

FACILE AND ECONOMIC SYNTHESIS OF SILICA NANOPARTICLES

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Preparation and characterization of silica nanoparticles via an economic route through sol-gel processing using the widely available and economic sodium silicate as a precursor were investigated. Through some experiments, the optimal synthesis conditions for the preparation of silica nanoparticles were obtained and the produced silica nanoparticles were characterized by transmission electron microscope (TEM), X-ray diffraction (XRD), infrared spectra (IR) and thermogravimetric analysis (TG). The results indicated that the silica nanoparticles were successfully formed. The XRD analysis indicated the amorphous structure of the synthesized silica nanoparticles while the transmission electron microscope image exhibited monodispersed nanosized silica particles with a size ~25 nm.

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1. Introduction

The monodispersed nanometer-sized particles have a great importance in both scientific field and various industrial applications, e.g. catalysts, pigments, pharmacy, etc. [1]. Of these particles, amorphous SiO₂ nanoparticles are used in fabrication of electronic substrates, thin film substrates, electrical insulators, thermal insulators, humidity sensors [2]. In addition, it can be used as ideal support for magnetic nanoparticles as it can easily provide functionalities, prevent the anisotropic dipolar magnetic attraction in the absence of external magnetic fields, and enhance the wear and corrosion resistance of magnetic nanoparticles etc. [3, 4]. The silica particles play a different role in each of these products; the quality of these products is highly dependent on the size and size distribution of the particles [1].

Bogush and Zukoski [5] obtained monodispersed silica particles having sizes ranging from 40 nm to several micrometers by controlled hydrolysis of tetraethylortho-silicate (TEOS) in ethanol, followed by condensation (polymerization) of the dispersed phase material. Also, Sung Kyoo Park [2] prepared silica nanoparticles from tetraethylortho-silicate (TEOS) dissolved in ethanol by using a semi-batch process in order to control the particle properties. Ryu [6] had also prepared amorphous silica by oxidation of silicon. Janet et al. [7] produced porous silica gels with high surface areas from tetraethylorthosilicate and polyacrylic acid of high molecular weight in acidic media by sol-gel method. Porous silica glass was prepared through sol-gel processing using tetramethylorthosilicate (TMOS) as precursor, with HNO₃ and HF as catalysts [8].

The sol-gel technique presents many processing merits for several material production methods, mainly owing to facility, versatility, purity, homogeneity and modifications of material properties by changing synthesis parameters [9, 10]. The mean pore size, the interconnectivity and the pore size distributions can be controlled by changing the molar ratio water/precursor, type of catalyst or precursor, temperatures of gelation, drying, and stabilization. Moreover, the sol-gel technique is in-expensive and the silica xerogels produced are non-toxic materials [11].

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In the present work, we reported a facile and economic method for preparing amorphous silica nanoparticles through the sol-gel techniques employing the economic sodium silicate as a precursor. The optimal parameters for the synthesis of amorphous monodispersed silica nanoparticles were presented.

2. Materials and experimental procedure

2.1. Materials

Commercial sodium silicate and HCl analytical grade were used as starting materials for preparation of silica nanoparticles. All chemicals were used as purchased and used without further purification. The chemical analysis of sodium silicate is illustrated in Table 1.

Table 1: Chemical analysis of sodium silicate

Component	Weight %
SiO ₂	24.9
Na ₂ O	20.9
H ₂ O	54.2
SiO ₂ :Na ₂ O = 1.2	

2.2. Preparation of silica nanoparticles.

For comparison, two methods of preparation were used. In the first one, solid silica gel was produced by drop-wise addition (~ 2 drops/s) of diluted sodium silicate to 28 ml of 2.5% HCl with stirring for 250 rpm at 60°C until a cloudy, viscous gel was formed. The volume of sodium silicate was noted down to be 10 mL. It was then thoroughly washed with distilled water until free from Cl⁻ ions. Diluted silver nitrate solution was added to the filtrate for testing the removal of Cl⁻ ions. Its presence was indicated by the formation of a white precipitate. This test was repeated until no white precipitate was formed on addition of silver nitrate. The product was then dried in oven at 100°C for more than 24 hours, and calcined in air at 1000°C for 1 hour.

In the second method of preparation, 2.5% HCl was added drop wisely to diluted sodium silicate until a cloudy colloidal precipitate was formed. The obtained precipitate was filtered, washed and dried by the same way.

2.3. Characterization of the amorphous silica nanoparticles

The characterization of the prepared silica nanoparticles was carried out by transmission electron microscopy (TEM) (JEOL 1200 EX) at an accelerator voltage of 80 kV., infrared spectra (IR) using a Perkin– Elmer 577 spectrophotometer, covered the range from 400–4000cm⁻¹. IR spectra of solid samples were detected using the KBr disc method, X-ray diffraction (XRD) patterns were recorded on a diffractometer (Rigaku, D/Max2500VB2+/PC) with CuKα radiation of wavelength 0.154056 nm and thermogravimetric analysis (TG) using a Delta series A7 thermoanalyzer with differential scanning calorimeter cell. The rate of heating was 10 °C/min in a stream of air with a flow rate of 30cm³/min.

3. Results and discussion

It is evident from Fig. 1a that nano-sized silica particles with an average particle diameter ~25nm and narrower particle size distribution were formed through our optimal synthesis

conditions. Furthermore, the particles were dispersed and had almost well-defined and regular spherical structures.

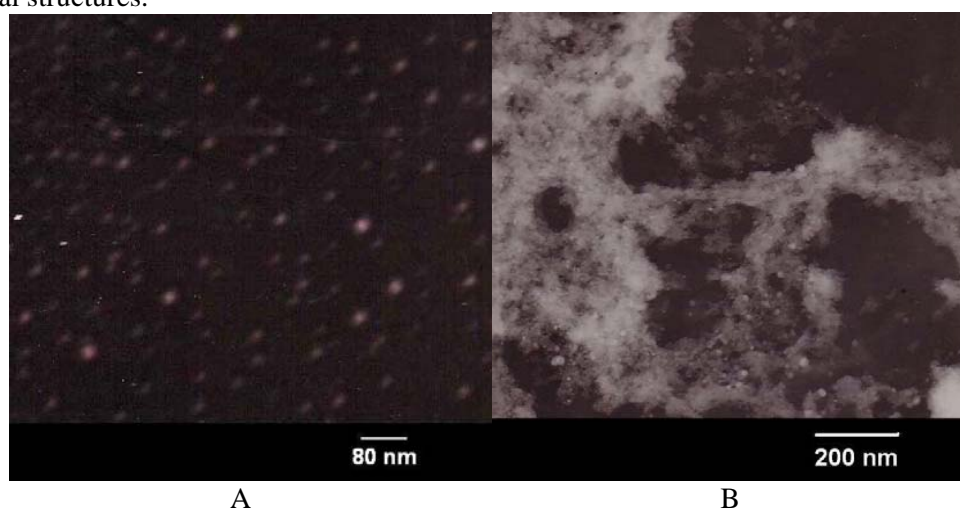


Fig. 1: TEM images of the prepared silica nanoparticles (a) with 250 rpm stirring and 60°C temperature i.e prepared by first method (b) at room temperature without stirring i.e. prepared by second method

This kind of well dispersed structures could be used for different applications. For instance, a silica nanoparticle can only act as a core around which a shell is coated, if its structure is regular and no obstruction to the coating process e.g. agglomeration.

Based on our previous knowledge and study [12,13,14], it was found that the following synthesis parameter must be taken into consideration in synthesis of monodispersed silica nanoparticles using sodium silicate as a source of silica. They are the stirring rate, SiO₂ wt. %, HCl concentration and the temperature of reaction. These optimal parameters are represented in Table 2.

Table 2: Optimal parameters for synthesis of monodispersed silica nanoparticles

Temperature, °C	Stirring rate, rpm	SiO ₂ , wt.-%	HCl concentration, %
60	250	24	2.5

Chosen of a proper temperature is required to achieve the fastest reaction rate with good quality of silica nanoparticles. As a result, we have found that a moderate temperature is needed, because if the temperature is low, the agglomeration of the silica nanoparticle will be occurred as seen in Fig. (1b).

Stirring rate should be set at 250 rpm, because it is the optimal speed required for mixing to obtain well-defined spherical nanoparticles. The higher stirring rate may cause the formed silica nanoparticles to have irregular shapes and agglomerate, while the lower rate would make it hard to reach the required mixing and hence, retarding the formation of nanoparticles

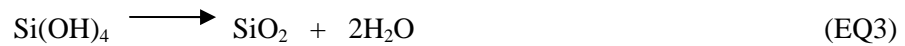
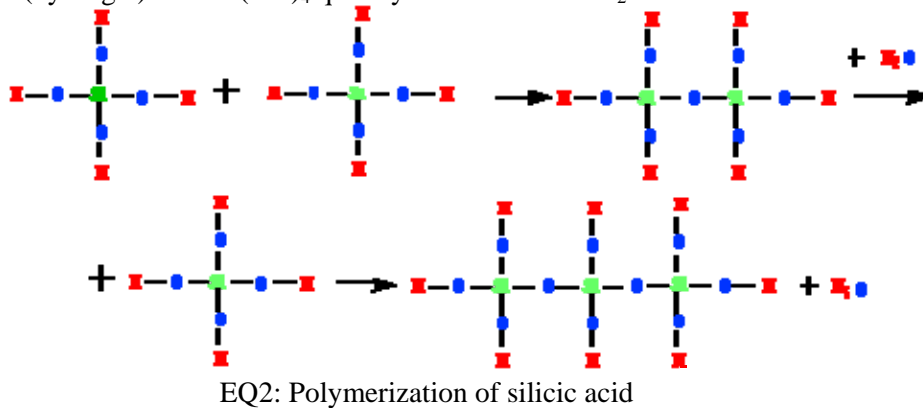
The silica weight percent is an important parameter. If it is very high, the formed silica nanoparticles agglomerates and the regularity of the particles shape will be influenced. As well as, the concentration of HCl has a significant effect on monodispersed silica nanoparticles preparation. A low concentration of HCl is required to avoid the agglomeration of the nanoparticles.

Through our synthesis rout, the initial step in the formation of silica nanoparticles is the release of silicic acid by hydrolysis of sodium silicate with hydrochloric acid according to the following equation:



Then, the silicic acid starts to polymerize with the elimination of water (EQ2). The polymer continues to grow with the removal of water eventually forming polymeric spheres called primary silica particles, and their size range is equal nearly few Angstroms (10⁻¹⁰ m). At a certain

size these primary particles start to attach to each other through the silanol groups (SiOH) to form silica gel (hydrogel). The $\text{Si}(\text{OH})_4$ quickly condenses to SiO_2 with the removal of water (EQ3).



Figs. 2 and 3 show the IR spectra of silica nano particle (prepared by the first method) before and after calcination at 1000°C , respectively. The three main characteristic peaks of Si–O–Si bonds vibrational modes are detected around 460 , 800 and 1070 cm^{-1} which are attributed to O–Si–O rocking vibration band [15], Si–O bending vibration band and Si–O–Si antisymmetric stretching vibration band, respectively [16, 17]. The most noticeable difference between the two Figures is the broad peak between 3000 and 4000 cm^{-1} . This peak is characteristic to the OH group [17] that exists in water. This confirms the elimination of all water molecules after calcination to form xerogel.

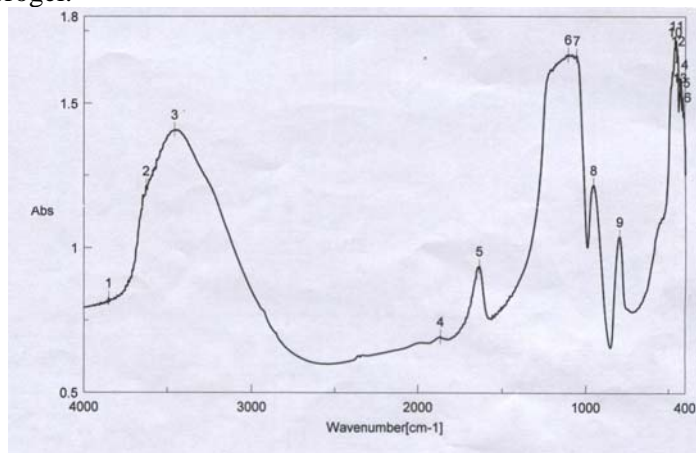


Fig. 2: Infrared spectra of silica gel prior to firing (hydrogel)

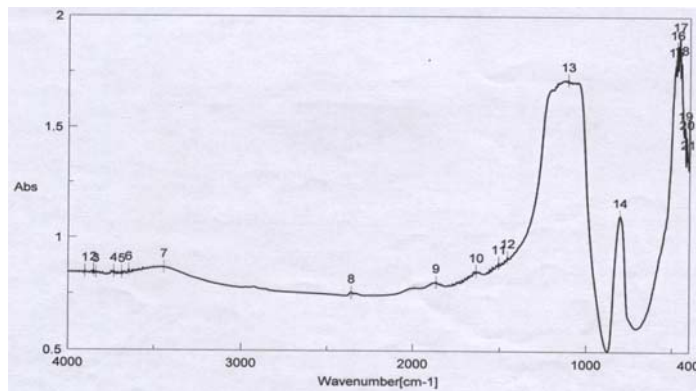


Fig. 3: Infrared spectra of silica gel after firing at 1000°C

There is also another detected peak at 1635cm^{-1} in the IR spectrum of unfired sample which disappeared after firing of the silica samples. This band is attributed to Si-H₂O flexion (16).

In XRD analysis, it was found that the two XRD patterns before and after firing (Figs.4 &5) are identical. This indicates that the obtained silica is only partially crystalline, and predominantly amorphous.

The TG thermogram of the as-prepared silica (Fig.6) is identical to that in the literature review [18]. The first 17% weight loss between 20 and 100°C (A) is due to the loss of absorbed water and moisture in the sample. The second 6% loss in weight between 100°C and 400°C (B) is due to the loss of strongly bonded (hydrogen bonded) water molecules. The final 16% loss between 400°C and 1100°C (C) is due to the condensation of silanol groups (Si-OH) to siloxane bonds (Si-O-Si) with the removal of water.

4. Conclusions

Amorphous silica nanoparticles with a diameter ~25 nm and regular spherical structure were obtained successfully using the economic sodium silicate as a precursor. This will enhance the use of silica in many potential applications in many fields such as controlled release applications, catalysis and dielectric materials. In order to achieve the best conditions for the fabrication of the amorphous silica nanoparticles, the temperature should be maintained at 60°C and the stirring speed is adjusted at 250 rpm.

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