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Characteristics of silica nanopowders and sol containing immobilized nanoparticles of copper or silver

RAPID COMMUNICATION

Summary — Silica nanoparticles (NP's) with immobilized NP's of copper or silver were synthesized by means of sol-gel process. The optimization of silica NP's synthesis was carried out under different conditions of temperature and stirring rate. Our results confirmed that the stirring rate plays an important role in growth, polydispersity and stability of nanoparticles. The properties of nanosilica containing immobilized nanosilver or nanocopper were examined by scanning electron microscopy (SEM), atomic absorption spectroscopy (AAS), photon correlation spectroscopy (PCS) and zeta potential analysis.
Keywords: nanosilica, copper nanoparticles, silver nanoparticles, zeta potential, photon correlation spectroscopy.

CHARAKTERYSTYKA NANOPROSZKÓW I ZOLI KRZEMIONKOWYCH ZAWIERAJĄCYCH NANOCZĄSTKI MIEDZI LUB SREBRA
Streszczenie — Nanocząstki krzemionkowe syntetyzowano w procesie zol-żel. Syntezę prowadzono w kilku wybranych wartościach temperatury oraz stosując różną szybkość mieszania. Na podstawie badań wielkości i polidyspersyjności otrzymanych nanocząstek wybrano optymalne warunki prowadzenia tego procesu pozwalające na zapewnienie małej polidyspersyjności (rys. 1—4). Następnie, tak otrzymaną nanokrzemionkę modyfikowano nanocząstkami srebra lub miedzi. Właściwości nanokrzemionki, zawierającej immobilizowane nanocząstki srebra lub miedzi, badano metodami: skaningowej mikroskopii elektronowej (SEM), atomowej spektroskopii absorpcyjnej (AAS), korelacyjnej spektroskopii fotonów (PCS) oraz charakteryzowano wartością potencjału zeta (tabela 1).
Słowa kluczowe: nanokrzemionka, nanocząstki miedzi, nanocząstki srebra, potencjał zeta, korelacyjna spektroskopia fotonów.

The synthesis of nanoparticles (NP's) has attracted considerable interest due to their unique electronic, magnetic, optical, biological and chemical properties [1, 2]. The properties of nanoparticles depend on their size and particle size distribution which is important in such applications. Recently nanoparticles with embedded biocides have been extensively investigated. The antimicrobial activity of silver and copper is well established, especially when metals are applied in the form of NP's [3, 4]. The agglomeration of silver or copper NP's in colloids can result in decrease of their antimicrobial and antifungi properties. Colloidal silver particles can be stabilized by the protective colloids [5]. The use of such stabilized silver colloids is limited due to unfavorable effect of stabilizers on the properties of the obtained material. Copper nanoparticles can be stabilized by the implantation of copper ions on silica gels by a laser of appropriate wavelength [6].

This study is focused on the method of effective stabilization of silver or copper NP's to prevent agglomeration resulting in the decrease of antimicrobial and antifungi properties. The problem of NP's stability was solved by the development of silica nanospheres containing immobilized NP's of silver or copper. In this study, series of syntheses of silica nanoparticles and silica nanoparticles containing immobilized NP's copper or silver were performed.

EXPERIMENTAL

Materials

Tetraethoxysilane (TEOS, technical grade) was purchased from Wacker Chemie, Germany. TEOS used as alkoxysilane precursor was distilled immediately before use for the preparation of nanoparticles.

The following chemicals supplied by POCh S.A. (Poland) were also applied: aqueous ammonia (reagent grade, 25 wt. %, density $d = 0.91$ g/cm^3), ethyl alcohol (absolute, reagent grade), silver nitrate and copper acetate.

Synthesis of nanopowders

Nanopowders were obtained according to the procedure described in [7, 8]. Ethyl alcohol, aqueous ammonia and distilled water were mixed to obtain the reaction mixture. The initial pH of reaction mixture was measured with pH-meter of Schott Instruments LAB850. Syntheses were carried out at three temperatures (25, 40 and 65 °C). TEOS was added to reaction mixture which was stirred for 2 h with one of four constant speed values of 100, 250, 500 or 1000 rpm. The reaction mixture containing TEOS/EtOH/H_2O in the mole ratios 0.023/0.500/0.477 was used for the synthesis. The particle size of obtained silica NP's depends on the initial pH value, which should be carefully controlled during the synthesis. To obtain particles of the average diameter of 30, 60 and 130 nm three variant of syntheses were performed with the initial pH equal 10.4 (svI), 10.85 (svII) and 11.25 (svIII), respectively.

The final pH range was 7.5—10.8 and further *in situ* modification of reaction product with nanoparticles of copper or silver was carried out. For that purpose aqueous solution of copper acetate and γ-glicydoxypropyltrietoxysilane (copper NP's) [8] or silver nitrate and reductor *i.e.* formaldehyde (silver NP's) [7] was dropped to the reaction mixture and stirring was continued for 1 hour to achieve a characteristic (dark brown) color of mixture. The sample of sol was dried in two steps at the temperatures of 90 and 250 °C [3]. All syntheses were performed three times using the same recipes to achieve better credibility of measured products properties, which were presented as the average value for samples obtained in three identical syntheses.

Methods of testing

Characteristics of sol

Particle size (Z average diameter) and particle size distribution (polydispersity) in resulting sols of unmodified and modified silica NP's were measured by photon correlation spectroscopy (PCS). The experiments have been carried out with a Zetasizer Nano ZS apparatus (Malvern). The Zetasizer Nano ZS was also used to determine zeta potential using Smoluchowski approximation. The instrument offers high sensitivity, accuracy and resolution of the measurement of zeta potential. The measuring error of particle size was ±10 nm and of zeta potential ±0.1 mV, accordingly. This is achieved by a combination of laser Doppler velocimetry and phase analysis light scattering (PALS) in Malvern's patented M3-PALS technique [9]. The results were registered as the curve of particle size distribution. The resulting peak analysis by intensity, volume and number was performed.

Characteristics of nanopowders

Silver or copper content was determined by atomic absorption spectroscopy (AAS) using AAS Spectrometer 5100 PC (PerkinElmer).

RESULTS AND DISCUSSION

Silica NP's

A series of silica NP's synthesis was performed to optimize the sol-gel process conditions. The stirring rate and the temperature were selected as two most important factors affecting particle size (Z average diameter), particle size distribution (polydispersity) and zeta potential. Silica NP's synthesised using different initial pH to obtain particles with three average size (variants of synthesis svI, svII and svIII) were characterised.

The effect of stirring rate

The effect of stirring rate on polidyspersity of particles synthesised at constant temperature 25 °C using three synthesis variants is presented in Figure 1. This effect is evident for all investigated silica NP's. The highest polydispersity was observed for particles obtained in svI synthesis, especially when synthesised at the stirring rate of 100 rpm. The lowest polidyspersity for all variants of synthesis was found when mixture was stirred at 250 rpm.

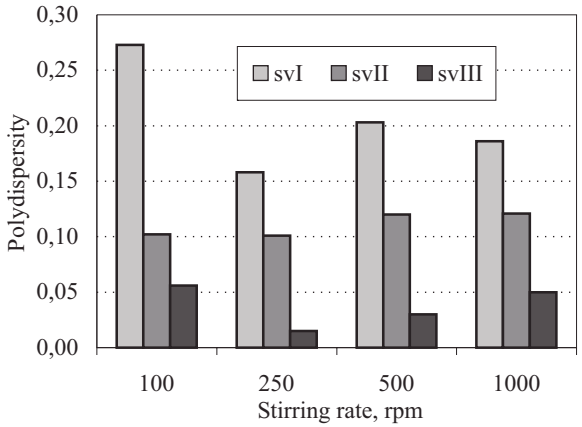

Fig. 1. The effect of stirring rate and variant of synthesis (see text) on polydispersity of particle size

The stirring rate also affects the Z average diameter as shown in Figure 2. This effect is evident for silica NP's obtained in svII and svIII variants of synthesis. In the cases of the svI and svIII variants the lowest particle size was observed for silica NP's synthesised at the stirring rate 250 rpm, while in the case of svII — 1000 rpm, respec-

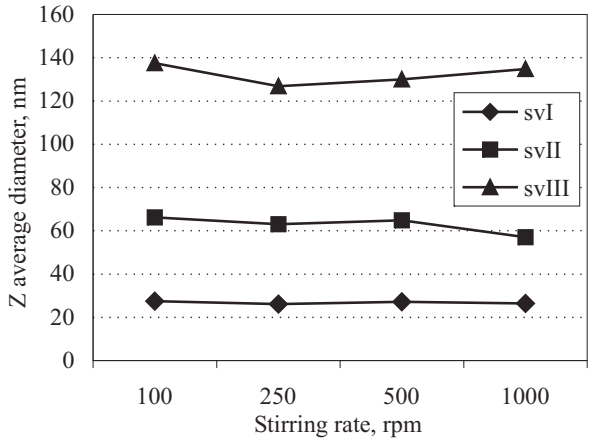

Fig. 2. The effect of stirring rate and variant of synthesis (see text) on Z average diameter of particles

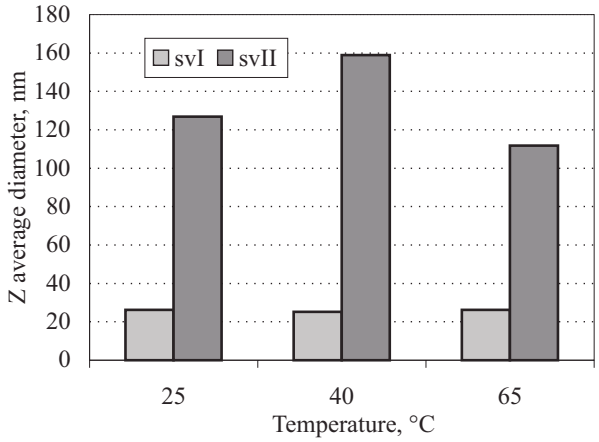

Fig. 4. The effect of temperature and variant of synthesis (see text) on Z average diameter of particles

tively. The stirring rate of 250 rpm was selected on the basis of the presented results as the optimized value and applied to further experiments.

The effect of temperature

To examine the effect of temperature on size and size distribution the nanosilica particles were synthesized at temperatures of 25, 40 and 65 °C under the conditions described as vsI and vsIII variants at stirring rate of 250 rpm. The influence of temperature on polydispersity of such particles is shown in Figure 3. The lowest polidispersity was observed for reaction temperature of 25 °C for all synthesized silica NP's.

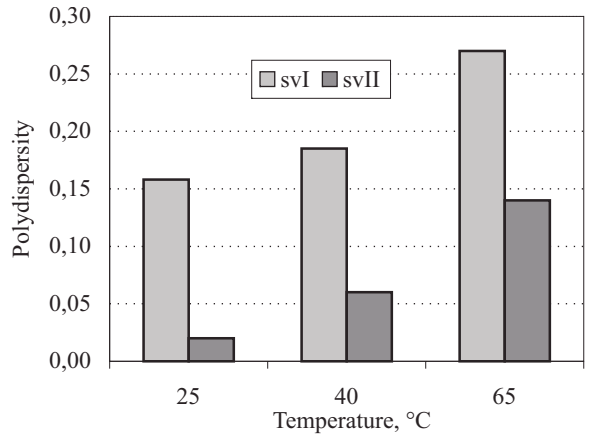

Fig. 3. The effect of temperature and variant of synthesis (see text) on polydispersity of particle size

The effect of temperature on Z average diameter for the same silica NP's is shown in Figure 4. In the case of svI variant of synthesis there was no influence of temperature on particle size. However, in the case of svIII variant Z average diameter of particles obtained in synthesis carried out at 40 °C is significantly higher than in other temperatures.

As a result of these studies the samples synthesized at 25 °C were selected for the further investigation.

Silica NP's containing immobilized copper or silver NP's

Nanosilica synthesized at 25 °C and 250 rpm stirring rate in the conditions corresponding to the vsI and vsIII variants were modified with copper or silver. In sols containing modified nanosilica as well as control samples 1 and 2, corresponding to unmodified nanosilica sols, polidyspersity and zeta potential was determined. Furthermore, AAS method was used to specify copper or silver content in the modified nanosilica. These results are summarized in Table 1. In fact, the modifications of nanosilica do not affect the polydispersity of the particles. The content of immobilized silver in NP's does not depend on the size of particles (a variant of synthesis), while the copper content is higher in nanosilica with smaller particles (svI variant). The modification with copper or silver results in considerable changes in the zeta potential. Negative values of the potential for unmodified silica were changed to positive after the modification and the absolute values of zeta potential were increased significantly as well and resulted in the increased stability of the obtained sols.

T a b l e 1. The characteristics of silica sols containing immobilized nanoparticles copper or silver and appropriate control samples with unmodified silica

Sample	Variant of synthesis	Polidispersity	Copper content wt. %	Silver content wt. %	Zeta potential (Smoluchowski approximation) mV
1	svI	0.24	4.45	–	18.6
2	svI	0.25	–	6.93	23.4
3	svIII	0.04	3.44	–	13.1
4	svIII	0.11	–	6.93	33.0
1 control	svI	0.24	–	–	-7.93
2 control	svIII	0.04	–	–	-8.69

CONCLUSIONS

The optimal parameters for obtaining modified silica nanopowders (*e.g.* stirring rate 250 rpm and synthesis temperature 25 °C) were determined. Zeta potential measurements confirmed the validity of the application of Smoluchowski approximation. It was found that the zeta potential changed from negative in unmodified nanosilica sols to positive in modified ones. Moreover, it was observed that absolute value of zeta potential of modified NP's is significantly higher in comparison with values measured for unmodified NP's sols. It confirmed the high stability of silica sols containing immobilized nanoparticles of copper or silver.

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