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RESEARCH ARTICLE

Effect of various amount of mmonium hydroxide on morphology of silica nanoparticles grown by sol-gel

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Abstract

Silica nanoparticles have drawn significant intentions for their potential in solar cell coating applications. These products occupy a noticeable position in a scientific research because of their easy preparation and wide uses for different technological applications. The quality of silica nanoparticles are highly dependent on the size. This study reports the synthesis of monodisperse silica nanoparticles by hydrolysis of tetraethyl orthosilicate (TEOS) in a mixture of ethanol and DI water as a solvent and ammonium hydroxide solution (NH_4OH) as a catalyst. The solutions are stirred overnight and dried in a low-pressure furnace under 100 mbar for 3 hours at 60°C. Various-sized silica nanoparticles in the range 80 nm – 250 nm were examined under field emission scanning electron microscopy (FESEM). With the increasing volume of ammonia solution, an increase in the size of silica nanoparticles were observed.

***Keywords*:** Silica nanoparticles; sol-gel; field emission scanning electron microscopy

INTRODUCTION

Silica nanoparticles are favorable for science and technology fields in electronic, aerospace, defense, medical and prominent areas in scientific researches. The designing, synthesis, characterization and application of materials and devices on nanometer scale have made ceramic nanoparticles into new classes of advanced materials which meet the demands from high-tech applications. Many researchers have been studying the silica because of their simple preparation and extensive uses and also, they are favorably subject on the size distribution of these particles [1][2].

Stober *et al.* [3] developed spherical silica particles of uniform in micron sizes between $0.05\ \mu m - 2\ \mu m$ by a chemical reactions of hydrolysis of alkyl silicates and subsequent condensation of silicic acid alcoholic solutions. The formation of silicas have achieved by two main mechanisms which are nucleation and growth [2][4]. The particles or nuclei aggregate with one another or larger aggregates by ammonia-catalyzed reactions of TEOS with water in low-molecular-weight alcohols which produced monodisperse and spherical silica nanoparticles [3]. In general, the hydrolysis and condensation reactions are given as [2][5][6],

$$\equiv Si - OR + H2O \leftrightarrow \text{hydrolysis}$$

$$\equiv Si - OH + ROH \quad (1)$$

$$\equiv Si - OR + \equiv Si - OH \leftrightarrow \text{alcohol condensation}$$

$$\equiv Si - O - Si + ROH \quad (2)$$

$$\equiv Si - OH + \equiv Si - OH \leftrightarrow \text{water condensation}$$

$$\equiv Si - O - Si \equiv + H2O \quad (3)$$

where R is an alkyl group C_xH_{2x+1}. For (Eq.(1])), the hydrolysis of alkoxide groups (OR) were substituted by hydroxyl groups (OH). The condensation reactions between the silanol groups and ethoxy groups or between silanol groups yield siloxane bridges ($Si - O - Si$) and either alcohol (ROH) for (Eq.(2)) and water (H2O) for (Eq.(3)).

More recently, Meier *et al.* [7] have used ethanolamine as a replacement of the basic catalyst ammonia via a modified Stober synthesis route to produce nanometric silica particles in alkaline media at elevated reaction temperatures. The use of ethanolamine in a sealed reaction tubes as a modified Stober synthesis inherent a good agreement of reaction kinetics that resulting the spherical silica nanoparticles with diameters between 28 – 647 nm at high temperatures and ambient pressure. In addition, Petcu *et al.* analyzed the drying of the silica from the volatile compounds and dispersed in ethanol in a vacuum state at ambient temperature and formed ~150 nm diameter silica nanoparticles in spherical shape. Rahman *et al.* reported [8] the higher ratio of H_2O/TEOS and lower ammonia concentration at slower feed rate produced particles in the range of 10 – 14 nm. The homogeneous and stable silica nanoparticles size were controlled by the optimum experimental conditions such as concentration of the reactants, ammonia feed rate, temperature and mixing mode. Besides that, the addition of small amount of anion electrolytes such as Br- and I- have the highest effect on reducing the particle size by 73% – 78% and were free from contamination [9]. In this study, the effect of the volume of ammonium hydroxide on the morphology and the size of the silica nanoparticles grown modified Stober method under a vacuum state was studied.

EXPERIMENTAL

Materials

Tetraethyl orthosilicate (TEOS, 99%), ethanol (extra pure), distilled water and ammonium hydroxide (NH_4OH, 28%) were used as received without further retreatment.

Synthesis of silica nanoparticles

The silica nanoparticles were prepared by hydrolysis of TEOS (6.9 ml) and ethanol (15 ml) that were initially introduced in 3 different of 30 ml vials with continuous stirring on the stirrer (400 rot/min). While stirring, a mixture of DI water (2.20 ml) and various amount of ammonium hydroxide solution (0.5 ml, 1.0 ml and 1.50 ml) were added into each vials after 10 minutes and kept stirring for 4 hours until the mixture turned into milky solution. Then, the 3-different mixtures were put into the petri dishes and dried in the tube furnace at low pressure (100 mbar) at 60℃ for 3 hours. After drying, about 1 g of silica nanoparticles for each petri dishes were obtained and characterized.

Characterization

The structure and the particle size of silica nanoparticles were observed and measured using Field Emission Scanning Electron Microscopy (FESEM). The samples have been coated with gold and the micrographs were taken at 3 random spots.

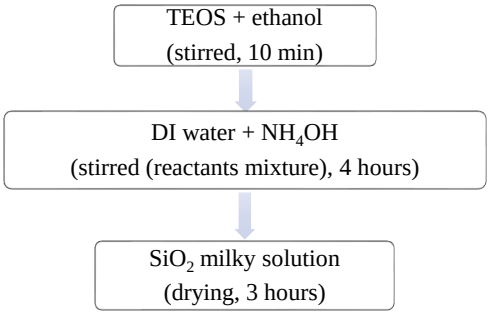


Fig. 1 Flow chart of preparation of silica nanoparticles.

RESULTS AND DISCUSSION

Synthesis of silica nanoparticles

A systematic experiment was carried out by sol-gel process via Stober synthesis route [7] and the results are discussed. The preparation of different series of silica nanoparticles (samples a, b, c) stated in Table 1. The size of the silica nanoparticles, which were controlled by the volume of NH_4OH was one of the parameters that show a vital role in the size distribution of silica nanoparticles.

The FESEM micrographs of each samples are shown in Fig 2. The size of the silica nanoparticles were measured by FESEM and Image J where compatible. Three spots were taken at each samples to get the uniformity of the average particle sizes. Ammonium hydroxide acts as a catalyst for hydrolysis and condensation of TEOS in ethanol escalating the rate of the reaction. The decreasing volume of ammonium hydroxide with decreasing weight ratio (20.4%, 13.6% and 6.8%) led to smaller size of the silica nanoparticles. The decreasing volume of ammonium hydroxide in the mixture of TEOS, ethanol and DI water ensures the constant concentration of ammonia (25M) which formed the smaller silica nanoparticles.

Table 1 Preparation of different size silica nanoparticles.

Samples	TEOS (ml)	C_2H_5OH (ml)	DI water (ml)	NH_4OH (ml)	Average particle size (nm)
a	6.9	15	2.2	1.5	214.1
b	6.9	15	2.2	1.0	162.4
c	6.9	15	2.2	0.5	93.5

As seen in Fig. 2, the structure of the silica particles for each samples was different in terms of the diameter. The particles were bigger in sample a which is in average size between 150 nm – 250 nm with the highest amount of ammonium hydroxide compared to the samples b (100 nm – 160 nm) and c (80 nm – 100 nm) due to the controlled aggregation. The addition of monomer triggered the nucleation growth of the particles and continuously reacted resulting the particles to aggregate together and form larger particles [5][2]. Besides that, according to Szekers *et al* [10], high concentration of water enlarged the size of the particles. This was due to the high nucleation rate of the hydrogen bond of SiO_2 that causes the agglomeration and ended with the large particles as shown in Fig. 3.

The solubility of the nanoparticles were essentially liable to agglomeration of the powder especially during the drying process [11]. A thorough process hints the formation of well-dispersed particles, whereas drying in the presence of water could outcome in agglomeration phenomenon [5]. This was as of the particle behavior from the condensation reactions at interparticle contacts throughout the drying process and also could be the Brownian motion and hydrodynamic effect. Thus, the ethanol was used as the suspension medium to moderate the agglomeration effect but somehow the amount of the ethanol did not show a major role in order to acquire monodispersed and smaller size particles when raising the volume of the ammonia, as presented in Fig.2. However, these silica nanoparticles were dried in a tube furnace at low pressure (100 mbar) which accelerated the drying process at 60℃.

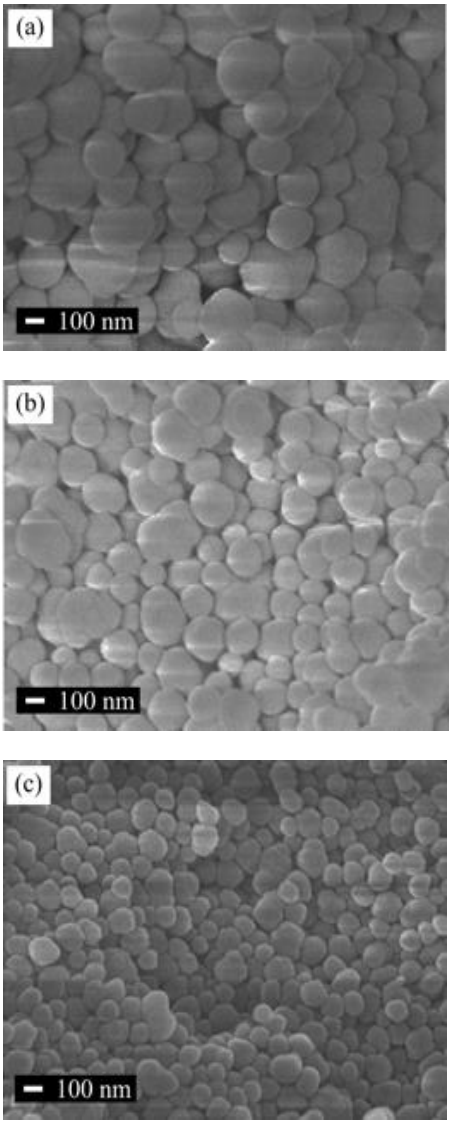
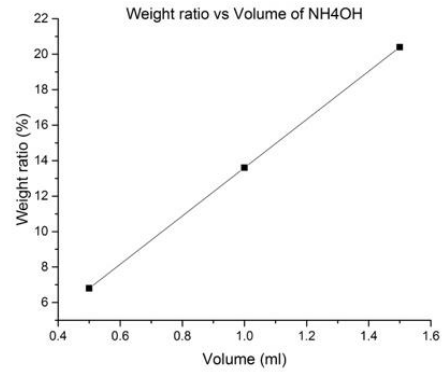
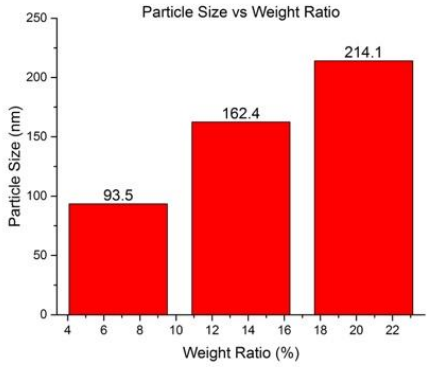


Fig. 2 FESEM images of silica nanoparticles synthesized by sol-gel method.



(a)



(b)

Fig. 3 (a) Relationship between volume and concentration of NH_4OH, (b) Effect of NH_4OH on average particle size

CONCLUSION

The present method is a convenient modification of Stober method conducted in a vacuum state at low temperature to produced various size of silica nanoparticles. The use of the ethanol as a solvent and ammonium hydroxide as a catalyst allows silica to form into spherical shape and well controllable diameters between 80 to 250 nm.

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