

## Synthesis Submicro- and Nanoscale Spherical Silica Particles with 3-aminopropyl Groups in the Surface Layer

I.V. Melnyk, V.V. Tomina, Yu.L. Zub

*Chuiiko Institute of Surface Chemistry of NAS of Ukraine, 17, General Naumov Str., 03164 Kyiv, Ukraine*

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Stöber's method and two-component systems (considering alkoxy silanes) were used to develop techniques for the synthesis of spherical silica particles with  $\equiv\text{Si}(\text{CH}_2)_3\text{NH}_2$  groups in the surface layer. The influence of synthesis conditions on the size of synthesized spherical particles and concentration of functional groups were studied. DRIFT, SEM and acid–base titration were used to identify the composition of the surface layers and morphology of the obtained silica particles. There was analyzed the influence of the order entry components, the stirring time, the drying mode, the ratio of reacting of alkoxy silanes, the temperature, and the amount of water and solvent on the morphology, the size of synthesized spherical particles and the content of functional groups in the silica spheres.

**Keywords:** Stöber's method, silica submicro- and nanoparticles, amino groups.

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### 1. INTRODUCTION

There have recently been published papers describing synthesis of non-porous silica nano- and submicro-spheres with functional groups in the surface layer [1,2]. The suggested technique was based on Stöber method [3]. These silica spheres due to their excellent properties, such as adjustable size and surface layer composition, along with their chemical stability and biocompatibility, are promising materials for application in wide range of areas (chromatography, controlled drug delivery, bioseparation, chemo- and biosensors, biocatalysis). There are two most commonly used techniques for the synthesis of functionalized silica nano- and submicro-spheres. The first of them is based on the surface modification of silica spheres obtained by Stöber method with trifunctional silanes,  $(\text{RO})_3\text{SiR}'$ . The second technique applies one-step synthesis. In other words, the structural agent (usually tetraethoxysilane, TEOS) and functionalizing agent are entered simultaneously or sequentially (in some order) in the reactive solution. However, the very first works showed that, despite their simplicity, both approaches are characterized by the existence of unknown factors affecting the shape and size of particles, the content of functional groups, hydrolytic stability of the surface layer, and even the final product yield. Thus, in the first studies examining the preparation of nanoparticles with 3-aminopropyl groups, it was shown that heating suspension in DMF at 100°C for 24 h does not increase the content of surface amino groups, but improves the stability of the surface layer [2]. It was determined [1] that the introduction of 3-aminopropyltriethoxysilane (APTES) to TEOS alkosol at a molar ratio of 1/1 yields nanoparticles with an average diameter about 66 nm, but their surface layer contains almost no amino groups. At 3/1 TEOS/APTES molar ratio, the surface layer contains amine groups (1.56 mmol/g), but the particle size decreases to about 9 nm. When the order of components was changed, the content of functional groups increased to 3.2 mmol/g; however, according to  $^{29}\text{Si}$  NMR spectroscopy, the

number of  $\text{Q}^4$  structural units decreases. This may indicate the looseness of the particles polysiloxane network.

Therefore, the current paper is aimed to establish a number of factors affecting the morphology of spherical silica, their particle size, the content of the functional groups. As functional groups, there was chosen complexing 3-aminopropyl group.

### 2. EXPERIMENTAL PART

#### 2.1 Reagents

The following substances were used as precursors for synthesis of the samples: tetraethoxysilane,  $\text{Si}(\text{OC}_2\text{H}_5)_4$  (Aldrich, 98%); 3-aminopropyltriethoxysilane,  $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$  (Fluka, 98%); ethanol (96%); ammonium hydroxide (25% aq.) (reagent grade, "Makrohim", Ukraine). Reagents for acid-base titration: 0.1 N solutions of HCl and NaOH prepared from fixanal; indicator was methylene orange.

#### 2.2 Syntheses

**Sample 1.** 4.5  $\text{cm}^3$  of TEOS were added at constant stirring to ethanol-ammonium solution (see Table 1). Opalescence was appeared after 5 min. and it was increased with time. 1.5  $\text{cm}^3$  of APTES were added to the suspension after stirring for 1 h. The suspension was stirred 23 h and the precipitate was centrifuged (for 10 min at 5000 rpm), and washed triply with ethanol. The sample was dried in air and after that in the drying oven at 100°C for 1 day.

**Samples 2-7.** 21  $\text{cm}^3$  of 25% aq.  $\text{NH}_4\text{OH}$  and 14  $\text{cm}^3$  of distilled water (besides sample 7) were added at constant stirring to 100  $\text{cm}^3$  of ethanol. In several minutes, 2  $\text{cm}^3$  APTES (6  $\text{cm}^3$  in the case of sample 2, 1  $\text{cm}^3$  in the case of sample 3) were added to the mixture. The solution immediately turned cloudy; however, in few minutes it got transparent again. Then 6  $\text{cm}^3$  of TEOS were added to it. In two minutes, the solution was cloudy again, and the amount of precipitate started increasing. The suspension was stirred for some hours

(see Table 1), and was centrifuged, washed and dried like sample 1 (except for sample 6 - it was dried in air, and 6\* - it was dried under vacuum at 100°C for 3 h).

Sample 8. 1 cm<sup>3</sup> of TEOS and 1 cm<sup>3</sup> of APTES were added at constant stirring to 6 cm<sup>3</sup> of ethanol in an ice bath. In 15 min. obtained sol was left at room temperature. In 30 min. it turned cloudy, and after 24 h sediment was observed throughout the all volume. It was crushed and dried like sample 1.

Sample 9. TEOS and APTES were mixed in ethanol in an ice bath. After the appearance of opalescence (45 min.) the solution of ammonia was added. The suspension was stirred for 2h 15min. more and carried out similar to the sample 1.

Sample 10. Synthesis of the sample was carried out similarly to the sample 9, but at room temperature (20 °C). The solution of ammonia was added after the appearance of opalescence (30 min.).

Sample 11. Synthesis of the sample was carried out similarly to the sample 9, but with heating to 45 °C. The solution of ammonia was added after the appearance of opalescence (15 min.).

The composition of the reaction solution and other parameters of syntheses are presented in Table 1.

### 2.3 Characterization

For SEM studies by JSM-6060LA Analytical Scanning Electron Microscope (Jeol, Tokyo, Japan) using secondary electrons at accelerating voltage of 30 kV, the samples were fixed on the surface of objective table. To prevent the accumulation of the positive charges and to receive contrasting images, the surface of the samples was covered with thin continues layer of gold or platinum by cathodic sputtering in vacuum.

The content of amino groups was determined by acid–base titration [4]. Batches of the samples (0.1 g) were treated with a 0.1 N HCl solution (20 cm<sup>3</sup>) for 24 h. The resulting precipitates were filtered and the filtrate was titrated with 0.1 M NaOH in the presence of the indicator. The amine concentration was estimated using the difference between the content of protons in solution before and after sorption.

## 3. RESULTS AND DISCUSSION

The search for the methods of synthesis of spherical silica particles with 3-aminopropyl groups in their surface layer dates back to the 1990s. Some authors have suggested single [2] and two-stage [1,2] techniques, at room temperature [5] and with boiling solution [1], and using different solvents [2]. Firstly, we synthesized sample 1 using the technique of [6]. Indeed, there was observed the formation of silica particles under these conditions (Fig. 1), but IR spectroscopy and acid-base titration analyses showed no amine groups on their surfaces. Therefore, in the following synthesis (sample 2) there was used a method of successive addition of APTES and, later, TEOS, to the ethanol-ammonia medium [1]. However, sample 2 contained both spherical particles and non-spherical (Fig. 1). It was found, that the increasing molar ratio of TEOS/APTES improves the morphological characteristics of the samples (Fig. 1, samples 3 and 4). However, with the increase in the molar ratio to 6/1, the number

of functional groups is significantly reduced (Table 1, sample 3). Therefore, in the following syntheses, we adhered to the optimal ratio of TEOS/APTES equal to 3/1 (Table 1, sample 4). It should be noted, that the increasing stirring time caused the reduction of functional groups content (see samples 4 and 5, Table 1) and the product yield. Therefore, the stirring was less than 1 h, which was marked in other papers [7]. Changing the drying mode (Table 1, samples 4, 6 and 6\*) does not affect the morphology of samples (Fig. 1). However, the content of amine groups slightly increases for sample 4 due to more complete removal of water. For this reason, all the next samples were dried in the oven at 100°C for 24 h.

**Table 1** – The composition of the reaction solution and some properties of the synthesized samples

Sample	EtOH, cm <sup>3</sup>	H <sub>2</sub> O, cm <sup>3</sup>	NH <sub>4</sub> OH, cm <sup>3</sup>	TEOS, cm <sup>3</sup>	APTES, cm <sup>3</sup>	Time, h	Size, nm	C <sub>NH<sub>2</sub></sub> , mmol/g
1	40	-	21	4.5	1.5	24	450	not determ
2	100	14	21	6	6	2	200	2.1
3	100	14	21	6	1	1.5	700	0.3
4	100	14	21	6	2	1	400	1.3
5	100	14	21	6	2	6	400	0.7
6	100	14	21	6	2	1	300	1.1
6*	100	14	21	6	2	1	300	0.9
7	100	-	21	6	2	1	300	1.1
8	6	-	-	1	1	24	100	2.1
9	100	-	1.8	4	1.4	3	100	1.3
10	100	-	1.8	4	1.4	2	300	1.4
11	100	-	1.8	4	1.4	1.5	700	1.7

Some authors believe, that the amount of water in the syntheses should be increased [1,2], but others consider that water from ammonia solution is enough for the reaction of hydrolytic polycondensation [8]. Comparing samples 6 and 7 (Table 1 and Figure 1), it is easy to conclude, that the additional amount of water does not affect the particle size and number of functional groups.

Finally, there was analysed the effect of the synthesis temperature on the particle size and the content of functional groups, in terms of samples 9, 10, and 11. It should be mentioned, that in addition to the temperature variation, the stirring time for these samples was also varied (Table 1). The fact is that after 1 h stirring time (sample 9), there was observed the formation of particles, too small to be centrifuged in our conditions. However, in our opinion, this factor (stirring time) would not significantly affect the particle size, and the temperature of hydrolytic polycondensation reaction of alkoxy silanes has a more significant effect. Comparing the size of these samples (Table 1), it is easy to conclude, that the increase in temperature from the ice bath ( $\approx 2^\circ\text{C}$ ) to 45°C leads to 7 times increase in diameter of the particles. It is also accompanied by the increase in the content of functional groups (Table 1).

It is interesting to note, that during the synthesis of xerogels with 3-aminopropyl groups [9] these groups created alkaline medium in water for hydrolytic polycondensation reaction. Indeed, the synthesis of sample 8 at TEOS/APTES ratio of 1/1, without using ammonia

solution (water source was 96% ethanol), the formation of spherical silica particles was also observed (Fig. 1). In the synthesis under similar conditions, but without TEOS, the appearance of precipitate was not observed even when the solution was heated. Compared with the sample 2, where the same ratio of alkoxysilanes was used, we found that the diameter of the particles for sample 8

is twice less, but both samples are characterized by the same content of amino groups (Table 1). Thus, nanoscale spherical silica particles with amino groups can be obtained without introducing ammonia. However, the synthesis of the sample 8 requires further research for improving the morphology of the particles.

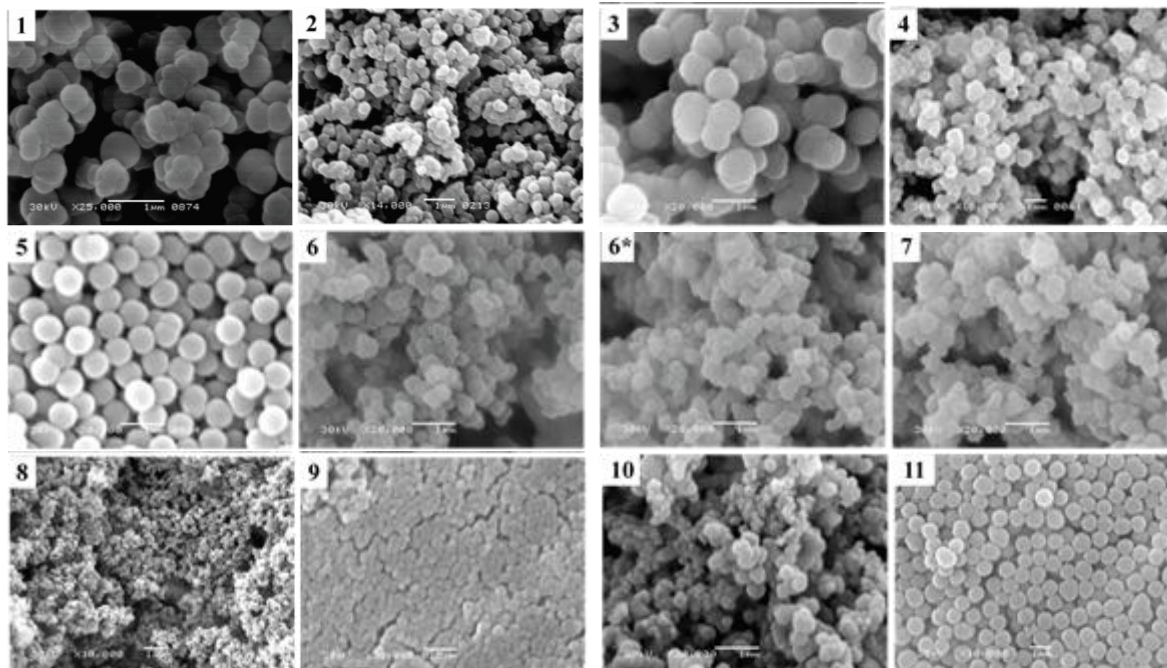


Fig. 1 – Photomicrographs of synthesized samples obtained by SEM

#### 4. CONCLUSIONS

The influence of factors, such as the order entry components, the stirring time, the drying mode, the ratio of reacting of alkoxysilanes, the temperature, and the amounts of water and solvent on the morphology and the content of functional groups in the silica spheres was analysed. It was shown, that the shape and size of the particles are majorly affected by the synthesis temperature, and the ratio of reacting alkoxysilanes determines the content of 3-aminopropyl groups.

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