Morphology and absorption properties control of silver nanoparticles deposited on two types of sol–gel spherical silica substrates

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ABSTRACT

In this work, the size, distribution, morphology and optical absorption properties of silver nanoparticles are regulated by controlling the type of spherical silica substrate. Two different types of SiO_2 microparticles with unmodified and amino-functionalized surface are used as a matrix for Ag nanocrystals deposition. In both cases, silver ions are located on the substrate surface and then are thermally reduced to metallic silver, however, modification of silica spheres with $-NH_2$ groups enables the accomplishment of Ag ions reduction at considerably lower temperatures. Controlled surface functionalization of silica substrate clearly affects the morphology and optical absorption properties of obtained silver nanoparticles. Amine functional groups have a significant influence on the silica dense coverage by Ag nanoparticles. Dense packing of nano-sized metallic silver particles causes red shifting and broadening of surface plasmon resonance (SPR) absorption peak compared to sparse nanoparticles distribution. The size of obtained Ag nanocrystals is ranged from 3 nm to 20 nm depending on the selected silica substrate as well as silver concentration.

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1. Introduction

Silver nanoparticles with uniform size and shape are of great interest for many applications including photonics, sensors, catalysts, pigments, adsorbents, pharmaceuticals and medical diagnostics [1–3]. Since fascinating properties of nanometals strongly depend not only on size, shape and surface properties, but on the manner of their preparation as well, great efforts have been devoted to the controlled synthesis of silver nanoparticles in recent years [4,5].

Depending on the desired future application Ag nanocrystals are synthesized in forms of pure nanoparticles or composites formed by silver and oxide matrix. Recently, there are many reports on the deposition of Ag onto SiO_2 microspheres [3–9]. Silica spheres are very convenient as a substrate for metal deposition mainly because of their fine chemical durability and high active surface area. Nanoparticles can obtain improved chemical stability and size monodispersity through deposition onto the silica support.

Undisputed advantage of silica particles is also their possibility for surface functionalization. The modification of the silica particle surface can be used to enhance the attachment of silver nanoparticles as well as to control their growth. There are many papers published for the synthesis of silver nanoparticles located on unmodified [6–8] and amino-modified SiO_2 substrate [9–12].

However, to the best of our knowledge, there are no reports comparing properties of Ag nanocrystals depending on the silica substrate type. Comparative study between two different types of silica substrate is particularly interesting considering different functional groups on the unmodified and amino-functionalized SiO_2 particles surface. It has been observed that the presence of –NH_2 groups effectively improves the anchoring of several metal ions to the silica [9,11]. Accordingly, in this paper two types of silica microspheres were used as substrates for silver nanoparticles deposition. The aims were twofold, first to develop a rapid and simple method for silver ions deposition and reduction, and second, to investigate differences between resulting nanoparticles depending on the type of silica substrate.

The unmodified silica microspheres were produced by modified Stöber sol–gel method [13]. Synthesis of SiO_2 modified with amino groups was similar to process described by Wu et al. [14]. Nevertheless by contrast with method reported by Wu the procedure was simplified and the reaction time was remarkably shortened. Fabrication of silica micro-sized spheres, surface functionalization of SiO_2 substrate with amino groups, and moreover deposition of Ag ions were performed in one process without necessity of intermediate steps like centrifugation and redispersion.

Silver ions deposited on both types of SiO_2 microspheres were reduced by a simple thermal reduction process without hazardous reducing agents (i.e. organic compounds like hydrazine, sodium borohydride and formaldehyde) or expensive and unsafe high temperature gaseous hydrogen reducing atmosphere.

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2. Experimental

2.1. Samples synthesis

Fig. 1 shows the flow chart for the preparation of both unmodified and amino-functionalized SiO_2 micro-sized spheres with silver nanoparticles on their surface.

All reagents were of analytical grade and used as received without further purification.

2.1.1. Preparation of unmodified silica spheres doped with silver nanoparticles (SiO$_2$/Ag)

Silica spheres were prepared according to the Stöber method by hydrolysis and condensation of 3.1 ml of tetraethoxysilane (TEOS, Alfa Aesar, 98%) in a mixture with 42 ml of ethanol (POCH, 96%) and distilled water, using aqueous ammonia solution (POCH, 25%) as catalyst to initiate the reaction. The solution was constantly stirred using a magnetic stirrer for 2 h at room temperature. Then, the adequate amount of $AgNO_3$ solution (Ag quantities was equal to 6%, 12%, 20% and 50% compared to the weight of SiO_2) was added to the resulted solution and the reaction was allowed to continue for additional 2 h with stirring. The obtained suspension of particles was dried in air at 55 °C. After air drying, the obtained powder, hereinafter referred to as SiO_2/Ag, was reduced in the ambient atmosphere at 600 °C.

2.1.2. Preparation of amino-functionalized silica spheres doped with silver nanoparticles (SiO$_2$–NH$_2$/Ag)

The amino-functionalized silica spheres doped with silver were prepared using facile one-pot method. Firstly, colloidal suspension of the silica particles was obtained as described above. After 2 h of reaction, 0.1 ml of (3-Aminopropyl)triethoxysilane (APTES, POCH, 99%) was added to the solution and stirring was continued for further 2 h. Then, the adequate amount of $AgNO_3$ solution (Ag quantities was equal to 6%, 12%, 20% compared to the weight of SiO_2) was added to the resulted solution and the reaction was allowed to continue for additional 2 h with stirring.

The obtained particles, marked as SiO_2–NH$_2$/Ag, were then separated by centrifugation, washed with ethanol and distilled water several times to remove excess of silver ions. The obtained material was dried at room temperature and subsequently Ag^+ ions were reduced to metallic silver by thermal treatment at 300 °C.

2.2. Characterization

The surface morphology of samples was superficially characterized by a scanning electron microscope (HITACHI S-3400 N) equipped with an EDS system for elemental analysis. Transmission electron microscope (FEI Tecnai G^2 20 X-TWIN) was used to accurately characterize the size and shape of silver nanoparticles located on the surface of silica matrix. Absorption spectral measurements were carried out using a UV–Vis spectrophotometer (Thermo Nicolet Evolution 100). The X-ray powder diffraction data were collected on a Rigaku Ultima IV X-ray diffractometer equipped with a Cu radiation source. SEM, UV–Vis and XRD measurements were made in Sol-Gel and Nanotechnology Materials Laboratory of Lower Silesian Center for Advanced Technologies in Wroclaw.

3. Results and discussion

Thermally-induced formation of the metallic silver deposited on the surface of silica substrate is a result of electron attachment to Ag^+ ions from organic substances of the sol–gel substrate or their decomposition products during their sintering at correspondingly high temperatures. Complete thermal reduction of Ag^+ ions deposited on unmodified SiO_2 substrate occurs after annealing for two hours at 600 °C. Thermal-induced formation of silver nanoparticles in the amino-functionalized silica matrixes starts at lower temperatures due to the alone pair electrons of amine groups providing additional capacity to reduce Ag^+ to metallic silver. It was found that the temperature of complete reduction process for Ag^+ ions deposited on amino-functionalized silica spheres can be successfully reduced. Finally, SiO_2–NH$_2$/Ag composites were reduced at 300 °C.

Fig. 2 shows the powder X-ray diffraction pattern for the SiO_2/Ag and SiO_2–NH$_2$/Ag composites for different loadings of silver. The XRD patterns for all the composites are characterized by a broad peak characteristic for amorphous silica matrix at around $2\theta = 23$. No silver diffraction peaks were detected for SiO_2/Ag with 6% concentration of nanoparticles. For SiO_2–NH$_2$/Ag composites XRD silver peaks are visible even for lowest concentration of nanoparticles what confirm better capability of –NH$_2$ groups for linking metal ions.

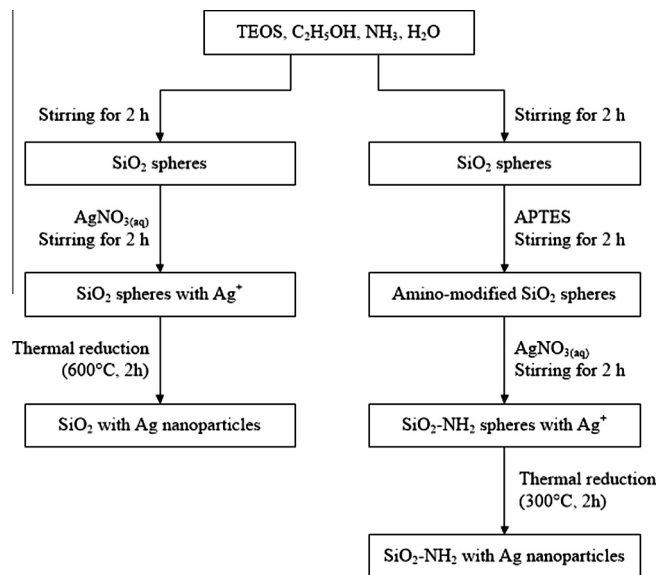**Fig. 1.** Chart for the preparation of SiO_2/Ag and SiO_2–NH$_2$/Ag particles.

Characteristic peaks representing pure metallic silver were not very prominent in the samples with low concentrations of Ag. However, with increasing concentration of metal a peaks at $2\theta = 38$, 44 and 64 corresponding to the face-centered cubic structure of silver are clearly visible. From Fig. 2 it is evident that for SiO_2/Ag composites diffraction peaks become more intense and narrow with the increasing concentration of silver suggesting that the average silver particle size also increases. Contrary for SiO_2–NH$_2$/Ag composites width and intensity of silver diffraction peaks are not metal concentration dependence suggesting that the average Ag particles size is similar for different contents of silver.

SEM micrographs of the prepared particles are shown in Fig. 3 and demonstrate that the unmodified and amino-functionalized silica spheres are spherical with uniform size and shape. In both composites selected for presentation in Fig. 3 the concentration of silver is equal to 20%. Images also provide rational evidence that modification of silica surface with –NH$_2$ groups enhances the attachment of nanosilver and enables a dense coverage of Ag on the substrate surface.

Fig. 4 shows the typical TEM images of the unmodified and amino-functionalized silica particles covered by silver for three different concentrations of Ag for which metallic silver XRD diffraction peaks were detected (12%, 20%, 50% for SiO_2/Ag and 6%, 12%, 20% for SiO_2–NH$_2$/Ag composites).

As can be seen in Fig. 4 the functional groups present on the surface of the silica substrate had a profound influence on the coverage by silver nanoparticles. Close inspection of TEM images reveals that smaller silver particles are present on the amino-functionalized SiO_2 surface. What is more, silver decoration density is apparently larger for this type of silica substrate what can be explained by the fact that modified silica except the OH^- binding groups has NH_2^- groups on the surface.

The mean size of Ag nanoparticles deposited on amino-functionalized silica surface for Ag concentration of 6%, 12% and 20% was estimated to be 3 nm, 3 nm and 5 nm respectively. From TEM observation it can be seen that the silver nanoparticles located on SiO_2–NH$_2$ matrix are well separated, spherical in shape and spacing between nanoparticles is extremely short. A gradual decrease in interparticle spacing was observed for increasing concentration of silver. There is also a visible tendency for silver particles to form a few aggregates with increasing Ag concentration. Nevertheless, the size of silver aggregates, even at 20% Ag concentration, does not exceed 100 nm.