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Characterisation and preparation of sonochemically synthesised silver–silica nanocomposites

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Properties of nanoparticles differ from those of bulk phase or individual molecules. The metal form of these particles shows chemical and physical properties that can be used in fields such as optics, optoelectronics and catalysis. Silver nanoparticles can be used as an antimicrobial agent in wound dressings and as surface coatings, e.g., catheters. In this work, silver nanoparticles were deposited on silica submicrospheres using ultrasounds. A mixture of silver nitrate solution with silica submicrospheres was sonificated under an atmosphere of argon gas in order to eliminate oxygen and decrease both the cavitational threshold as well as the intensity of the ultrasounds. Duration of irradiation was varied between 90 and 180 min at a the frequency of 24 kHz.The resulting silver–silica nanocomposites were characterized with Fourier transform infrared (FTIR), high resolution transmission electron microscopy (HR-TEM), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX) and X-ray florescence (XRF). The results of SEM micrographs show submicrospheres of silver-silica nanocomposites, with the 16–64 nm size distribution. Furthermore, HR-TEM micrographs show that the particle size distribution does not depend on time of irradiation. The particle size distribution of silver nanocomposite in all samples was approximately 4–30 nm. EDAX and FTIR measurements show that, with increasing $AgNO_3$ concentration, the percentage of deposited silver on silica increases. XRF patterns show that the amount of silver deposited on silica can be increased by increasing the ultrasound power.

Key words: *energy dispersive X-ray analysis; high resolution transmission electron microscopy (HR-TEM); scanning electron microscopy; silver nanocomposite; sonochemical treatment*

1. Introduction

Nanoparticles of noble metals have been extensively studied due to their potential applications in microelectronics, and their optical, electronic and catalytic properties [1, 2]. There is particular interest in nanoparticulate Ag, due to its ability to act as both an electron sink as well as a redox catalyst. Antimicrobial properties of silver were

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well known to the ancient Egyptians and Greeks, for example Hippocrates mentions silver as a treatment for ulcers [3]. Silver nanoparticles can be used as an antimicrobial agent in applications such as wound dressings and as surface coatings e.g., catheters [4, 5]. Silver has been shown to inhibit energy production by inhibiting the respiratory chain of *E. coli* [6].

In order to obtain high performance materials, it is of paramount importance that particle size and structure be controlled [7, 8]. One significant approach is to synthesize them in the presence of a porous solid such as alumina, silica, or zeolite. Mesoporous solids, due to their small pore size, high opening pore volume, and large internal surface area, have found great utility. Different techniques for improving the formation of metal particle loaded mesoporous composites have been developed [9, 10] but recently there has been a rapid increase in the application of unconventional methods. Different than other traditional chemical methods, sonochemistry is based on acoustic cavitation, that is, the formation, growth and collapse of bubbles in a liquid [11]. Being a sound wave, ultrasounds are transmitted through any substance, be it solid, liquid or gas, which possesses elastic properties. For liquid and gases, particle oscillation takes place in the direction of the wave, and produces longitudinal waves. This causes the layer of liquid or gas closest to the ultrasound source to be displaced, which then causes other neighbouring layers to be displaced in an iterative manner, thus the layers become compressed. This is the compression cycle of the process. When some layers are compressed, others are expanded. This is called the rarefaction cycle of the process. Besides the variation in the positions of molecules, when an ultrasound wave travels through a liquid or gas, there is a variation in pressure. At the point where the layers are crowded together (i.e., where the molecules are compressed), the pressure is higher than normal at the given instant, whereas in the region where the layers are furthest apart (i.e. the rarefaction region), the pressure is lower than normal. This pressure is called the applied acoustic pressure. The total pressure, P in the liquid is given by: [12]

$$P = P_h + P_a \tag{1}$$

In this equation, P_h, is the ambient pressure (usually hydrostatic) in the liquid. If a sufficiently large negative pressure P_c is applied to the liquid (here it will be the acoustic pressure on rarefaction, $P_c = P_h - P_a$) such that the average distance between the molecules exceeds the critical molecular distance, the liquid breaks down and cavities will be created (bubble formation). These cavities may grow in size until the maximum of the negative pressure has been reached (bubble growth). The total collapse of the bubbles, due to enormous energies involved, produces a shock wave.

The adiabatic process associated with an implosive collapse generates localized hot spots with transient temperatures of about 5000 K and pressures of 181.8 MPa [13]. The chemical effects of ultrasounds are attributed to the cavitation producing strong reactants from aqueous solutions, thereby reducing metal salts *in situ*.

The use of ultrasound in liquid–solid systems for the preparation of nanostructure of metals, especially in the presence of porous solid, however, is rarely reported in the literature [14]. In this paper, we report on the ultrasound-assisted preparation of Ag/SiO_2 nanocomposites, their microstructure characterizations, and we also study the effects of such parameters as ultrasound power, concentration of $AgNO_3$ and irradiation time on the particle size of nanocomposites, and the amount of silver deposited on silica by this method.

2. Experimental

Pieces of the mesoporous silica (1 g) were immersed into aqueous solutions containing metal ionic precursor (say, 0.2, 0.3, 0.4 and 0.5 g $AgNO_3$). The liquid–solid mixture (about 100 cm^3in total) charged in the conical flask, was placed in the water pool and irradiated with ultrasounds at the frequency of 24 kHz. Ultrasonic irradiation was accomplished by using an ultrasonic processor UP200H with 186 to 480 W/cm^2 output power. During irradiation, the flask was purged with Argon gas to eliminate oxygen and to decrease both the cavitational threshold and the intensity of the ultrasound power. A water flow was used to cool the glass vessel in the bath. Then the mesoporous silica containing $AgNO_3$ was irradiated with ultrasounds for 90 to 180 min. Each solid sample was washed with distilled water and dried at 100 °C for 30–40 min.

The structures of the as-prepared composites were characterized mainly by the Fourier transform infrared (FTIR), high resolution transmission electron microscopy (HR-TEM), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX) and X-ray florescence (XRF).

3. Results and discussion

The presence of silver, silicon and oxygen in the coated materials was examined with EDAX. The EDAX spectrum was also used to obtain a quantitative estimate of the silver content and the Ag/Si ratio. Figure 1 shows this silver silica nanocomposite EDAX spectrum.The silver content in the sample was about 4.48 wt. %.

The SEM spectra of the sample are shown in Fig. 2. Due to the limit of the resolution, only large silver nanocomposites can be seen. The particle size distribution of silver nanocomposites is 16–64 nm, which is shown in Fig. 3. More than 16% of the particles have the diameter of approximately 44–46 nm.

The effect of increasing the irradiation time, for 90, 120, 150 and 180 min, on the particle size is demonstrated by the HR-TEM spectrum in Fig. 4. HR-TEM is used to study small particles, due to its higher resolution. The size distributions and the shape of the metal nanoparticles were obtained from HR-TEM micrographs. HR-TEM measurements were performed with a Philips model EM208.

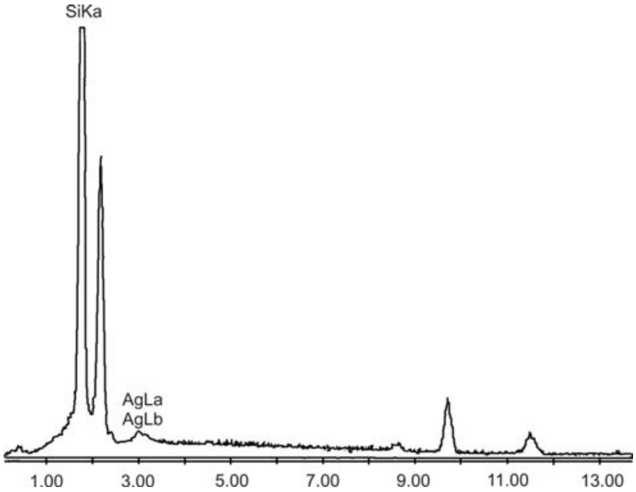

Fig. 1. The EDAX spectrum of silver silica nanocomposite

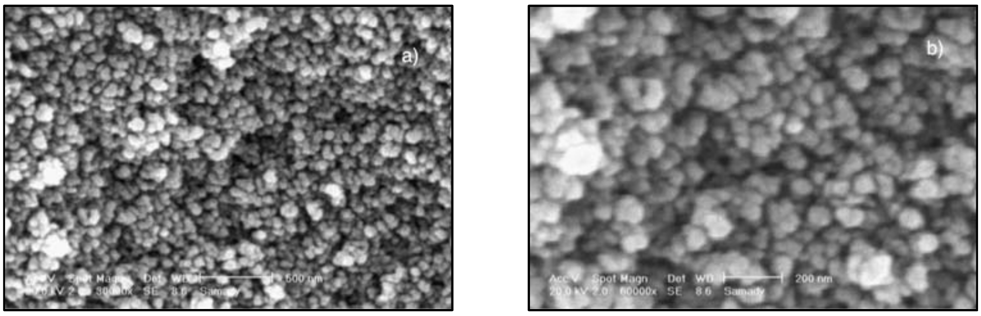

Fig. 2. Scanning electron micrographs of silver silica nanocomposite
with magnification: a) 30000×, b) 60000×

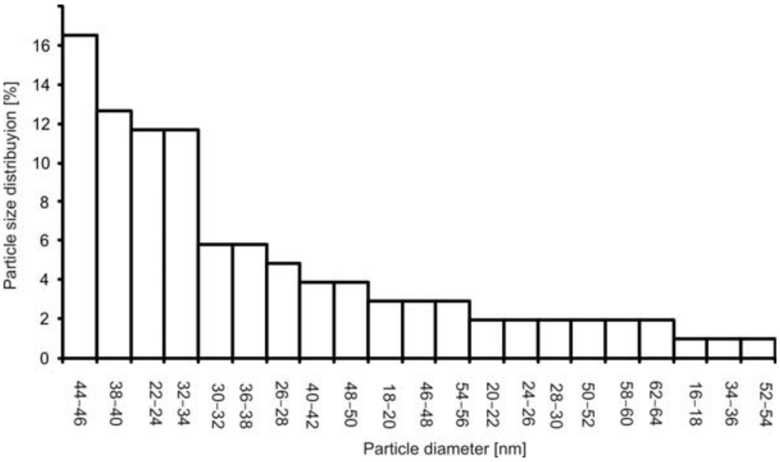

Fig. 3. Particle size distribution of silver nanocomposite

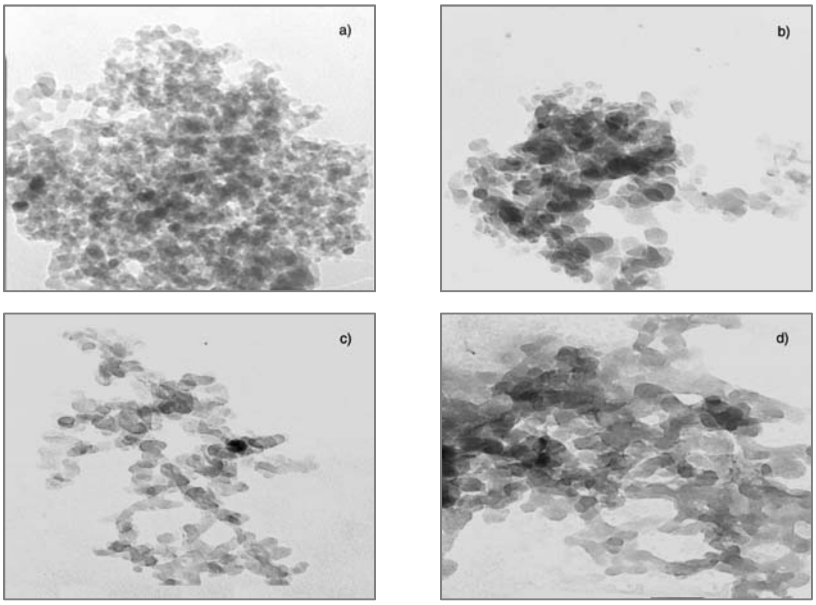

Fig. 4. HR-TEM micrographs of silver silica nanocomposites with irradiation time:
a) 90 min, b)120 min, c)150 min, d)180 min

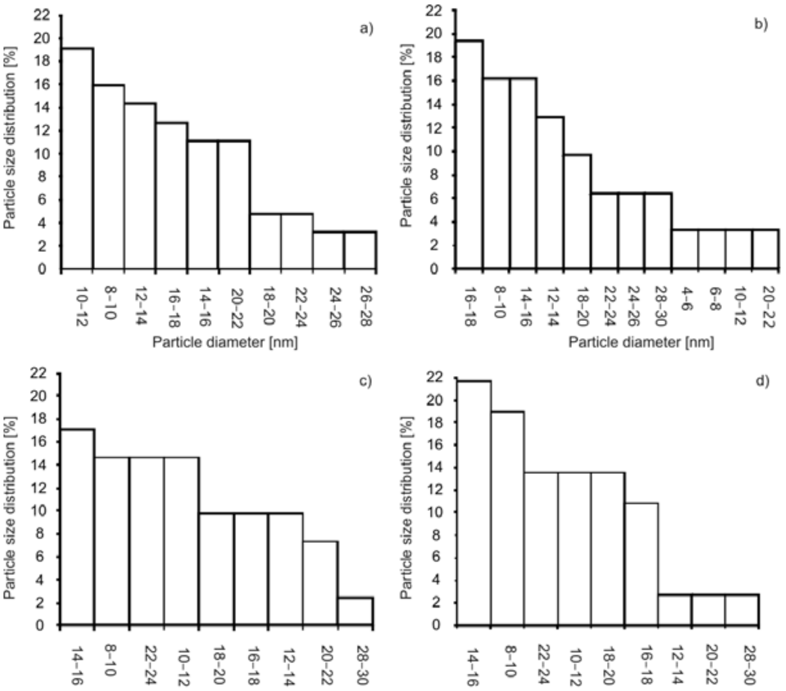

Fig. 5. Particle size distributions of samples with various irradiation times:
a) 90 min, b) 120 min, c) 150 min, d)180 min

The particle size distributions of the obtained samples of silver nanocomposites are shown in Fig. 5. The particle size distribution in all samples is about 4–30 nm. Thus there is no significant difference between the particle size distributions of samples having different irradiation times, but increasing the irradiation time does prevent agglomeration of particles.

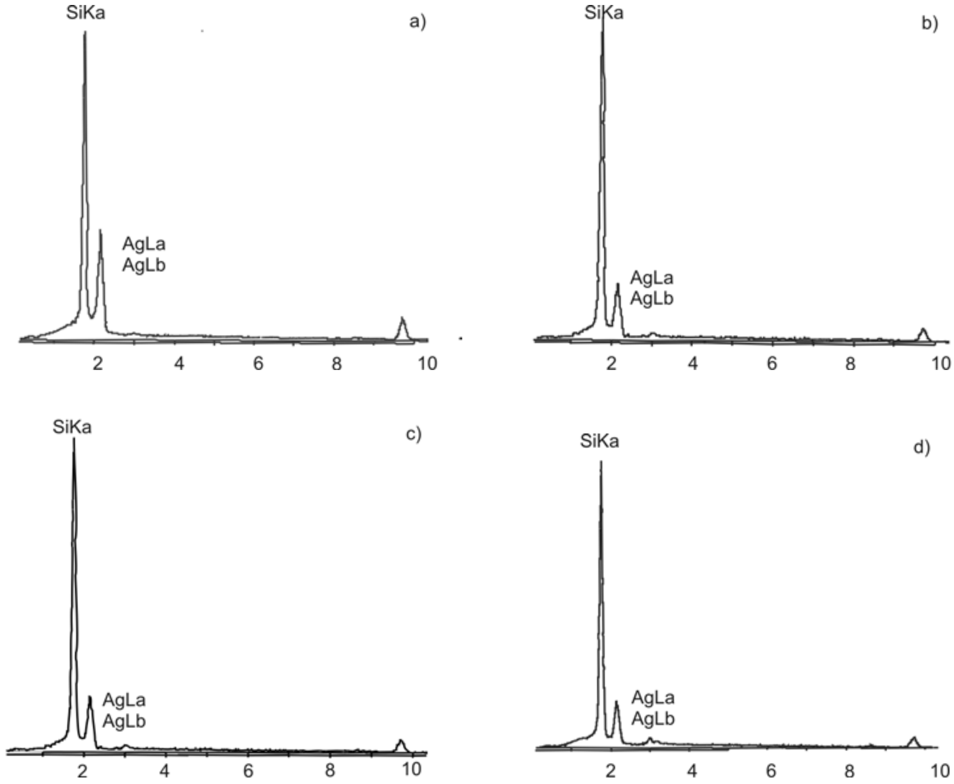

Fig. 6. The EDAX spectra of silver silica nanocomposites with various $AgNO_3$ concentrations: a) 0.2 g/100 cm^3, b)0.3 g/100cm^3, c) 0.4 g/100cm^3, d) 0.5 g/100cm^3

Effects of $AgNO_3$ concentration (0.2- 0.3- 0.4- 0.5 g/100 cm^3) on the deposition of Ag particles on silica are demonstrated by EDAX spectra in Fig. 6. Also, Figure 7 shows that the percentage of deposited silver on silica increases as the $AgNO_3$ concentration increases.

FTIR spectra, shown in Fig. 8, confirm the presence of silver on silica spheres. FTIR absorption is used in order to assess the extent of interaction between the metal and the surface. This interaction drastically changes the nature of the coated material. The comparison between silica spectra with different silver nanocomposite spectrum confirms this result. One of the main changes between these spectra is a decrease in the intensity of the peaks in the broad, 1000–1100 cm^{-1} range, for the surface -deposited samples. This range corresponds to the asymmetric stretching (AS) vibration mode of the Si–O–Si bridge of the siloxane link [15]. Also, a relatively strong peak at 810 cm^{-1}, corresponding to the symmetric stretching of the Si–O–Si group, is decreased in intensity. This result might be explained as follows. During a sonochemical reaction, the energy produced during bubble collapse is sufficient to rupture the strained surface Si–O–Si bonds. This activates the surface of the silica spheres, producing better adhesion of the formed silver nanoparticles.

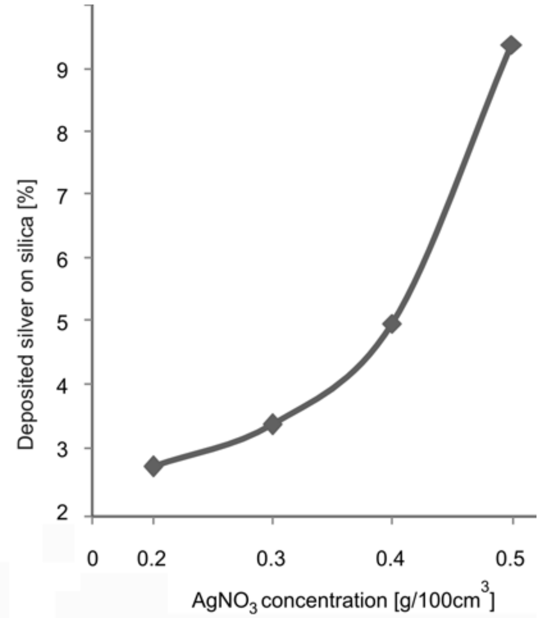

Fig. 7. Effect of AgNO$_3$ concentration
on the percentage of deposited silver on silica

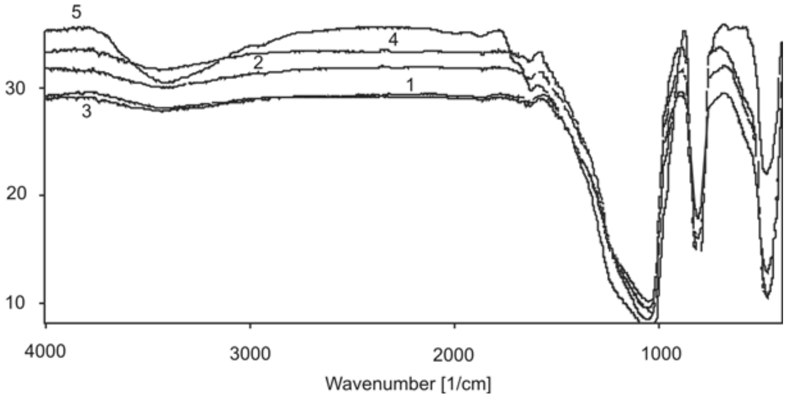

Fig. 8. FTIR spectra of silver silica nanocomposite samples with:
1– 0.2, 2 – 0.3, 3 – 0.4, 4 – 0.5 g/100cm^3 of AgNO$_3$ and 5 – silica spectrum

Table 1. The effect of ultrasound power

Ultrasound power [W/cm^2]	Silica content [wt. %]
480	96.64
368	97.6
276	98.15
186	98.56

Finally, the effect of ultrasound power was investigated by the XRF analysis. The result is shown in Table 1. As the ultrasound power is increased from 186 to 480 W/cm^2, the percentage of silica is decreased and therefore the percentage of deposited silver on silica is increased.

4. Conclusions

Nanosized silver-silica nanocomposite with a 16–64 nm size distribution is obtained by ultrasound power using a basic aqueous solution containing Ag$^+$ ions. The importance of bubbling Argon gas prior to and during the sonication lies in the elimination of oxygen gas and in the decrease both of the the cavitational threshold as well as the intensity of the ultrasound power. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX) were used to characterize the resulting silver–silica nanocomposite. The weight percentage of silver deposited on submicrospheres silica ranges from 2.96 to 9.37. The effect of increasing irradiation time on the particle size was investigated by HR-TEM. The particle size distribution of silver nanocomposite in all samples is about 4–30 nm. Thus, there is no significant difference between the particle size distributions of samples having different irradiation times, but increasing the irradiation time does prevent agglomeration of particles. The effect of $AgNO_3$ concentration on the deposition of Ag particles on silica is shown by the EDAX spectra and Fourier transform infrared (FTIR) analysis. The percentage of deposited silver on silica increases as the $AgNO_3$ concentration increases. Finally, we can say that the advantages of this process are its simplicity, effectiveness and short preparation time, as compared with other methods which take a minimum of 14.15 to 24 h.

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