Characterization and Colloidal Stability of Surface Modified Zinc Oxide Nanoparticle

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Abstract. This paper mainly studies the characterization and colloidal stability of surface modified zinc oxide nanoparticle and pure zinc oxide nanoparticle. According to IUPAC definition, ultrafine particles are always in the range of within 100 nm called nano-sized particle which expressed in term of perfect spherical diameter. Nanotechnology has immersed into various sector of oil and gas industries. In recent decades, vast amount of research has been done using zinc oxide nanoparticle related products effect on disjoining pressure mechanism in porous medium, interfacial tension (IFT) and wettability. Several types of nanoparticles have been evaluated through interfacial tension and wettability. Disadvantage of poor colloidal stability of nanoparticle in fluid is aggregation and sedimentation which leads poor heat transfer. In this study, zinc oxide nanoparticle was used as core to be functionalized. Surfactant was used to surface modify ZnO nanoparticle. Surface modified ZnO nanoparticle and pure ZnO nanoparticle were characterized using Scanning Electron Microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR). Stability and hydrodynamic size of surface modified and pure zinc oxide nanofluid are examined using Zetasizer Nano ZS. Rheological behavior of nanofluids were determined through rheometer. The peak of surface modified and pure ZnO nanofluid were 62.94 nm and 386.4 nm respectively. There is a decrease of 83.71% of hydrodynamic size of nanoparticle after surface modified. ZnO nanofluid has the stability of -14.2 mV while surface modified ZnO has the zeta potential of -45.4 mV. Increase of 219.72 % more stable compared to pure ZnO nanofluid. Pure ZnO nanofluid showed viscosity increment which could because of the sedimentation of nanoparticle occurs. Lower viscosity of surface modified ZnO nanofluid might due to SDS surfactant.

1. Introduction

According to IUPAC definition, ultrafine particles are always in the range of within 100 nm called nano-sized particle which expressed in term of perfect spherical diameter. Nanoparticle have been studied for decades for the commercialization and scientific purposes [1]. The advantages of using nanoparticle for various application are due to low costs and environmental friendly. Zinc oxide is one of the metal oxide with low toxicity and biodegradability, making it attractive for application in the biomedical [2], agriculture [3], bio-sensing and antibacterial field [4]. In recent years, success application of nanoparticles was shown in the Table 1.

Nanotechnology has immersed into various sector of oil and gas industries. In recent decades, vast amount of research has been done using zinc oxide nanoparticle related products effect on disjoining pressure mechanism [5] in porous medium, interfacial tension (IFT) [6] and wettability [7]. It has been projected that the involved in nanoparticle reduces interfacial tension between two immiscible liquid and wettability alteration from strongly oil-wet to water-wet.
In the past decades, nanotechnology has penetrated upstream processing of oil and gas industry. Basically particles within hundred nano-meter defined as nanoparticles which are used for different applications such as exploration, reservoir, drilling and completion and production [8]. From the latest review paper by Xiaofei Sun et al. done research on various nanofluids in porous medium [9], nanoparticles such as silica [10], titanium dioxide [6], alumina [11], and zirconium oxide [12] have been studied. Interfacial tension and alteration of wetting behavior [4], [10–12] of nanoparticles on sandstone, limestone [16] were studied. SiO$_2$, TiO$_2$, Al$_2$O$_3$, and NiO proved to reduce more IFT of crude oil and nanofluid. Nwidee et al. [16] found that 0.05 wt% of zirconium oxide and nickel oxide greatly alter the oil-wet limestone to water-wet limestone which has brine as dispersant agent. Results have shown oil separated from the surface due to adsorption of nanoparticle.

### Table 1. Zinc oxide nanoparticles application in upstream oil and gas industries

| Nanoparticle | Size(nm) | Dispersion Agent | Area | Function | Ref. |
|--------------|----------|------------------|------|----------|------|
| ZnO          | 14-25    | Drilling mud     | Drilling fluids | Removal of toxic gas | [17] |
| ZnO          | <50      | Xanthan gum, PEG, PVP | Drilling fluids | Fluid loss reduction | [18] |
| ZnO          | 20       | Distilled water, 4wt% KCL | Coal Bed Methane | Control clay swelling | [19] |
| ZnO          | 5-35     | Clay             | Drilling fluid | Withstand HPHT condition, Rheologically stable, good colloidal dispersion | [20] |
| ZnO          | 1.1      | Arabic gum, brine | IFT | Interfacial reduction, wettability alteration | [21] |

In recent years, many researchers explored nanofluids the oil and gas application. Zinc oxide nanoparticles have proven the profound influence in removal of toxic gas, control fluid loss, control clay swelling and IFT reduction in porous medium. In porous medium, zinc oxide nanoparticles have been experimented numerous times individually [22], [23], coated [24], improve CO$_2$ flooding. In the latest review of nanotech for porous medium, C. Negin et al. [25] summarized that zinc oxide was one of the nanoparticles needed to be investigated deeper as when doing fluid injection, zinc oxide tend to agglomerates and cause porous medium permeability problems.

Nanofluid that injected into the porous medium must fulfill two criteria, which are (i) hydrodynamic size and (ii) stability. For hydrodynamic size, dispersing nanoparticle in fluid should be maintained in less than 100 nm to prevent the agglomeration and sedimentation due to gravitational effect. For stability, zeta potential can be used as to optimize the suspension and prevention of flocculation. Dynamic light scattering (DLS) is an instrument that measure a nanofluid sample in fast and effective way. It detects Brownian motion of the particles in the liquid. Random motion of nanoparticles and their spherical size can be detected based on the scattered light. Using Rayleigh scattering method, particles in fluid can be determined for their dispersity. Colloidal stability of nanoparticles can be assessed using zeta potential. Stable nanofluid can be achieved when the value more than ±30 mV. Choi et. al. resulted polymer coated silica nanoparticles has higher zeta potential compared to normal nanoparticle.

The aim of this study is to examine the dispersion stability of surface modified and pure ZnO suspension, zeta potential and their rheological behavior.

### 2. Experimental section

#### 2.1. Materials and Preparation of Surface Modified Zinc Oxide Nanoparticle

Zinc oxide nanoparticle was purchased from Aldrich Chemistry and sodium chloride (NaCl) was obtained from Merck. For surface coating purposes, sodium lauryl sulphate which as known as sodium...
dodecyl sulphate (SDS) from R&M Chemicals. Distilled water was prepared from Water Still-WS 4L. The morphology and characteristic of ZnO nanoparticle was determined by Variable Pressure Field Emission Scanning Electron Microscope (VPFESEM) and Fourier-transform infrared spectroscopy (FTIR) respectively. Energy-dispersive X-ray spectroscopy (EDX) was used to analyze each element in the sample.

For the chemical modification experiments, 20 g of pure ZnO nanoparticle was continuously mixing with 2 wt% of SDS surfactant solution under heating of 50 °C for 2 days. Coated nanoparticle was undergoing centrifugation method to be separated from SDS solution. Subsequently, nanoparticles were washed repeatedly and filtered to remove excessive surfactant. The surface modified nanoparticles were dried at 50 °C for another 3 days to ensure dried nanoparticle can be obtained [26].

Brine solution with the concentration of 3 wt% was prepared as dispersant agent using sodium chloride to mimic the salinity of seawater. Most researchers have found 500 ppm of nanoparticle concentration gave the best colloidal stability [4], [21–23]. Nimbus® analytical balance was used to measure precision up to 0.0001 g for the accuracy in obtaining nanoparticle’s weight. MCR Anton Paar 302 mainly analyze shear rate, shear stress and dynamic viscosity of fluid. To prevent agglomeration and sustain longer suspension for nanoparticle in solution, nanofluid was subjected to undergo 1 hour of ultrasonication before test for particle size analysis and zeta potential measurement.

2.2. Hydrodynamic Size of Nanofluid

Nanoparticle suspended in brine solution was analyzed with the dynamic light scattering (DLS) method. Particle Size Analyzer (PSA) can measure size range between 0.6 nm and 6 µm which has covered the nano-range of particle dispersed in solution. Prior to testing, nanofluid was sonicated hours for better suspension. Nano solution of 1 ml was injected into a designed cuvette which used 173° for light scattering through the sample. Hydrodynamic diameter of nanoparticle was determined through DLS and as in equation (1).

\[
d(H) = \frac{kT}{3\pi\eta D}
\]

where, \(d(H)\) = diameter of solid particles in fluid, \(D\) = translational diffusion coefficient, \(k\) = Boltzmann’s constant, \(T\) = temperature @ 25 °C, and \(\eta\) = viscosity of nanofluid.

Zeta potential of nanofluid can be determined through electrophoresis method. By applying electric field across the nanofluid, charged nanoparticle will be attracted by opposite charges and cause a constant velocity. The particle velocity in the electric field is known as electrophoretic mobility while zeta potential can be related through Henry equation as in equation (2):

\[
U_E = \frac{2\varepsilon z f(\kappa \alpha)}{3\eta}
\]

where, \(U_E\) = electrophoretic mobility, \(z\) = zeta potential, \(\varepsilon\) = dielectric constant, \(\eta\) = viscosity and \(f(\kappa \alpha)\) = Henry’s function.

| Nanopowder       | Particle size (BET) | Molecular Weight | Contain   |
|------------------|---------------------|------------------|-----------|
| Zinc Oxide       | <50nm               | 81.39            | 6% Al dop |

Table 2 Content of zinc oxide nanopowder
2.3. Rheological Behavior of Nanofluid
Modular Compact Rheometer (MCR 302) was used to determine the viscosity of nanofluid. Behavior of the nanofluid mainly depending on the shear rate. Viscosity of surface modified and pure ZnO nanofluid was measured at the same shear rate over 100 min to determine the average viscosity of nanofluid.

3. Results and discussion
3.1. Characteristic of Surface Modified and Pure ZnO Nanoparticles
Scanning Electron Microscope (SEM) was done on the surface modified nanoparticle and pure nanoparticle at 50 k times of magnification. Morphology of pure ZnO nanoparticle was seen in Figure 1(a) and surface modified ZnO nanoparticle in Figure 1(b). Few nano-meters increased for surface modified ZnO nanoparticle compared to pure ZnO nanoparticle, where it ranges from 40-60 nm diameter. Figure 3 and 4 show the EDX of pure ZnO nanoparticle and surface modified ZnO nanoparticle respectively. The molecular formula of SDS is C_{12}H_{25}NaO_4S. From the EDX, it shows the surface modified ZnO included all the element of the ZnO and SDS in the sample.

![Figure 1. SEM of pure ZnO nanoparticles](image1)
![Figure 2. SEM of surface modified ZnO nanoparticles](image2)

![Figure 3. EDX of pure ZnO nanoparticles](image3)
![Figure 4. EDX of surface modified ZnO nanoparticles](image4)

FTIR with wavelength range of 650 – 4000 cm\(^{-1}\) measured surface modified and pure ZnO nanoparticle shown in Figure 5. Pure ZnO nanoparticle shows IR peaks at 3378.5 cm\(^{-1}\), 2321.2 cm\(^{-1}\), 1980 cm\(^{-1}\), 2047.1 cm\(^{-1}\), 1498.9 cm\(^{-1}\), 1381.4 cm\(^{-1}\), 1040.1 cm\(^{-1}\), 945 cm\(^{-1}\), 827.6 cm\(^{-1}\), 693.3 cm\(^{-1}\). Surface modified ZnO nanoparticle show IR peaks at 3372.9 cm\(^{-1}\), 2919.8 cm\(^{-1}\), 2852.6 cm\(^{-1}\), 2371.5 cm\(^{-1}\), 2080.7 cm\(^{-1}\), 1991.1 cm\(^{-1}\), 1733.8 cm\(^{-1}\), 1543.6 cm\(^{-1}\), 1493.3 cm\(^{-1}\), 1375.8 cm\(^{-1}\), 1163.2 cm\(^{-1}\), 1040.1 cm\(^{-1}\), 939.5 cm\(^{-1}\), 889.1 cm\(^{-1}\), 827.6 cm\(^{-1}\), 704.5 cm\(^{-1}\). Sharp peak was observed at 3378.5 cm\(^{-1}\).
at pure ZnO and surface modified ZnO due to the O-H stretching and deformation by water adsorption on the metal oxide. 1498.9 cm\(^{-1}\) and 693.3 cm\(^{-1}\) from both ZnO corresponded to Zn-O stretching and deformation respectively. The results for O-H and Zn-O bond matched with the literature values [30]. C-H stretching at frequency of 2919.8 cm\(^{-1}\) and 2852.6 cm\(^{-1}\) and presence of C-O bond at 1040.1 cm\(^{-1}\) in surface modified ZnO indicated the layer of surfactant on the ZnO nanoparticle.

![FTIR of surface modified (orange) and pure ZnO (blue)](image)

**Figure 5.** FTIR of surface modified (orange) and pure ZnO (blue)

3.2. Stability and Rheology of Zinc Oxide Nanofluid

Stability of nanoparticle in liquid is crucial as it determines the sedimentation and agglomeration occurs. Result of hydrodynamic size for surface modified and pure ZnO nanoparticle was shown in Figure 6. The peak of surface modified and pure ZnO nanofluid were at 62.94 nm and 386.4 nm respectively. There is a decrease of 83.71% of hydrodynamic size after surface modification. For surface modified ZnO, size ranges from 40 – 90 nm. It showed low agglomeration of nanoparticle in the fluid. However, for pure ZnO nanoparticle has range of 250 – 400 nm. The DLS results obtained for pure ZnO nanofluid much alike to the result done by Tso et. al. with pure water as carrier fluid [31].

Dispersion stability of nanofluid can be measured through absolute value of zeta potential. Nanofluid can be ensured as colloidal stability of dispersion with the absolute zeta potential more than 30 mV [32]. Table 3 shows the colloidal stability of nanofluid measured using zeta potential. Without surface modified, ZnO nanofluid has the stability of -14.2 mV. Low stability and high possible on particle aggregation. For surface modified ZnO, the zeta potential is -45.4 mV. Higher than 30 mV considered the nanofluid is at better colloidal stability condition.

**Table 3.** Zeta potential of surface modified and pure ZnO nanofluid

| Nanofluid       | Zeta Potential (mV) |
|-----------------|---------------------|
| ZnO             | -14.2               |
| Surface Modified| -45.4               |
| ZnO             |                     |
Dynamic viscosity of ZnO nanofluid was shown in Figure 7. Compared to pure ZnO nanofluid, surface modified ZnO nanofluid presented approximate of 0.45 mPa.s over the time. Pure ZnO nanofluid showed viscosity increment over a period of 500 s. Some of the nanoparticles was found to be depositing during the measurement. From 0.55 mPa.s, pure ZnO nanofluid increased for 26.55% to 0.696 mPa.s. Compare to pure ZnO nanofluid, surface modified ZnO nanofluid has lower viscosity but very stable with time.

![Size Distribution by Intensity](image)

**Figure 6.** Hydrodynamic size distribution of surface modified and pure ZnO nanofluid

![Viscosity vs Time](image)

**Figure 7.** Viscosity of surface modified ZnO and pure ZnO nanofluid

4. Conclusions

ZnO nanoparticle was surface modified using simple method of mixing, centrifuge, washing and filtering repeatedly with SDS for better dispersion. The prepared pure ZnO and surface modified ZnO nanoparticles were proven that nanoparticle was surface modified through SEM and FTIR. Dispersion stability were determined through ZetaSizer. The size of surface modified ZnO nanoparticle did not
vary much compared to pure ZnO nanoparticle. The peak of surface modified and pure ZnO nanofluid were 62.94 nm and 386.4 nm respectively. ZnO nanofluid has the stability of -14.2 mV while surface modified ZnO has the zeta potential of -45.4 mV. There is an increase of 219.72 % colloidal stability with the surface modified ZnO nanofluid. Pure ZnO nanofluid showed viscosity increment which could be due to the sedimentation of nanoparticle occurs. Surface modified ZnO nanofluid has lower viscosity compared to pure ZnO nanofluid can be attributed to the SDS surfactant.

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