PARTICULATE SCIENCE AND TECHNOLOGY
2017, VOL. 35, NO. 1, 67–70
http://dx.doi.org/10.1080/02726351.2015.1131787

Role of surfactants on the stability of nano-zinc oxide dispersions

Anand K. and Siby Varghese

Technical Consultancy Division, Rubber Research Institute of India, Kottayam, Kerala, India

ABSTRACT

Nowadays, stable colloidal dispersions with ultra-fine or nanosized particles are getting importance due to their higher activity. In this article, methods for the preparation of stable aqueous dispersions of zinc oxide (ZnO) were discussed. The quality of the dispersion was improved by capping with different types of surfactants say non-ionic, cationic, and anionic. Accordingly, Triton X 100, polyethylene glycol-6000 (both non-ionic), cetyltrimethylammonium bromide (cationic), and sodium dodecyl sulfate (anionic) were selected for the study. Effect of these surfactants on particle size of ZnO was followed through dynamic light scattering (DLS) studies and zeta potential measurements. Particle size analysis and zeta potential measurement indicated that ZnO dispersions stabilized with anionic surfactants (sodium dodecyl sulfate) showed better stability. Further, the effect of ultrasonication on particle size distribution was examined and optimized.

KEYWORDS

Dispersion stability; nano-ZnO; surfactants; ultrasonication; zeta potential

Introduction

A stable colloidal dispersion is expected to remain without sedimentation even after prolonged periods of storage. The settling behavior of dispersions depends mainly on the size and density of the dispersed particles. Dispersion of nanopowders into liquids is a challenging task. The high surface area and surface energy which are responsible for the beneficial effects of nanomaterials cause agglomeration of particles which leads to poor-quality dispersions.

Stabilization of metal oxide nanoparticles are extensively studied over the past few years (Tkachenko et al. 2006; Zhang et al. 2008). As a promising semiconductor material, ZnO finds lot of applications in optoelectronic devices, photocatalysts, cosmetics, pigments, paints, ceramics, solar cells, varistors, sensors etc. (Kanade et al. 2006; Promsawat, Watcharapasorn, and Jiansirisomboon 2012). The properties of ZnO can be tailor-made by reducing the size, whereby the specific surface area gets increased, which increases the chemical activity.

Surfactants/capping agents are usually employed to control the size and dispersion of nanoparticles. The presence of capping molecule appears to affect the kinetics of nucleation and accretion in such a way that the growth of large particles slows down gradually. When no capping agents are introduced, particle–particle interaction will be much higher, accounting for the instability of the sample (Guo et al. 2000). Stabilization of colloidal dispersions of several commercial and synthesized metal oxide nanopowders by electrostatic and steric interactions was reported (Heijman and Stein 1995; Widegren and Bergstrom 2002; Mandzy, Grulke, and Druffel 2005). Synthesis of sulfur nanoparticles in aqueous media and the effect of different surfactants on particle size is studied by Chaudhuri and Paria (2010). Naeini et al. (2012) used UV-visible spectroscopy to investigate the dispersion and stability of titania nanoparticles in aqueous media with different types of dispersants. Effect of dispersant types and concentration on dispersion of titania nanopowders was reported by Fazio et al. (2008). They used zeta potential measurements and particle size distribution to characterize the nanotitania suspensions.

The main difficulty associated with nanoparticles is to convert it into a stable dispersion. Though the benefits of nanoparticles are widely appreciated, there exist difficulties in the preparation and storage stability of such dispersions. The key problem is the particle agglomeration. *Van der Waals* and other attractive forces are responsible for the formation of aggregates or agglomerates. This impedes the effective usage of nanoparticles and makes the production cost much higher. With increasing energy costs and raw material prices, it is important to explore the efficiency of the manufacturing process associated with fine-particle dispersions.

Most of the nanomaterials are produced *via* dry process. As a result, they should be dispersed well in liquid formulations. Breakage of agglomerates is also a critical issue. Therefore, effective methods for de-agglomeration and dispersion of particles are required to explore the full potential of nanoparticles in aqueous dispersions. Ultrasonication is a well-established method for particle size reduction. Further, storage stability of nanodispersions is important for various applications.

In the present work, dispersion of synthesized ZnO nanopowder was stabilized with different types of surfactants. The stability of the resulting dispersion was assessed by particle size analysis, zeta potential measurements, and sedimentation tests. Effect of ultrasonication on the size reduction is also attempted.

CONTACT Siby Varghese ✉ siby@rubberboard.org.in Technical Consultancy Division, Rubber Research Institute of India, Kottayam, Kerala, India.

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/upst.

Experimental

Materials

Nano-ZnO with an average particle size of 35 nm, synthesized through a mechano-chemical route (Anand, Varghese, and Kurian 2014) was used to prepare aqueous dispersion. Briefly, 1 M $Zn(OAc)_2$ $2H_2O$ and 0.3 M cetyltrimethylammonium bromide (CTAB) were ground in an agate mortar for about 20 min. 6 g of NaOH was added to the above mixture and further ground for 45 min at room temperature. The resulting pasty mass was washed with 100 ml distilled water for two to three times and sonicated. It is then centrifuged at 600 rpm. The resulting supernatant solution was decanted off. The precipitate is filtered, dried, and calcined at 300°C for 2 h.

$Zn(OAc)_2$ $2H_2O$ and NaOH used were of AR grade supplied by MERCK, Mumbai, India. CTAB was procured from CDH (New Delhi). HPLC grade distilled water (Spectrochem, Mumbai) was used for the synthesis of nano-ZnO. The surfactants used are Triton X 100, PEG 6000 (both non-ionic), CTAB (cationic), and sodium dodecyl sulfate (SDS) (anionic). Triton-X 100 and SDS were purchased from Sigma-Aldrich (Germany). PEG 6000 was procured from MERCK and LR grade CTAB from NICE chemicals, Kochi, India. Millipore distilled water having a conductivity of 0.240 µS/cm was used for the preparation of surfactant solutions. Details of the surfactants are given in Table 1.

Methods

Preparation of ZnO dispersion

Surfactant solutions with a concentration of 0.22 wt% was prepared by adding 0.11 g of each surfactant in 50 ml distilled water and stirred to get a homogeneous solution. It was then divided into four aliquots and nano-ZnO was added to each with continuous stirring. The concentration of resulting dispersion was maintained at 0.5 wt%. The stirring process was continued for few more hours to get a uniform dispersion of ZnO. Around 13–15 ml of that is taken in four different test tubes (designated as **a, b, c**, and **d**) and are used for the storage stability studies (sedimentation test). [*__a__ and __b__ represents ZnO dispersed in Triton X 100 and PEG 6000, respectively. __c__ indicates ZnO dispersed in CTAB and __d__ represents ZnO dispersed in SDS.*]

Particle size analysis was performed in a particle size analyzer (Zetasizer Nano S, Malvern, UK) using dynamic light scattering (DLS) technique. A Vibra Cell ultrasonicator (model VCX-750) at a frequency of 20 kHz having 750 W power rate was used to break down the agglomerates in the dispersions. Zeta potential was measured by a Zetasizer (Nano Z, Malvern, UK) at 25°C.

Results and discussion

The morphological characteristics of synthesized ZnO nanoparticles were studied using transmission electron microscopy (TEM) and are given in Figure 1. Particles have a rod-like morphology as evident from the TEM image. The average particle size is in the range of 35–60 nm and is in good agreement with our previous results (Anand, Varghese, and Kurian 2014).

Impact of various surfactants on ZnO dispersion

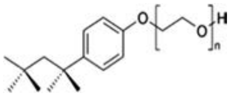
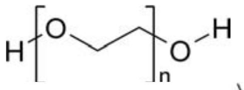
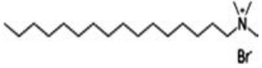
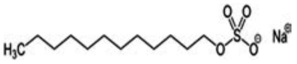
Particle size of ZnO in various surfactants

Figure 2 displays the particle size distribution curves of aqueous dispersions of ZnO in the presence of different surfactants. The average particle size $D(50)$ was discussed. It can be seen that among the three kinds of surfactants used, nano-ZnO stabilized with SDS showed the lowest particle size (186 nm). The share of particles (vol.%) was 36%, whereas in CTAB, almost 50% particles recorded a size of 191 nm. Among the non-ionic surfactants tried, ZnO particles showed a size of 442 and 716 nm, respectively, in Triton X 100 and PEG 6000. The higher size exhibited by ZnO in PEG 6000 might be due to aggregation between ZnO nanoparticles.

Size after storage

The storage stability of nano-ZnO dispersions stabilized using various surfactants was checked after keeping the samples for 1 week. The size distribution curves are shown in Figure 3. In all the cases, the size of the particles is higher than the initial. The particle size, $D(50)$ of ZnO in Triton X 100, PEG 6000, and CTAB are 1590 nm (32%), 1162 nm (43%), and 1365 nm (38%), respectively. A bimodal distribution curve having size 227 nm and 4951 nm was observed for ZnO stabilized with SDS. The increased size is due to agglomeration, which might

Table 1. Details of the surfactants used.

Surfactant used	IUPAC name	Formula	Molar mass (g mol^{-1})	Structure
Triton X 100	Polyoxyethylene octyl phenyl ether	$(C_{14}H_{22}O(C_2H_4O)_n)$	647	
PEG 6000	Poly(oxyethylene)	$H\text{-}(O\text{-}CH_2\text{-}CH_2)_n\text{-}OH$	5000–7000	
CTAB	Hexadecyl-trimethyl-ammonium bromide	$(C_{16}H_{33})N(CH_3)_3Br$	364.45	
SDS	Sodium dodecyl sulfate	$NaC_{12}H_{25}SO_4$	288.37	

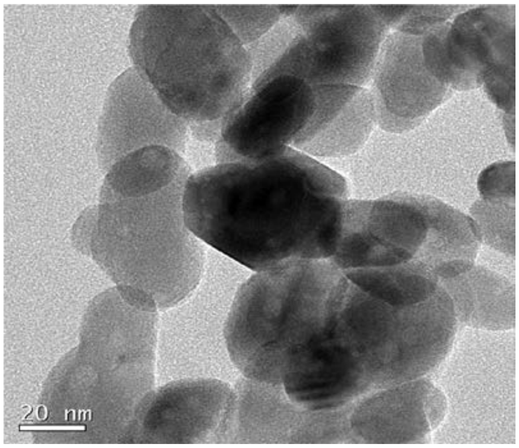


Figure 1. TEM image of nano-ZnO (synthesized).

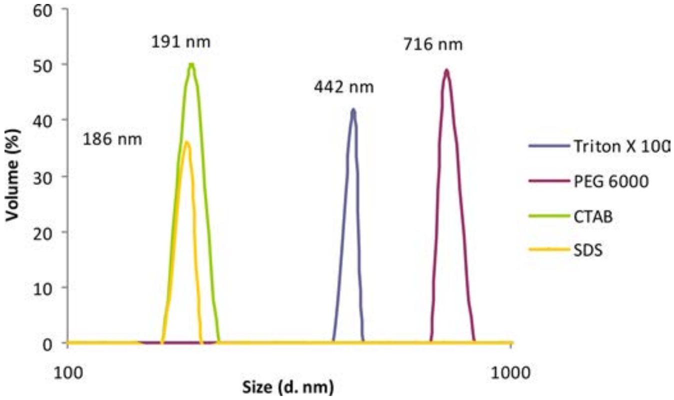


Figure 2. Size distribution of ZnO in different surfactants.

be due to incomplete capping of ZnO nanoparticles with SDS. Large surface area and high surface activity of nanoparticles cause agglomeration on prolonged storage. Smaller particles have a higher number concentration and a larger diffusion coefficient as compared with larger ones at the same mass concentration, which aggregated rapidly in water by Brownian motion (Tso et al. 2010).

Effect of sonication

Ultrasonication is an effective tool for preparing aqueous dispersions of ultra-fine/nanoparticles. Ultrasonic cavitation can break the primary particles and the *Van der Waals* forces in agglomerates (Anand, Varghese, and Kurian 2015). The effect of sonication on size distribution of ZnO dispersions stabilized in non-ionic (Triton X 100 and PEG 6000), cationic (CTAB), and anionic (SDS) surfactants are shown in Table 2. The highest size of 3541 nm was observed for ZnO stabilized with PEG 6000 after 3 min sonication (Table 2). Earlier reports indicated that re-agglomeration process prevails even after sonication (Mandzy, Grulke, and Druffel 2005). For CTAB-stabilized system, in addition to a peak at 347 nm, particles having size closer to 100 nm (exactly 114 nm) were also observed after 2 min sonication (Table 2). The share of particles at this size range was only 6%. By increasing the sonication time, particle–particle interaction predominates which results in agglomeration. Sonication in the presence of SDS reduces the agglomerates, and hence the proportion of lower-sized particles increases accordingly. In SDS, ZnO exhibited bimodal distributions after 3 and 4 min sonication. Particle size of ZnO after 3 min sonication was 74 nm (21%) and 868 nm (5%), which further decreased to 45 nm (32%) and 317 nm (3%) after 4 min sonication. Increasing the sonication time (>4 min) leads to the growth of particles (Ostwald ripening).

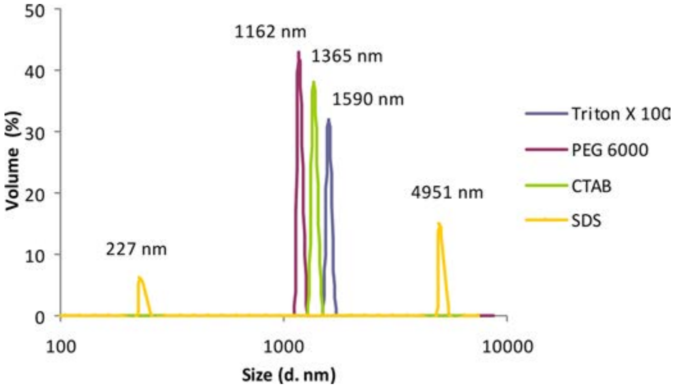


Figure 3. Size distribution curves of ZnO in various surfactants after 1 week.

Table 2. Effect of sonication on the particle size of nano-ZnO dispersions.

	Sonication time (min.)		
Surfactant used	2	3	4
Triton X 100	201* (35%)**	223 (36%)	485 (25%)
PEG 6000	254 (48%)	3541 (16%)	370 (38%)
CTAB	114 (6%) 347 (17%)	805 (30%)	223 (18%)
SDS	195 (13%)	74 (21%) 868 (5%)	45 (32%) 317 (3%)

*Size of the particles (in nm) after sonication in different surfactants.
**Volume (%) of particles with corresponding size.

Stability of ZnO dispersion

The stability of colloidal suspensions can be assessed by measuring their zeta potential. The magnitude of zeta potential determines the stability of the dispersion. Surfactants added into aqueous solution will decrease the contact angle of solid particles. An increase in the contact angle may cause the particle to flocculate from the dispersion or to float over to the surface. A decrease in contact angle may increase dispersibility (Rosen and Kunjappu 2012). Figure 4 illustrates the zeta potential of aqueous dispersions of nano-ZnO in various

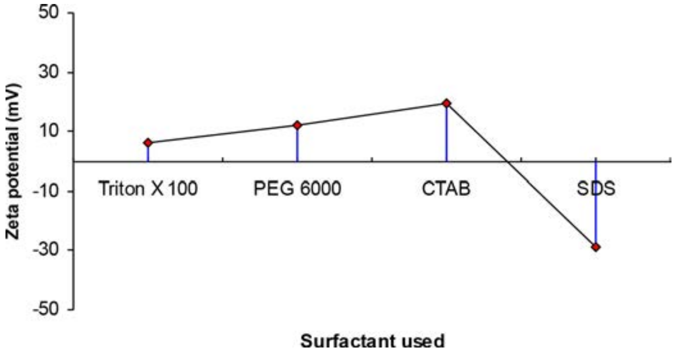


Figure 4. Zeta potential of ZnO dispersion in various surfactants.

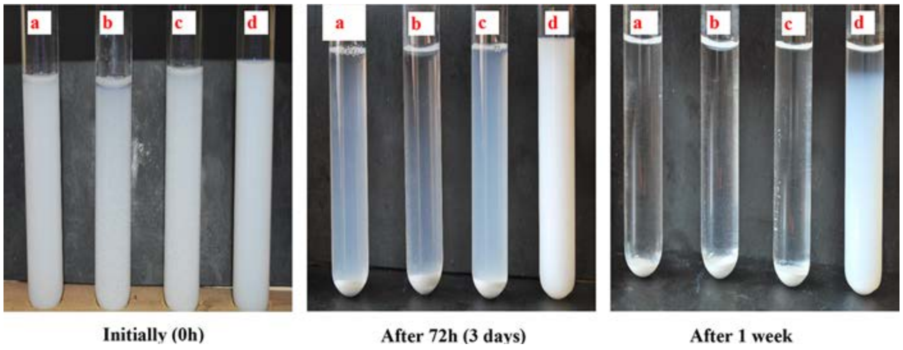


Figure 5. Sedimentation of ZnO nanodispersions in (a) Triton × 100, (b) PEG 6000, (c) CTAB, and (d) SDS.

surfactants. Among them, ZnO–SDS combination exhibited better stability. The zeta potential of the resultant dispersion was −28.9 mV. This might be due to the higher level of adsorption of SDS molecules on ZnO surface. Zeta potential of ZnO in Triton X 100, PEG 6000, and CTAB is 5.92, 12.3, and 19.6 mV respectively. Therefore, agglomeration tendency of ZnO nanoparticles in non-ionic surfactants is high because of low zeta potential value. In order to compare the storage stability of nano-ZnO, sedimentation tests were conducted. Photographs showing the dispersion state of ZnO nanoparticles in various surfactants are displayed (Figure 5. ZnO dispersed in non-ionic surfactants obviously settles down after 3 days. ZnO dispersed in cationic surfactant (CTAB) too started sedimentation after 3 days, but it was observed to be a slow process. After 3 days, complete settlement was observed in both non-ionic and cationic surfactants (Figure 5 [II]). The results are in accordance with zeta potential values. The lower the zeta value, lower will be the stability. Among the four kinds of surfactants used, nano-ZnO dispersed in SDS showed maximum stability even after 1 week. Particle settling velocity is related to the size and density of the particle. The larger the particle, higher the settling velocity (Ni, Shen, and Zhang 2006). The results showed that ZnO dispersed in SDS has lesser agglomeration among the particles indicating better dispersion.

Conclusions

The study was mainly focused on the role of different surfactants on the stability and the particle size distributions of ZnO in aqueous media. Optimal dispersion conditions for the preparation of stable aqueous dispersion of nano-ZnO were presented. Surfactants play a major role in lowering the particle size. Among the non-ionic, cationic, and anionic surfactants studied, the quality of dispersion was better with anionic surfactants (SDS). Dispersion of ZnO in SDS retained more number of particles in the nanosize range. Sonication in the presence of SDS further enhanced the share of lower-sized particles. As revealed from the zeta potential studies, the colloidal stability of ZnO dispersed in SDS was also found to be higher (−28.9 mV).

Funding

Anand K gratefully acknowledges the financial support from Rubber Board (Ministry of Commerce and Industry), India, under RRII Research Fellowship Scheme (2/88/RF Scheme/2010/Res).

References

Anand, K., S. Varghese, and T. Kurian. 2014. Synthesis of ZnO nano rods through mechano-chemical route: A solvent free approach. *International Journal of Theoretical and Applied Sciences* 6 (1):87–93.

Anand, K., S. Varghese, and T. Kurian. 2015. Preparation of ultra-fine dispersions of zinc oxide dispersions by simple ball-milling: Optimization of process parameters. *Powder Technology* 271:187–92. doi:10.1016/j.powtec.2014.11.009.

Chaudhuri, R. G., and S. Paria. 2010. Synthesis of sulfur nanoparticles in aqueous surfactant solutions. *Journal of Colloid and Interface Science* 343:439–46. doi:10.1016/j.jcis.2009.12.004.

Fazio, S., J. Guzman, M. Colomer, A. Salomoni, and R. Moreno. 2008. Colloidal stability of nanosized titania aqueous suspensions. *Journal of European Ceramic Society* 28 (11):2171–76. doi:10.1016/j.jeurceramsoc.2008.02.017.

Guo, L., S. Yang, C. Yang, P. Yu, J. Wang, W. Ge, and G. K. L. Wong. 2000. Synthesis and characterization of poly(vinylpyrrolidone)-modified ZnO nanoparticles. *Chemistry of Materials* 12 (8):2268–74. doi:10.1021/cm9907817.

Heijman, S. G. J., and H. N. Stein. 1995. Electrostatic and sterical stabilization of TiO2 dispersions. *Langmuir* 11 (2):422–27. doi:10.1021/la00002a010.

Kanade, K. G., B. B. Kale, R. C. Aiyer, and B. K. Das. 2006. Effect of solvents on the synthesis of nano-size zinc oxide and its properties. *Materials Research Bulletin* 41 (3):590–600. doi:10.1016/j.materresbull.2005.09.002.

Mandzy, N., E. Grulke, and T. Druffel. 2005. Breakage of TiO_2 agglomerates in electrostatically stabilized aqueous dispersions. *Powder Technology* 160:121–26. doi:10.1016/j.powtec.2005.08.020.

Naeini, Y. S., M. Aminzare, F. G. Fard, F. Khorasanizadeh, and E. Salahi. 2012. Suspension stability of Titania nanoparticles studied by UV-VIS spectroscopy method. *Iranian Journal of Materials Science and Engineering* 9 (1):62–68.

Ni, X. Y., J. Shen, and Z. H. Zhang. 2006. *The physicochemical properties and application of nanomaterials*. Beijing: Chemical Industry Press.

Promsawat, M., A. Watcharapasorn, and S. Jiansirisomboon. 2012. Effect of ZnO nanoparticulate addition on the properties of PMNT ceramics. *Nanoscale Research Letters* 7 (1):65.

Rosen, J. M., and J. T. Kunjappu. 2012. *Surfactants and interfacial phenomena*, 4th ed. Hoboken, NJ: John Wiley and Sons.

Tkachenko, N. H., Z. M. Yaremko, C. Bellmann, and M. M. Soltys. 2006. The influence of ionic and nonionic surfactants on aggregative stability and electrical surface properties of aqueous suspensions of titanium dioxide. *Journal of Colloid and Interface Science* 299 (2):686–95. doi:10.1016/j.jcis.2006.03.008.

Tso, C. P., C. M. Zhung, Y. H. Shih, Y. M. Tseng, S. C. Wu, and R. Doong. 2010. Stability of metal oxide nanoparticles in aqueous solutions. *Water Science & Technology* 61 (1):127–33. doi:10.2166/wst.2010.787.

Widegren, J., and L. Bergstrom. 2002. Electrostatic stabilization of ultrafine titania in ethanol. *Journal of the American Ceramic Society* 85 (3):523–28. doi:10.1111/j.1151-2916.2002.tb00127.x.

Zhang, Y., Y. Chen, P. Westerhoff, K. Hristovski, and J. C. Crittenden. 2008. Stability of commercial metal oxide nanoparticles in water. *Water Research* 42 (8–9):2204–12. doi:10.1016/j.watres.2007.11.036.