

DOI: <https://doi.org/10.24425/amm.2024.147789>PRATIK S. KAPADNIS<sup>1</sup>, KYUNGSUN KIM<sup>1</sup>, HYUNG-HO PARK<sup>2</sup>, HAEJIN HWANG<sup>1\*</sup>

## FABRICATION OF SILVER-IMPREGNATED SILICA AEROGEL COMPOSITE FOR ENERGY APPLICATIONS

In this study, Ag-impregnated silica aerogel composites were fabricated via wet impregnation. In this approach, silver salt was reduced with ethylene glycol in the presence of polyvinylpyrrolidone (PVP) at reaction temperature 80°C. PVP was used as a capping agent to protect the Ag nanoparticles (NPs) from agglomeration. Wet impregnation was used to synthesize the Ag/SiO<sub>2</sub> composite by combining the reduction of AgNO<sub>3</sub> with a silica aerogel slurry. Experimental results showed that the AgNO<sub>3</sub> concentration and PVP: AgNO<sub>3</sub> ratio had an active influence on the growth of Ag NPs on silica surfaces. The X-ray diffraction (XRD) patterns of the composite material showed no imprints of impurities or parasitic materials except for Ag and SiO<sub>2</sub>. Scanning electron microscopy (SEM) images revealed that the Ag NPs were well impregnated into the porous silica aerogel structure. It was found that SiO<sub>2</sub> aerogel surfaces were homogeneously surrounded by the Ag NPs.

*Keywords:* Silver nanoparticle; Silica aerogel; Poly(vinylpyrrolidone); Impregnation; Composite material

### 1. Introduction

The focused study of silica aerogels covered by metallic nanoparticles have gained increasing interest in energy applications because of their active involvement. Due to its great thermal stability, transparency, and Capacity to manage varying thickness and density, TEOS is a significant coating precursor for silica aerogels [1,2]. Most research are mainly focused on composite ceramic materials doped with Ag nanoparticles (NPs) [3]. Ag NPs are the most beneficial metallic NP because of their optical and conductive properties and particularly desirable due to its high solubility and low orbital energy [4,5]. Therefore, the potential benefits of highly catalytic Ag NPs with active materials in energy applications have attracted considerable attention [6].

Several methods have been investigated for fabricating Ag-impregnated silica aerogels. These methods are based on reducing precursors using various chemical reducing agents [7]. However, most of the approaches demand high temperatures and long reaction times. In contrast, wet impregnation of metal NPs on the surfaces of the support material is a simpler method for fabrication. During wet impregnation, metallic NPs and the matrix were formed consecutively, resulting in a uniform particle size distribution. The wet impregnation method does not require high reaction temperatures and saves time.

Various reducing agents have been employed to synthesize morphology-controlled uniform Ag NPs. However, most of them have a significant reducing potential, and the reaction is completed rapidly. The molecular weight, concentration, and ratio between the metal precursor and reducing agent affect the reaction mechanism. The use of polyvinylpyrrolidone (PVP) as a capping agent in the reaction allows the metal NPs to accelerate and produce a small size distribution.

In this study, an Ag-impregnated composite silica aerogel was fabricated via wet impregnation in the presence of a capping and reducing agent (PVP). Scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS) and X-ray diffraction (XRD) were used to characterize the morphology, chemical composition, and structure of the Ag/SiO<sub>2</sub> composite material.

### 2. Experimental

#### 2.1. Preparation of surface-modified silica aerogel powder

Surface-modified silica aerogel powder was synthesized by the thermal gelation method [8]. Briefly, a water glass (sodium silicate) solution (silica content: 28-30 wt. %, SiO<sub>2</sub>:Na<sub>2</sub>O = 3.4:1,

<sup>1</sup> INHA UNIVERSITY, DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING, INCHEON 22212, REPUBLIC OF KOREA

<sup>2</sup> YONSEI UNIVERSITY, DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING, SEOUL 03722, REPUBLIC OF KOREA

\* Corresponding author: [hjhwang@inha.ac.kr](mailto:hjhwang@inha.ac.kr)



Young Il Chemical Co., Ltd., Incheon, Korea) (5.3-8.7%) was diluted with deionized water. Next, 75 ml of water glass was blended with acetic acid (99.5%, Samchun Pure Chemical, Pyeongtaek, Korea), ethyl alcohol (95.0%, Samchun Pure Chemical), and named the above water glass solution. Subsequently, 85 ml of n-hexane (95%, Samchun Pure Chemical) was mixed with the surfactant sorbitan monooleate (Span80, Junsei Chemical Co., Ltd., Tokyo, Japan). The waterglass-to-n-hexane ratio was maintained at 1:1. Water glass and n-hexane were blended at 6000 rpm for 10 min using a homogenizer (UltraTurrax IKA T25:S25D-10G-KS; IKA Werke, Königswinter, Germany). The obtained water glass/n-hexane solution was heated at 100°C for condensation (thermal gelation). After 90 min. wet silica gel immersed in 150ml ethyl alcohol. Ethyl alcohol, a solvent-exchange agent, may affect the hydrogel-to-alcogel transition. The silica alcogel sphere surfaces were chemically modified in a 150 ml solution of 20% hexamethyldisilazane (HMDS, 98%, Samchun Pure Chemical)/n-hexane at 100°C for 3 h with magnetic stirring at 100 RPM. The silylated silica wet-gel spheres were washed in an ethyl alcohol/n-hexane solution to remove any remaining surface modification agents and reaction products. The silica wet gel spheres were dried at 100°C under ambient pressure for 1 h. The obtained surface-modified silica aerogel powder was used for further characterization and Ag/SiO<sub>2</sub> composite synthesis.

## 2.2. Preparation of Ag/SiO<sub>2</sub> composite

AgNO<sub>3</sub> solution with molar concentration (0.05 M) was prepared by adding silver nitrate (AgNO<sub>3</sub>, 99.9%, Alfa Aesar) in 50 ml ethylene glycol under a vigorous stirring. AgNO<sub>3</sub> was used as Ag precursor. Then, under magnetic stirring, 0.0002 M polyvinylpyrrolidone (PVP-40000, Sigma-Aldrich) was added to 50 ml ethylene glycol (99.5%, Samchun Pure Chemical, Pyeongtaek, Korea) at 80°C and After 30 min as prepared 1 g of SiO<sub>2</sub> powder slurry (100 ml ethyl alcohol/ethylene glycol) was

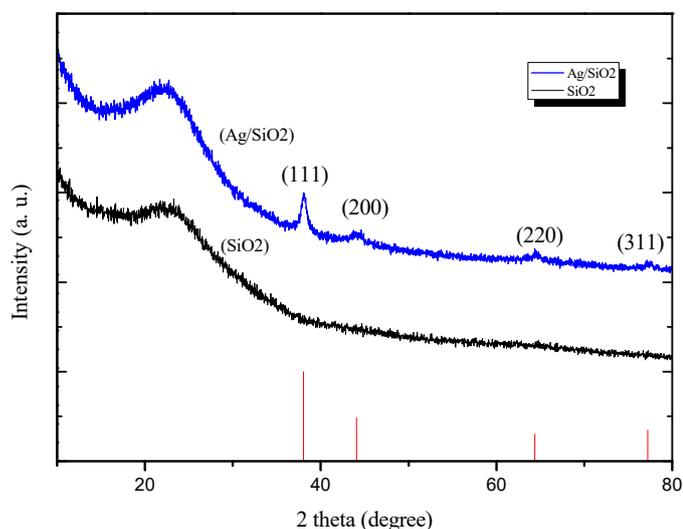


Fig. 1. X-ray diffraction patterns of SiO<sub>2</sub> microsphere and Ag/SiO<sub>2</sub> composite synthesized by wet impregnation

dispersed in the PVP solution then dropwise addition of AgNO<sub>3</sub> solution was conducted with a magnetic stirring at 80°C for 2 h. The weight ratio of AgNO<sub>3</sub> and PVP was maintained at 1:1. When AgNO<sub>3</sub> solution was added, the color of the solution gradually shifted to pale yellow, clearly showing the formation of Ag/SiO<sub>2</sub> composite. The obtained solution was filtered by ethyl alcohol (95.0%, Samchun Pure Chemical) and dried at 100°C in ambient pressure. The synthesized composite powder was used for further characterization. Other reactions were conducted using two different AgNO<sub>3</sub> concentrations (0.01, 0.1M). The weight ratio of AgNO<sub>3</sub> to PVP was the same as that used for the above reaction.

XRD (HR-XRD-standard analysis institute), SEM, and EDS (FESEM S-4300, Hitachi) were used to perform morphological and structural analysis.

## 3. Result and Discussion-

### 3.1. Characterization of Ag/SiO<sub>2</sub> Composite material

#### 3.1.1. XRD analysis

The XRD patterns of the synthesized SiO<sub>2</sub> microspheres and Ag/SiO<sub>2</sub> composites are shown in Fig. 1. The silica aerogel powder synthesized by the thermal gelation method showed a wide characteristic diffraction (2θ) peak at 22.9°, which is related to amorphous SiO<sub>2</sub> in pure silica. These results demonstrated that the synthesized silica aerogel powder was in an amorphous phase. Four diffraction peaks 2θ values at 38.6°, 44.0°, 64.3° and 77.1° were attributed to the face-centered cubic (FCC) structure of Ag crystal planes of (111), (200), (220) and (311) respectively as per ICDD card no. 01-087-0719 [9]. However, the intensity of the crystalline peaks increased with increasing molar concentration of the Ag precursor. This is because the crystal size of the Ag NP was small. It can be seen that the peaks are less intense, wider than those of bulk Ag indicating Ag nanoparticles with small size. This perfectly nanosized Ag was achieved in the presence of a well-known capping agent, PVP. Hence, the wet impregnation method for the synthesis of Ag/SiO<sub>2</sub> was found very effective.

#### 3.1.2. SEM and EDS analysis

SEM micrographs of the Ag/SiO<sub>2</sub> composite synthesized by wet impregnation are shown in Fig. 2(a,b). As can be seen in Fig. 2(a), silica aerogel powder synthesized by thermal gelation method showing the spherical morphology, and an average estimate of silica particle size is in between 10 and 30 μm. The high-magnification SEM images (Fig. 2(a) indicate that the silica particles had a highly porous three-dimensional network structure. In a previous study on silica aerogel powder, it was concluded that the concentration of waterglass did not significantly affect the shape and morphology of the silica particles. The Ag NPs had a homogeneous size distribution, ranging be-

tween 50 to 80 nm. The high-magnification SEM image shows the presence of Ag NPs on the surface of the silica aerogel particles. The presence of polyvinylpyrrolidone (PVP), which covers the Ag nanoparticles and prevents agglomeration, allows for the rapid reduction of Ag to a controlled size and shape. By comparing Fig. 2(a) and (b), even after surface capping by PVP and decoration by Ag nanoparticles, the silica spheres maintained their spherical shape and average size of approximately 10 to 30  $\mu\text{m}$ . From Fig. 2(a), we can conclude that the silica aerogel particles have a spherical morphology and porous structure, whereas Fig. 2(b) shows spherical Ag-decorated silica aerogel particles. This result suggests that Ag nanoparticles were homogeneously dispersed on the surfaces of the silica aerogels, and

the silica aerogel maintained its original morphology even after being composited with another material.

The chemical composition of the Ag/SiO<sub>2</sub> composite with Ag content of 2.24% was investigated using EDS analysis. As shown in Fig. 3, the elemental mapping of Ag/SiO<sub>2</sub> shows that, except for the Si, O, and Ag peaks, no additional peaks were detected, indicating homogeneous doping of Ag on the SiO<sub>2</sub> surface. The small size and appropriate concentration of the Ag precursor allowed Ag NPs to be modified on the pores of the silica particles, and without any thermal treatment, we successfully doped homogeneous Ag NPs on the surface of the silica aerogel particles. To examine the variation in the molar concentration, the chemical compositions with different molar

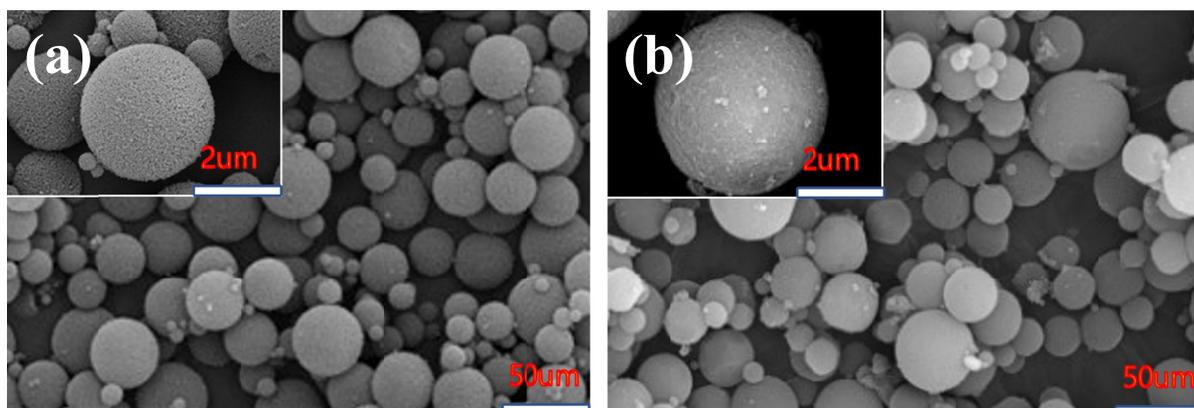


Fig. 2. SEM micrographs of (a) spherical SiO<sub>2</sub> and (b) Ag/SiO<sub>2</sub> composite sphere

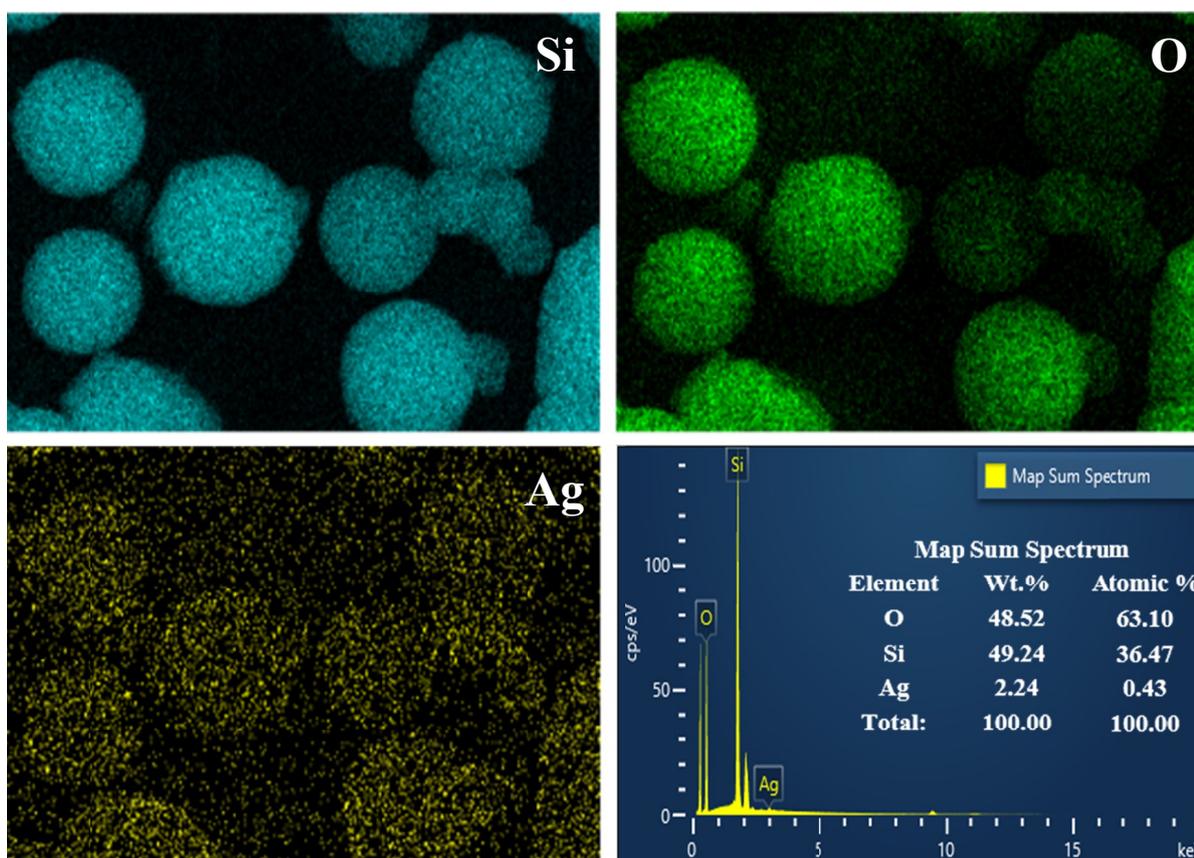


Fig. 3. EDS mapping of Ag/SiO<sub>2</sub> composite with 2.24 wt. % of Ag on SiO<sub>2</sub> surface

concentrations of  $\text{AgNO}_3$  were studied using EDS analysis. The surface capping and presence of Ag NPs were lower than the above concentrations of  $\text{AgNO}_3$ . The doping of the Ag NPs seemed to be inhomogeneous because of the lower concentration of the Ag precursor.

As shown in TABLE 1, we fabricated Ag/SiO<sub>2</sub> composite material with varying  $\text{AgNO}_3$  concentrations to investigate the effect of  $\text{AgNO}_3$  on the composite material. During the EDS analysis, a dramatic shift in the concentration of Ag on the silica particles was observed owing to the principle of chemical equilibrium and the concept of limiting reactants. At lower concentrations, the amount of Ag was insufficient to react actively and homogeneously with SiO<sub>2</sub>. Similarly, at higher concentrations, a large amount of Ag precipitated individually, and further agglomeration was observed. However, Sample 2, with an appropriate concentration of Ag, showed homogeneous solubility, proper interactions, and impregnation with SiO<sub>2</sub> microspheres. Thus, the concentration variations indicate that a suitable concentration of  $\text{AgNO}_3$  (0.05 M) is beneficial for the plausible loading of Ag NPs on SiO<sub>2</sub> particles.

TABLE 1

Ag weight % of Ag/SiO<sub>2</sub> composite powder synthesized with different Ag: PVP concentrations. The molar concentration of Ag: PVP was 1:1

Sr. No.	$\text{AgNO}_3$ (M)	PVP (M)	SiO <sub>2</sub> (gm)	Ag (%)
1.	0.01	0.00004	1	1.24
2.	0.05	0.0002	1	2.24
3.	0.1	0.0004	1	1.50

#### 4. Conclusions

In this study, we fabricated an Ag-impregnated silica aerogel composite material by a wet impregnation method using PVP as both a capping and reducing agent. We successfully demonstrated that the presence of PVP prevented the agglomeration of Ag NPs and ensured their homogeneous dispersion of Ag particles on the SiO<sub>2</sub> surface. The XRD and SEM results indicated that the Ag particles had a face-centered cubic structure and the Ag/SiO<sub>2</sub> composite particles had a spherical morphology. The silica aerogel particles maintain their spherical morphology. EDS results confirmed that the surface of SiO<sub>2</sub> was homogeneously surrounded by Ag particles, and the fluctuations in the concentrations of  $\text{AgNO}_3$  and PVP clarified the substantial variations in the presence of Ag on the surface of the silica particles. Hence, impregnation is a cost-effective and rapid technique for obtaining Ag/SiO<sub>2</sub> composites.

#### Acknowledgement

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. 2020R1A5A1019131). This work was also supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. 2022M3H4A1A04085322).

#### REFERENCES

- [1] M. Park, A. Choi, S. Kim, Study of SiO<sub>2</sub> coating and carboxylic surface-modification on Mg-based inorganic fiber by one-step reflux reaction. *J. Korean Ceram. Soc.* **59**, 869-875 (2022). DOI: <https://doi.org/10.1007/s43207-022-00227-8>
- [2] M. Park, W. Shim, Y. Kim, A Study of Various SiO<sub>2</sub> Coating Control on White TiO<sub>2</sub> Pigment for Cosmetic Applications. *Powder Mater.* **29** (3), 207-212 (2022). DOI: <https://doi.org/10.4150>
- [3] S. Kim, M.S. Nam, Y.S. Oh, S. Nahm, J. Shin, H. Kim, B.S. Oh, Fabrication of Light weight Ceramic Insulation Materials by Using Oxide Ceramic Fibers for Reusable Thermal Protection systems. *Powder Mater.* **9** (6), 477-484(2022). DOI: <https://doi.org/10.4150/KPMI.2022.29.6.477>
- [4] Ersoz, O.A. Yildirim, Green Synthesis and Characterization of Ag-doped ZnO nanofibers for photodegradation of MB, RhB and MO dye molecules. *J. Korean Ceram. Soc.* **59**, 655-670 (2022). DOI: <https://doi.org/10.1007/s43207-022-00202-3>
- [5] Z. Deng, M. Chen, L. Wu, Novel Method to Fabricate SiO<sub>2</sub>/Ag Composite Spheres and Their Catalytic, Surface-Enhanced Raman Scattering Properties. *J. Phys. Chem. C.* **111** (31), 11692-11698 (2007). DOI: <https://doi.org/10.1021/jp073632h>
- [6] C. Burda, X. Chen, R. Narayanan, M.A. El-Sayed, Chemistry and Properties of Nanocrystals of Different Shapes. *Chem. Rev.* **105** (4), 1025-1102 (2005). DOI: <https://doi.org/10.1021/cr030063a>
- [7] Q.Y. Han, G.A. Li., D.X. Wang, E.J. He, J. Dong, W. Gao, J.N. Li, T.Z. Liu, Z.Y. Zhang, H.R. Zheng, Synthesis of Ag-SiO<sub>2</sub> Composite Nanospheres and Their Catalytic Activity. *Sci. China Chem.* **57**, 881-887 (2014). DOI: <https://doi.org/10.1007/s11426-014-5068-0>
- [8] K.J. Lee, J.M. Lee, K.S. Nam, H. Hwang, Thermal Gelation for Synthesis of Surface-Modified Silica Aerogel Powders. *Gels.* **7** (4), 242 (2021). DOI: <https://doi.org/10.3390/gels7040242>
- [9] T. Ung, L.M. Liz-Marzán, P. Mulvaney, Redox Catalysis using Ag@ SiO<sub>2</sub> Colloids. *J. Phys. Chem. B.* **103** (32), 6770-6773 (1999). DOI: <https://doi.org/10.1021/jp991111r>