Preparation of Sub-micro SiO_2 Particles by Sol-gel Method

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***Abstract*—In this paper, the sub-micro silica particles were prepared successfully by sol-gel method. The ammonia was introduced as a catalyst and silane coupling agent as surfactant. The impact of reaction temperature, ethyl orthosilicate (TEOS) concentration, the amount of silane coupling agent and the order added to the solution on the size of particles were investigated. The sub-micro SiO_2 particles were determined by SEM. The result showed that the average size of particles changed from 200nm to 600nm while the reaction temperature was from 20℃ to 50℃, concentration of TEOS was 0.2mol/L to 0.3mol/L and 0.075 to 0.125ml dispersant was added after reaction. At room temperature, the silica particles grew up more easily on the condition that the concentration of TEOS was 0.3 mol/L and added 0.075 to 0.125ml dispersant after the reaction, the sub-micro silica particles with the average size of 600nm were prepared.**

***Keywords-silicon; sub-micro; sol-gel method; silane coupling agent; TE*OS**

I. INTRODUCTION

SiO_2 particles are widely used in the column packing, structural ceramic materials and cosmetics, paint, ink additives, etc. due to its mobility and high mechanical strength[1-2]. At the same time, it becomes functional because of no toxicity, high biological activity and it is suitable for its surface silanols as modified bridges [3].The system of sub-micro SiO_2 is 100nm to 1000nm, sub-micro SiO_2 can be applied to liquid body armor [4]. The main component of liquid armor is a special "shear dense liquid" (STF), the extremely small spherical particles (such as SiO_2 spherical particles) of this substance will be mixed into a liquid which is non-volatile, non-toxic and with good mobility forming a suspension or gel. This new liquid material usually very easily deformed, the extremely small hard particles is in suspension. However, once under the attract, the previous suspension collision point charged into the hard particles aggregating into clusters of particles, so that the shear thickening fluid instantly becomes very hard to stop the deadly strike from the human body[5].

There are many methods to prepare nano-silica microspheres, such as mechanical alloying method, hydrothermal synthesis method[6-7], microemulsion method[8], sol-gel method[9], precipitation, radiation synthesis preparation method[10]etc. The sol-gel method has become one of the preferred methods of preparation of spherical SiO_2 because it's simple process and low cost. Ultrasonic agitations were introduced based on the traditional sol-gel method in this article [11]. Sub-micro SiO_2 particles were prepared by TEOS hydrolysis reaction, then centrifuged, washed and dried at the end of reaction.

II. EXPERIMENTAL PROCEDURE

Preparation of A solution: mixing 28% concentrated ammonia, ethanol and deionized water in a flask, then carried on ultrasonic agitation; Preparation of B solution; mixing TEOS and ethanol uniform; Then the solution B was added to solution A rapidly, adding a certain amount of silane coupling agent KH-570, and reduced the strength of the ultrasound after a minute, the reaction was continued at room temperature for 3 to 6 hours. The resulting material was centrifuged, washed and spin-steamed grinding flour. The silica particles were analyze by scanning electron microscopy (SEM).

III. RESULTS AND DISCUSSION

A. The Effect of Order of Adding the Dispersing Agent KH-570 on the Particles

The volume of the reaction system (made up by ethanol, water, ammonia, and TEOS) was controlled to about 100ml. Solution A was 9ml 28% concentrated aqueous ammonia, 16.25 ml ethanol and 22.50ml water. Solution B was 6.75ml TEOS and 45.5ml ethanol. Solution B was mixed uniformly and then added into solution A rapidly. The ultrasound intensity was 35W at the moment then the ultrasound intensity was adjusted to 20W after a minute. Finally, the powder was prepared by rotary evaporation and grinding after 4h reaction at room temperature. The SEM images of the particles were showed as Figure 1. The SiO_2 particles were spherical particle and their size was about 600 nm, shown as in Figure 1 (a, c). The concentration of the TEOS was 0.3 mol/L. The dispersing agent KH-570 immediately was added after the solution B was added, shown as Figure 1 (b, d). The TEOS was not complete hydrolysis in Figure 1 b, however, the particle was liked as floc in Figure 1 d, which because that the SiO_2 nucleation was packaged by silane coupling agent KH-570. They prevented further growth and agglomeration, and the nanoparticles were easily formed. It can be seen that dispersing agent KH-570 was added to the solution suitably after reaction complete, namely, the agglomeration of SiO_2 particles can be improved after the nucleation.

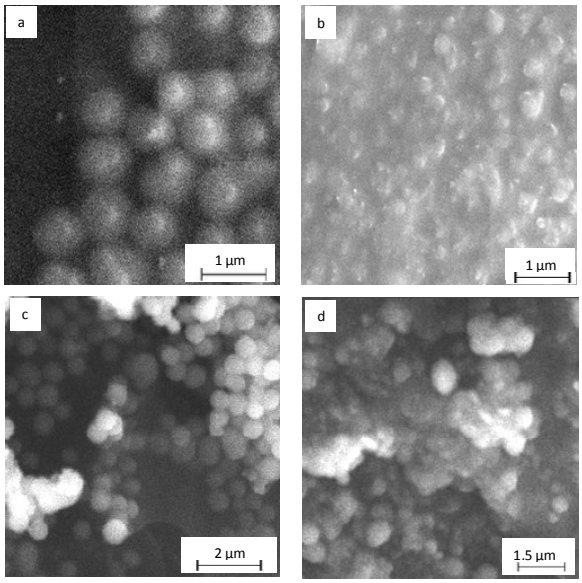

FIGURE I. SEM IMAGES OF SiO_2 PARTICLES (a) 0.075 ml KH-750 ADDED AFTER REACTION; (b) 0.075 ml KH-750 ADDED ONLY AFTER ADDING THE B SOLUTION; (c) 0.125 ml KH-750 ADDED AFTER REACTION; (d) 0.125 ml KH-750 ADDED ONLY AFTER ADDING THE B SOLUTION.

B. The Effect of the Amount of the Dispersing Agent KH-570 on the Particles

The volume of the reaction system (made up by ethanol, water, ammonia, and TEOS) was controlled to about 100ml. Solution A was 9ml 28% concentrated aqueous ammonia, 16.25 ml ethanol and 24.75ml water agitated at the 35W ultrasound intensity . Solution B was 4.5ml TEOS and 45.5ml ethanol. Solution B was mixed uniformly and then added into solution A rapidly. The ultrasound intensity was adjusted to 20W after a minute. Finally, the particles were prepared by rotary evaporation and grinding after 4h reaction at room temperature. Figure 2a showed the 300nm SiO_2 particles was prepared at the room temperature (20 ℃), the concentration of TEOS was 0.2 mol/L, and the silane coupling agent KH-570 was 0.15ml. Figure2b showed that SiO_2 were floc while adding 0.15ml silane coupling agent KH-570 immediately after the solution B was added. And the SiO_2 particles of 500 nm were prepared by adding 0.075 ml silane coupling agent KH-570 after reaction as Figure2c. Silica hydrolysis was not complete hydrolysis by adding 0.125ml silane coupling agent KH-570, shown as Figure2d. Because the hydroxyl (-OH) was informed by unmodified SiO_2 microsphere surface reaction with water molecules. The hydroxyl interacted in anhydrous ethanol and combined by chemically or hydrogen and the silane coupling agent occurred hydrolysis during preparing the SiO_2. The inorganic group of hydrolysis was adsorbed on the surface of SiO_2 particles which were joined with hydroxyl on the surface of SiO_2 network structure by dehydration synthesis, hindering the role of hydrogen bonding between the particles and preventing agglomeration. If the amount of coupling agent was too small, the surface of SiO_2 particles was incomplete and modified was ineffective; and if opposite, it will cause unnecessary waste, and excess coupling will cause reunion.

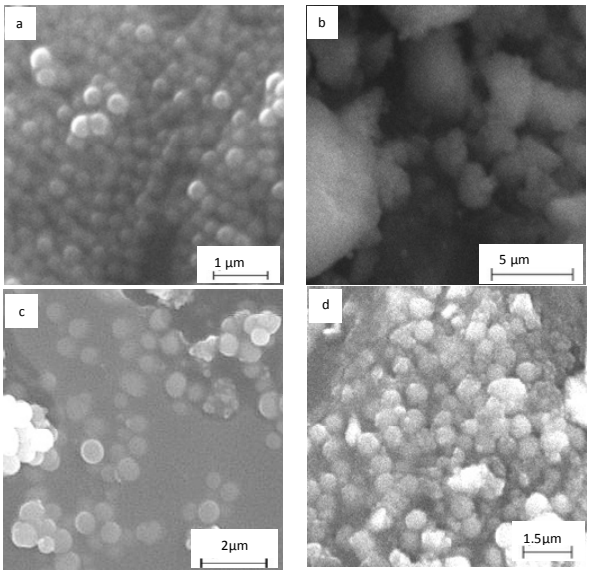

FIGURE II. SEM IMAGES OF SiO_2 PARTICLES (a) 0.15 ml KH-570; (b) 1.5 ml KH-570; (c) 0.075 ml KH-570; (d) 0.125 ml KH-570.

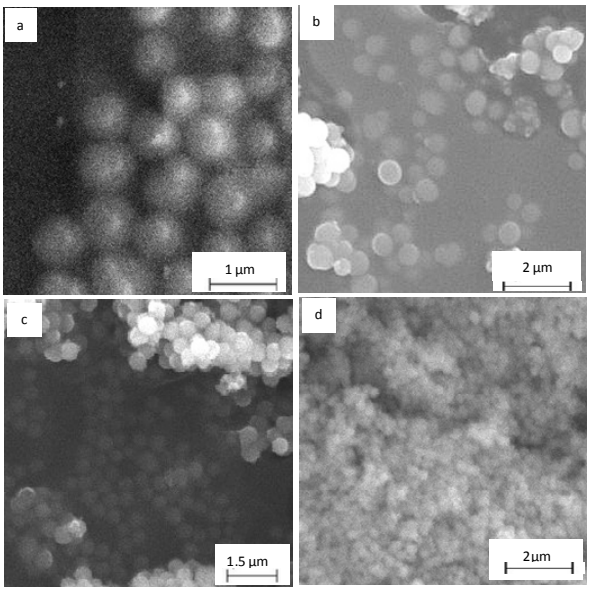

FIGURE III. SEM IMAGES OF SiO_2 PARTICLES (a) T=20℃, CTEOS: 0.3 mol/L, 0.075mlKH-570; (b) T=20℃CTEOS: 0.2 mol/L, 0.075mlKH-570; (c) T=50℃, CTEOS: 0.3 mol/L, 0.125mlKH-570; (d) T=50℃, CTEOS: 0.2 mol/L, 0.125mlKH-570.

C. The Effect of Concentration of TEOS on Synthetic Silica Particles

Figure 3 (a,b) showed the SiO_2 particles were prepared by adding 0.075ml dispersant after reaction, and the concentration of TEOS was 0.3 mol/L or 0.2 mol/L at room temperature (20 ℃). Figure 3 c and d showed the SiO_2 particles were prepared by adding the 0.125ml dispersant, and the concentration of TEOS was 0.3mol/L and 0.2 mol/L at 50 ℃. Figure 3 (a) shows the size of SiO_2 particle size about 600 nm was slightly larger than the particle size about 500 nm shown in Figure b. Figure 3 (c) showed the size of SiO_2 particle

approximately 400 nm. It was because the main source of Si was TEOS; the concentration of TEOS affected the particle size. When the other reaction condition was same, the change of concentration of TEOS in the system caused the change of rate of hydrolysis and polymerization, and therefore affected the size of SiO_2 particles.

IV. CONCLUSIONS

(1)The average size with 200-600 nm of sub-micro SiO_2 particles was prepared successfully by sol-gel method. The SiO_2 particle was spherical while the silane coupling agent KH-570 was added after the reaction.

(2) The 200-600 nm SiO_2 particles were prepared with the concentration of TEOS was 0.2-0.3 mol/L, 0.075-0.125 ml dispersant, and the reaction temperature is from 20℃ to 50℃. The silica particles grew up more easily on the concentration of TEOS was 0.3mol/L, the dispersant was added after reaction at room temperature 20 ℃ and the particle size was about 600 nm.

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