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Properties and applications of silica submicron powders with surface Ag nanoclusters

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Spherical silica powders with uniform, submicron grain diameter have been obtained using the sol-gel technology. Subsequently, metallic silver nanoparticles have been produced on the surfaces of the grains. Raman scattering spectra of such SiO_2–Ag^0 powders impregnated in ethanol solutions of tris(2,2'-bipyridyl)ruthenium(II) can be recorded for solutions four orders of magnitude more diluted than the lowest possible concentration detectable for complex liquid solutions in the same experimental conditions (the SERS effect). Also, such silver-doped silica powders display anti-microbial capabilities and can be used to obtain doped thin-film coatings, e.g. for the production of bacteriostatic textiles.

1. Introduction

Nanostructured materials possess unique mechanical, chemical and optical properties [1]. Nanometre-sized metal and semiconductor particles have attracted much attention due to their novel properties significantly different from those of correspond-

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ing bulk materials, such as the quantum-size effect, nonlinear optical properties and unusual luminescence [2–4].

Sol-gel technology [5–7] provides an excellent way of obtaining transparent and mechanically stable glasses and glass-like materials (xerogels). The sol-gel technique is based on the hydrolysis of liquid precursors and formation of colloidal sols. The precursors are usually organosilicates (e.g. tetraethoxysilane, TEOS) yielding silicate sol-gel materials. In the case of the most often employed silicate sol-gel matrices, manufactured from hydrolyzates of various alkoxysilanes, the chemical reactions involved in gel formation are shown below.

The hydrolysis:

$$\equiv\mathrm{Si{-}OR} + \mathrm{H_2O} \xrightarrow{\mathrm{H^+/OH^-}} \equiv\mathrm{Si{-}OH} + \mathrm{ROH} \qquad (1)$$

and subsequent formation of the silicate network:

$$\equiv\mathrm{Si{-}OH} + \mathrm{HO{-}Si}\equiv \longrightarrow \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{HOH} \qquad (2)$$

$$\equiv\mathrm{Si{-}OR} + \mathrm{HO{-}Si}\equiv \longrightarrow \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{ROH} \qquad (3)$$

Another interesting property of sol-gel materials stems from the fact that they are prepared from liquid solutions, which allows doping by dissolving or suspending dopants in the hydrolyzates. An alternative way of introducing various substances to sol-gel matrices is via their impregnation in solutions/suspensions of the target molecules. Various oxide matrices obtained by the sol-gel method are essential for the development of a broad variety of advanced materials such as electrochemical solar cells, photocatalytic materials, electron-sensitive devices, optical coatings, etc. A very attractive and new development of the sol-gel technology is its application to manufacturing free and doped uniform silica spheres of submicron sizes [8–10]. Films of self-organized silica nanospheres deposited on a glass support exhibit the photonic crystal effect [10]. Such materials are potentially appliccable in a variety of fields such as medicine or optoelectronics. In the last decade, the synthesis and optical properties of photonic crystalline structures have been intensely investigated. Photonic crystals are characterized by frequency-forbidden band-gaps in a broad frequency region of electromagnetic radiation [5, 11–13]. The characteristic feature of such materials is their opalescence. It has been demonstrated [14–17] that photonic crystals offer a number of potential applications as filters, inhibitors of spontaneous emission, or thresholdless lasers.

Raman spectroscopy can be a powerful and flexible tool for detecting and characterizing organic and biological molecules. This method is, in general, quite sensitive and capable of detecting low quantities of analytes. However, in certain situations (especially in the case of biological and forensic studies) the need arises to detect molecules at concentrations below a typical limit of detection of conventional Raman techniques. It is well known that in certain cases the adsorption of organic molecules on silver or gold electrodes results in a significant increase of the intensity of Raman scattering of adsorbed molecules. This phenomenon is known as Surface Enhanced Raman Scattering (SERS) [18]. Such enhancement has also been observed for molecules adsorbed on aqueous Ag sols [19], on silver nanoparticles embedded in a cellulose film [20], and on Ag evaporated onto SiO_2 nanoparticles [21]. The sol-gel method has been successfully used for obtaining sol-gel matrices doped with various nanoparticles of metals (e.g., Ag, Pt, etc.) and semiconductors (e.g., Ag_2S, CdS, etc.) [22–24]. Silica submicron spheres with surface-deposited metallic silver nanoclusters have been shown to exhibit the SERS effect for organic dye molecules adsorbed on the Ag islands [25]. This phenomenon can also be observed for submicromolar concentrations of organometallic complexes as presented in this contribution. Also, such Ag-doped powders possess bacteriostatic properties and can be used for doping various layered materials (e.g., textile impregnation thin films), giving them anti-microbial capabilities.

2. Experimental

Uniform, submicron-sized silica particles were synthesized following the base-catalyzed polycondensation of tetraethoxysilane (TEOS) in an alcoholic medium [5]. Briefly, ethanol (99.6%; POCh Gliwice) and a water solution of ammonia (POCh Gliwice) were mixed with the precursor (TEOS, 99%; Fluka). The solution was stirred in a plastic flask at room temperature for 2 h. During the stirring, the silica powder was formed and after filtering it was impregnated in an aqueous solution of $AgNO_{3(aq)}$. The impregnated silica powders were soaked in a series of solutions in order to reduce Ag^+ to Ag^0 ($NaOH_{(aq)}$, $formaldehyde_{(aq)}$, $NaBH_{4(aq)}$ [20]). Tris(2,2'-bipyridyl)ruthenium(II) ($Ru(bpy)_3^{2+}$) was obtained from Aldrich and used as received. For the SEM measurements, an XL 30 Philips CP microscope equipped with EDX, SE, BSE and Robinson detectors was used. Raman scattering spectra were obtained with a Raman Spectrometer Bruker RFS 100/S. In order to analyze the antibacterial effects of the SiO_2–Ag powders on bacteria, the *Escherichia coli* ATCC 25922 strain was used. To investigate the inhibition of bacteria growth, the standard agar diffusion method was used, according to the protocols of the National Committee for Clinical Laboratory Standards [26]. The overnight bacterial cultures, diluted 1000 times, were plated on Petri dishes containing Mueller–Hinton II Agar, (Becton, Dickinson Comp.). Next, 50 μl aliquots of water suspensions of the silver-doped powders were dropped on the surface of the medium and the plates were incubated at 37 °C for 24–48 h. After incubation, the diameter of the zones around the plated material (indicating inhibition of bacterial growth) were measured. The diameters of the zones are proportional to the amount of the anti-microbial agent, the way of its immobilization, the solubility of the agent, and the diffusion coefficient. As a control, water suspensions of pure (without silver) silica powders were dropped onto medium. The coated textile samples were prepared on PES/CO 67/33 fabric supports by doping a Dicrylan SL-MPU/SL-MPA polymeric paste with the SiO_2–Ag powders.

3. Results and discussion

Figure 1 presents a SEM micrograph of silica submicron spheres obtained by the sol–gel method. The diameter of the spheres is about 500 nm. As can be seen, the grains have a natural tendency to form very regular layers, which results in their photonic behaviour [10].

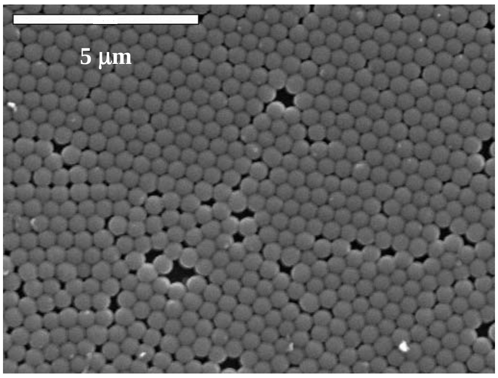

Fig. 1. Scanning electron micrograph of submicron sol-gel silica spheres

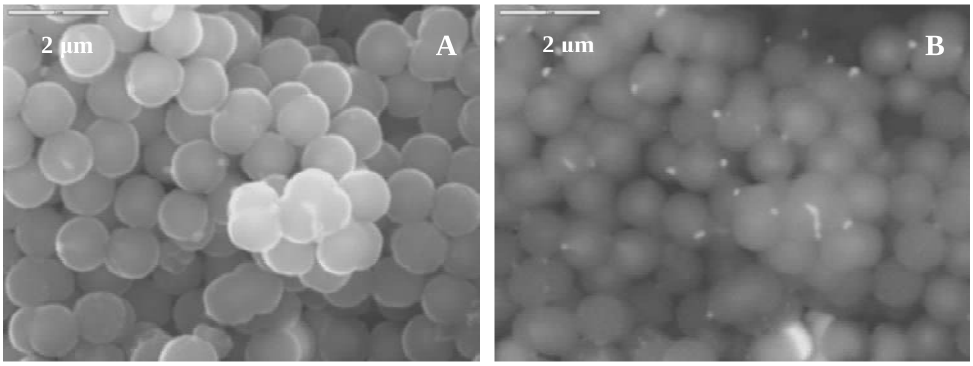

Fig. 2. SEM (A) and SEM-BEI (B) pictures of submicron silica spheres with silver “islands”

Silver nanoparticles obtained on the surfaces of silica submicron spheres are shown in Figure 2. Figure 2A presents a conventional SEM micrograph of silica spheres with Ag^0 clusters on their surfaces, while Figure 2B presents the BEI (Back-Scattered Electron Image) picture of the hybrid powder. Analogous nanoparticles have been obtained during the preparation of Ag/TiO_2 and Au/TiO_2 hybrid materials [27]. However, the sizes and shapes of those Ag^0 (Au^0)-doped TiO_2 nanoparticles are significantly different from those of the reported Ag^0-doped SiO_2 particles. The size of the silica spheres plays an important role in stabilizing the silver nanoparticles. Their interaction with silver ions or clusters inhibits aggregation of larger particles [28].

Silica powders with grains containing Ag^0 “islands” on their surfaces have been demonstrated to work as “amplifiers” of Raman scattering in the case of a simple organic dye [25]. In order to establish if the SERS effect also works for organometallic molecules possessing D_3 symmetry adsorbed on silver nanoclusters, the SiO_2–Ag^0 powders were soaked in $Ru(bpy)_3^{2+}$ ethanol solutions. Subsequently, the powders were filtered, washed, dried and their Raman spectra obtained.

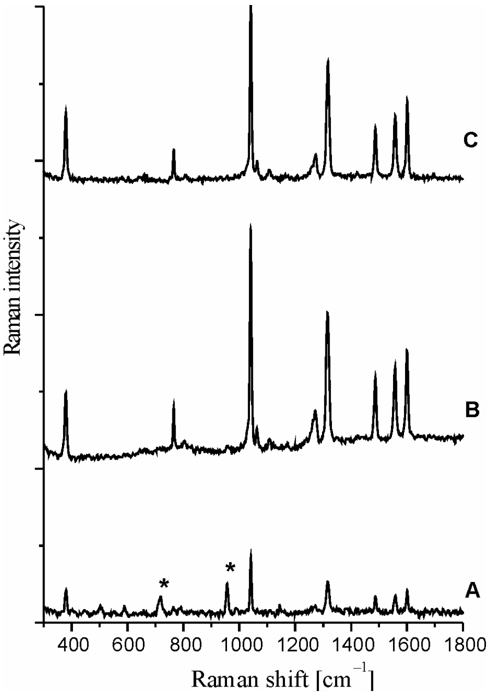

Fig. 3. FT-Raman spectra of the Ag^0-doped submicron silica powders after impregnation in solutions of tris(bipirydyne)ruthenium(II) with the complex concentrations of: 5.2×10^{-7} M (Trace A), 7.81×10^{-6} M (Trace B) and 7.81×10^{-5} M

Figure 3 presents the FT-Raman spectra of Ag^0-doped submicron silica powders after impregnation in solutions of tris(bipirydyne)ruthenium(II) with complex concentrations of: 5.2×10^{-7} M (Trace A), 7.81×10^{-6} M (Trace B) and 7.81×10^{-5} M. As can be seen, the $Ru(bpy)_3^{2+}$ Raman spectrum can easily be observed even for concentrations as low as ca. 5×10^{-7} M. Comparison with the results obtained for aqueous solutions of the ruthenium complex reveals that using the Ag^0-doped silica powders for SERS measurements allows the $Ru(bpy)_3^{2+}$ detection limit to be lowered by approximately four orders of magnitude (with the experimental setup used). It is important to note that in the case of silica powders without silver nanoclusters no Raman signal was observed upon their impregnation even in the concentrated $Ru(bpy)_3^{2+}$ solutions.

Thus, such materials could be used for improving analytical methods employed in, for example, medicine (detection of drugs or important metabolites), crime prevention (detection of chemical or biological weapons), environmental sciences (spills of dangerous substances), etc.

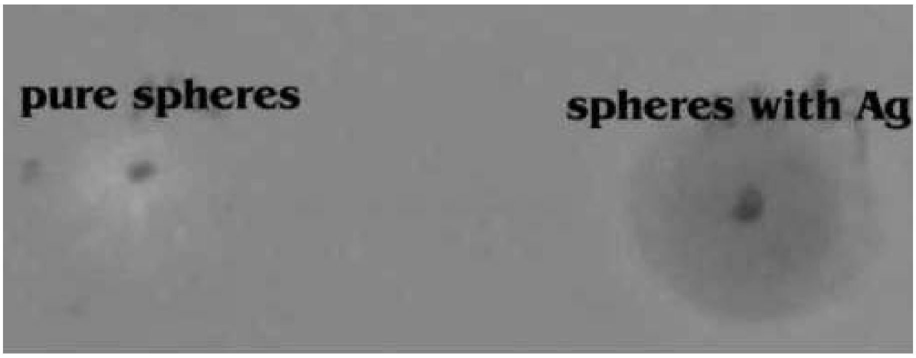

Fig. 4. A plate with E. Coli culture. Left – with pure silica particles, right – silica particles with Ag^0 nanoclusters

The obtained silica powders with silver intrusions display bacteriostatic properties. The inhibition of *E. coli* growth on an agar plate is shown in Figure 4. In this case, the lack of effect of pure silica spheres can be compared to the growth inhibition zone caused by the silica spheres doped with silver. An analogous effect has been observed for *Salmonella techimurium*, *Staphylococcus aureus* and *Hafnia alvei*.

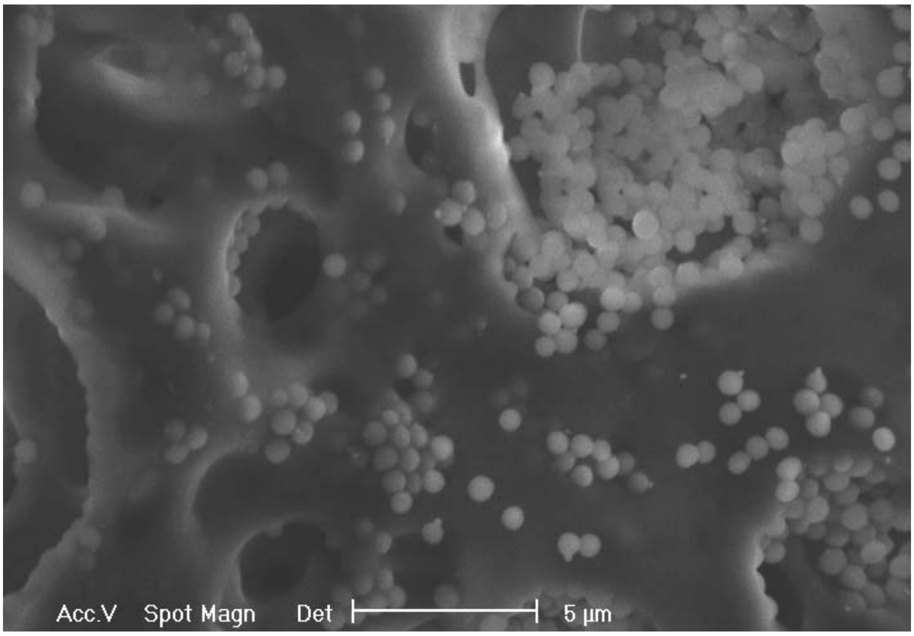

Fig. 5. SEM micrograph of a textile coating with SiO_2–Ag^0 powder

Such powders can be added to thermo-polymeric films used for the impregnation of textiles. Figure 5 presents a SEM micrograph of a doped textile coating surface. One of the practical problems to be overcome in the production of such doped coatings is avoiding particle agglomeration. It is expected that textiles equipped with well-dispersed nanoclusters of metallic silver on their surfaces will become bacteriostatic. This could be employed for the production of, for example, medical fabrics.

4. Conclusions

A sol-gel based method for the preparation of submicron spherical silica particles doped with Ag^0 clusters is reported. Sphere morphology has been studied by the SEM method. It has been found that all silica particles have identical size (ca. 450 nm). SEM micrographs show that the silver clusters produced by chemical reduction occur on the surface of the silica spheres. Good quality FT-Raman spectra of $Ru(bpy)_3^{2+}$ molecules adsorbed on the doped powder grains have been obtained. Concentrations of the soaking solutions were a few orders of magnitude smaller than the concentrations of the reference solutions capable of yielding direct Raman spectra. The observed phenomenon can be explained by the enhancement of the Raman signal from molecules adsorbed on metallic Ag^0 particles (Surface Enhanced Raman Spectroscopy - SERS). Such materials offer a broad scope of potential applications in various fields of analytical chemistry. This effect could be employed in the detection of trace amounts of chemicals. Possible applications of such detection systems range from forensic investigations, through medicine, and to environmental issues. The SiO_2-Ag^0 powders also exhibit bacteriostatic properties. The powders can be used as additives to thin-film textile coatings, yielding textiles with anti-microbial capabilities. Such materials could be used e.g. for medical purposes.

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