm, and when the pressure is 100 Torr, it would be 395 nm. From the results illustrated in Fig. 10 and the above discussion, it is known that smaller particles can be obtained under lower pressure, regardless of whether inert gas is added or not.

Figure 11 demonstrates the relationship between the shear stress and shear rate of ZnO nanoparticle suspension
under different pH values. This figure shows that except the pH value of 9.45, all the shear stress range of nanoparticle suspension lies within 0.5 Pa, in which the rheological curve is closest to linear form in pH 11.8. Also demonstrated from the figure, the acquired nanosuspension particles having different pH values are all similar to pseudo-plastic fluid having yield stress. Besides, by using Eq. (4) to fit the experimental data obtained from pH values of 3.3, 4.2, 9.45 and 11.9, respectively, the $A$ and $n$ values under respective pH values are 1.577 9 and 0.166 1, 0.883 1 and 0.239 3, 0.838 9 and 0.428 1 as well as 0.245 7 and 0.580 6.

Figure 12 shows the relationship between the viscosity of nanoparticle suspension and pH value when the shear rate is 12.56 s$^{-1}$. This figure indicates that when the pH value lies within the range of 4–8, the viscosity of nanoparticle suspension would drop rapidly, resulting from a fluid which is similar to the Newtonian Fluid while the particle dispersion is more satisfying. Figure 13 shows the relationship between the pH value of nanoparticle suspension and Zeta potential. When the pH value of nanoparticle suspension is 7.3, the Zeta potential is 0 mV, but when the pH value is larger than 7.3, it becomes a negative value. From this, when the pH value is smaller than 7, the particles can hardly agglomerate because the nanoparticle suspension has a higher surface electric potential, and thus acquiring the particles of a smaller particle size.

Figure 14 shows the relationship between the wave length and transmittance upon the exposure of Ultraviolet-Visible spectroscopy (UV-Vis) of the produced ZnO.
this figure, when the radiating wave length is smaller than 380 nm, the transmittance of light source on the nanoparticle suspension is less than 12%. In other words, the nanoparticle suspension produced by this study has a good capability of absorbing UV light. Besides, within this scope of wave length, the nanoparticle suspension having an average size of 50 nm possesses a better UV light absorption than those having an average size of 100 nm.

5. Conclusions

This study aims at developing a high frequency induction process for the production of nanoparticles. Through the experimental result, the following conclusion is acquired:

(1) Under lower pressure and cooling temperature, the particle produced is smaller with a size of approximately 50 nm.

(2) The addition of inert gas change the rheology of the nanoparticle suspension, whereas the addition of Ar can have a greater effect on the shear stress of the nanoparticle suspension.

(3) When the pH value of ZnO lies within the range of 4 to 8, and its viscosity tends to fall, then the fluid is similar to the Newtonian Fluid. When the pH value of the produced ZnO nanoparticle suspension is 7.3, the Zeta potential is 0, and when this pH value is smaller than 7.3, the Zeta potential is a positive value.

(4) It was identified by the UV-Vis spectrophotometer that the absorption wave length of UV light of the TiO2 Nanoparticles is less than 380 nm. The nanoparticle suspension produced by this study has a good capability of absorbing UV light.

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References

(1) Richard, P.F., There’s Plenty of Room at the Bottom, Annual Meeting of the American Physical Society, (1959), December 29.


(10) Patel, M.R., Barrufet, M.A., Eubank, P.T. and