Influence of pH on the Spherical Shape and Particle Size of the Freeze Drying Assisted Sol-gel Derived Silica Nano-Particles (SNPs)

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Abstract: The spherical silica nanoparticles (SNPs) are synthesized by freeze drying assisted sol gel method and the effect of pH on morphology and particle size is studied. The Tetraortho silicate (TEOS) was used as silane source and Polyethylene Glycol 6000(PEG 6000) was used as capping agent for controlling the shape of the particles. The synthesized (SNPs) were analyzed using Zeta size Analyzer which confirmed the particle size in the range of 24-1090 nm at different pH values of the solution. The Fourier Transform Infrared (FTIR) Spectroscopy was used to characterize the functional moieties present in the synthesized material which confirmed the presence of functional vibration groups corresponding to silica particles which are mainly Si-O-Si asymmetric stretching (1034-1120 cm\textsuperscript{-1}), Si-O rocking (443-487cm\textsuperscript{-1}) and Si-O bending (760-800 cm\textsuperscript{-1}) , X-Ray Diffraction (XRD) analysis of the synthesized nano silica particles confirmed the amorphous nature and Scanning Electron Microscope (SEM) was used to study the morphology of the synthesized (SNPs) which confirmed the spherical shape of the (SNPs) and it was found that shape tend to deform on increase of the pH of the solution.

1. Introduction

The nanoparticles have gained an important platform in research as well as industrial level due to its excellent properties from their macro size counterpart, which entitles it as one of the most prominent candidate in the development of pigments, catalysis, thin film substrates, pharmaceutical industries, nanocomposite, nanoceramics, micro reactor as well as biomedical and drug delivery systems\cite{1-3}. Among them, SNPs are used extensively as nano filler material for synthesis of advanced synthetic and natural nanocomposites due to its improvement of thermal, mechanical and chemical properties by the addition of SNPs \cite{4-6}. The silica particles available from natural resources are contaminated with metal impurities which are not beneficial for advanced scientific and industrial applications due to which the need for synthesis of synthetic silica particles aroused \cite{7-8}. The Various methods that have been used to obtain silica nanoparticles particles are sol-gel process, reverse micro emulsion, flame synthesis, plasma synthesis, hydrothermal technique, chemical vapor deposition, spin coating, etc. \cite{9-13}. There are various methods being reported for the mono disperse silica particle synthesis using the stobers method and modified stobers method in which the particle was reduced to 40 nm to few micrometers \cite{14-15}. Later on further the particle size was decreased to 13.7 ± 4 nm by park et al and thereafter kim et al reported the synthesis of silica nanoparticles by 17.4 nm by the addition of appropriate electrolyte \cite{17-18}. The particles size depends on the type of precursor of silane group and alcohol and based on the above parameters M. Jafarzadeh et al has studied the effect of reactants and drying techniques on the particle size distribution\cite{19}. Recently ultrasonic methods have been developed and the effect of particle size has been studied \cite{20-21}. The sol gel process basically comprises of three main processes comprising of hydrolysis, condensation and ageing. During hydrolysis, silanol groups are formed and during condensation the siloxane chains are formed. The sol-gel process is widely used to synthesize silica nanoparticles due to its ability to control the particle size distribution and surface morphology through methodical controlling of reaction parameters \cite{22-23}.

In the present work, spherical silica nanoparticles were synthesized by sol-gel process assisted by freeze drying using polyethylene glycol as a capping agent by varying pH level at fixed molar concentration of TEOS, ethanol and water as (1:08:08).it was found that as the pH value of the solution was varied from 2 to 14 with an increment of 2 it was found that there is an increase in the
particle size and the morphology of the particle also changes from spherical to irregular shape.

2. Materials and Method

2.1. Reagents and Chemicals

Tetraethyl Orthosilicate (TEOS) (99.99% Across organics, India) is used as precursor, ethanol(EtOH) (99.99%, Changshu Yangyuan Chemicals, China) was used as solvent, and Hydrochloric acid (HCL) (Finar chemicals, India) and 25% Ammonium hydroxide (NH₄OH) solution were used as catalyst and Polyethylene glycol (PEG 6000) (RFCL ltd, India) as a capping agent. All these chemicals were of analytical grade and used without any further purification. Distilled water (H₂O) was used throughout the synthesis of silica nanoparticles.

2.2. Experimental procedure

Preparation of solutions

The molar concentrations of the solutions was maintained for TEOS/ (EtOH)/ (H₂O) as 1/8/8 for both acidic and basic water. Further, Polyethylene glycol 6000 grade was used as a capping agent. Polyethylene glycol solution (5% w/v) was prepared in ethanol using bath sonication for 45 minutes. 0.1M HCl solution was prepared in distilled water to maintain the pH level (for acidic medium) of the solution as per our designed processing route and 25% NH₄OH solution was prepared in distilled water to control the pH level of solution for basic medium.

Sol processing method Synthesis of SNPs

Silica nanoparticles synthesis is based on the hydrolysis and polycondensation of silane containing compound. TEOS which was used as silane source was mixed with ethanol, and the mixture was stirred at room temperature for 15 minutes to achieve proper mixing of solution. A known amount of (5% w/v) PEG 6000 was added to the solution drop by drop using burette. The Calculated amount of acidic water was then added drop wise into TEOS-EtOH-PEG 6000 mixture by using Burette at the rate of 1 ml/min. The pH of the solution was varied using the acidic water till 6 and each time after the addition of acidic water the mixture was allowed to stir at 460 rpm continuously at room temperature without any disturbance for 22 hours until complete hydrolysis of the reactants take place. The same process was repeated with calculated amount of basic water and pH was varied till 12. The pH was varied alternatively due to minor change in the result of the nearby pH variations. After the stirring the solution was put 24 hrs for ageing resulting into a viscous gel. The obtained viscous gels from the solution was then washed with ethanol and distilled water and further centrifuged at high 4000 rpm speed. After the centrifugation the solution was transferred into a round neck flask and the solution were allowed to solidify under deep freezing at 0°C for 48hrs. After the solidification, the solidified solution was introduced for freeze drying (GOLD-SIM Freeze dryer instrument) under auto controlled vacuum and inert atmosphere condition during the reaction. The temperature of the solidified solution was then further decreased slowly to near -85°C and was kept for 24 hours for obtaining silica nanoparticles. These SNPs were further subjected to 100°C heat treatment for the removal of the capping agent introduced during the initial stage of synthesis.

3. Characterization Techniques

Fourier Transform Infrared (FTIR) Spectroscopy IR-4100 (Jasco Instruments, Japan) was used to confirm the presence of functional vibration groups corresponding silica nano particles by KBr pellet method. The Particle size analyser (Zetasizer Nano ZS, Malvern Instrument, UK) was used to measure the particle size at different pH values. The Structural characteristics of silica nanoparticles were studies by using X-ray diffraction system (Discover D8, Bruker, Germany) with CuKα radiation = 1.54060Å. Scanning Electron Microscope (LEO-440i) was used to study the morphology of nanoparticles synthesized.

4. Result and discussion

4.1. Fourier Transform Infrared (FTIR) Studies

FTIR characterization of silica nanoparticles figure 1(a) after drying indicates the same vibration with slight shift in peak due to change in size of nanoparticles. In figure.1 (b) FTIR taken for powder after heat treatment there was no vibration peak observed near 920-97 cm⁻¹ relates with Si-OH bending vibration and ~ 1600 cm⁻¹, which belong to the stretching vibration of O-H bending of the free or absorbed water. There was no major absorptions of PEG are specified to the -CH (CH₂) n- due to heat treatment. FT-IR spectra of SNPs at different pH level with constant molar ratios of TEOS, ethanol and water were recorded for detail functional groups analysis. FTIR in figure.2 of silica nanoparticles indicates the vibration band at 443-487 cm⁻¹ which is due to Si-O rocking and the band around 760-800 cm⁻¹ corresponds to Si-O bending. It was also observed band at 1034-1120 cm⁻¹ which represents Si-O-Si asymmetric stretching and the absorption around 910-87 cm⁻¹ relates with Si-OH bending vibration.
Two broad bands were also observed at 3400-3560 cm\(^{-1}\) and \(\sim 1560-1600\) cm\(^{-1}\), which belong to the stretching vibration of O-H bending of the free or absorbed water. IR analysis is also showing that the band was slightly shifted to lower wave number as the particle size is reduced. The characterization result recommends a conversion in the native bonding structures of Si and O atoms at lesser particle size. Hence functional moieties of SNPs are confirmed.

![FTIR spectra of SNPs](image)

Figure 1. FTIR spectra of SNPs (a) After freeze drying and (b) After heat treatment.

![FTIR spectra of SNPs](image)

Figure 2. FTIR spectra of SNPs (a) pH level-2, (b) pH level-4, (c) pH level-6, (d) pH level-8, (e) pH level-10 and (f) pH level-12.

4.2. X-ray diffraction studies (XRD)

The XRD analysis of the synthesized SNPs .fig.2 (a) shows the characteristics broad peak obtained between 22-23° confirms the amorphous nature of prepared silica particles after drying and heat treatment.
4.3. Particle size analysis
As the pH level of the solution with respect to fixed molar concentration TEOS: Ethanol: Water (1:8:8) increases the obtained particle size also increases continually. The fig shows the particle size of SNPs increase with increase in the pH level of solution from the lowest 24nm obtained at pH 2 and further increase of pH level increases the particle to 1092 nm when the pH level 12 was measured in solution. The study shows the role of catalyst in the reaction at fixed molar concentration also effect on particle size. It was found that in the basic region the particle tends to agglomerate more and the cluster were formed relative to the acidic region.

4.4. Morphological studies
Scanning electron microscopy shows the different size range particles are present in sample. The synthesized SNPs were dispersed in acetone, and the resultant suspensions were sonicated for 20 min and drop casted on a silicon wafer. Scanning electron
microscopy shows the presence of typical nanoparticles with size range from 50nm to 500nm. Figure 5(a) shows spherical nanoparticles with size range around 50nm at pH 2 which is acidic medium and the shape of the particles were spherical and figure (b,c,d,e,f) shows the particle at different pH levels 4,6,8,10,12 respectively. It is clear from the figure that as the pH value is increased particle size increases along with which the spherical shape of the particles also changes. It is observed the spherical structure start to elongate from one of the sides which is uncertain leading to an irregular shape. From the image it is also observed that the particle start to agglomerate in the basic region forming nanoclusters of the order of few microns.
Figure 6. SEM image SNPs of different sizes (a) around 50 nm, (b) around 210 nm, (c) around 450-500 nm and (d) around 1000-1100 nm. (e) Agglomerated (f) Agglomerated nanocluster formation

5. Conclusions
In this study, we have successfully synthesised SNPs and we have studied the influence of pH on the particle size and morphology of the SNPs. The results obtained by Zeta size Analyser have confirmed the size of silica nano-particles in range of 24-1090 nm (average size). Scanning Electron Microscope (SEM) confirmed the effect of pH on the size and shape of the synthesized SNPs. Hence it can be concluded that in solution gelation method along with drying temperature and reactants involved in the synthesis; the particle size distribution and morphology also depends on the pH value of the solution.

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7. References


