Preparation of ZnO Nanoparticles Water-based Dispersion

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Abstract. In this work, an attempt was made to stabilize ZnO NPs as water-based dispersion. The dispersing agents used are 3-glycidoxypropyltrimethoxysilane (GPTMS), polyvinyl alcohol (PVA) and oleic acid (OA). These dispersing agents were combined with sodium dodecyl sulfate (SDS) to facilitate better dispersion stability. Different w/v% content of modified ZnO NPs such as 0.2, 0.4, 1 and 3% w/v was used at a fixed ratio of ZnO NPs:SDS:dispersing agent. The highest dispersion stability was achieved at 1% w/v content of modified ZnO NP, whereas some precipitate was observed at 3% w/v. The result reveals that sonication at 30 minutes produced the highest dispersion stability whereas extended sonication led to re-agglomeration of ZnO NPs. The optimum ratio of ZnO NPs:SDS:dispersing agent which produced about 98% dispersion stability was at 1:0.25:0.2. The zeta potential (ZP) values of ZnO NPs/GPTMS, ZnO NPs/PVA, and ZnO NPs/OA dispersions are -51, -29 and -15 mV, respectively. The ZP values was influenced by the electrical charge surrounding the particles which was also caused by the functional group of the dispersing agents. However, the stabilization mechanisms of modified ZnO NPs in water was complicated. It did not only depend on the electrostatic value but also on electrosteric stabilization caused by the steric effects hindering the dispersing agents. Interactions between the dispersing agents and ZnO NPs was confirmed through FTIR analysis.

1. Introduction

ZnO NPs has been widely used in cosmetic, plastic, pharmaceuticals, rubber, textile, and catalysts due to its antibacterial and low-cost properties. It is an inorganic compound, appearing as a white powder which is insoluble in water. So, whereas ZnO NPs can disperse in organic system, it is difficult to disperse it in an aqueous system. Therefore, it is essential to modify the surface of ZnO NPs [1-3]. Moreover, ZnO NPs possesses small size with large surface area. This often led to agglomeration of particles and formation of sediments at the bottom of dispersion containers.

To overcome this problem, ZnO NPs particles have been modified with some organic compounds or polymers to reduce the attraction between the particles. This is performed so that the surface charges could repel the particle from each other and achieve stabilization through electrostatic stabilization. In case of functionalized particles, the hindrance of large molecules would keep the distance between particle, through steric stabilization. The combination of both phenomena is called electrosteric stabilization. Poly(vinyl alcohol) (PVA), oleic acid (OA) and 3-Glycidyloxypropyl trimethoxysilane (GPTMS) contain hydroxyl, carboxyl and silanol functional groups which interact with ZnO NPs [4-6]. Since GPTMS, PVA and OA possess different functional groups and molecular weight, the stabilization mechanism might be different. Hence, SDS is commonly used as dispersing agent. It contains strong negative charge which can effectively stabilize the dispersion. Therefore, it is quite interesting to study the dispersion efficiency, using a combination of SDS and other dispersing agent as it can help...
to provide different dispersion stability. In fact, the synergistic effect of SDS and dispersing agent was reported in the study conducted by Xiaofei [7]. On the other hand, ultrasonication is a common technique to break up the agglomeration of nanoparticles. The adhesive interparticle forces cause agglomeration and reduced repulsion [7]. So, the vibration from ultrasound would generate voids between the aggregated particles, thereby separating the small particles from each other. As such, the dispersion would be stable for a longer time.

In this work, ZnO NPs dispersions were carried out in an aqueous solution. Three types of dispersing agents such as (3-Glycidyloxypropyl) trimethoxysilane (GPTMS), poly(vinyl alcohol) (PVA) and oleic acid (OA) were used to modify the ZnO NPs surface with a combination of Sodium dodecyl sulphate (SDS). The content of modified ZnO NPs in water, sonication time and ratio of ZnO NPs:SDS:dispersing agent were optimized for the dispersion stability. The surface charge was evaluated with a Zetasizer while the functional groups on the particle surface was investigated through FTIR analysis.

2. Materials and methods

2.1 Materials

The zinc oxide nanoparticles (ZnO NPs) were purchased from Nano materials technology, Chonburi, Thailand. On the other hand, 3-Glycidyloxypropyl trimethoxysilane (Molecular weight=236.34 g/mol), and poly(vinyl alcohol) (Molecular weight ~31,000-50,000) were purchased from Sigma-Aldrich, St. Louis, USA. Oleic acid (Molecular weight=282.47 g/mol), pharma grade was procured from PanReac AppliChem, Darmstadt, Germany while Sodium dodecyl sulphate (SDS) was purchased from KEMAUS, Australia.

2.2 Preparation of ZnO NPs dispersions with various conditions

The ZnO, SDS, and dispersing agents were mixed into 10 ml of water and then stirred using a magnetic stirrer for 10 mins. The mixtures were then sonicated at room temperature for 10 mins. The dispersion contains modified ZnO NPs at different wt% content such as 0.2, 0.4, 1 and 3% w/v while the amount of SDS and dispersing agent (1:1) was fixed at 50% w/w of ZnO NPs. Three types of dispersing agents; (3-Glycidyloxypropyl)trimethoxysilane (GPTMS), Oleic acid (OA) and poly(vinyl alcohol) (PVA) were used separately. The dispersions were prepared as formulations summarized in Table 1.

The optimum content of ZnO NPs in the dispersion was used to further study the effects of various sonication time using three types of dispersing agents. The sonication was performed at 5, 10, 15, 30 and 60 mins (sample numbers 19-33). Subsequently, the dispersion with above optimum condition (ZnO content, sonication time) was studied at different ratio of ZnO NPs:SDS:dispersing agent as presented in Table 1 (sample numbers 34-48).

2.3 Characterizations

2.3.1 Dispersion stability. The prepared dispersions were placed in the test tube for 10 ml to observe the precipitation. The tubes were put on racks and placed in a stable condition without disturbance. The dispersion stability was calculated using equation (1) which was modified from Batmunkh’s work [8]. The height of dispersion was obtained from the cloudy area, see details in Figure 1.

\[
\% \text{Dispersion stability} = \frac{\text{dispersion height}}{\text{initial height of dispersion}} \times 100\% \tag{1}
\]

2.3.2 Zeta potential value. The charge (Zeta potential) on surface of the modified ZnO NPS particles in dispersions were determined by using a Zetasizer (MALVERN, ZSP).

2.3.3 Fourier Transform Infrared Spectroscopy (FTIR). The functional groups of the ZnO NPs, modified ZnO NPs and dispersing agents were characterized through Fourier Transform Infrared Spectrophotometry using a NICOLET iS50 FT-IR spectrophotometer over a wavenumber range from 400 to 4000 cm\(^{-1}\). The prepared dispersions were dried and washed with ethanol. Then, the dried ZnO NP powder was grinded with KBr and then pressed into a pellet for characterization.
3. Results and discussion

3.1 Effect of modified ZnO NPs content

Figure 1 presents the stability of ZnO NPs dispersion. The ZnO NPs were dispersed in water by adding dispersing agent and SDS for synergic stabilization. Preliminary experiment revealed that dispersions without any dispersing agent or surfactant precipitated rapidly after sonication. It was also found that using merely dispersing agent or SDS presented lower stability compared to their combination. Both SDS and dispersing agents produced electrostatic stabilization. This is because SDS possesses strong electrostatics while dispersing agents may present high hindrance to their molecules. Dispersions containing various ZnO NPs contents such as 0.2, 0.4, 1 and 3% w/v with fixed ratio of ZnO NPs:SDS:dispersing agent (1:0.25:0.25) are included in Figure 1. The dispersion stability increases when the modified ZnO NPs content was increased. Hence, dispersion at 1% w/v of modified ZnO NPs gave better stability (about 96.25% dispersion stability) compared to other contents for the three types of dispersing agents. However, at 3% w/v of modified ZnO NPs precipitates were formed at the bottom of the tube (Figure 1 (c)). It is noticeably that at low content of modified ZnO NPs, the dispersion efficiency was low. This might be due to the presence of small amount of SDS and dispersing agent in the dispersion system which were not only adsorbed on the modified ZnO NPs, but also freely distributed in the aqueous [9]. At 0.2 and 0.4 % w/v, the remained SDS and dispersing agent might not be sufficient to cover the particles surface. Hence, the optimum amount of ZnO NPs in this case was 1% w/v [10]. However, at higher content of ZnO NPs (3% w/v) undesirable flocculation or aggregation might have been induced maybe because the particles got too close to each other, thereby producing larger clusters of particles [11]. This invariably resulted in low dispersion efficiency.

![Figure 1](image-url)  
**Figure 1.** Dispersion stability of dispersions containing ZnO NPs:SDS:dispersing agent (1:0.25:0.25) with various content of ZnO NPs at 0.2% w/v (a) 0.4% w/v (b) 1% w/v (c) 3% w/v (d).

3.2 Effect of sonication time

Dispersions containing the three types of dispersing agent and 1% w/v ZnO NPs was selected to study the effect of sonication time as presented in Figure 2. It was found that dispersion stability increased when sonication time was increased from 10 mins to 30 mins. However, the dispersion stability achieved at 60 min of sonication was reduced. The results showed that the optimum sonication time is at 30 mins (97.5-98.75%
dispersion stability). Generally, sonication could break the agglomeration of ZnO NPs by vibration. Therefore, the longer time helped to facilitate effective deagglomeration which resulted in improved dispersion stability. However, when the sonication period was increased 60 mins, more sonication energy was imparted on the particles which might induce re-agglomeration of the nanoparticles [12,13]. This is believed to be responsible for the reduced dispersion stability at 60 mins of sonication. Similar observation was reported in literature by Zhou et al. [14] and Anand et al. [15].

### 3.3 Effect of ratio of ZnO NPs:SDS:dispersing agent

The optimum ratio of SDS and each dispersing agent was investigated by fixing the content of ZnO NPs at 1% w/v and sonication time at 30 min (Figure 3). Dispersions were prepared at various ratios of ZnO NPs: SDS: dispersing agent as followed; 1:0.25:0.05, 1:0.25:0.1, 1:0.25:0.2 and 1:0.25:0.3 which are presented in Figure 3(a-e). Results showed that the dispersion with GPTMS, PVA and OA at 1:0.25:0.2 gave the highest stability (97.5-98.75% dispersion stability). In this work, it was observed that dispersions could be stabilized by electrosteric stabilization emanating from particle charge and hindrance of dispersing agent molecules [16-18]. As a result, the dispersion stability increases with increasing ratio of dispersing agent. Hence, as more ratio of dispersing agent was added, more molecules were possibly anchored on the ZnO NPs surface. This causes the hindrance effect which provided the greater repulsive force between the particles and prevents agglomeration [18]. However, the optimum ratio (saturation) of dispersing agent or SDS and particle are required. In case of too high dispersing agent, the molecular chains may cover the particle surface with too thick layer, thereby causing entanglement with the ones on other particles [10]. The interaction force resulted in flocculation of the system and then the loss of the dispersion stability [19,20].

### 3.4 Zeta potential

Table 2 shows the zeta potential (ZP) values of ZnO NPs aqueous dispersions containing GPTMS, OA and PVA. The measurement of all the dispersions was taken at pH 8. The recorded ZP values of ZnO NPs/GPTMS, ZnO NPs/PVA and ZnO NPs/OA dispersions are -51.3, -25.6 and -19.3 mV, while generally, the ZP value of pristine ZnO NPs dispersion is around 4-20 mV [21,22]. After modification, the ZP values turned to negative charges and presented higher values compared to the pristine ZnO NPs dispersions. It is believed that the
mixture of SDS and dispersing agent might have enhanced the ZP values of ZnO NPs dispersion. The obtained ZP values of each dispersion are from the combined particles charges of NPs, SDS and dispersing agent. However, the effect of different type of dispersants on the ZP value at the same amount of ZnO NPs and SDS was clearly shown. It was predicted that the molecules of GPTMS straightened and turned the silanol groups to interact with ZnO NPs. GPTMS containing epoxy ring would present the negative charge in aqueous. In addition, it exhibits low molecular weight indicating that large number of molecules with large number of negative charges in the system were obtained. The ZnO NPs/PVA dispersion gave the lower ZP value, even though the hydroxyl groups of PVA would wrap as a thick layer or clump on the ZnO NPs. This might have reduced the influence of particle charge and cause lower ZP. In the case of OA, the straightened molecules may form a bilayer or multilayer to stabilize the ZnO NPs in water. It is noteworthy that the ZP values did not agree with the %dispersion stability. This is probably because GPTMS, PVA and OA possess different functional groups, molecular structures, and size, thereby manifesting different dispersion mechanism. Therefore, this might have produced different effects from both particle charge and hindrance to molecules.

| Table 2. Zeta potential values of the obtained dispersions |
|----------------------------------------------------------|
| Dispersion (at ratio 1:0.25:0.2) | Zeta potential (mV) |
| ZnO NPs:SDS:GPTMS | -51 |
| ZnO NPs:SDS:PVA | -25 |
| ZnO NPs:SDS:OA | -19 |

3.5 FTIR analysis

The FTIR spectra of ZnO NPs and ZnO NPs modified with GPTMS (ZnO NPs/GPTMS), PVA (ZnO NPs/PVA), and oleic acid (ZnO NPs/OA) are illustrated in Figure 4. The powder samples were washed by ethanol for several times before characterization. The pristine ZnO NPs presented the peak at 400-500 cm\(^{-1}\) which corresponds to Zn-O stretching. The broad peak at 3404 cm\(^{-1}\) and the band in the region of 1384 to 1503 cm\(^{-1}\) corresponds to the hydroxyl group from atmospheric moisture [23].

![Figure 4. FTIR spectra of ZnO NPs, dispersing agents and modified ZnO NPs.](image)

In contrast, the FTIR spectrum of ZnO NPs/GPTMS reveals the peak at 1090 cm\(^{-1}\) which is assigned to the Si-O-Si asymmetrical stretching [24]. This peak disappeared after coating ZnO NPs surface due to the anchorage of functional groups and ZnO NPs particle [25]. On the other hand, the FTIR spectrum of ZnO NPs/PVA shows the band at 1495 cm\(^{-1}\) and 1096 cm\(^{-1}\) corresponding to CH\(_2\) bending and C-O stretching, respectively [26]. In the case of ZnO NPs/OA a band is present at 1215 cm\(^{-1}\) which is believed to have originated from the C-O stretching of carboxylic acid. The band at 1415 cm\(^{-1}\), 1542 cm\(^{-1}\) corresponds to COO-Zn stretching. Significantly, the band at 1713 cm\(^{-1}\) which represents C=O is almost absent in the spectrum of ZnO NPs/OA [27]. Based on these observations, it can be inferred that GPTMS, PVA and OA were incorporated onto the ZnO NPs.
4. Conclusions
Highly stable aqueous ZnO NPs dispersion was successfully prepared using GPTMS, PVA and OA as dispersing agent combined with SDS. The highest stability dispersions was obtained from the concentration of 1% modified ZnO NPs w/v at ZnO NPs:SDS:dispersing agent ratio of 1:0.25:0.2 and by sonication for 30 minutes. The ZP values of ZnO NPs/GPTMS dispersion was higher than ZnO NPs/OA and ZnO NPs/PVA, respectively. The interaction between ZnO NPs and GPTMS, PVA or OA was confirmed from the FTIR result.

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