ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Synthesis and Characterization of Titanium dioxide (TiO_2) Nanoparticles.

R Srikanth*, and H Joga Rao.

Department of Chemical Engineering, GMR Institute of Technology, Rajam, 532127, AP, India

ABSTRACT

Nano sized Titanium dioxide (TiO_2) powder was synthesized via sol-gel method using titanium dioxide (TIO_2), as the precursors. TiO_2metal oxide nano particles were prepared by following the Sol-gel process of bottom up method. The characterized SEM results obtained showed that pure crystalline particles of spherical and rod shape were formed with some clusters and agglomerates. TiO_2 surface area ranged between 0.2µm² to 0.9µm². The estimated properties viscosity (8.814 cp), thermal conductivity(1.226 W/m.K), specific heat(1082.25 *J/kg k)* varied for TiO_2. TiO_2had a high thermal conductivity, viscosity, Specific heat with reference to base fluid when compared to NiO. Especially, TiO_2nano fluid proved to be efficient for heat transfer enhancement as its thermal conductivity increased in 1.99 times of the base fluid of water.

Keywords: Nanoparticles, Titanium dioxide, Sol-Gel Method, Nanofluid, Property estimation.

Corresponding author

INTRODUCTION

Nanoparticles (NP) are defined as particles with a diameter smaller than 100 nm. Nanostructure materials are single phase or multiphase polycrystalline solids with a typical average size of a few nanometers (1nm = 10^{-9}m) [1]. Nanoparticles have different physical and chemical properties metals (e.g., lower melting points, higher specific surface areas, specific optical properties, mechanical strengths, and specific magnetizations), properties that might prove attractive in various industrial applications. Though the name is 'Nano' it is not only limited to tiny science, but often also employed in bulk materials and large surfaces. Nano Technology deals with these nano particles, mainly production and manipulation of these nano ranged materials[2]. Also, these particles have great potential uses in the electronic, chemical and mechanical industries, as well as in the related technologies using catalysts, drug carriers, sensors, pigments, also as well as in magnetic and electronic materials.

Types of nano particles

There are various approaches for classification of nanomaterials. Nanoparticles are classified based on one, two and three dimensions and also based on their morphology, composition, and Uniformity and agglomeration state. In the Nano scale one dimensional particle are typically surface coatings, thin films and also includes anti-reflection and hard coatings on Eye-glasses [3]. Among these thin films find a wide range of application since decades and they can be formed as a monolayer by various deposition methods. Some technological applications of these films are information storage systems, chemical and biological sensors, fiber-optic systems; magneto-optic and optical device. Two-dimensional nanomaterials have two dimensions in the nanometer scale range. These include 2D nano structured films, free particles with large aspect ratio, dimensions in the nano scale range [15]. Asbestos fiber and carbon nanotubes are an example of this material. Materials that are nanoscaled in all three dimensions are considered3D-nanomaterials[12]. These include thin films deposited under conditions that generate atomic-scale porosity, colloids, and free nanoparticles with various morphologies.

Morphological characteristics to be taken into account are: flatness, sphericity, and aspect ratio. In reality, this is a generalization of the Aspect-ratio concept. A general classification exists between high- and low-aspect ratio particles. High aspect ratio nanoparticles include nanotubes and nanowires, with various shapes, such as helices, zigzags, belts, or perhaps nanowires with a diameter that varies with length. Small-aspect ratio morphologies include spherical, oval, cubic, prism, helical, or pillar [13]. Collections of many particles exist as powders, suspension, or colloids. Nanoparticles can be composed of a single constituent material or be a composite of several materials. The nanoparticles found in nature are often agglomerations of materials with various compositions. Agglomerates are an assembly of primary particles and/or aggregates whose total surface area does not differ appreciable from the sum of the specific surface areas of primary particles [14]. While pure single-composition materials can be easily synthesized today by a variety of methods. Based on their chemistry and electro-magnetic properties, nanoparticles can exist as dispersed aerosols, as suspensions/colloids, or in an agglomerate state and can also form clusters. For example, magnetic nanoparticles tend to cluster, forming an agglomerate state, unless their surfaces are coated with anon-magnetic material [4]. In an agglomerate state, nanoparticles may behave as larger particles, depending on the size of the agglomerate. Hence, the factors that must be taken into account when deciding considering health and environmental regulation of new materials are, nanoparticle size, agglomeration, and surface reactivity, along with shape [5].This chapter deals with the information regarding the general synthesis methods and characterization techniques from various literatures that have been collected.

MATERIALS AND METHODS

Synthesis, Preparation and Characterization Methods

The following aspects involved for synthesizing nanoparticle are neutral pH, low cost and environmental friendly fashion. The synthesis of nanomaterial, can be well accomplished by two approaches [6]. Firstly, by “Bottom Up” method where small building blocks are produced and assembled into larger structures. Where the main controlling parameters are morphology, crystallinity, particle size, and chemical composition. Secondly, by “Top Down” method where large objects are modified to give smaller features. For example: film deposition and growth, nano imprint /lithography, etching technology, mechanical polishing, etc. the main reason of alteration in different mechanical, thermal and other property is due to increase in surface to volume ratio. Top Down approach is by nature non-economical and isn't easy to manufacture whereas Bottom Up approach is less expensive and its fabrication cost is also very less. So, on a large scale Bottom Up techniques are employed. High energy ball milling, the only top-down approach for nanoparticle synthesis, is used for the generation of magnetic and structural nanoparticles. The technique, which is already a commercial technology, has been considered dirty because of contamination problems from ball-milling processes. However, the availability of tungsten carbide components and the use of inert atmosphere and/or high vacuum processes have reduced impurities to acceptable levels for many industrial applications [7]. Common drawbacks include the low surface area, the highly poly disperse size distributions, and the partially amorphous state of the as prepared powders.

The sol-gel process is very long known since the late 1800s. Sol-gel is a chemical solution process used to make ceramic and glass materials in the form of thin films, fibers, or powders. A sol is a colloidal (the dispersed phase is so small that gravitational forces do not exist; only Vander Waals forces and surface charges are present) or molecular suspension of solid particles of ions in a solvent. A gel is a semi-rigid mass that forms when the solvent from the sol begins to evaporate and the particles or ions left behind begin to join together in a continuous network [8].The sol-gel process is a wet-chemical technique that uses either a chemical solution (sol short for solution) or colloidal particles (sol for nanoscale particle) to produce an integrated network (gel). Metal alkoxides and metal chlorides are typical precursors. They undergo hydrolysis and polycondensation reactions to form a colloid, a system composed of nanoparticles dispersed in a solvent. The sol evolves, then towards the formation of an inorganic continuous network containing a liquid phase (gel). Formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymersin solution. After a drying process, the liquid phase is removed from the gel. Then, a thermal treatment (calcination) may be performed in order to favor further polycondensation and enhance mechanical properties.

Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and X – Ray Diffraction (XRD) analyses were used for characterizing the nanoparticles. Different classical models were suggested and also Experimental studies were carried out to estimate the viscosity, thermal conductivity and specific heat of nanoparticles.

EXPERIMENITAL

Materials

Chemicals such as, Titanium dioxide, Nitric Acid, Citric Acid, were of pure and analytical grade and were used without further purification. Citric acid was used as Chelating agent as it is experimentally proved to be simple and cost effective. Ethylene glycol was used as gelating agent for the formation of gel.

General procedure for preparation of Titanium Dioxide nano particles

Titanium dioxide is insoluble in organic solvents as it is a transition metal. So, it was dissolved in Hydrofluoric acid for complete dissolution and left until it is dissolved(approx 3 days). As Hydrofluoric acid can produce dangerous fumes it should be added carefully in a fume cupboard with necessary precautions. For 1.582 g of weighed $TiO_2$1.66 times of citric acid is weighed and added. It is subjected for continuous heating with magnetic stirrer. As the solution gets thicker added ethylene glycol for complete gel formation. Auto-ignition starts as the temperature is reached and gel is completely burned. After complete combustion the burnt powder is collected and subjected for sintering at various temperatures. Sintering was done at three different temperatures. The whole sample was first sintered at 500°C and one-third part of the sample was weighed and taken aside from it. The as taken part is then Sintered at 600°Cand repeating the above step further sintered at 700°C. Also three different samples were prepared again by the above mentioned procedure and sintered at three different temperature 500°C, 600°C, 700°C respectively.

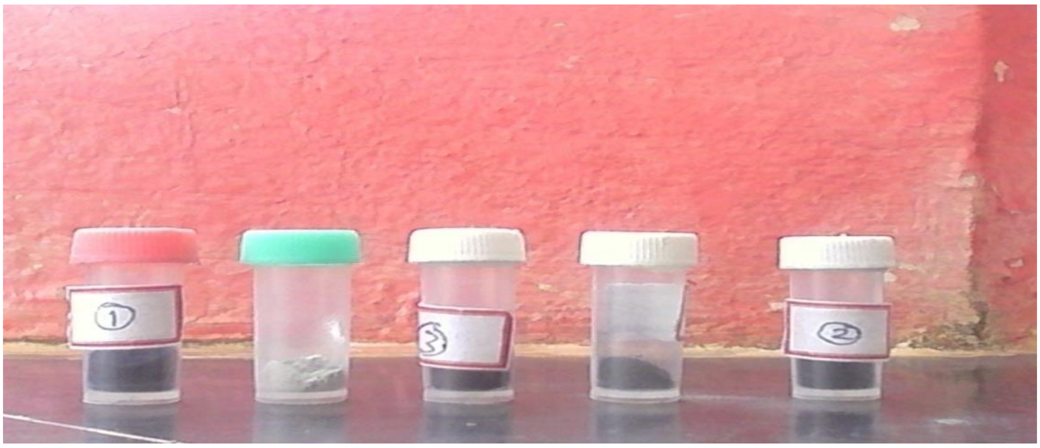

Fig 1: Prepared Samples of TiO_2

Characterization with Scanning Electron Microscopy (SEM) method

The synthesized nano powders of Titanium Dioxide (TiO_2) were characterized to know the size and morphology of the prepared samples. These testing's were carried out at 'Centurion University' located at parlakhemudi. The SEM generates a beam of incident electrons in an electron column above the sample chamber. The energy of the incident electrons can be as low as 100 eV or as high as 30 keV depending on the evaluation objectives. The electrons are focused into a small beam by a series of electromagnetic lenses in the SEM column. Scanning coils near the end of the column direct and position the focused beam onto the sample surface.

Dispersion of synthesized nano powders

The nano powders that were synthesized and characterized were now subjected for dispersion in order to get nano fluids with nano particles dispersed completely. For the dispersion the base fluid taken was water of about 500ml. The Samples of NiO and TiO_2 of which the SEM results obtained with high accuracy were considered and added to the water. Three samples of which two of them are NiO and one was TiO_2 were dispersed in the base fluid and processed further with continuous stirring. These samples were stirred continuously for 30 minutes before moving forward to sonication. Now after the completion of stirring they were kept in sonicator for another 30 minutes so that complete dispersion can be possible under the ultrasonic waves that results from the sonicator.

Property estimation of the nano fluids

Estimation of viscosity

In order to compare the viscosity of the nano fluids with base fluids the nano fluid's viscosity was calculated using the Red wood Viscometer. The cup of the Viscometer was first cleaned and filled with the base fluid and then after with nano fluid. A 50 ml volumetric flask was placed below to collect the fluid. Now the ball rod was taken out and stop watch was on. Time taken to collect50ml of the sample was noted. Two readings were taken randomly for all the fluids and the viscosity was calculated based on the formulae [9]

$$At - \frac{B}{t} \qquad (1)$$

where A and B are the constants and t is time taken to collect the sample.

Estimation of thermal conductivity

The specific heat of the nano fluids was calculated using classic models that were suggested by Maxwell. Maxwell's formula shows that the effective thermal conductivity of nanofluids relies on the thermal conductivity of the spherical particle, the base fluid and the volume fraction of the solid particles. The Maxwell formula is [10].

$$\frac{k_{eff}}{k_f} = \frac{k_p + 2k_f + 2\emptyset(k_p - k_f)}{k_p + 2k_f - \emptyset(k_p - k_f)} \quad (2)$$

where, k_{eff} is the effective thermal conductivity that is to be calculated, k_f is the thermal conductivity of the base fluid taken, Ø is the volume fraction of the particles in the suspension,

k_p is the thermal conductivity of the solid particle, k_f is the thermal conductivity of the base fluid.

Calculation of thermal conductivity of TiO_2 Nano fluid:

Thermal conductivity of water at 30°C (k_f)=0.615.4 *W/m*, Thermal conductivity of TiO_2 (k_p) = 7.7 *W/m.k*, Volume fraction is calculated by Volume= mass/density, where a mass of TiO_2taken is 1.77g, Volume fraction of TiO_2 is $8.42*10^{-4}$,Volume fraction of water is 0.9991.

From equation (1)

$$\frac{k_{eff}}{0.6154} = \frac{7.7 + (2 * 0.6154) + 2 * (8.42 * 10 - 4) * (7.7 - 0.6154)}{7.7 + (2 * 0.6154) - (8.42 * 10 - 4) * (7.7 - 0.6154)}$$

k_{eff} obtained upon calculation was 1.226*W/m.k*.

Estimation of Specific Heat of the nano fluids

A correlation for nanofluids was presented by Pak and Cho, taking the idea from the liquid-particle mixture theory as [8]

$$C_{p,nf} = \emptyset \times C_{p,s} + (1 - \emptyset)C_{p,bf} \quad (3)$$

Where $C_{pnf}$is the specific heat of the nanofluid, C_{ps} is the specific heat of the solid nanoparticle, Ø is the particle volumetric concentration and C_{pbf} is the specific heat of the base fluid.

Subsequently Xuan and Roetzel [8]modified this correlation by assuming thermal equilibrium between the nanoscale solid particles and the liquid phase by rewriting the above equation to include the density.

$$C_{p.nf} = \frac{\emptyset * C_{p,s} + (1 - \emptyset) * \rho_{b,f} * C_{p,bf}}{\rho_{nf}} \quad (4)$$

where $\rho_s$is the density of the solid nanoparticle, $\rho_{bf}$is the density of the base fluid, and $\rho_{nf}$is the density of the nanofluid.

Calculation of Specific heat of*TiO_2:* Ø=$8.42*10^{-4}$, $\rho_{s=}$ 4.23 *g/cm*^{3},C_{ps}= 690 *J/kg k*, ρ_{bf} =1000 *g/cc*, C_{pbf}=4200 *J/kg k*, ρ_{nf} = 3.9 *g/cm*^{3}

$$C_{p,nf} = \frac{(8.42 \times 10^{-4}) \times 423000 \times 690 + (1 - (8.42 \times 10^{-4})) \times 1000 \times 4200}{3900000}$$

=1082.25 *J/kg k*

RESULTS AND DISCUSSION

Nano powder of TiO_2 was prepared by using Sol-gel method of Bottom-up technique and sintered at 1800°C, 1100°C, 500°C, partly and 500°C, 600°C, 700°C respectively. Repeated sintering showed an influence on the distribution of the nano particles which was observed in the SEM characterization.

DISCUSSION FOR SYNTHESIZED TIO_2 NANO PARTICLES

TiO_2nano powder was synthesized using Sol-gel technique which resulted in fine ash colored particles unlike NiO. It also resulted in an increased mass of 5g in total. The difference in their size and morphological properties were also observed in SEM analysis.

SEM Results for TiO_2 sample

The TiO_2 samples sintered at 600°C, the particle surface area was observed between 0.269 µm² to 0.919µm².Scanning electron imaging was done with a resolution of 8500 and a width of 13mm with a 2µm scale. The particles were of a rod shape.

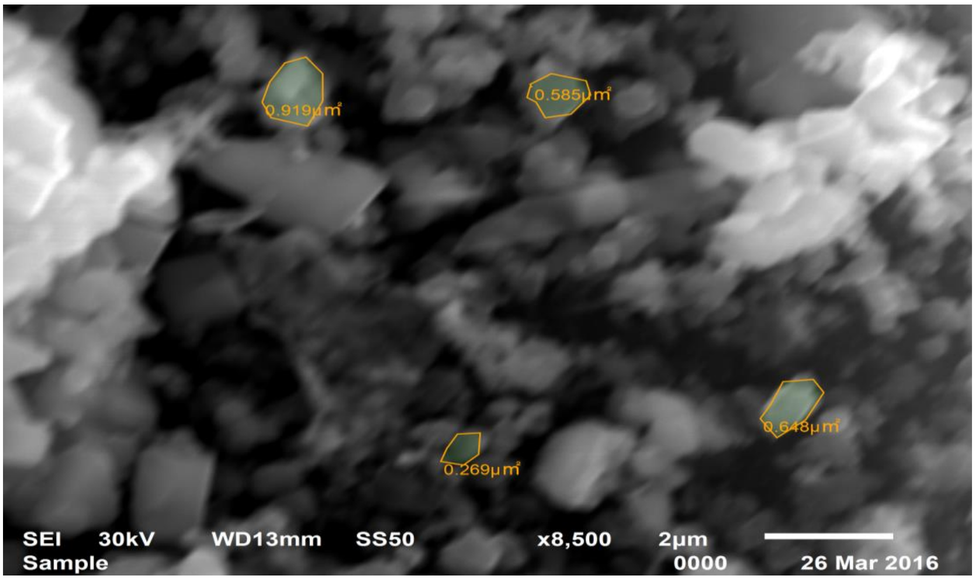

Fig2: SEM image for TiO_2 for samples sintered at 600°C

Results for Estimated Viscosity of TiO_2

The viscosity of the base fluid was found to be 0.765cp at 30°C. For TiO_2 it was increased to 8.814cp at the same temperature[2]. Which shows that this increase in viscosity of the nano fluid makes it as a better choice than the base fluid as it supports in the improvement of heat transfer coefficient [3].

Results for thermal conductivity of TiO_2

There was an improvement in the calculated thermal conductivity of TiO_2nano fluid when compared to the base fluid [11]. The thermal conductivity of the TiO_2 was obtained as 1.226 W/m.K while that of water(base fluid) was observed as 0.6154 i.e., it was increased by 1.99 times.

Results for Specific Heat of TiO_2

The calculated value of the specific heat of the TiO_2 was 1082.25 J/ kg.K. It was mor than that of NiO . As per the literature a decrease in the value Should be noticed with reference to the base fluid which was observed with the calculations performed according to the Xuan and Roetzel's model [8].

CONCLUSION

- TiO_2metal oxide nano particles were prepared by following Sol-gel process of bottom up method.
- The characterized SEM results obtained showed that pure crystalline particles of spherical and rod shape were formed with some clusters and agglomerates.
- TiO_2 surface area ranged between 0.2µm² to 0.9µm². The estimated properties viscosity (8.814 cp), thermal conductivity(1.226 W/m.K), specific heat(1082.25 *J/kg k)* varied for TiO_2.

- TiO_2had a high thermal conductivity, viscosity, Specific heat with reference to base fluid when compared to NiO.
- Especially, TiO_2nano fluid proved to be efficient for heat transfer enhancement as its thermal conductivity increased in 1.99 times. Whereas, NiO was decreased to 0.023 times of base fluid which results in less heat transfer coefficient when compared to TiO_2.

REFERENCES

[1] MannaPK, MohantaGP, MannavalanR,JanaU,PalSL,Journal of Applied Pharmaceutical Science 2011;2 (1): 228

[2] SrikanthR, International Journal of ChemTech Research 2016; 10(5):145.

[3] HeeraP,ShanmugamS, International Journal of Current Microbiology and Applied Sciences2015; 4: 379.

[4] BuzeaC, BlandinoIIP, RobbieK, Journal of Biointerphases2007; 2:17.

[5] HanumanthuSC, International Journal of engineering Science and Innovative technology 2015; 4:101.

[6] EvelynL.Hu,David ShawT, Tropical Journal of Pharmaceutical Research2006;4:561.

[7] HuseynovE, GaribovA,MehdiyevaR,Journal of materials research and technology2015;184:122.

[8] JongWHD,BormPJa, International Journal of Nano medicine2008;2:133.

[9] Xian-QiW, Arun MujumdarS, Brazilian Journla of Chemical Engineering2008;25: 613.

[10] Vajjha Ravi kanthS, Debendra DasK, Journal of Heat Transfer2009;131:273.

[11] ShanmugavelT, Gokul RajS, Ramesh KumarG, RajarajanGSravananD, Journal of King Saud University-Science 2015; 27:176.

[12] Mukesh kumarPC, KumarJ, SureshS, International Journal of Engineering Innovation and Research 2012;1: 2277.

[13] KumarPM, KumarJ, TamilarasanR, SendhilnathanS, SureshS, Engineering Journal2015; 19:342.

[14] SinghAK, Defence Science Journal2008;58: 600.

[15] Sheng Qi Z, RuiN, Journal of Applied Physics 2008; 92:93.