

Continuous Synthesis of Surface-modified Zinc Oxide Nanoparticles using Supercritical Methanol

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ABSTRACT

Surface-modified zinc oxide (ZnO) with diameters of 400 nm were synthesized rapidly and continuously in supercritical methanol at temperature 400 °C and at pressure 30 MPa by using a flow type reactor system and decanoic acid (C₉H₁₉COOH) as an organic modifier. Transmission electron microscopy (TEM) showed that the usage of supercritical methanol and the addition of decanoic acid changed the shape and size of the nanoparticles. Wide angle X-ray diffraction (WAXD) analysis revealed that the surface-modified nanoparticles had ZnO crystalline structure. Dispersion test in solvents including water, ethylene glycol and transformer oil showed that the addition of organic modifier into the reaction system significantly affected the dispersion stability of nanocrystals. The results of Fourier transform infrared (FT-IR) demonstrated that reagents comprised of aliphatic groups associated with decanoic acid and hydroxyl group chemically bounded onto the surface of ZnO nanoparticles.

INTRODUCTION

Zinc Oxide (ZnO) has become the most widely studied metal oxide material. The tremendous interest is provoked by the multifunctional character of ZnO, the option to vary its properties via the adjustment of morphology (size and shape), and the ease of synthesis of even very complex ZnO materials. It is used in various technologies such as varistor, gas sensor, UV photodetector material, high-efficient green phosphor, field emission displays, solar cell, and other applications [1]. Due to its importance and the potential of ZnO, it is obvious that enormous efforts have been made to explore expedient synthetic ways to ZnO with different particle size, various particle shapes and surface modification of ZnO nanoparticles. ZnO particles can be produced by several techniques such as precipitation [2],

spray pyrolysis [3], thermal decomposition [4], and hydrothermal synthesis [5, 6]. In particular, hydrothermal synthesis is well known as an environmental safe and simple process because it does not require any organic solvents and additional processing such as calcination.

Nanoparticles of various materials have been widely prepared continuously using supercritical water (scH₂O) [7-12]. Recently, surface-modified metal oxide nanoparticles have been synthesized with supercritical hydrothermal synthesis in a batch mode [8-14]. By using organic ligands molecules that are miscible with scH₂O, crystal growth can be inhibited and surface hydroxyl groups can be replaced with the organic ligands. This results in highly dispersible, nonagglomerated metal oxide nanoparticles in organic media. However, continuous synthesis of surface-modified metal oxide nanoparticles in supercritical media has not been reported yet.

This study describes the first use of supercritical methanol (scMeOH) for synthesis of surface-modified zinc oxide nanoparticles in a continuous mode to prepare highly dispersible nanofluids. Instead of using scH₂O, we use scMeOH as a reaction medium in the continuous synthesis of surface-modified nanoparticles because (1) homogeneous metal salt solution and organic surface modifier solution can be introduced into a flow type reactor continuously, and (2) line and filter clogging problems by unreacted, precipitated surface modifier in water at ambient condition can be avoided.

MATERIALS AND METHODS

The surface-modified zinc (ZnO) nanoparticles were prepared by introducing a solution of zinc nitrate hexahydrate (Zn(NO₃)₂) and decanoic acid (as a surface modifier) in methanol to a continuous flow reactor system. A schematic diagram of the reactor system is shown in Figure 1. All hot sections of the system were insulated in boxes of ceramic board and the temperature was monitored directly using a thermocouple. The system temperature was controlled by a temperature controller. The DDI water or methanol flow rate was fixed to 6 mL/min while the precursor solution (with or without surface modifier solution) flow rate was fixed to 2 mL/min. Temperature, pressure and flow rate in the system were monitored. Typically, the temperature of the reactor and the mixing tee can be maintained at 400 ± 3 °C over the length of the reactor and the pressure can be maintained at 30 ± 0.1 MPa over the entire reaction time. After the reaction, the particles in the metal filters were collected. The nanoparticles were washed with methanol and filtered with PTFE membrane filter. The obtained nanoparticles were further purified by dissolving in methanol, sonicating, and then separated by using centrifugation. The procedure for the purification was carried out in triplicate and the purified nanoparticles were dried at 60 °C in a vacuum oven for 24 h. For the dispersion test, a known weight (0.01-1 wt%) of the purified nanoparticles was charged in water, transformer oil and ethylene glycol and dispersed with ultrasonication for 15 min.

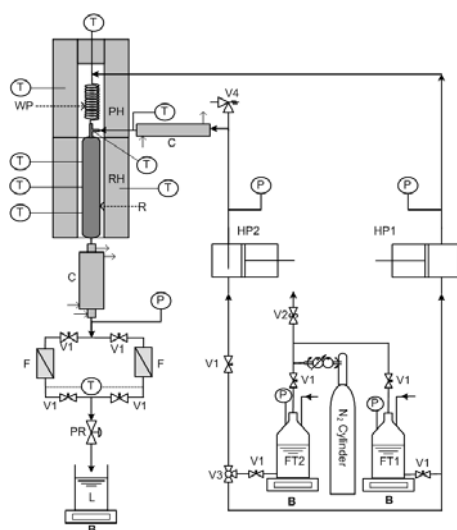


Figure 1. Schematic diagram of flow reactor system. B, balance; C, condenser; F, filter; P, pressure gauge; R, reactor; T, thermocouple; V, valve; FT, feed tank; HP, high pressure pump; PH, preheater; PR, pressure regulator; RH, reactor heater.

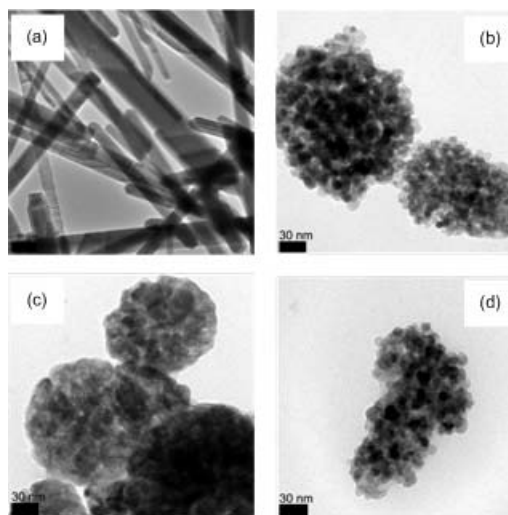


Figure 2. TEM image of zinc oxide nanoparticles synthesized using (a) scH_2O , (b) scMeOH , (c) scMeOH with 0.05 M $\text{Zn}(\text{NO}_3)_2$ and 0.3 M decanoic acid, (d) scMeOH with 0.01 M $\text{Zn}(\text{NO}_3)_2$ and 0.3 M decanoic acid. Nanoparticle synthesis conditions were 300 bar, 400 °C, and a residence time of ~ 40 s.

RESULTS AND DISCUSSION

Figure 2 shows the representative transmission electron microscopy (TEM) images of the zinc oxide nanoparticles synthesized at 300 bar, 400 °C, and residence time of ~ 40 s. When scH_2O was used, nanorods shape particles with clear facet was obtained. This result agrees well with the previously reported work [15]. When scMeOH was used, spherical shape particles with 40-80 nm in diameter were obtained (Figure 2b). When a lower molar ratios of surface modifier were used (molar ratio to $\text{Zn}(\text{NO}_3)_2$ precursor 6:1) was used with scMeOH as the reaction medium, the particle morphology did not change much compared to those of the particles synthesized without decanoic acid (Figure 2c). Significant changes of particle size morphology was observed with the use of large amount of decanoic acid (molar ratio to $\text{Zn}(\text{NO}_3)_2$ precursor 30:1) (Figure 2d). Primary particles with 5-10 nm in diameter were loosely aggregated and formed secondary particles with size of 30-40 nm. Thus the presence of the organic modifier significantly affected the particle shape and morphology. X-ray diffraction (XRD) analysis as shown in Figure 3 revealed the surface-modified nanoparticles had ZnO crystalline structure

Fourier transform infrared (FT-IR) analysis was conducted to investigate surface characteristics of the nanoparticles. Figure 4 shows FT-IR spectra of the zinc nanoparticles synthesized using (a) scH_2O , (b) scMeOH , (c) scMeOH with 0.05 $\text{Zn}(\text{NO}_3)_2$ and 0.3 M decanoic acid, and (d) scMeOH with 0.01 $\text{Zn}(\text{NO}_3)_2$ and 0.3 M decanoic acid. No functional

groups were observed in the particles synthesized using scH₂O (Figure 4a). In contrast, spectrum of the zinc nanoparticle synthesized using scMeOH shows broad -OH stretch peak at 3000-3750 cm⁻¹ and -CH₃ bend peak at 1330 cm⁻¹(Figure 4b). Thermal gravimetric analysis (TGA) results in Figure 5 showed that the weight of the particles synthesized using scH₂O did not change much while the weight of the particles synthesized using scMeOH decreased to ~ 98% at a temperature above 800 °C. This indicates that the surface of the zinc nanoparticles synthesized using scMeOH are modified with CH₃O- functional groups. The zinc nanoparticles synthesized using scMeOH with decanoic acid have -COO stretch peak at 1533 cm⁻¹, -CH₂- stretching peak at 2850 cm⁻¹ and -CH₃ stretching peak at 2920 cm⁻¹, along with the characteristic peaks of -CH₃ (1330 cm⁻¹) and OH (3000-3750 cm⁻¹) (Figure 4 c and d). The weight of the particles decreased to ~ 97.7% when temperature increased to 800 °C (see Figure 5). This suggests that some portion of the particle surfaces were chemically modified with decanoic acid. The presence of -COO peak may suggest that the carboxyl groups of decanoic acid are chemically bonded on the surface of the nanoparticles.

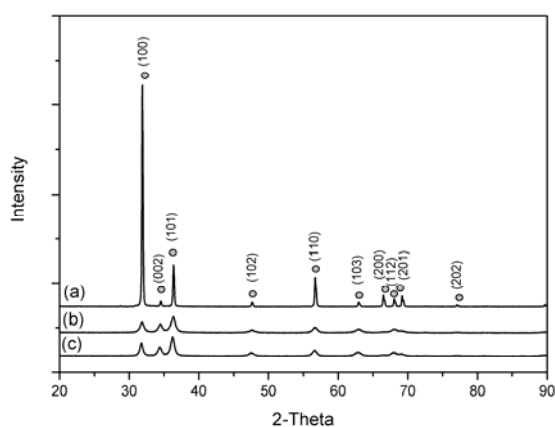


Figure 3. XRD pattern of zinc oxide nanoparticles synthesized using (a) scH₂O, (b) scMeOH, (c) scMeOH with 0.3 M decanoic acid.

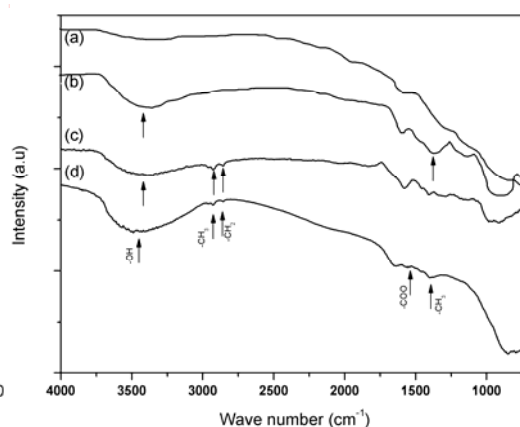


Figure 4. FT-IR spectra of zinc oxide nanoparticles synthesized using (a) scH₂O, (b) scMeOH, (c) scMeOH with 0.05 M Zn(NO₃)₂ and 0.3 M decanoic acid, (d) scMeOH with 0.01 M Zn(NO₃)₂ and 0.3 M decanoic acid.

Figure 6 shows dispersability of the zinc nanoparticles synthesized using scH₂O and scMeOH without using decanoic acid, and scMeOH using decanoic acid. Water, ethylene glycol and transformer oil were used as the base fluids. The transformer oil consists of cycloalkanes with a low portion of n-alkanes. The pictures in Figure 6 were taken after two weeks. All of the nanoparticles, synthesized using either scH₂O or scMeOH with or without using decanoic acid, aggregated and precipitated at the bottom of the vials when 0.1 wt% of the nanoparticles were dispersed in water. Similarly, when 0.1 wt% of the nanoparticles were dispersed in the transformer oil, all of the particles were precipitated. Aggregation and precipitation were observed when 1 wt% and 0.01 wt% of the nanoparticles were dispersed in

water or the transformer oil. The surface-modified nanoparticles dispersed in ethylene glycol showed better stability behavior. When 0.01 wt% of the nanoparticle synthesized using scH_2O were dispersed in ethylene glycol, most of particles were precipitated (Figure 6-1). Some portion of the particles synthesized using scMeOH was still dispersed and the other portion precipitated (Figure 6-2). When the surface of the particles was modified with lower molar concentration of decanoic acid, the dispersability was similar to that of the nanoparticles synthesized using scMeOH (Figure 6-3). In sharp contrast, perfect dispersion in ethylene glycol was observed in the nanoparticles synthesized using scMeOH with higher molar concentration of decanoic acid (Figure 6-4).

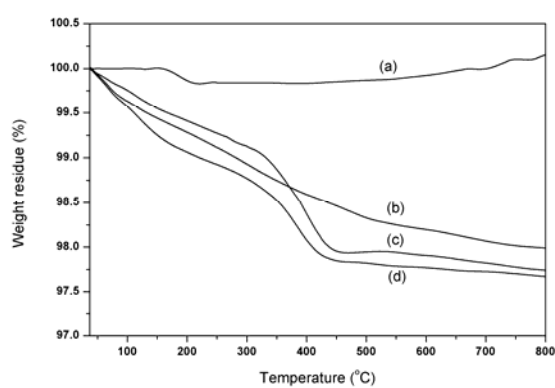


Figure 5. TGA thermograms of zinc oxide nanoparticles synthesized using (a) scH_2O , (b) scMeOH , (c) scMeOH with 0.05 M $\text{Zn}(\text{NO}_3)_2$ and 0.3 M decanoic acid, (d) scMeOH with 0.01 M $\text{Zn}(\text{NO}_3)_2$ and 0.3 M decanoic acid.



Figure 6. Dispersability of zinc oxide nanoparticles in ethylene glycol. The zinc oxide particles were synthesized using (1) scH_2O , (2) scMeOH , (3) scMeOH with 0.05 M $\text{Zn}(\text{NO}_3)_2$ and 0.3 M decanoic acid, (4) scMeOH with 0.01 M $\text{Zn}(\text{NO}_3)_2$ and 0.3 M decanoic acid. The bottom pictures were the bottom view of the vials.

Thus, surface-modified zinc oxide nanoparticles show much better dispersion stability in ethylene glycol. This may be due to the unique surface property of the surface-modified nanoparticles. As discussed previously, both of hydroxyl group and aliphatic group were present in the surface-modified nanoparticles. Thus the hydrophilicity of the particles can be a point between hydrophilic and hydrophobic. This may result in the particle precipitation in the hydrophilic fluid (water) and the hydrophobic fluid (transformer oil), but good dispersion in the medium hydrophilic fluid (ethylene glycol).

CONCLUSION

Surface-modified zinc oxide nanoparticles were synthesized using scMeOH in a continuous mode. The nanoparticles showed good dispersion stability in ethylene glycol. This method should also be applicable to various surface-modified metal oxides such as CuO ,

Fe₂O₃, AlOOH, and so on. This continuous method is amenable to large-scale production of nanofluids or other applications such as catalysts, cosmetics, bio-imagings, and optics by scale-up from laboratory to commercial scale.

ACKNOWLEDGEMENT

This research was supported by Nano R&D program through the Korea Science and Engineering Foundation funded by the Ministry of Education, Science and Technology (2008-02344). The authors acknowledge Energy and Environmental Research Division at Korea Institute of Science and Technology for additional support.

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