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Biocide Silver Nanoparticles in Two Different Silica-Based Coating

A. Babapour1, B. Yang1, S. Bahang1, W. Cao1,2

1. Center for Condensed Matter Sci. & Tech, Harbin Institute of Technology, Harbin, 150080, China
2. Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania 16802, USA

Abstract. Silica-based coatings containing biocide silver nanoparticles have been synthesized using low temperature sol-gel method. Two different silane based matrices, phenyltriethoxysilane (PhTEOS) and tetraethyl orthosilicate (TEOS), were selected as precursor to prepare silica-based film. The films were analyzed by using UV–visible spectrophotometry, atomic force microscopy (AFM) and scanning electron microscopy (SEM) for their optical, surface morphological as well as structural properties. Optical properties of nanosilver in these two matrices showed that the peak absorption observed at different wavelength, which is due to the fact that optical absorption of nanoparticles is affected by the surrounding medium. It is also found that the silver absorption has higher intensity in PhTEOS than in TEOS matrix, indicating higher concentration of silver nanoparticles being loaded into the coating. To study silver release property, the films were immersed in water for 12 and 20 days. AFM and SEM analyzes present that higher concentration of silver nanoparticles and smaller particle sizes were synthesis in PhTEOS coating and consequently, more particles remains on the surfaces after 20 days which leads to longer antibacterial activity of PhTEOS coating.

Keywords: Nanocomposites, Sol-Gel, Silver Nanoparticles, Antibacterial Coating.

PACS: 81.07.-b

INTRODUCTION

Metallic nanoparticles dispersed in solid materials have been the subject of extensive research in the past several years. In particular, noble metal nanoparticles (e.g., Au and Ag) with their remarkable plasmon resonance have generated great interest in many fields, such as catalysis [1, 2], anti-reflective films [3], sensors, particularly biosensors, [4, 5, 6] and nonlinear optical devices [7, 8].

Silver nanoparticle-embedded organic or inorganic matrices show extraordinary physical and chemical properties that are size and shape dependent [9,10,11]. Silver-incorporated materials have antibacterial capability that can be used in the medical field [12]. Silver is one of the most interesting biocide materials due to its strong and broad spectrum antimicrobial activities [13,14]. Biocide silver containing coatings have been applied onto implant materials such as bioglass [15], implant materials [16, 17] and ceramic orthopedic implants [18] to activate antibacterial function and to reduce the incidence of postoperative infections. Incorporate silver in various organic or inorganic matrices is a useful approach to prepare antibacterial materials. In this respect, silver-embedded silica based material has unique merits compared to their organic counterparts due to their high chemical and environmental durability, heat resistance, and long-term high antibacterial activity. Low temperature Sol-gel method is an easy way of preparing silver-containing coatings on glass or silica substrates in compare with some other processing techniques, such as sputtering, ion implantation, melt quenching, and ion exchange [19]. Taking into account that high initial release of antibacterial agent is significant during the early stage of device insertion for preventing bacterial attachment, a reduction of available surface silver ions is undesirable [20]. Consequently, preparing high concentration surface nanosize silver-doped material can increase antibacterial activity of coating. In addition, high density silver with controllable release rate can extend the lifetime of biocide silver release. According to our previous study, Silver nanoparticles tend to retain in upper layers of silica coating at low temperature which is necessary for the purpose of high initial silver release. However, this characteristic causes a limitation on silver particles concentration distribution, which reduces long-term bio activity of these coatings.
nanoparticles containing film. In the present study, we report the preparation of silver nanoparticles into two different silica-based coatings, TEOS and PhTEOS and study their physical and optical properties. Both of these nanocomposite films have very high loading of silver nanoparticles near the surface of the coating and can release particles at a desired rate. As silver can be load in PhTEOS higher than that in TEOS, this PhTEOS composite coating has longer silver release time and consequently, antibacterial activity.

MATERIALS AND METHODS

Film Preparation

The procedure of preparing silica-based thin films containing different amounts of silver nanoparticles has been previously reported [21]. Briefly, both sols were prepared using phenyltriethoxysilane (PhTEOS) and tetraethyl ortho silicate (TEOS), ethanol, DI water, nitric acid (HNO₃) and silver nitrate (AgNO₃) as precursors. After 30 min stirring, DI water was added to the solution. Then, different amounts of AgNO₃ along with a constant value of HNO₃ were added to the solution. The molar ratios of phTEOS/C₂H₅OH/H₂O/AgNO₃ and TEOS/C₂H₅OH/H₂O/AgNO₃ were 1:3.8:4:n, where n = 0, 0.02, 0.04, 0.08 and 0.16 is the nominal molar ratio of Ag/Si. The Ag colloid-containing sols were aged until the viscosity reached approximately 2–4 cP. All composite films were dried in air at 100 ºC for 1 h, which leads to transparent light brown color films.

Characterization

Surface morphology, particle size and distribution in the thin films were studied by Atomic Force Microscopy (AFM). A UV-visible photo spectrometer was used to determine the optical absorption spectra of the films in the wavelength range of 300–800 nm. The ability to prevent biofilm growth of silver-containing coatings was first proved by the zone of inhibition test and then was quantitatively assessed using scanning electron microscopy (SEM). Escherichia coli were used as the antibacterial test. After sterilizing, glass slides (10 mm × 10 mm), one group coated with silver-containing films and another group coated with silver-free films, were immersed in a nutrient-rich bacterial suspension of approximately 10⁸ CFU (colony forming units) ml⁻¹ and incubated for 15 and 30 days at 37 ºC. After incubation, the glass slides were removed and washed with DI water. In order to correctly count the grown bacterial colonies, 0.1 ml of the treated solution was diluted with DI water to a suitable volume. Then, the diluted solution was spread on a nutrient agar plate and incubated at 37 ºC for 48 h to count the bacterial colonies.

RESULTS AND DISCUSSION

The optical absorption spectra of the sol–gel derived silica-based coating with different silver concentrations are shown in FIGURE 1. As expected, all samples show an absorption peak around 430 nm with significant nanosilver surface Plasmon absorption, clearly indicating the presence of silver nanoparticles in the coating. It is seen that the absorption curves of films with higher AgNO₃ concentration show a red-shift. This shift happens because of particle size changes. It has been shown that higher AgNO₃ concentration leads silver nanoparticle’s size increcent [22]. Nanoparticles of different size in same medium have different absorption peak. For the absorption peak at 456 nm, it goes down to 408 nm when the Ag concentration decreases from 0.16 to 0.02 mol Ag (in TEOS, fig 1.a.). In addition, coatings with higher Ag concentrations show increased absorption intensities.

![FIGURE 1. Optical absorption spectroscopy of silver containing silica-based coating a) Ag-TEOS and b) Ag-PhTEOS with different silver concentration.](image-url)
distribution of particle size. The absorption intensity here is higher than Ag in TEOS, which confirms higher concentration of silver nanoparticles in the film. The surface morphology of silver nanocomposite thin films prepared by different TEOS and PhTEOS precursor were examined by AFM. **FIGURE 2** shows the AFM images of silver nanoparticle containing different amount of AgNO₃ in both matrices dried at 100 ºC. In order to extend the silver release time, high loading of silver nanoparticles in the composite film is vital. Therefore, the amount of AgNO₃ must be adjusted in the sol to maximize the concentration of silver nanoparticles in the matrix without losing nanosized particles. Our previous study demonstrated that there is an upper limit in loading AgNO₃ to the matrix. Increasing the concentration beyond this limit will cause the silver particles to lose semi-spherical shape and lead to particle agglomeration [23]. This limitation varies for different matrix. In this work, we found that more AgNO₃ can be loaded to PhTEOS than to TEOS without losing surface particle morphology. Because of the present of Phenyl groups in PhTEOS matrix, which open up more spaces, consequently more silver nanoparticles can be loaded into the composite film. **FIGURE 2.A1** and **A2** show Ag-PhTEOS composite and **FIGURE 2.B1** and **B2** present Ag-TEOS composite with 0.08 and 1.6 mol % Ag. For same AgNO₃ concentration, silver nanoparticles have bigger mean particle size in TEOS matrix than in PhTEOS matrix.

Because the antibacterial activity of the prepared silver-containing films is our purpose, understanding surface properties and amount of silver particles and their distribution are important. In order to study the concentration changes and washing resistant of silver nanoparticles on the surface of both coatings, scanning electron microscopy was utilized. Silica-based coatings of Ag-PhTEOS and Ag-TEOS were immersed in water as a test liquid. **FIGURE 3** shows SEM images of same concentration silver nanoparticles in both PhTEOS and TEOS films after 12 and 20 days immersion in water. As it was seen in AFM images, Nanoparticles in TEOS coating have bigger particle size in TEOS coating and consequently lower amount of surface particles. **FIGURE 3.a&b** present 12 days immersion of films in water. The concentration of particles on the both surfaces is still considerable and our previous study showed that this concentration can effectively inhibit bacteria attachment on the surfaces of coatings [21]. **FIGURE 3.c&d** demonstrate 20 days immersion of coating. The silver nanoparticles on TEOS surface are substantially lower than that on PhTEOS surface. According to this matter, it is conclude that Ag nanoparticles are more firm on PhTEOS surface and the concentration on the surface even after 20 days immersion is considerable.

**FIGURE 3.** SEM images of silver containing silica-based coating after a&b) 12 days and c&d) 20 days immersion in water. a&c) Ag-PhTEOS and b&d) Ag-TEOS

As it was mentioned, silver nanoparticles tend to maintain in upper layers and on surface of the silica based composites. For the same concentration of AgNO₃, higher amount of nanoparticles sustain on the surface of TEOS coating which cause bigger particle size and higher silver release and consequently leads to shortening antibacterial activity of the composite. This also proved the fact that higher silver nanoparticles can be loaded into PhTEOS. Due to higher silver concentration, there are still biocide nanoparticles present on the surface of the PhTEOS-silver nanocomposite coating even after 20 days. Therefore, we conclude that silver nanoparticles in PhTEOS matrix is a better choice in terms of long-time activity. For short time, both types of silver nanocomposites have strong biocide capability.
CONCLUSION

Silica-based coatings containing biocide silver nanoparticles have been synthesized using low temperature sol-gel method. Two different materials, TEOS and PhTEOS, were selected as precursor to prepare silica-based film. Optical properties of nanosilver in these two matrices showed that the peak absorption happens at different wavelength, which is due to the fact that optical absorption of nanoparticles is affected by the surrounding medium. We also found that the silver absorption has higher intensity in PhTEOS than in TEOS matrix, indicating higher concentration of silver nanoparticles being loaded into the coating. As demonstrated experimentally, higher silver nanoparticles lead to longer time biocide activity of the coating. Based on our experimental results, PhTEOS is more suitable candidate to be host of biocide silver nanoparticles.

REFERENCES


[23] A. Babapour, B. Yang, S. Bahang and W. Cao, IEEE, Symposium on Photonics and Optoelectronics (SOPO), 2011