

Preparation of Silver-Doped Silica Powder and Particles by Sol-Gel Method

Y.L. Li^{1,2,*}, F. Li² and C.Y. Wu²

¹Department of Physics, Nankai University, Tianjin 300071, P.R. China

²Department of Physics, Tianjin University of Science and Technology, Tianjin 300457, P.R. China

*Corresponding author: Fax: +86 22 60601332; Tel: +86 22 28194516; E-mail: jijl_ljl@sina.com

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Silver-doped silica has attracted widely interests in science and technique fields. In this research, silver-doped silica have been synthesized via a two-step sol-gel process at room temperature, where silver nitrate has been employed as silver resource, tetraethyl orthosilicate as silicon precursors and 3-mercaptopropyltrimethoxysilane as a chelator for silver. After the sol-gel process was completed, silver ions were reduced by formaldehyde. Silver-doped silica powder, silica colloidal particles and silica/silver/silica trilayer particles have been prepared by changing the experimental conditions. The morphologies of obtained materials were observed by field emission transmission electron microscopic images and scanning electron microscopy. Energy dispersive X-ray spectroscopic analysis was used to investigate the element composition of the resulted materials and the results revealed the existence of S, Si, O, C and Ag in the obtained materials. This strategy provides a facile, low-cost and green methodology for the creation of silver doped silica materials.

Key Words: Sol-gel, Colloidal nanoparticles, Silver, Hybrid material, Nanomaterial.

INTRODUCTION

Silver nanoparticles have attracted intensive attentions in the past few years, because they usually display excellent optical, catalytic and electronic properties that bulk materials do not usually exhibit, which can be applied in many areas that imaging^{1,2}, catalysis^{3,4} and electronics^{5,6} and the development of antimicrobial coating^{7,8}. However, it is difficult to utilize directly original nanostructured form because silver nanoparticles undergo fast oxidation and easily aggregate in solutions. Such inevitable aggregation of silver nanoparticles damages their inherent functionality and eventually yields ordinary bulk materials. One way to improve the stability of the nanoparticles is to incorporate them into various matrices.

Silica gel is considered as an ideal supporting materials for silver nanoparticles, because it is inert, stable, biocompatible and optical transparent from the near UV region through the near infrared. Recently, silica materials containing silver have been reported in powder^{9,10}, colloidal particles^{11,12} and coating form¹³⁻¹⁵. They have been prepared by, either direct filling of silver salt into the pores of silica¹⁶⁻¹⁹ or addition of the salt into one of the aqueous sol-gel precursors^{20,21}. Subsequently, the silver ions could be reduced to metallic particles by thermal treatment in air or in a hydrogen atmosphere or by irradiation with UV light or γ -rays. However, many previous reports involved using surfactants¹¹ or high temperature^{9,10} or precious device²², which made the preparation process

complicated. In addition, little attention has been paid to understand the effects of the preparation conditions on the size, the distribution and the morphology of hybrid materials; all of which are critical for technical applications. Optical and antibacterial properties as well as long-term chemical durability are directly related to the silver size and its distribution in the silica matrix.

In present study, we reported a two-step method using a silane coupling agent and a chemical reducing method for the preparation of silver-doped silica. We also studied the influence of (i) distilled water, (ii) the nature of the coupling agent and (iii) the concentration of silver nitrate on the size of the silver nanoparticles and morphology of silica matrix. The obtained materials were characterized by field emission transmission electron microscopy images (FETEM), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis.

EXPERIMENTAL

Tetraethyl orthosilicate (TEOS) and silver nitrate were obtained from Kemiou Chemical Reagent (Tianjin, China). Ethanol, formaldehyde and ammonium solution (28-30 % NH_4OH) were obtained from North Medical Chemical Reagent (Tianjin, China). 3-Mercaptopropyltrimethoxysilane (MPTMS) was purchased from Alfa Aesar (Tianjin, China). All the reagents were used as-received without further purification.

Deionized water ($> 18.2 \text{ M}\Omega \text{ cm}$) was obtained from a Millipore Milli-Q purification system.

Preparation of silver-doped silica: The procedure was carried out based a two-step procedure as follows. First, 0.15 mL of 3-mercaptopropyltrimethoxysilane was added to solution of silver nitrate in ethanol. Then acetic acid or base as a catalyst was added into the mixture. The homogenous mixture was then stirred overnight at room temperature to form gel-A. In the second step, 3 mL of tetraethyl orthosilicate was added dropwise into the mixed solution of ethanol (80.0 mL) and aqueous solution of ammonia (25-28 %, 5.0 mL), or of ethanol (80.0 mL), aqueous solution of ammonia (25-28 %, 5.0 mL) and distilled water (5.0 mL), under magnetic stirring with a speed *ca.* 300 rpm. This solution is referred as B. Subsequently, the gel-A and 4 mL of tetraethyl orthosilicate was also added drop by drop to the solution-B in sequence. The mixtures were then stirred for 2 h at room temperature. At last, formaldehyde was added into the solution and stirred for 1 h. The obtained precipitate was subjected to centrifugation to collect the silver doped silica materials, which were washed three times with fresh alcohol and water, respectively, to remove residual NH_4OH and unreacted tetraethyl orthosilicate.

Characterization: Samples for field emission transmission electron microscopy were deposited onto carbon-coated copper electron microscope grids and dried in air. Field emission transmission electron microscopy analysis was performed using Tecnai F20 G² (FEI Company, Netherland.). Energy dispersive X-ray spectroscopy analysis was performed using a system attached to the field emission transmission electron microscopy. Scanning electron microscopy was performed using SU-1510. (HITACHI SU-1510, Japan). Fourier transform infrared (FTIR) spectra were obtained at a resolution of 1 cm^{-1} with a Bruker FT-IR spectrophotometer between 4000 and 400 cm^{-1} . The IR measurements of the powder samples were performed in the form of KBr pellets.

RESULTS AND DISCUSSION

Preparation and morphology of silver-doped silica: In this research, tetraethyl orthosilicate as silica precursors, silver nitrate as silver resources, 3-mercaptopropyltrimethoxysilane as a chelator and formaldehyde as a reducing agent for silver ions were employed to synthesize silver-silica hybride materials by the two-step strategy. First, silver nitrate and 3-mercaptopropyltrimethoxysilane was dissolved in ethanol to form gel A in the presence of acetic acid, in which silver and 3-mercaptopropyltrimethoxysilane interacted through cleavage of the S-H bonds and spontaneous formation of S-Ag bonds. In the second step, part of tetraethyl orthosilicate was first added into the mixture of ammonia, ethanol and distilled water and then the gel A and surplus tetraethyl orthosilicate were added successively for the preparation of sample 1. The similar preparation conditions were employed to prepare sample 2 except that distilled water was not added into the mixed solvents in the second step. The field emission transmission electron microscopy images of samples 1 and 2 were shown in Fig. 1a and b, respectively. Sample 1 was pale brown (inset of Fig. 1a) and the morphology was spherical particles with an average size of 180 nm in diameter (Fig. 1a). A pale yellow

and irregular powder was obtained when deionized water was omitted from the mixed solvents in the preparation process of sample 2 (inset of Fig. 1b). The size and distribution of silver in silica matrix was further observed by the higher magnified field emission transmission electron microscopy.

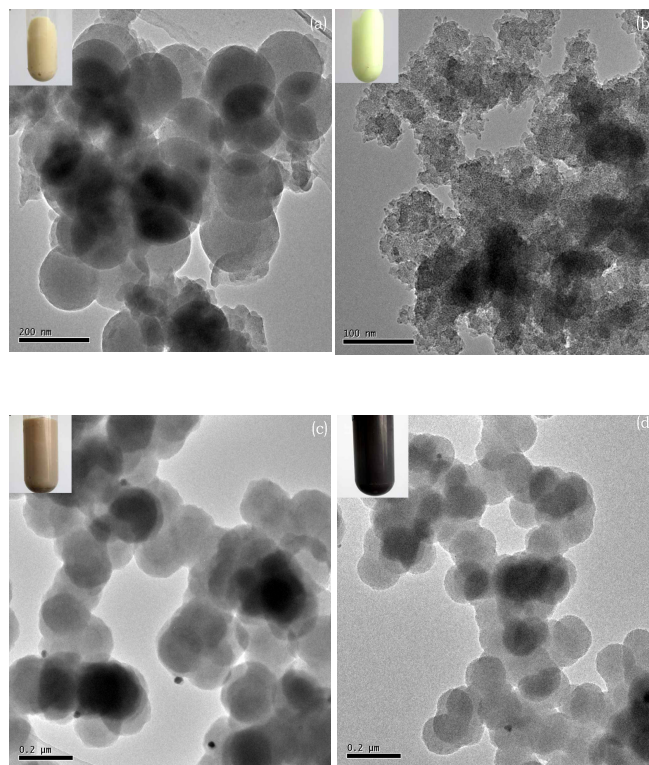
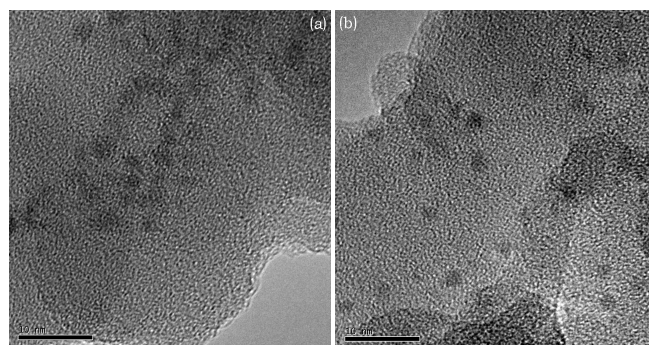


Fig. 1 Transmission electron microscopic image of silver-doped silica. (a) sample 1; (b) sample 2; (c) sample 3; (d) sample 4.

Fig. 2a showed that the silver nanoparticles in sample 1 were heterogeneous and nanocluster shape with an average size of 2.5 nm in diameter. However, the spherical silver nanoparticles with a diameter of 2-3 nm were uniform dispersed in sample 2 (Fig. 2b). The materials were also characterized by scanning electron microscopy (Fig. 3a and b). From Fig. 3a, it could be observed that the silica particles were irregular spherical structures with diameters in the range of 180-200 nm besides flocculated structures. However, a powder was obtained when distilled water was not added into the mixed solvents in the second step (Fig. 3b). All results indicated that water played an important role in the control of the morphology of silver doped silica material and the dispersion of silver nanoparticles in silica.



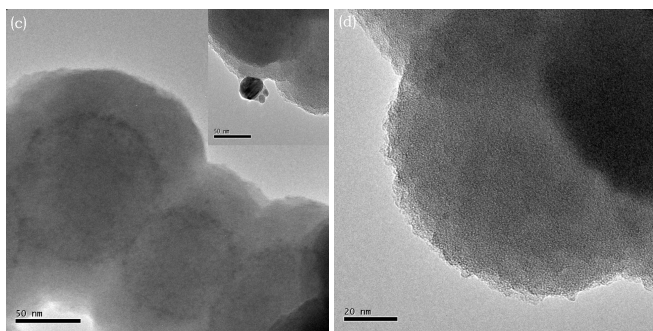


Fig. 2. Magnified transmission electron microscopic images of silver-doped silica. (a) sample 1; (b) sample 2; (c) sample 3; (d) sample 4.

By using ammonia instead of acetic acid in the first step, the sample 3 was prepared under the similar conditions with the sample 1. A brown product was obtained (inset of Fig. 1c). Large silver particles and interconnected silica particles were coexisted in sample 3 (Fig. 1c). From Fig. 2c, the structure of silica/silver/silica trilayer interconnected nanoparticle was easily observed and the large silver nanoparticles was ellipse morphology (inset of Fig. 2c). The interconnected worm shaped particles could be observed from scanning electron microscopy image (Fig. 3c). The results suggested that the kind of catalyst used in the first step had a significant effect on the morphology of silver doped silica material and the dispersion of silver nanoparticles.

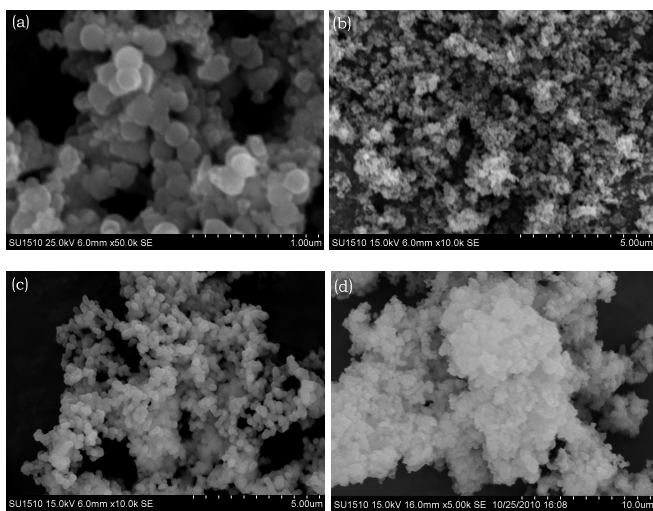


Fig. 3. Scanning electron microscopic image of silver-doped silica. (a) sample 1; (b) sample 2; (c) sample 3; (d) sample 4

Sample 4 was prepared under the similar conditions with sample 1, except that silver nitrate concentration was changed from 0.0125 M to 0.0625 M. The resulted material was black (Inset of Fig. 1b). This indicated that larger silver particles might be formed. In the transmission electron microscopy images (Fig. 1d), the granular silica and dark particles were observed. The silver nanoparticles could not be observed from the silica particles (Fig. 2d). This may be attributed to that higher silver concentration resulted in inhomogeneous mixing and phase separation of silver precipitates. Scanning electron microscopy imaging showed agglomerates of small grains (Fig. 3d). Thus, the concentration of silver nitrate apparently influenced distribution and the morphology of silver doped silica.

Energy dispersive X-ray spectroscopy analysis: The elemental composition of the obtained silver-doped silica was performed using the energy dispersive X-ray spectroscopy on the field emission transmission electron microscopy. Fig. 4a and b showed the energy dispersive X-ray spectroscopy spectrum of the samples 1 and 3. The peaks around 3.40 keV is correspond to silver. The peaks situated at binding energies of 0.25 KeV and 2.3 KeV belongs to carbon of the propyl hydrocarbon chains and sulfur of the thiol groups of 3-mercaptopropyltrimethoxysilane, respectively. The peak around 1.74 KeV belong to silicon of silica network was also detected. The copper peaks corresponding to transmission electron microscopy holding grid were observed at 8.06 and 8.94 KeV. The result indicated that Ag has been successful incorporated in silica.

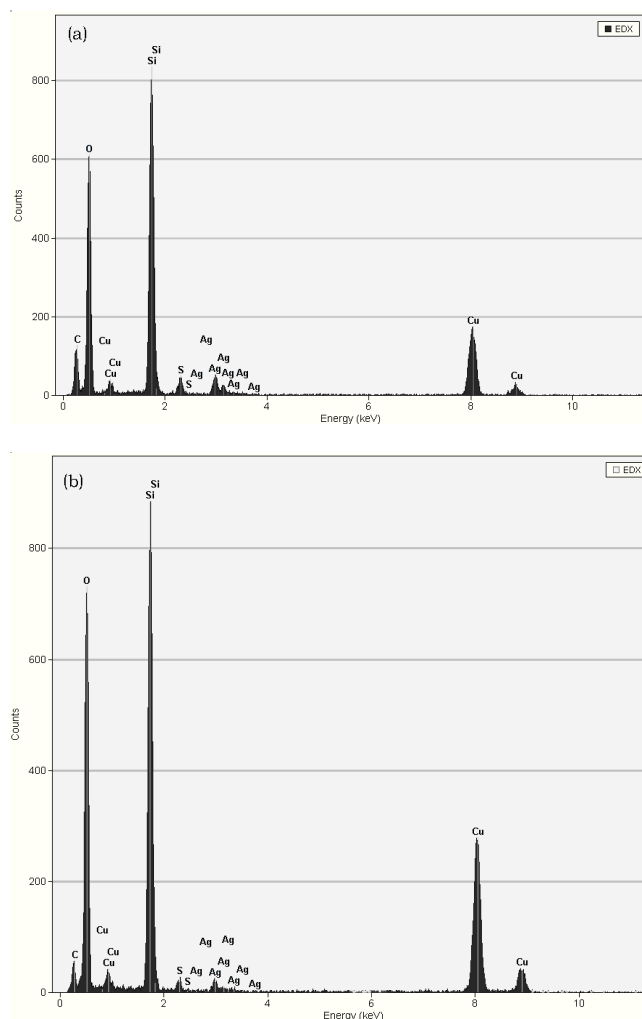


Fig. 4. EDS analysis of silver-doped silica. (a) sample 1; (b) sample 3

Fourier transform infrared spectroscopy analysis: In order to qualitative identification of the organic functional groups, the samples 1 and 3 were also characterized by FTIR spectroscopy. Fig. 5a and b illustrated the FTIR spectra of the silver doped silica materials. The bands at 1097, 802 and 470 cm^{-1} are assigned to the typical Si-O-Si bands of the condensed silica network. The weak bands at 1465 and 1384 cm^{-1} are attributed to bending vibrations of methylene groups and the weak frequency bands at 2960 and 2925 cm^{-1} corresponding

to the methylene stretching vibrations of the propyl chains of 3-mercaptopropyltrimethoxysilane. The absorbance at 954 cm^{-1} is associated with Si-O stretching of terminal nonbridging groups. The broad band around 3424 cm^{-1} and the strong peak around 1629 cm^{-1} are due to the stretching and bending vibrations of adsorbed H_2O . Although EDX analysis showed sulfur elemental present, the peak associated with the S-H bond could not be observed in its IR spectrum. It may be attributed to the low absorption coefficient of the S-H stretching²³.

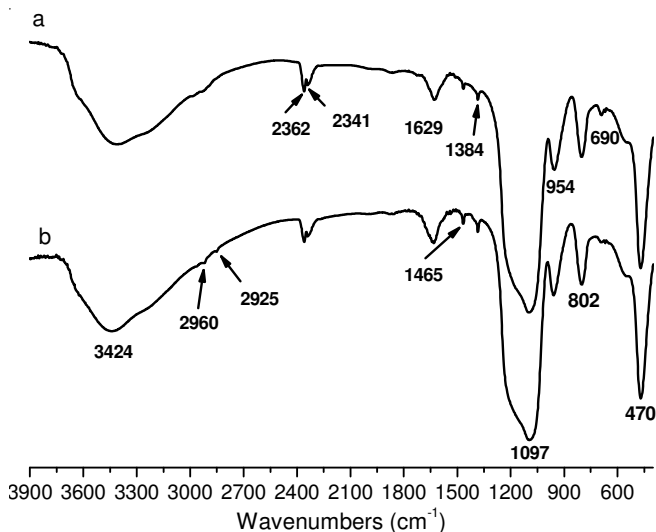


Fig. 5. FTIR spectra of silver-doped silica. (a) sample 1; (b) sample 3

Conclusion

Series of silver-doped silica were prepared by a two-step method. Careful control of synthetic conditions is essential for the formation of particular morphologies and distribution of silver and silica matrix. Catalysis, nature of coupling agent and concentration of silver nitrate affected the size and distribution of the resulting silver nanoparticles and morphology of silica matrix.

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