Effect of Surfactants on the Wet Chemical Synthesis of Silica Nanoparticles

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Abstract: Silica (SiO₂) nanoparticles have found applications in many advanced areas. This research work is concerned with the preparation of silica nanoparticles by the hydrolysis of tetraethyl orthosilicate (TEOS) in ethanol medium and the effect of different surfactants such as cetyl trimethylammonium bromide (CTAB), sodium dodecyl sulphate (SDS) and poly vinyl pyrrolidone (PVP) on the final particle size of silica nanoparticles. The synthesized nanoparticles were systematically characterized by XRD, EDAX analysis, FTIR, UV-visible spectroscopy, particle size analysis and SEM. The XRD results revealed the amorphous nature of silica nanoparticles. Atomic percentage of silicon and oxygen was measured by EDAX analysis. FTIR spectroscopy confirmed the presence of Si-O in all the samples. UV-visible spectra have shown an absorption band at around 225 nm in all the samples (dissolved in hot NaOH) which is accountable for silica. The sample prepared with the particle characteristics data also.

Keywords: Silica nanoparticles; wet chemical process; surfactants; physical characterization.

1. Introduction

Recently, interest in the scientific research of silica nanoparticles has increased because of their easy preparation and their wide uses in various industrial applications, such as catalysis, pigments, pharmacy, electronic and thin film substrates, electronic and thermal insulators, and humidity sensors [1]. The silica particles play a different role in each of the above applications; the quality of these products is highly dependent on the size and size distribution of the particles [2]. Stober et al. [3], in 1968, reported a pioneering method for the synthesis of spherical and monodisperse silica nanoparticles from aqueous alcohol solutions of silicon alkoxides in the presence of ammonia as a catalyst, and different sizes of silica nanoparticles were prepared ranging from 50 nm to 1 μ m with a narrow size distribution. The size of particles depends on the type of silicon alkoxide and alcohol. Chruściel and Ślusarski have reported the formation of nanosized silica particles from a precursor formed by trans-esterification reaction of astabilizer and an emulsifier [4]. Smaihi et al. [5] have developed a new method for the synthesis of silica nanoparticles using oil microemulsion technique to create silica nanoparticles of

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homogenous size distribution. Further, the size of the particles can be controlled by the composition of the microemulsion. Venkatathri [6] has synthesized silica nanoparticles using tetraethylorthosilicate, water, aqueous ammonia, ethanol and octadecyltrimethoxy silane as constituents. Venkatathri [7] has synthesized silica nanosphere using homogeneous and heterogeneous systems, respectively. Homogeneous system contains a mixture of ethanol, water, aqueous ammonia and tetraethylorthosilicate (TEOS). In the case of heterogeneous system, only ethanol was absent. In homogeneous system, silica spheres were synthesized without cetyltrimethylammonium bromide (CTAB), which gave bimodal particle size and lower yield (77%). To improve the yield, CTAB was added and found that the yield was very high (100%). The particle was in nm range, but the particle sizes are bimodal. To avoid it, reaction in heterogeneous system using CTAB was carried out. Nanosized silica sphere with uniform size (vield, 94%) was observed. Guo et al. [8] have reported a new method of synthesis of silica nanoparticles by hydrolysis of silica powder. According to them, the solution composition and temperature of the reaction influenced the synthesis. The particle size distribution was not uniform but that was rectified by facile regrowth procedure in the same reaction. Jafarzadeh et al. [9] have reported a modified preparation of silica nanoparticles via sol-gel process. The ability to control the particle size and distribution was found highly dependent on mixing modes of the reactants and drying techniques. The mixture of tetraethoxysilane and ethanol followed by addition of water (Mode-A) produced monodispersed powder with an average particle size of 10.6 ± 1.40 nm with a narrow size distribution. The freeze drying technique (FD) further improved the quality of powder. Zawara et al. [10] have prepared and characterized silica nanoparticles via an economic route through sol-gel processing using the widely available and economic sodium silicate as a precursor. Amorphous silica nanoparticles with a diameter ~25 nm and regular spherical structure were obtained. For best results, temperature should be maintained at 60 °C and the stirring speed, adjusted at 250 rpm in the above process. Ibrahim et al. [11] have reported that the diameter of silica nanoparticles is mainly affected by the relative contribution from nucleation and growth. Experimental results indicated that the size of silica colloids decreased with increasing with tetraethyl orthosilicate and ammonia concentrations. Furthermore, they have studied the effect of a surfactant namely hexamethyldisilazane on the dispersibility of silica nanoparticles. Auger et al. [12] have synthesized silica nanoparticles from tetraerthylorthosilicte and tetramethylorthosilicate using ethanol and water. Luminophores were encapsulated and were studied. According to them, the photo-physical characteristics of the dyes are retained upon their encapsulation into the silica matrix, leading to fluorescent silica nanoparticles.

A series of mesoporous silica nanoparticles (MSN) with varied physical properties were synthesized via liquid crystal templating (LCT) mechanism by varying the molar concentrations of the reagents by Wanyika et al. [13]. It was established that a delicate balance between all the reagents in the reaction mixture is necessary in order to synthesize nanoparticles with desirable properties. According to them, liquid-based MSN synthesis methods are versatile and robust. Tuan Noraidhan Azila et al. [14] have studied the possibility of synthesizing nanosilica fillers for use in the fabrication of experimental dental nanocomposites and evaluated their properties, including surface and mechanical properties. They used the surfactant namely silane coupling agent γ -methacryloxypropyltrimethoxysilane (MPS) to reduce agglomeration of nanosilica. According to them, the synthesised nanosilica is a promising material for the fabrication of dental nanocomposites for tooth-filling applications. Singho and Johan synthesized silica nanoparticles by sol-gel method from tetraethoxysilane (TEOS), ethanol (C₂H₅OH), water and ammonium hydroxide (NH₄OH) as catalyst. They mentioned that the morphology and structure

of colloidal silica particles formed depended on the molar ratio of reagents. Complex impedance spectroscopy study showed the presence of both bulk and grain boundary effects in the material, as well as the presence of temperature dependent electrical relaxation phenomena in the method [15]. Hak-Sung Jung et al. employed aminofunctional trialkoxysilanes such as aminopropyl trimethoxysilane (APTMS) and (3-trimethoxysilylpropyl) diethylenetriamine (DETAS) as surface modification molecule for generating monolayer modification on the surface of silica (SiO₂) nanoparticles. They confirmed that the reactivity of amino groups on the surface-modified silica nanoparticles could be maintained in ethanol for more than 1.5 months without showing any significant differences in the reactivity [16]. From the above literature, it was clear that research efforts are now-a-days focussed towards synthesizing SiO₂ nanoparticles for different applications. The present work is one such effort to synthesize SiO₂ nanoparticles by wet chemical synthetic route and to study the effect of different surfactants such as cetyl trimethylammonium bromide (CTAB), sodium dodecyl sulphate (SDS) and poly vinyl pyrrolidone (PVP) on the final particle size of synthesized silica nanoparticles.

2. Materials and methods

2.1. Preparation of SiO₂ nanoparticles by wet chemical synthesis

Tetraethylorthosilicate (Merck, Germany), ammonium hydroxide (Merck, India), absolute ethanol solution (Changshu Yangyuan,China), Cetyl trimethylammonium bromide (SD Fine Chemicals, India), Poly Vinyl Pyrrolidone (Loba Chemie, India) and Sodium Dodecyl Sulphate (Sisco Research Lab, India) were used in the process. All the chemicals were used as received, without further purification. Double distilled water was used throughout the experiment.

During the preparation of SiO₂ nanoparticles, ethanol and water mixture were initially taken in a beaker and stirred well. Then, 5.6 ml of TEOS (Tetraethyl orthosilicate) was added to the above mixture drop-wise. Stirring was carried out for about 10 minutes. During the addition of TEOS into ethanol / water mixture, the pH was maintained between 9.5-10.5 by the addition of 25 % ammonia (~ 3 ml) drop-wise. To the above solution, 2 ml of 5 % / 10 % CTAB or PVP or 2 ml of 2 % / 3 % of SDS (prepared in ethanol) was added with continuous stirring. The stirring speed was maintained as 400 rpm. For this study, 2% / 3 % SDS was chosen as the dissolution of above 5 % SDS was not possible in ethanol. After the addition of surfactant, the entire mixture was stirred for about 1 hour. After this, the beaker was covered with an aluminum foil and left over during night hours (~12 hours) without any disturbance. The resulting white coloured product was washed with absolute ethanol and centrifuged (typically 4000-10000 rpm for 30-45 minutes). After which, the sample was heat treated at 600° C for 2 hours. After heat treatment, white colored silica nanoparticles were formed. The flow chart to prepare SiO₂ nanparticles by wet chemical synthesis is indicated in Figure 1. The following chemical reactions may take place during the process.

$Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH$	(1)
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$$Si(OH)_4 \rightarrow SiO_2 + 2H_2O$$
 (2)

2.2. Characterization of SiO₂

The powder XRD study was carried out using a Shimadzu XRD 6000 X-ray diffractometer using CuK α radiation. EDAX analysis was performed with JEOL Model JSM-6360 instrument

to find out the percentage of elements present in the samples. The FTIR spectra for the samples were taken using Shimadzu IR Prestige-21 model FTIR spectrometer. The UV-Visible spectra for the samples were taken using JASCO V-670 UV-visible spectrometer. The particle size of the powder was measured using a Malvern Particle Size Analyzer using triple distilled water as medium. The morphology of the particles was studied by means of JEOL Model JSM-6360 scanning electron microscope.



Figure 1. Flow chart to prepare SiO₂ nanoparticles by wet chemical synthesis

3. Results and discussion

3.1. X-ray diffraction studies

The XRD patterns obtained on silica nanoparticles prepared without any surfactant and with the addition of 10 % CTAB, 5% CTAB, 10% PVP, 5% PVP, 3% SDS and 2% SDS are indicated in Figure 2 (A)-(G) respectively. Zhang Le-Tian et. al have prepared the SiO₂ film by flame hydrolysis process and confirmed the amorphous nature of the film [17]. Xiaovi Shen et. al have prepared monodisperse spherical SiO₂ by microwave hydrothermal method and they have reported that the as-prepared SiO_2 particles were amorphous with no crystallized phases [18]. The XRD peaks of all the samples show a typical broad halo, clearly assigned to amorphous silica as reported in Ref.[18]. The broad XRD reflection peaks may be due to the small size and incomplete inner structure of the particles. No well defined peaks are observed in all the samples as indicated in Ref.[19]. This demonstrates that a high percentage of these particles are amorphous in all the samples [15]. Gorji et.al have prepared SiO₂ nanoparticles prepared by sol-gel method and they have reported that a high percentage of particles are amorphous but few of them are crystalline as per XRD data [20]. SiO₂ particles prepared by chemical method of dissolution-precipitation resulted in amorphous nature as described by Hamid Khorsand et.al very recently [21]. From the reported data, it is clear that amorphous SiO₂ can be prepared by wet chemical methods.



Figure 2. XRD patterns obtained on calcined SiO₂ powder prepared by the wet chemical method (A) without any surfactant; (B) with 2 ml of 10% CTAB; (C) with 2 ml of 5% CTAB; (D) with 2 ml of 10% PVP; (E) with 2 ml of 5% PVP; (F) with 2 ml of 3% SDS; (G) with 2 ml of 2% SDS

3.2. Energy dispersive spectroscopy (EDAX) studies

The energy dispersive spectra (EDAX) obtained on silica nanoparticles synthesized by the wet chemical method without surfactant and with surfactants is reported in Figure 3 (A)-(G). E-DAX spectra of the samples show peaks for Si and O only and not for any other impurities in the samples. The chemical composition data obtained on SiO₂ by EDAX analysis is given in Table 1. The data confirmed the presence of silicon and oxygen in all the samples. Similar result was reported by Venkatathri and Yoo recently [22]. From the EDAX data, it was found that the weight percentage of silicon is varied between 36-47 % and for oxygen is 52-63%. The variation in the percentage of elements (Si and O) may be due to the reaction conditions during the preparation of silica nanoparticles [23].



Figure 3. EDAX spectra obtained on calcined SiO₂ powder prepared by the wet chemical method (A) without any surfactant; (B) with 2 ml of 10% CTAB; (C) with 2 ml of 5% CTAB; (D) with 2 ml of 10% PVP; (E) with 2 ml of 5% PVP; (F) with 2 ml of 3% SDS; (G) with 2 ml of 2% SDS

Process	Weight % of elements
Without any surfactant	Si - 43.37 O - 56.63
10% CTAB	Si – 44.01 O – 55.99
5% CTAB	Si – 47.85 O – 52.15
10% PVP	Si - 44.42 O - 55.58
5% PVP	Si - 45.05 O - 54.95
3% SDS	Si - 40.96 O - 59.04
2% SDS	Si - 36.36 O - 63.64

Table 1.	Chemical compos	sition data	obtained c	on SiO ₂ (prep	pared by w	vet chemical	method)
	by EDAX analysi	3					

3.3. FTIR Studies

Figure 4 (A)-(G) show the FTIR spectra obtained on silica nanoparticles prepared by the wet chemical method. FTIR measurements were done using KBr method at RT. The spectra of all the samples show the absorption band at about 470 cm⁻¹ which corresponds to the Si-O rocking vibration where the oxygen atom moves perpendicular to the Si-O-Si plane [15]. The band appeared at about 800 cm⁻¹ may be due to the Si-O bending vibration where the oxygen move at right angle to the Si-Si lines in the Si-O-Si plane [15]. The peak appeared at about 3400 cm⁻¹ is related to the O-H stretching vibration of H₂O in the sample [24]. It was reported that SiO₂ nanoparticles can absorb water molecules from atmospheric air as per the recently published article [25]. The FTIR analysis shows that the silica nanoparticles are found to be hygroscopic in nature. Rest of the peaks was almost similar with each other which indicate the formation of pure amorphous phase of SiO₂.

3.4. UV-Visible spectroscopic studies

The prepared silica nanoparticles were dissolved in hot sodium hydroxide (1 M) and the UV analysis was performed. Pure sodium hydroxide (1 M) was used as blank for the entire studies. Figure 5 (A)-(G) show the UV-visible spectra obtained on silica nanoparticles prepared by wet chemical method. The absorption for all the samples reported at around 225 nm which shows the similar optical properties in all the samples [26].



Figure 4. FTIR spectra obtained on calcined SiO₂ powder prepared by the wet chemical method (A) without any surfactant; (B) with 2 ml of 10% CTAB; (C) with 2 ml of 5% CTAB; (D) with 2 ml of 10% PVP; (E) with 2 ml of 5% PVP; (F) with 2 ml of 3% SDS; (G) with 2 ml of 2% SDS



Figure 5. UV visible spectra obtained on SiO₂ (dissolved in 1 M hot NaOH) (A) without any surfactant; (B) with 2 ml of 10% CTAB; (C) with 2 ml of 5% CTAB; (D) with 2 ml of 10% PVP; (E) with 2 ml of 5% PVP; (F) with 2 ml of 3% SDS; (G) with 2 ml of 2% SDS

3.5. Particle size analysis

The particle size distribution curves obtained with silica nanoparticles prepared by the wet chemical method are shown in Figure 6 (A)-(G). For all the measurements, 0.001 g of silica was sonicated in 30 ml triple distilled water for about 10 minutes and after which the sample was subjected for particle size analysis. The particle characteristics data obtained on silica nanoparticles particles is indicated in Table 2. From the particle size data (Table 2), it was understood that the particle size is not influenced much with the addition of surfactants. The presence of bigger particles (> 500 nm) in the samples may be due to high temperature treatment. It was reported that the higher temperature will cause agglomeration to occur more readily [27].



Figure 6. Particle distribution curves obtained on calcined SiO₂ (sonicated in water) (A) without any surfactant; (B) with 2 ml of 10% CTAB; (C) with 2 ml of 5% CTAB; (D) with 2 ml of 10% PVP; (E) with 2 ml of 5% PVP; (F) with 2 ml of 3% SDS; (G) with 2 ml of 2% SDS

	Pea	Peak 1		Peak 2		Peak 3		
Process	% Intensity	Diameter (nm)	% Intensity	Diameter (nm)	% Intensity	Diameter (nm)	particle size (nm)	particle size (nm)
Without any surfactant	63.8	385.3	36.2	94.84			296.7	
10% CTAB	80.1	281.7	19.9	99.47			468.2	
5% CTAB	100	505.0					608.6	
10% PVP	66	369.9	34	105.8			315.8	
5% PVP	60.5	190.9	37.2	662.6	2.3	5474	310.3	
3% SDS	71.9	438.0	28.1	108.0			495.2	
2% SDS	62.2	853.7	36.6	141.3	1.4	5560	390.1	

Table 2. Particle characteristics data obtained on SiO₂ nanoparticles prepared by chemical precipitation method

3.6. SEM studies

The surface microstructure of SiO₂ nanoparticles was studied with SEM. The SEM photographs of SiO₂ nanoparticles are shown in Figure 7 (A)-(G). SEM analysis provides the information about the size and shape of the particle and pore. From the SEM photographs, it was understood that the samples consist of small and big grain. However, the samples prepared with SDS (both 3% and 2%) show microstructures with low grain size (70-90 nm). Larger particles present in the samples may be due to agglomeration during high temperature treatment (600 °C).





Figure 7. SEM photographs obtained on calcined SiO₂ nanoparticles prepared by the wet chemical method (A) without any surfactant; (B) with 2 ml of 10% CTAB; (C) with 2 ml of 5% CTAB; (D) with 2 ml of 10% PVP; (E) with 2 ml of 5% PVP; (F) with 2 ml of 3% SDS; (G) with 2 ml of 2% SDS

4. Conclusions

Wet chemical synthesis of SiO₂ nano particles using tetraethyl orthosilicate (TEOS), ethanol, water and ammonium hydroxide with surfactants (CTAB, PVP and SDS) is reported. The XRD data obtained on SiO₂ powder shows that all samples are amorphous in nature. The EDAX data confirmed the presence of silicon and oxygen in all the samples. From the FTIR data, it is shown that all samples exhibited characteristic peaks for SiO₂. The particulate properties obtained on SiO₂ powder suggest that the particles are present from nano to micrometer size. SEM data revealed that SiO₂ samples prepared with the addition of 2 % or 3 % SDS (surfactant) resulted in less particle size than other samples.

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