Nanostructure surfaces

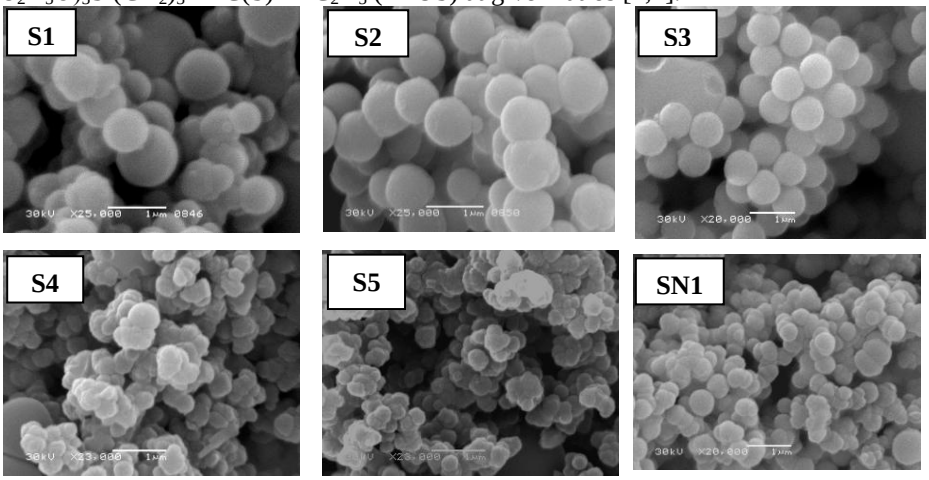
Effect of synthesis conditions on the formation of spherical silica particles with sulfur-containing surface layer

G.I.Nazarchuk, I.V.Melnyk, Yu.L.Zub

Chuiko Institute of Surface Chemistry, Natl. Acad. of Sci. of Ukraine, 17 General Naumov Str., Kiev-03039, Ukraine.
E-mail: dhi@online.ua; nazarchuk_g@isc.gov.ua

Nano- and microspheres of silica with functionalized surface layer have been of particular attention in the recent years. Such layer endows them with new specific properties, which significantly extends the scope of their practical application. A common method to obtain monodisperse spherical silica particles of 50-2000 nm in size is Stoeber method, which is the hydrolytic polycondensation of tetraethoxysilane (TEOS) in an environment of low molecular weight alcohol (with ammonium hydroxide as catalyst). The aim of current research is to determine the conditions that affect the formation of silica particles with sulfur-containing complexing groups, -SH or –NHC(S)NH, in the surface layer.

The synthesis of spherical particles was conducted using tetraethoxysilane (TEOS) and 3-mercaptopropyltrimethoxysilane (MPTMS) or trifunctional silane $(C_2H_5O)_3Si(CH_2)_3NHC(S)NHC_2H_5$ (ETUS) at given ratios [1,2].



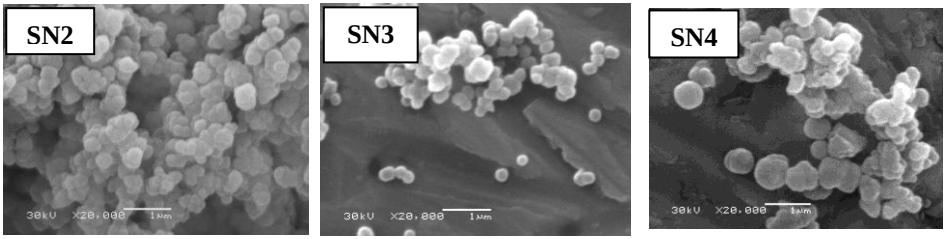


Fig. 1. SEM images of samples: **S1** – 3/1 (without cat.), $d_{aver.}$=740 nm; **S2** – 3/1 (H^+), $d_{aver.}$ =760 nm; **S3** – 3/1 (F^-), $d_{aver.}$=510 nm; **S4** – 6/1 (H^+), $d_{aver.}$= 410 nm; **S5** – 6/1 (F^-), $d_{aver.}$ = 330 nm), **SN1** – 3/1 $d_{aver.}$= 400nm, **SN2** – 6/1 (T-15^{0}C, 2h) $d_{aver.}$= 270 nm, **SN3** – 6/1 (T-15^{0}C, 12h) $d_{aver.}$= 260 nm, **SN4** – 6/1 (T-40^{0}C, 12h) $d_{aver.}$= 400 nm.

It was determined, that in ethanol-ammonia solution, trifunctional silane ETUS does not form a separate phase, but for MPTMS the formation of separate phase is observed. Varying the nature of the catalyst used for MPTMS hydrolysis, and the ratio of the reacting alkoxysilanes, there can be obtained spherical silica particles 330-760 nm in size, containing 3-mercaptopropyl groups in the surface layer. However, when ETUS is used with TEOS, there is observed the formation of functionalized silica particles of submicron size, which is confirmed by IR and NMR spectroscopy, and elemental analysis. It was determined, that stirring time virtually has no effect on the average size of the particles formed during the synthesis. However, the size of submicron particles can be influenced by varying the ratio of the reacting components, the order of reagents addition, and temperature of the solution. The possible application of such materials can be the removal of heavy metal ions from aqueous solutions.

We express our gratitude to the Ukrainian State Program “Nanotechnologies and Nanomaterials” (Project No. 6.22.5.42) for financial support of the present work.

1. *Nazarchuk G., Melnyk I., Zub Yu.* Synthesis of spherical silica particles with 3-mercaptopropyl groups in their surface layer // Chem. J. Moldova.-2012.-**7.** -P.157-161.

2. *Nazarchuk G., Melnyk I., Papayanina O., Zub Yu.* Synthesis of spherical silica particles with thiourea complexing-forming groups in their surface layer. // Nanosystems, nanomaterials, nanotechnologies.-2013.-**11**, N 4.-P. 769-780.