SYNTHESIS AND CHARACTERIZATION OF CERIA, CERIA-ZIRCONIA HYBRID AND SURFACTANT-MODIFIED HYBRID NANOPARTICLES FOR LUBRICANT APPLICATIONS

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Abstract
Conservation of materials and energy is becoming a very global issue. The main cause of energy loss in a mechanical system is friction which can be reduced by lubrication. Selection of a good combination of base-oil and proper additives is significant for effective lubrication. Recently nanoparticle additives have attracted world-wide attention in the area of the formulation of lubricants. Several researchers have investigated on lubricants added with nanoparticles and the results show a promising future. However, cost effective synthesis routes and characterization of nanoparticles is a general issue faced by various researchers. Achievements in the fields of chemistry and technology, nanoscience and nanotechnology provide the possibility of synthesis and characterization of various metal, metal oxide and non-metal nanoparticles. Over the last few years, interest in the synthesis and properties of colloidal inorganic nanoparticles has steadily grown because of the great expectations for their application in different fields of material science and technology, including the field of nanolubrication. Metal oxide nanoparticles play a very vital role in the area of chemistry, physics and material sciences, since they can be adapted to a wide variety of structural geometries with different electronic structure. Certain metal oxide nanoparticles such as ZnO, SiO_2, ZrO_2 have been widely investigated as possible boundary lubricant additives. Synthesis of nanoparticles can be classified into two broad categories; viz., physical processes and chemical processes. The major physical processes include high energy ball milling, inert gas condensation, arc discharge, laser ablation, ion sputtering, wire explosion, etc. However, these processes require large energy sources and the particle size variation is large. In chemical methods, nanoparticles are made starting from atoms. They include chemical reduction, solvo-thermal synthesis, precipitation method, photo chemical synthesis, electro-chemical synthesis, etc. The present work aims to synthesize and characterize hybrid nanoparticles for lubricant application. The base nanoparticle selected for synthesis is Cerium Oxide (CeO_2) nanoparticles. In order to hybridize CeO_2 nanoparticles for better performance in lubrication applications, a compound containing Zirconium (Zr) is used during the synthesis process. Further, to increase the dispersion stability of hybridized nanoparticles a suitable surfactant is utilized. Due to better control over the particle size and total yield of nanoparticles, precipitation method is employed in this work.

The characterization of nanoparticles include surface morphology analysis, particles size variation analysis, presence and composition of particles, and will be carried out by using Scanning Electron Microscopy (SEM), Energy Dispersive

Spectroscopy (EDS), Zeta potential measurement and Dynamic light scattering (DLS) analyses techniques.

Index Terms: Nanoparticles, Nanolubrication, Precipitation method, Surfactant.

I. INTRODUCTION

A. Tribology

Tribology is the science and engineering of interacting surfaces in relative motion. It includes the study and application of the principles of friction, lubrication and wear. Tribology is a branch of mechanical engineering and materials science.

1. Lubrication: Lubrication is the process or technique employed to reduce friction between, and wear of one or both, surfaces in proximity and moving relative to each other, by interposing a substance called a lubricant in between them. The lubricant can be a solid, (e.g. Molybdenum disulphide, MoS2) a solid/liquid dispersion, a liquid such as oil or water, a liquid-liquid dispersion (a grease) or a gas. With fluid lubricants the applied load is either carried by pressure generated within the liquid due to the frictional viscous resistance to motion of the lubricating fluid between the surfaces, or by the liquid being pumped under pressure between the surfaces. Lubrication can also describe the phenomenon where reduction of friction occurs unintentionally, which can be hazardous such as hydroplaning on a road.

B. Nanotribology

It is a branch of tribology which studies friction phenomenon at the nanometer scale. The distinction between nanotribology and tribology is primarily due to the involvement of atomic forces in the determination of the final behaviour of the system. Gears, bearings, and liquid lubricants can reduce friction in the macroscopic world, but the origins of friction for small devices such as micro- or nanoelectromechanical systems (NEMs) require other solutions. Despite the unprecedented accuracy by which these devices are nowadays designed and fabricated, their enormous surface-volume ratio leads to severe friction and wear issues, which dramatically reduce their applicability and lifetime. Traditional liquid lubricants become too viscous when confined in layers of molecular thickness. This situation has led to a number of proposals for ways to reduce friction on the nanoscale, such as superlubricity and thermolubricity. The major experimental tool which is used for nanotribological research is the Atomic Force Microscope (AFM), with its various modifications as well as Molecular Dynamics (MD) simulation.

C. Nanolubrication

One of the major aspects of tribology is lubrication. It is the most common way to prevent wear. The idea is to maintain a liquid or grease layer between the two solids and the compressive stresses generated in this layer keep the two solids from coming in contact. Theoretically, a good lubricant is supposed to: (1) Generate fluid pressures to keep the two surfaces separate. (2) Sacrificially wear off to protect the surface. (3) Redistribute the stresses at the contact. (4) Increase the contact area (lowering the contact pressure). Another important property of a good lubricant is its ability to produce boundary lubricating films when needed in situations when the film thickness is not sufficient to avoid contact (if the film thickness is lesser than the roughness of the surface), then the highest asperities of the two surfaces come into contact with each other. As the pressure increases, the deformation of these asperities becomes more and more plastic. This situation is referred to as ‘boundary lubrication’. However, in this situation (under the conditions of high temperature of the asperity tips), the lubricant and its additives react with the solid surface forming a protective chemical film. This film is sheered away, thus protecting the surface from any damage [3].

The effectiveness of a film depends on several factors like its adhesive and cohesive strength, density, its thickness, etc. Most of these properties can be measured by using the techniques mentioned above to study nanotribology. It is desirable to use a film that is thicker than the surface roughness which is capable of generating fluid pressures to avoid contact and which also has good adhesion and cohesion properties.

However, most of the time at the nanoscale, there is only a limited supply of lubricant and only one or two monolayers are available to do the job. In such a situation, even a small damage to the film (by shear or oxidation, which is why the lubricating film should be oxidation-resistant and non-volatile) can continue to get aggravated, exposing the surface to contact and hence strong frictional forces. This is very common with the Langmuir-Blodgett (LB) films. Therefore, it is highly essential for these films to have self-repairing properties. This is possible only if the molecules from another location can move in to cover the exposed surface. Thus, the molecules should be free to move around on the surface, and should not be chemically absorbed on the surface, which would result in low bonding strength. In order to overcome these two contradicting problems, we use mixed molecular films, wherein one species bonds to the surface, while the other is free to move. Thus a carefully designed molecular assembly, where in each molecule improves a certain property of the film, is required.

II. RESEARH BACKGROUND

A. Nanolubricants

A nanolubricant is lubricant containing nanometre-sized particles, called nanoparticles. The importance of nanolubrication and its necessities in the modern machines is of increasing demand nowadays. Hsu, S. M. (2004) [4] explained the concept and design of nanolubrication including the various methods which can be employed for implementation of the same. Recent developments in micro-electromechanical devices (MEMs), microsystems, nanotechnology, nano-electromechanical devices (NEMs) in communication, aerospace, biomedicine, and lab-on-a-chip all pose new requirements of lubrication at nanometre scale for better life.

There have been several investigations on the tribological properties of mineral oil based lubricants with different nanoparticles added. Many investigators have reported that the addition of nano particles to the lubricants is an effective method to reduce friction and wear. The friction-reduction and anti-wear behaviours are dependent on the characteristics of nanoparticles such as size, shape and concentration. The sizes of nanoparticles used were mostly in the range of 20-150 nm.

B. Nanoparticle Additives

Nanotechnology is regarded as the most revolutionary technology of the 21st century. It can be used in many fields and ushers material science into a new era. There has been many investigation on the tribological properties of the lubricants with different nanoparticles added. A large number of papers have been reported the addition of nanoparticles to lubricants is effective in reducing wear and friction. Wu et al. (2007) [11] shows that nanoparticles including CuO, TiO2 and Nano-Diamond used as additives in lubricating oils exhibits good friction reduction and anti-wear behavior, especially for CuO. The physical and chemical properties of nanoparticles determine the behaviour of lubricants to a large extend.

Spikes, H. (2015) [9] explains that the main potential advantages of using nanoparticles as lubricant additives are envisaged as: (1) the ability to use chemistries that are insoluble in non-polar base oils; (2) since their activity is limited to their surfaces, they should show less interaction with other additives present in a lubricant; (3) since their film formation is largely mechanical, they may form films on many different types of surface; (4) because their films form mechanically, they need to be less chemically reactive than normal additives and so will be more durable and less likely to react with other additives; and (5) they are likely to be highly non-volatile and thus not lost in high temperature conditions. And for a nanoparticle to be effective in controlling friction, three requirements must be fulfilled: (1) the dispersed particles must enter the contact in sufficient quantities; (2) once between the surfaces, the particles must impart low friction; (3) some adhesion of the particles to the surface is probably necessary.

The need for energy efficiency is leading to the growing use of additives that reduce friction in thin film boundary and mixed lubrication conditions. Several classes of such friction modifier additive exist, the main ones being organic friction modifiers, functionalised polymers, soluble organo-molybdenum additives and dispersed nanoparticles.

During the past few years many researches have been carried out using nanoparticles as additives in petroleum based oils and biodegradable oils to enhance the lubrication characteristics of the end lubricant. Results obtained by Dubey et al. (2013) [2] showed that the blending of nano-sized Potytetraflouoroethylene (PTFE) solid lubricant particles into a 150 N API Group II base oil improve the weld load, as well as the anti-wear and friction reduction properties of the nanolubricant formed. Koshy et al. (2015) [6] conducted the evaluation of coconut oil based bio-lubricant added with MoS2 nanoparticles, which showed enhanced thermo-physical properties of the lubricant.

C. Synthesis of Nanoparticles

Synthesis of nanoparticles can be classified into two broad categories; viz., physical processes and chemical processes. The major physical processes include high energy ball milling, inert gas condensation, arc discharge, laser ablation, ion sputtering, wire explosion, etc. However, these processes require large energy sources and the particle size variation is large. In chemical methods, nanoparticles are made starting from atoms. They include chemical reduction, solvo-thermal synthesis, precipitation method, photo chemical synthesis, electro-chemical synthesis, etc.

1. High energy ball milling

Yadav et al. (2012) [12] reported the synthesis of nanocrytalline cerium oxide by high energy ball milling. It is a ball milling process where a powder mixture placed in the ball mill is subjected to high-energy collision from the balls. This process was developed by Benjamin and his co-workers at the International Nickel Company in the late of 1960. It was found that this method, termed mechanical alloying, could successfully produce fine, uniform dispersions of oxide particles (Al_2O_2, Y_2O_3, ThO_2) in nickel-base super alloys that could not be made by more conventional powder metallurgy methods. Their innovation has changed the traditional method in which production of materials is carried out by high temperature synthesis. Besides materials synthesis, high-energy ball milling is a way of modifying the conditions in which chemical reactions usually take place either by changing the reactivity of as-milled solids (mechanical activation increasing reaction rates, lowering reaction temperature of the ground powders) or by inducing chemical reactions during milling (mechanochemistry). It is, furthermore, a way of inducing phase transformations in starting powders whose particles have all the same chemical composition: amorphization or polymorphic transformations of compounds, disordering of ordered alloys, etc.

2. Inert gas condensation

The inert gas evaporation–condensation (IGC) technique, in which nanoparticles are formed via the evaporation of a metallic source in an inert gas, has been widely used in the synthesis of ultrafine metal particles since the 1930s. A similar method has been used in the manufacture of carbon black, an ink pigment, since ancient times. The technique employed now for the formation of nanopowders, in reality, differs from that used to produce carbon and lampblack primarily in the choice of atmospheric composition and pressure and in the use of a chemically reactive source. Thus, although the technology is old, the application to the production of truly nanoscaled powders is relatively recent. In its basic form, the method consists of evaporating a metallic source, using resistive heating (although radio frequency heating or use of an electron or laser beam as the heating source are all equally effective methods) inside a chamber which has been previously evacuated to about 10-7 torr and backfilled with inert gas to a low pressure. The metal vapour migrates from the hot source into the cooler inert gas by a combination of convective flow and diffusion and the evaporated atoms collide with the gas atoms within the chamber, thus losing kinetic energy. Ultimately, the particles are collected for subsequent consolidation, usually by deposition on a cold surface.

3. Precipitation Method

Chen et al. (2004) [1] describes the synthesis of cerium oxide nanoparticles by homogenous precipitation method. Ceria ammonium nitrate is an inorganic compound with the formula $(NH)_2Ce(NO_3)_2$. This orange-red, water-soluble cerium salt is widely used as an oxidizing agent in organic synthesis and as a standard oxidant in quantitative analysis. Ammonium hydroxide is a precipitator which is added to ammonium cerium nitrate. Hydroxyl ions from ammonium hydroxide are also used to stabilize the ceria nanoparticles. As the concentration of hydroxyl ion increases, pH value increases and nanoparticles solution tends to stabilize. Concentration of hydroxyl ion can be measured using pH value of solution. As the reaction proceeds slowly the super-saturation state is reached and the nucleation of ceria nanoparticles starts to occur while the hydroxyl ions surrounds the ceria and surrounds it, thus creating electrostatic stabilisation. The presence of alcohol in the solvent can favour in the decrease of the particle size.

4. Solvothermal synthesis

Verdon et al. (1995) [10] proposed the synthesis of cerium dioxide microcrystallites using solvothermal synthesis. This process for making inorganic nanoparticles, comprises of (i) forming a suspension or solution comprising at least one group II-IV and lanthanide metal inorganic salt in a first medium (ii) disposing the suspension or solution in a sealed chamber having an interior pressure (iii) heating the suspension or solution to a peak temperature higher than the normal boiling point of the first medium (iv) elevating the interior pressure of the sealed chamber to an initial interior pressure prior to the heating and (v) forming a plurality of inorganic nanoparticles, wherein 80% of the plurality of inorganic nanoparticles has a diameter less than 100 nm. The solvents used were water and ethanol. The difference in size and morphology of the produced nanoparticles by using different solvents were also mentioned.

III. SYNTHESIS OF NANOPARTICLES

A. Synthesis of CeO_2 Nanoparticles

Cerium oxide/Ceria (CeO_2) nanoparticles are selected because of its excellent properties of wear resistance, chemistry erode resistance and good polishing effect as abrasive. Researchers also have discovered that CeO_2 nanoparticles could restrain the reunification among particles and strengthen the stability of nanoparticles in the organic liquid phase. Moreover, it is highly stable, non-toxic and used as a refractory ceramic material. CeO_2 nanoparticles are synthesized by means of precipitation method which is a chemical method. Chemicals used in this method were reagent-grade cerium (III) nitrate ($Ce(NO_3)_3{\cdot}6H_2O$) (supplied by Nice Chemicals (P) Ltd., purity 99%), analytical-grade isopropanol and 3M aqueous ammonia. The chemical reactions were carried out at temperature 60 °C. 0.1M cerium nitrate solution in water-isopropanol mixture in the volume ratio of 1:6 is prepared and is vigorously stirred by means of a magnetic stirrer. A fivefold excess of 3M aqueous ammonia solution is added to the solution. pH of the solution is adjusted to 10 by the addition of ammonium hydroxide, as alkaline medium gives smaller particles than acidic medium. After one hour the pale red coloured reactants turns to yellow, indicating the formation of cerium oxide nanoparticles.

The synthesized nanoparticles were transferred to a crucible silica dish and are calcinated in a muffle furnace at 500 °C for 4 hours for obtaining crystalline nanosized particles. The final product obtained is a yellow finely powdered material which is the CeO_2 nanoparticles

Figure 7.1 Stages of CeO_2 nanoparticle synthesis

B. Synthesis of Ce-Zr Oxide Hybrid Nanoparticles

Metal-doped cerium oxide/Ceria (CeO_2) in nanoparticle form is proven to give much better results in efficiency enhancement compared to large dimension powders. John et al. (2015) showed that the doping of zirconium with ceria nanoparticles improve its corrosion resistance. Cerium-zirconium oxide hybrid nanoparticles are synthesized by means of precipitation method which is a chemical method. Chemicals used in this method were laboratory-grade cerium (III) nitrate ($Ce(NO_3)_3{\cdot}6H_2O$) (supplied by Nice Chemicals (P) Ltd., purity 99%), laboratory-grade zirconium oxychloride and 3M aqueous ammonia. The chemical reactions were carried out at temperature 60 °C. 0.1M cerium nitrate and zirconium oxychloride solution in water is prepared and vigorously stirred by means of a magnetic stirrer. A fivefold excess of 3M aqueous ammonia solution is added to the solution. pH of the solution is adjusted to 10 by the addition of ammonium hydroxide, as alkaline medium gives smaller particles than acidic medium. After one hour the pale red coloured reactants turns to yellow, indicating the formation of cerium-zirconium oxide hybrid nanoparticles. The synthesized nanoparticles are calcinated in a muffle furnace at 500 °C for 4 hours for obtaining crystalline nanosized particles.

C. Surfactant Modification Of CeO_2, Ce-Zr Hybrid Nanoparticles

A surfactant has been used for obtaining better dispersion of ceria nanoparticles in the lubricant. For the preparation of surfactant-modified CeO_2 nanoparticles, Ce-Zr oxide hybrid nanoparticles, a suitable surfactant, viz., tween 20 (Polyoxyethylene sorbitan monolaurate, $C_{26}H_{50}O_{50}$, transparent liquid), is mixed with nanoparticles respectively.

The selection of surfactant depends on the hydrophilic lipophilic balance (HLB) of the surfactant, which is the relative degree to which the surfactant is water soluble or oil soluble. Tween 20 has a HLB value of 16.7 and is a stable compound with adhesive property, slight odour and is totally soluble in lubricant. The lipophobic part of the tween 20 molecule is embedded into the cerium oxide particle, leaving the lipophilic part of the molecule to interact with lubricant.

Figure 7.2 Stages of Ce-Zr oxide hybrid nanoparticle synthesis

The weight fraction of surfactant is 30% of the weight of CeO_2 nanoparticles. The mixture is then dried and calcinated at 80 °C and the resulting forms the surfactant-modified CeO_2 nanoparticles. Surfactant-modification depresses the possibility of agglomeration of CeO_2 nanoparticles in the lubricant thus giving better dispersion stability.

IV. RESULTS AND DISCUSSION

A. *Surface Topography And Morphology Analyses*

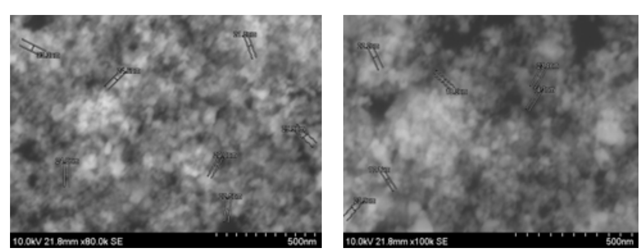
In this work, the various types of advanced laboratorial devices including SEM, EDS, Zeta potential and DLS analyses techniques are used to characterize the nanoparticles.

1. *Scanning Electron Microscopy (SEM)*

Scanning electron microscope is a novel equipment used for taking images of samples, by the application of high energy electrons emitting from a source at micro/nano scale. Electrons from an anode will hit on the sample surface. Some of the electrons may reflected, some may refracted and the remaining will absorbed by the sample. The SEM makes use of reflected electrons which are detected with the help of an electron detector (ET) which converts it to images. Depending up on the angle of reflectance the reflected electrons are of different types. SEM is equipped with different detector for detecting different reflected rays. In SEM a monochromatic electron beam is passed over the surface of the specimen which induces various changes in the sample. The resulting particles from the sample are used to create an image of the specimen. The information is derived from the surface of the sample.

The main advantage of SEM is its large depth of field. 2D images are available to study the topography and morphology of the specimen. The SEM image of the cerium oxide nanoparticles produced by precipitation method is shown in Figure 8.1. Cerium oxide has high optical and luminescence property and has high tendency to agglomerate in a faster rate than any other nanosized rare earth materials. The SEM images of cerium oxide won't give much clear information on the morphology and particle size. The SEM image of cerium-zirconium oxide hybrid nanoparticles is shown in Figure 8.2.

The size of CeO_2 nanoparticles and cerium-zirconium oxide hybrid nanoparticles obtained from SEM images ranges between 14.3 nm to 33.3 nm and 32.3 nm to 65.5 nm respectively.



The shape of both type of nanoparticles were found to be spherical.

Figure 8.1 SEM images of the synthesized cerium oxide nanoparticles

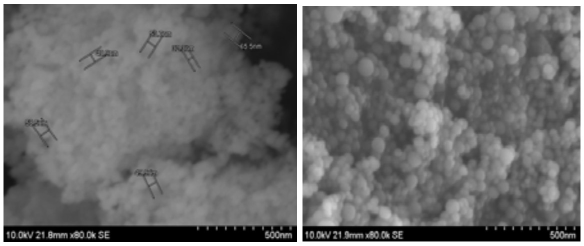


Figure 8.2 SEM images of the Ce-Zr oxide hybrid nanoparticles

2. *Energy Dispersive Spectroscopy (EDS)*

Energy dispersive spectrum (EDS) is taken for finding the elemental composition in the sample. EDS analysis was done on the synthesised cerium oxide nanoparticles and cerium-zirconium oxide hybrid nanoparticles which were prepared by the means of chemical method. The EDS spectrum of the synthesised cerium oxide nanoparticle is shown in Figure 8.3, which reveals the weight and atomic percentage of each component present in the synthesized sample as shown in Table 8.1.

Table 8.1 Weight and atomic percentage of elements present in synthesized cerium oxide nanoparticles from EDS data

Element	Weight%	Atomic%
O (K)	16.01	62.55
Ce (L)	83.99	37.45
Total	100	100

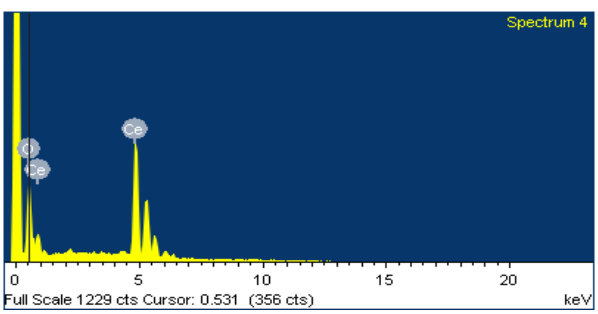


Figure 8.3 EDS spectrum obtained from primary nanocrystalline CeO_2

Table 8.2 Weight and atomic percentage of elements present in synthesized Ce-Zr oxide hybrid nanoparticles from EDS data

Element	Weight%	Atomic%
Zr	35.81	73.36
Ce	64.19	26.64
Total	100	100

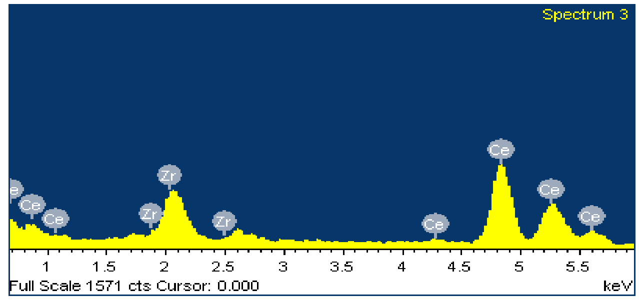


Figure 8.4 EDS spectrum obtained from nanocrystalline Ce-Zr oxide hybrid nanoparticles

Along with the spectrum the EDS gives the information about the percentage of atoms of each elemental component of interest. It also provides information on the weight percentage of each elemental component of interest. This is made possible by the analysis of X-Rays coming out of the specimen, when an electron beam hit in it. Here the spectrum indicates the presence of cerium and oxygen in the synthesized particles, thus acts as a primary characterization technique for giving the information about composition, of any sample under consideration. The EDS spectrum of the synthesised Ce-Zr oxide hybrid nanoparticle is shown in Figure 8.4, which reveals the weight and atomic percentage of each component present in the synthesized sample as shown in Table 8.2.

3. *Zeta potential and Dynamic Light Scattering (DLS)*

Zeta potential is a measure of the magnitude of the electrostatic or charge repulsion/attraction between particles, and is one of the fundamental parameters known to affect stability. Its measurement brings detailed insight into the causes of dispersion, aggregation or flocculation, and can be applied to improve the formulation of dispersions, emulsions and suspensions.

In the current study, zeta potential of the nanoparticles dispersed in a liquid medium (Hexane) is measured at a temperature of 30 °C. The input parameters required for the estimation of zeta potential are dynamic viscosity and dielectric constant and these parameters are experimentally determined using a rheometer and abbe refractometer, respectively at the required temperature. Table 8.3 shows that maximum zeta potential is obtained for the lubricant containing surfactant modified CeO_2 and cerium-zirconium oxide hybrid nanoparticles, 38.58 and 40.50 respectively, which proves the dispersion stability of surfactant modified nanoparticles over the unmodified cases.

Table 8.3 Zeta potential values of different samples

Sample No.	Description	Zeta potential (mV)
1	Hexane + CeO_2	28.92
2	Hexane + Ce-Zr oxide	31.70
3	Hexane + surfactant modified CeO_2	38.58
4	Hexane + surfactant modified Ce-Zr oxide	40.50

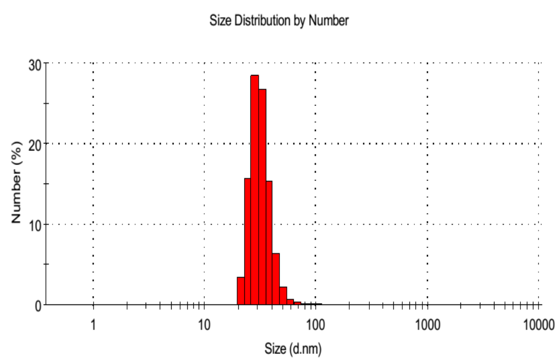


Figure 8.5 DLS plot obtained from primary nanocrystalline CeO_2

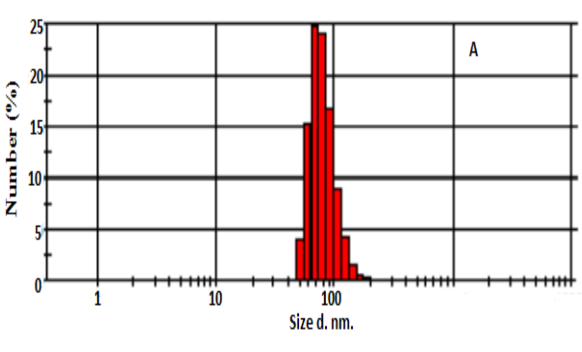


Figure 8.6 DLS plot obtained from nanocrystalline Ce-Zr oxide hybrid nanoparticles

The particle size of the ceria, ceria-zirconia hybrid nanoparticles are verified using DLS as shown in Figure 8.5 and Figure 8.6 respectively with hexane as base fluid. For CeO_2 nanoparticles the particle size varies from 20 to 80 nm and the average particle size is found to be 34.86 nm for the CeO_2 nanoparticles synthesized by precipitation method. Further, for ceria-zirconia hybrid nanoparticles the particle size varies from 45 to 110 nm and the average particle size is found to be 61.28 nm.

V. CONCLUSIONS

The following conclusions are derived on the basis of the synthesis processes carried out for preparation of ceria, ceria-zirconia hybrid, surfactant modified hybrid nanoparticles and the various surface morphology analyses conducted on them:

• Spherical CeO_2, ceria-zirconia hybrid nanoparticles are synthesized by precipitation method. From the SEM images, the average sizes of the nanoparticles were found to be 22.70 nm for the former and 51.46 nm for the latter. Further, the samples were surfactant modified using Tween 20 to compare the dispersion stability of the nanoparticles.

• Analyses of the synthesized nanoparticles were conducted using characterization techniques such as SEM, EDS, Zeta potential and DLS. SEM coupled with the EDS analyses proved the uniform distribution of spherical nanoparticles.

• From the dispersion and stability studies using zeta potential and DLS techniques, it is clear that the surfactant-modified CeO_2 nanoparticles in hexane settle down only after a longer duration of time which makes it more suitable for long term stationary applications. Moreover, the particle size distribution was obtained from the DLS plots.

• Precipitation method is proven to be a simple and cost effective method for the formulation of CeO_2 and ceria-zirconia hybrid nanoparticles. The production cost of the synthesized nano particles were found to be much less compared to their market prizes.

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REFERENCES

[1] Chen, H. I., & Chang, H. Y. (2004). Homogeneous precipitation of cerium dioxide nanoparticles in alcohol/water mixed solvents. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 242(1), 61-69.

[2] Dubey, M. K., Bijwe, J., & Ramakumar, S. S. V. (2013). PTFE based nano-lubricants. Wear, 306(1), 80-88.

[3] Goldstein, J., Newbury, D. E., Echlin, P., Joy, D. C., Romig Jr, A. D., Lyman, C. E., ... & Lifshin, E. (2012). Scanning electron microscopy and X-ray microanalysis: a text for biologists, materials scientists, and geologists. Springer Science & Business Media.

[4] Hsu, S. M. (2004). Nano-lubrication: concept and design. Tribology International, 37(7), 537-545.

[5] John, J., & Vandana, S. (2015, November). Experimental Investigation on the Effect of Zirconium on Corrosion Resistance of Ceria Nanoparticles. InASME 2015 International Mechanical Engineering Congress and Exposition(pp. V014T11A019-V014T11A019). American Society of Mechanical Engineers.

[6] Koshy, C. P., Rajendrakumar, P. K., & Thottackkad, M. V. (2015). Evaluation of the tribological and thermo-physical properties of coconut oil added with MoS_2 nanoparticles at elevated temperatures. Wear, 330, 288-308.

[7] Sajeevan, A. C., & Sajith, V. (2013). Diesel engine emission reduction using catalytic nanoparticles: an experimental investigation. Journal of Engineering, 2013.

[8] Sajith V, Mohamed Jihad PM, (2015). Development of stable cerium zirconium mixed oxide nanoparticles additive for emission reduction in biodiesel blends, Journal of Engineering and Technology.

[9] Spikes, H. (2015). Friction Modifier Additives. Tribology Letters, 60(1), 1-26.

[10] Verdon, E., Devalette, M., & Demazeau, G. (1995). Solvothermal synthesis of cerium dioxide microcrystallites: effect of the solvent. Materials letters, 25(3), 127-131.

[11] Wu, Y. Y., Tsui, W. C., & Liu, T. C. (2007). Experimental analysis of tribological properties of lubricating oils with nanoparticle additives. Wear,262(7), 819-825.

[12] Yadav, T. P., & Srivastava, O. N. (2012). Synthesis of nanocrystalline cerium oxide by high energy ball milling. Ceramics International, 38(7), 5783-5789.