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Young Hwan Kim [a], Don Keun Lee [a], Chang Woo Kim [a], Hyun Gil Cha [a], Young Soo Kang [a], Beong Gi Jo [b] & Jee Hean Jeong [b]

[a] Department of Chemistry, Pukyong National University, Nam-gu, Busan, Korea

[b] R&D Center, Coreana Cosmetics Co., Ltd., Cheoan-si, Korea

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Young Hwan Kim
Don Keun Lee
Chang Woo Kim
Hyun Gil Cha
Young Soo Kang
Department of Chemistry, Pukyong National University, Nam-gu, Busan, Korea

Beong Gi Jo
Jee Hean Jeong
R&D Center, Coreana Cosmetics Co., Ltd., Cheoan-si, Korea

Silica particle was deposited with Ag nanoparticles to achieve hybrid structure. First, silica nanoparticles were synthesized according to the well-known Stöber method by hydrolysis and condensation of TEOS in a mixture of ethanol with water, using ammonia as catalyst to initiate the reaction. These SiO_2 nanoparticles were dried at 100°C. We measured the size of these nanoparticles with transmission electron microscopy (TEM). Second, Ag-SiO_2 nanoparticles were synthesized by reaction with $AgNO_3$ and SiO_2 nanoparticles at room temperature for 12 hrs. Results show silica nanoparticles of about 110 nm size deposited with Ag nanoparticles. Ag-SiO_2 nanoparticles were investigated with TEM images, energy dispersive X-ray analysis (EDX) spectrum. The antibiotic property was examined with disk plate method.

Keywords: Ag-SiO_2 nanoparticle; antibiotic property; hybrid structures

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Address correspondence to Young Soo Kang, Department of Chemistry, Pukyong National University, 599-1 Daeyeon-3-dong, Nam-gu, Busan 608-737, Korea. E-mail: yskang@pknu.ac.kr

INTRODUCTION

Silver nanoparticles attracted considerable attention because of their catalytic, optical, and conducting properties [1,2]. The merits of inorganic antibacterial materials is superior to that of organic antibacterial materials in durability, heat resistant, toxicity, selectivity and so on. The usefulness of silver as an antimicrobial agent has been known for a long time. It is an effective agent with low toxicity, which is especially important in the typical antibacterial treatment [3]. Its synthesis has been achieved via various routes, including radiation methods, microemulsion techniques, supercritical techniques, sonochemical reduction, laser ablation, metal vapor synthesis, vacuum vapor deposition, etc [4–6]. These synthetic methods are time consuming work and carried out by using high expensive instruments. Also silver nanoparticles synthesized by using above methods are easily aggregated and then cause deterioration of its chemical properties and decrease antibacterial property.

To improve these problems, we synthesized silica nanoparticles deposited with silver nanoparticles. Also to increase antibacterial property, more silver nanoparticles were deposited on the surface of silica nanoparticle. If silver is deposited on porous hosts, the release time of silver can be delayed for a long time so that silver-supported materials will be of great potentials for antibacterial application.

At present, many antibacterial agents have been mainly based on organic material, which are often not stable under conditions where chemical durability is required [7,8]. However, silver supported inorganic materials can overcome this disadvantage well. Up to now, zeolites, calcium phosphate and carbon fiber have been developed as inorganic supports for antibacterial silver containing materials [9,10]. Especially, silver supported silica materials, such as silica glass and silica thin films, are expected to be good candidates for antibacterial materials due to their fine chemical durability and high antibacterial activity [11].

Core-shell or hybrid structures have been intensively studied recently, in particular since such structures exhibit peculiar properties which make them attractive for applications in optical and biological sensors and in optoelectronics [12,13]. In all coating methods, the monolayer covering is important, as the chemistry is specific to the shell. The monolayer of oxide-shell materials is rather involved and required multistep process, and scale-up is difficult. To this purpose, oxide nanospheres of nearly equal size, offering great flexibility of composition, are well suited [14,15]. The aim of producing hybrid structures requires one to achieve a high nucleation but low growth

rate, and these results in the high number density of metal nanoparticles without the formation of aggregates. In this study, the antibacterial properties of silver nanoparticles deposited on the surface of silica nanoparticles show very strong inhibitory effect to various microrganism because of most ultrafine silver nanoparticles evenly deposited on the surface of silica nanoparticle.

EXPERIMENTALS

Synthetic Method of Silver Deposition on the Surface of Silica Nanoparticle

Silica nanoparticles were synthesized according to the well-known Stöber method by hydrolysis and condensation of tetraethoxysliane (TEOS, Aldrich Co., 98%) in a mixture of ethanol with water, using ammonia as catalyst to initiate the reaction. The size of silica nanoparticles was controlled by the molar ratio of TEOS, water and ammonia. The reaction started with mixing and stirring of the components, required about 6 hrs and was finished by centrifugation. The separated products were dried at temperature below 100°C for 2 hrs [16]. To do silver deposition on the surface of silica nanoparticles, silver nitrate ($AgNO_3$, Aldrich Co., 97%) was added to silica nanoparticle solution. We synthesized the Ag-SiO_2 by reacting silica nanoparticle solution with 0.018 mol of $AgNO_3$ in the presence of catalyst (0.0055 mol ammonia solution) at room temperature for 6 hrs. The product was purified by washing with ethanol. They were filtered, centrifuged and dried at room temperature for 2 hrs. Finally, Ag-SiO_2 nanoparticles were obtained.

Analysis

TEM samples were prepared on the 400 mesh copper grid coated with carbon. Structural characterization of the products was done with transmission electron microscopes (TEM, HITACHI H-7500) and high resolution transmission electron microscopes (HR-TEM, JEOL JEM-2010). The elemental ratio of prepared nanoparticles were characterized by scanning electron microscope-energy dispersive X-ray (SEM-EDS, HITACHI S-2400).

Test of Antibacterial Property

For antibacterial experimentation, Pseudomonas aeruginosa (ATCC 17934, gram-negative bacteria), Staphylococcus aureus (ATCC 25923, gram-positive bacteria), Escherichia coli (ATCC 25922, gram-negative

bacteria), Enterobacter cloacae (ATCC 29249, gram-negative bacteria), Candida albicans (ATTC 11282, yeast), Penicillium citrinum (ATCC 42504, fungi) and Aspergillus niger (ATCC 64958, fungi) were selected as indicators. All disk and materials were sterilized in autoclave before experiments. The antibacterial activities of Ag-SiO_2 nanoaprticle were measured by paper disk diffusion method. The disk diffusion assay was determined by placing a 8 mm disk saturated by 50 μl of Ag-SiO_2 nanoparticle solutions onto agar plate seeded with various microorganisms. After 24 hrs of incubation, the diameters of the inhibition zones were measured [17,18].

RESULTS AND DISCUSSION

TEM image of silica nanoparticles is shown in Figure 1 (a). Most of the silica nanoparticles were spherical. The histogram of the size distribution of silica nanoparticles shows the diameter of 112.2 nm ± 5.4 nm. In the presence of catalyst, more silver nanoparticles were deposited on the surface of SiO_2 nanoparticles and the size of silver nanoparticles was lager than that without catalyst. Silver nanoparticles were easily deposited on the surface of SiO_2 nanoparticle compared to silver nanoparticle prepared without catalyst in Figure 2. Very even Ag nanoparticles deposited on the surface of silica nanoparticle were observed with high resolution TEM of Figure 2 (c). Alkaline condition produced strong nucleophiles via deprotonation of hydroxo ligands and then electrophilic material like metal reacted with these nucleophilic part. This mechanism was schematically illustrated in Figure 3.

Figure 4 shows the EDX spectra of Ag-SiO_2 nanoparticles excited by an electron beam (20 kV). Peaks for the elements of O, Si and Ag were observed at 0.5249 ($O_{k\alpha 1}$), 1.73998 ($Si_{k\alpha 1,2}$), 1.83594 ($Si_{k\beta 1}$), 2.9843 ($Ag_{L\alpha 1}$), 2.9782 ($Ag_{L\alpha 2}$), 3.1509 ($Ag_{L\beta 1}$) and 3.3478 ($Ag_{L\beta 2}$), respectively. There were only silica and silver atoms in EDS spectra. From the EDS spectra we could confirm that the nanoparticles in TEM images were pure hybrid type Ag-SiO_2 nanoparticles.

The antibacterial activities of Ag-SiO_2 nanoparticle against the microorganisms were qualitatively assessed by determining the presence of inhibition zones. The antibacterial effects, inhibition zones, evaluated by the disk diffusion assay of the Ag-SiO_2 nanoaprticles were shown in Figure 5. The inhibition zones of silver nanoaprticles deposited on the surface of silica nanoparticle against P. aeruginosa, C. albicans, P. citrinum and S. aureus were determined as 14, 11, 12 and 10 mm, respectively [19]. In the case of low concentration of Ag-SiO_2 (number 1), the inhibition zone was detected against

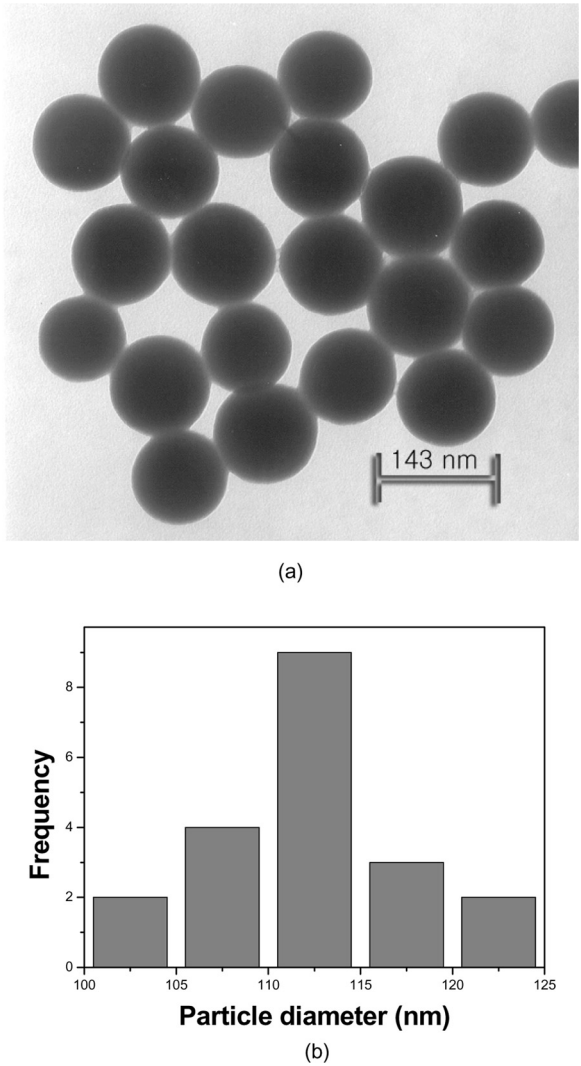

FIGURE 1 Transmission electron micrographs of silica nanoparticles (a) and the histogram of the size distribution (b).

P. aeruginosa, but it was not detected against other microorganisms. But, in the case of high concentration of Ag-SiO_2 (number 4), the inhibition zone was clearly detected against P. aeruginosa, C. albicans, P. citrinum and S. aureus. The values of inhibition zone against fungi and yeast were middle between the values of inhibition zone against

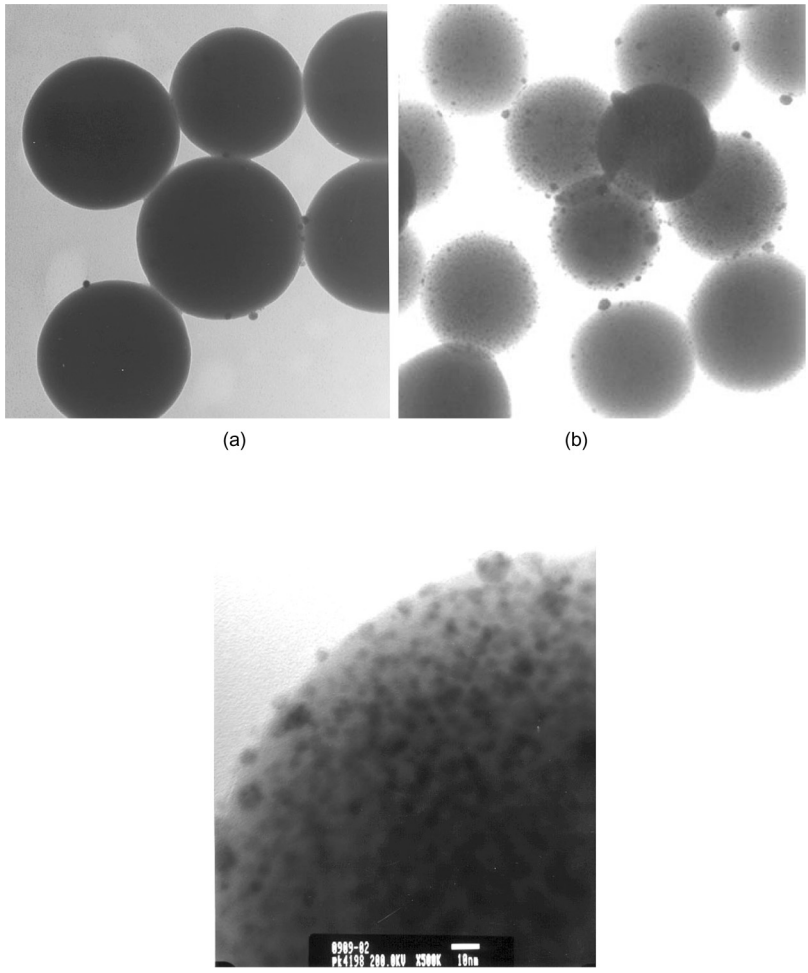

FIGURE 2 TEM images of silver deposited silica nanoparticles carried out without catalyst (a) and with catalyst (b), and high resolution TEM image of Ag-SiO_2 nanoparticle with catalyst (c).

gram-positive and gram-negative. The antibacterial effect, inhibition zone, for gram-negative bacteria such as P. aeruginosa showed less responsibility to the amount of Ag-SiO_2 nanoparticles. In contrast, gram-positive bacterium such as S. aureus was found to vary seriously depending on the amount of Ag-SiO_2. Besides the known antibacterial mechanism of silver, this phenomenon might also be partially

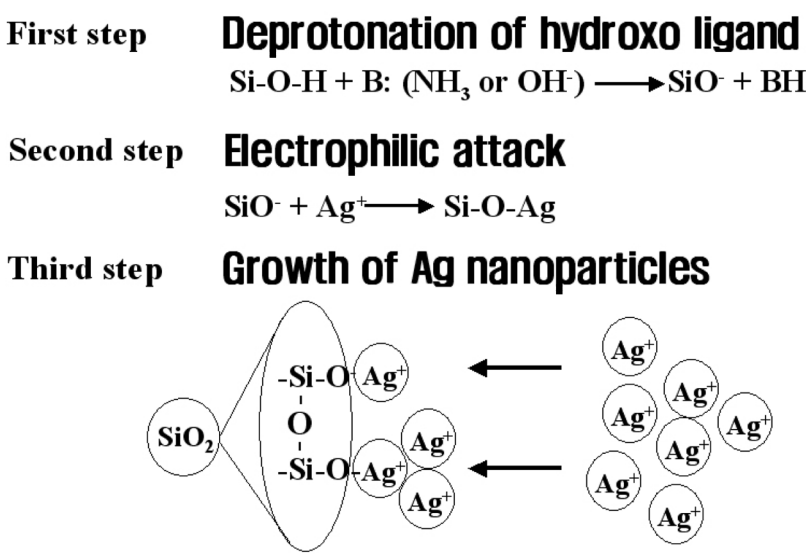

FIGURE 3 The mechanism of silver deposition on the surface of silica nanoparticle.

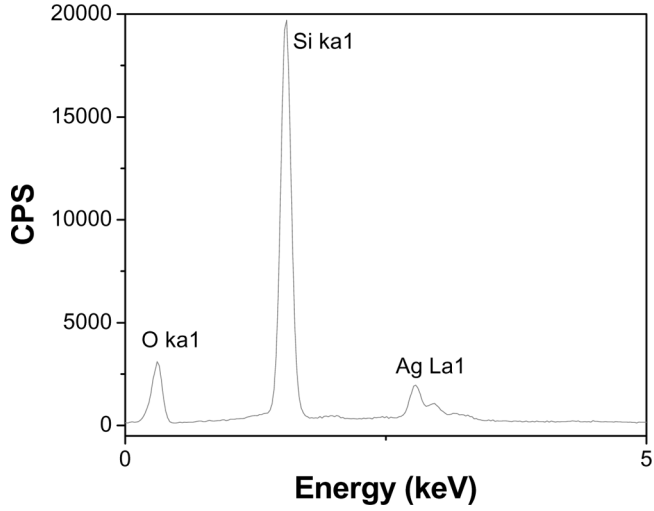

FIGURE 4 Energy dispersive X-ray spectrum of Ag-SiO_2 nanoparticles.

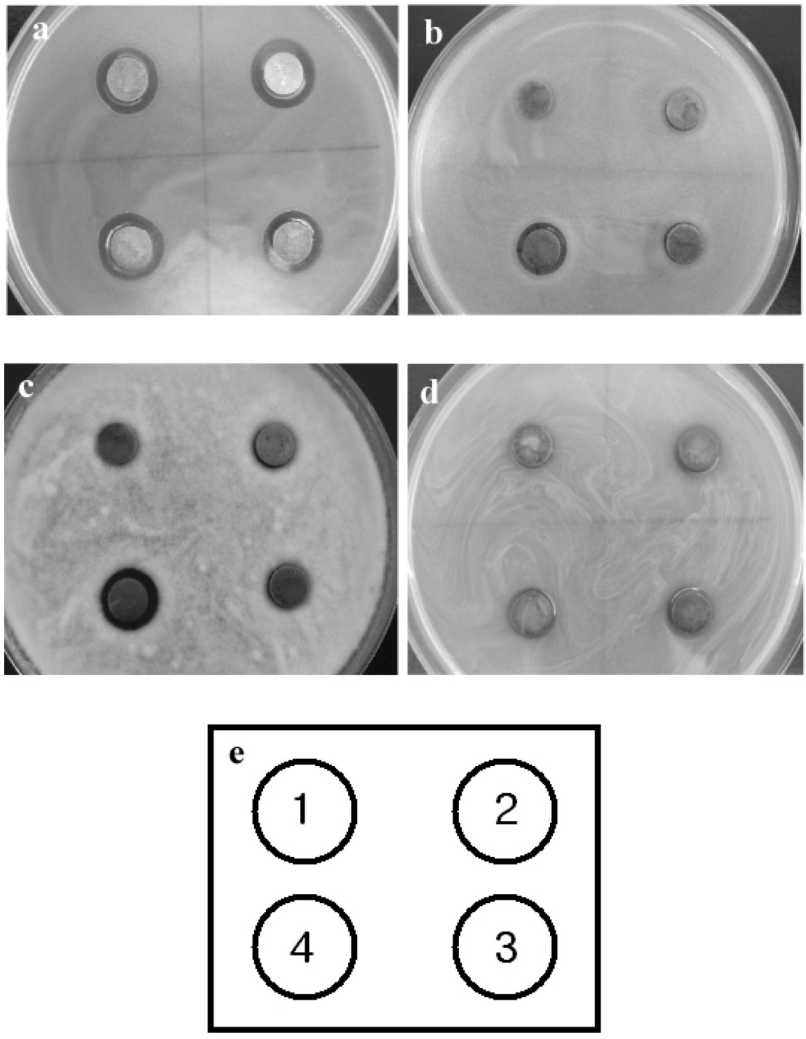

FIGURE 5 Photographs of the antibacterial test results on P. aeruginosa (a), C. allbicans (b), P. citrinum (c) and S. aureus (d) incubated on plates. In case of (e), concentration of number 1 is 0.24 mg of Ag-SiO_2 nanoparticle/1 μl of ethanol, 2 is 0.39 mg/μl, 3 is 0.56 mg/μl and 4 is 0.66 mg/μl.

explained with the fact that silver nanoparticles deposited on the surface of silica carried the opposite charge with gram negative, P. aeruginosa, thereby, killing them more easily than gram-positive bacteria due to the electrostatic attraction.

CONCLUSIONS

Silica deposited with silver nanoparticles was prepared at room temperature. This method was well suited for preparing silver metal nanoparticle deposition on the surface of silica nanoparticle. The effect of the presence of catalyst was more superior to that of without catalyst because strong nucleophiles produced by NH_3 via deprotonation of hydroxo ligands and then electrophilic material like metal reacted with nucleophilic sites. In the antibacterial test, Ag-SiO_2 nanoparticles showed high antibacterial activity against bacteria (E. coli, P. aeruginosa, S. aureus and E. cloacae) and yeast (C. albicans, P. citrinium and A. niger).

REFERENCES

[1] Joshi, S. S., Patil, S. F., Lyer, V., & Mahumuni, S. (1998). *Nanostruct. Mater*, *10*, 1135.
[2] Lee, J. J., Lee, S. J., & Kim, K. (2004). *Mol. Cryst. Liq. Cryst.*, *424*, 1.
[3] Li, Q. X., Tang, H. A., Li, Y. Z., Wang, M. Wang, L. F., & Xia, C. G. (2000). *J. Inorg. Biochem.*, *78*, 167.
[4] Dhas, N. A., Raj, C. P., & Gedanken, A. (1998). *Chem. Mater.*, *10*, 1446.
[5] Yeh, M. S., Yang, Y. S., Lee, Y. P., Lee, H. F., Yeh, Y. H., & Yeh, C. S. (1999). *J. Phys. Chem.*, *103*, 6851.
[6] Vitulli, G., Bernini, M., Bertozzi, S., Pitzalis, E., Salvadori, P., & Coluccia, S. Martra, G. (2002). *Chem. Mater.*, *14*, 1183.
[7] Ignatova, M., Labaye, D., Lenoir, S., Strivay, D., Jerome, R., & Jerome. C. (2003). *Langmuir*, *19*, 8971.
[8] Yeo, S. Y. & Jeong, S. H. (2003). *Int.*, *52*, 1053.
[9] Kawashita, M., Toda, S., Kim, H. M., Kokubo, T., & Masuda, N. (2003). *J. Biomed. Mater Res.*, *66*, 266.
[10] Park, S. J. & Jang, Y. S. (2003). *J. Colloid Interface Sci.*, *261*, 238.
[11] Kawashita, M., Tsuneyama, S., Miyaji, F., Kokubo, T., Kozuka, H., & Tamamoto, K. (2000). *Biomaterials*, *21*, 393.
[12] Sershen, S. R., Westcott, S. L., Halas, N. J., & West, J. L. (2000). *J. Biomed. Mater. Res.*, *51*, 293.
[13] Mayoral, R., Requena, J., Moya, J. S., Lopez, C., Ciontas, A., Miguez, H., Meseguer, F., Vazquez, L., Holgado, M., & Blanco, A. (1997). *Adv. Mater.*, *9*, 257.
[14] Romanov, S. G. & Sotomayor-Torres (2000). Three-dimensional lattices of nanostructures: the template approach. In: *Three dimensional Lattices of Nanostructures: The Template Approach: Handbook of Nanostructured Materials*, Nalwa, H. S. (Ed.), Academic Press: New York, Vol. 4, 232.
[15] Yonezawa, Y., Sato, T., Kuroda, S., & Kuge, K. (1991). *J. Chem. Soc. Faraday Trans.*, *87*, 1905.
[16] Stöber, W., Fink, A., & Bohn, E. (1968). *Colloid Interf. Sci.*, *26*, 62.
[17] Trewyn, B. G., Whitman, C. M., & Lim, V. S.-Y. (2004). *Nano letters*, *4*(11), 2139.
[18] Wilkinson, J. M., Hipwell, M., Ryan, T., & Cavagh, H. M.-A. (2003). *J. Agric. Food Chem.*, *51*, 76.
[19] Miyanaga, S., Hiwara, A., & Yasuda, H. (2002). *Science and Technology of Advanced Materials*, *3*, 103.