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Preparation of Silver Nanoparticles and Antibiotic Test of Its Polycarbonate Films Composite

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General synthetic methods for silver nanoparticles are reduction of metal salt in aqueous solution or alcoholic solution. However, the preparation of silver nanoparticles in organic solvent is rarely reported. The most common preparation methods for silver nanoparticles in organic solvent are based on transfer of nanoparticles from aqueous phase to organic phase by phase transfer agent. We describe an easy synthetic method to prepare dispersed silver nanoparticles (~10 nm) by reduction of silver cation in organic solvent such as toluene using a reducing agent and a capping agent. The synthesized silver nanoparticles and polycarbonate were mixed and molded to prepare a new composite in methylene chloride. The composite was tested to investigate antifungal effect by coliform (*Escherichia coil* ATCC 25922). The antifungal effect of the composite reached high after 24 h (99.9999%). The composite and the silver nanoparticles have been characterized using X-ray diffraction (XRD), UV-vis spectroscopy, transmission electron microcopy (TEM), and inductively coupled plasma (ICP).

Keywords: Nanocatalysis, Silver Nanoparticles, Organic Nano Sol, Antifungal Effect.

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1. INTRODUCTION

Nanoparticles show unique properties different from bulk materials, in the range of nanometer. The properties of nanomaterials are responsible for two fundamental factors, which are related to the size variations in nanocrystal properties.[1] As the particles size decreases, the surface to volume ratio increases and therefore this leads to the surface playing an important role in the properties of the materials. The properties are due to unusual properties such as specific activity and selectivity. Metal nanoparticles have various applications in the areas of catalysis,[2] opto-electronics,[3] and film growth seeding, etc. Moreover, these nanoparticles are interesting to investigate their optical properties, since they strongly absorb light in the visible region due to surface plasmon resonance.[4] The most common method for the preparation of Ag nanoparticle is reducing silver cation in solvent with surfactants. Reducing methods ϒ-ray or UV irradiation,[6] hydrogen gas treatment,[7] as well as using chemical reducing agents such as sodium borohydride,[8] hydrazine,[9] alcohol,[10] ethylene glycol,[11] and aldehyde.[12] Stabilizers are generally required to prepare Ag nanoparticles with controlled size and shapes. Alkylthiols,[9] alkylamines,[13] fatty acids,[14] carbon disulfide,[15] and polymers such as polyvinylpyrrolidine[16] have been used for the preparation of Ag nanoparticles with uniform size and shapes. In General, solution with reducing agents and stabilizers is used synthesized silver nanoparticles. The preparation methods of silver nanoparticles are divided into two classes depending on solvent; aqueous solution and organic solution. Generally, silver nanoparticles have been prepared by reduction of metal salt in aqueous solution. However, organic solvent has been rarely used except alcohol. The general preparation methods for silver nanoparticles in organic solvent are based on transfer of nanoparticles from aqueous phase to organic phase by phase transfer agent,[17] after synthesizing silver nanoparticles in aqueous phase. Sastry et al.[18] have demonstrated the phase transfer of aqueous colloidal silver into hexane using octadecylamine present in the organic phase. However, the preparation of organic colloidal silver by phase transfer method has problems such as requirements of much solvent and multi-step process.

Silver has an antifungal effect[19] on various microbes of about 650 species such as staphylococcus, klebsiella pneumoniae, coliform bacillus, and so on. Thus, many goods of living use silver nanoparticles for antifungal effect such as washing machine, cleaning water, nursing bottle, and

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so on. The antifungal effect increases in silver nanoparticles better than in bulk silver, because the surface to volume ratio increases in the nanoparticles. In the generality of cases, polymer goods containing silver nanoparticles were to mold the nanoparticles on surface for antifungal effect. But this method has demerit that peels off coating silver on polymer.

In this report, we describe an easy synthetic method to prepare dispersed silver nanoparticles by reduction of silver cation in organic solvent such as toluene using reducing agents. In detail, the method has the advantage of simple and easy formation of monodispersed silver nanoparticles in organic solvent without size selection and phase transfer process. Almost silver nanoparticles have well-dispersed in organic solvent. Also, polycarbonate films containing silver nanoparticles were prepared by molding method with simple and inexpensive process. Then, antifungal effect of these films was measured by film contact method (FC-TM-20). In this experiment, we used *Escherichia coil* ATCC 25922 as a standard microbe.

2. EXPERIMENTAL DETAILS

2.1. Material and Characterization

$AgClO_4$ (97%), $NaBH_4$ (98%), and dodecylamine (98%) were purchased from Aldrich. Oleic acid, toluene, methylene chloride, and methanol were used by low grade. All materials were used without further purification. Polycarbonate used in the work was Lexan 101. The X-ray diffraction patterns of Ag nanoparticles were recorded by employing Rigaku D/MAX-III-B (Cu Kα). UV-vis spectroscopy measurements (300–600 nm) were performed using SHIMADZU UV-2501PC spectrophotometer at room temperature. Transmission electron micrographs (TEM) were obtained by employing JEOL JEM 3011 micrographs under 300 kV.

2.2. Preparation of Silver Nanoparticles

Silver perchlorate and dodecylamine were dissolved in toluene at room temperature. Infinitesimal water to solve sodium borohydride was added in drops for 15 min. The transparent solution turned into yellow color from colorlessness. The color of the solution became dark over the reaction time for 30 min. But the dilute solution has yellow color. The precipitation of silver nanoparticles was separated from the solution by centrifugation and subsequently was washed with methanol for several times. The ultimate powders were then dried in vacuum at room temperature for 2 h. The final products had silver content of 80%. The powders showed deep purple and were well-redispersed in organic solvent such as toluene, hexane, and methylene chloride.

2.3. Preparation of Composite of Polycarbonate and Silver Nanoparticles

We prepared the polycarbonate films containing silver nanoparticles with varying the concentration of silver nanoparticles during mixing polycarbonate films and silver nanoparticles in solvent. Silver nanoparticles contents of samples were 0.5, 1.0, 2.0, and 3.0 wt%, respectively. The solution of polycarbonate films in methylene chloride was mixed with the dispersion of silver nanoparticles in methylene chloride. The mixture was poured into a mold at room temperature. The solvent was evaporated to dryness to give the composite of the polycarbonate films containing silver nanoparticles.

3. RESULTS AND DISCUSSION

Figure 1 shows X-ray diffraction patterns of silver nanoparticles. The peaks were assigned to diffraction from the (111), (200), (220), (311), and (222) planes of fcc silver, respectively. The average particle size of the metal nuclei (6.3 nm) calculated by the Scherrer equation, using the half width of the intense (111) reflection, was comparable with the value obtained from TEM images. Metal nanoparticles exhibit absorption bands or broad regions of absorption in the UV-vis range. These are known to be due to the excitation of plasma resonances or interband transitions, characteristic properties of the metallic nature of the particles. Figure 2 reveals UV-vis spectra of the silver nanoparticle (a) and silver nanoparticles (0.5 wt%) in polycarbonate film (b).

The silver nanoparticles display an optical absorption band peak at 424 nm, which is typical of the absorption of metallic silver nanoparticles due to the surface plasmon resonance. The low concentration of silver in organic solvent such as toluene, hexane, and methylene chloride were a bright yellow color due to the intense bands around the excitation of the surface plasmon resonance.

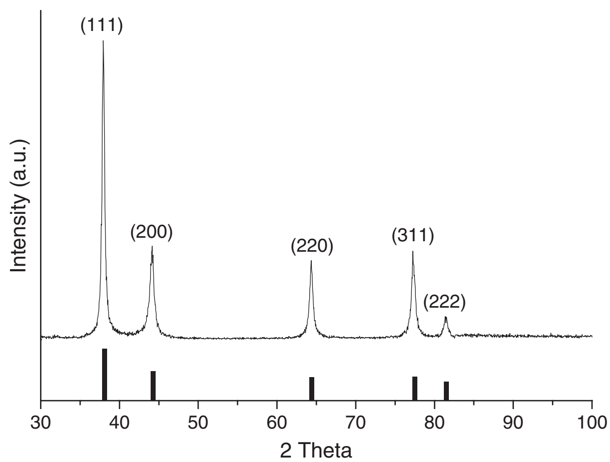

Fig. 1. XRD pattern of dodecylamine capped silver nanoparticles (bar: JCPDS no. 04-0783).

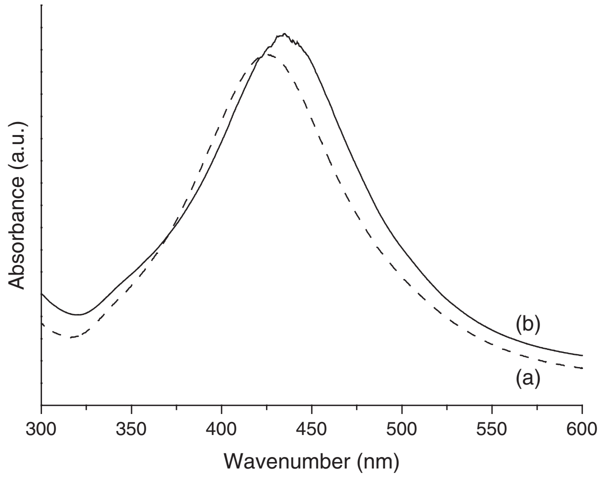

Fig. 2. UV-vis absorption spectrum of (a) dodecylamine capped on silver nanoparticles (b) silver nanoparticles (0.5 wt%) included in polycarbonate films.

Also UV-vis absorption spectrum of silver nanoparticles (0.5 wt%) included in polycarbonate films are observed to be slightly red-shifted. This red-shift of absorption bands can be attributed to the larger size of silver nanoparticles. Drop-coated films of the dodecylamine capped silver nanoparticles solution were formed on carbon-coated copper grids by solvent evaporation for TEM measurements. Figure 3 displays TEM image of dodecylamine capped silver nanoparticles and a plot of the particle size distribution histogram measured from an analysis of about 300 particles in TEM image. The spherical silver nanoparticles have average particle size of 5.52 ± 1.55 nm. Real particle size is similar with particle size calculated by XRD pattern. Dodecylamine is attached to the surface of the silver particle and the ratio of Ag to dodecylamine is approximately 80:20, as determined by ICP (inductively coupled plasma). Figure 4 exhibits transmission electron micrograph image

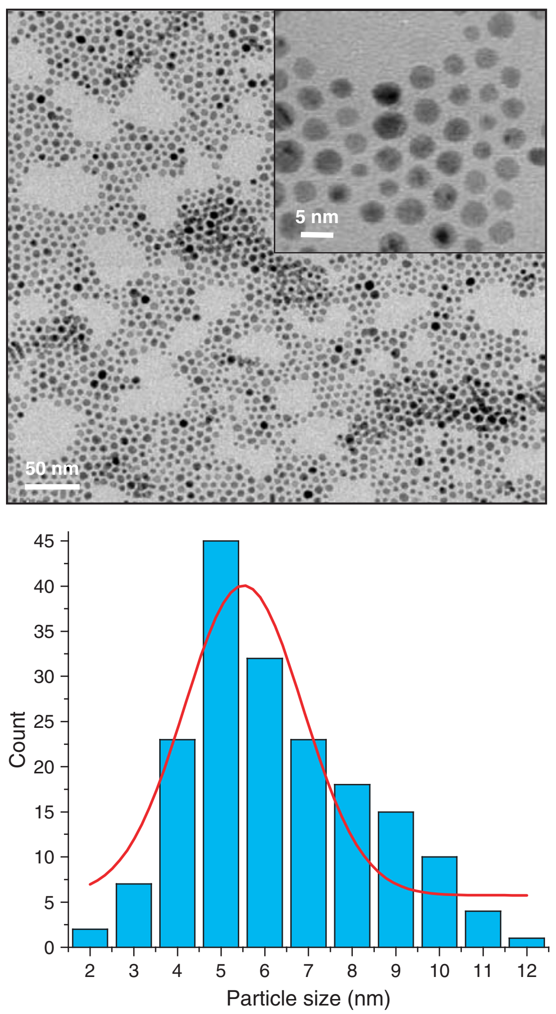

Fig. 3. Transmission electron micrograph image and particle size distribution histogram of dodecylamine stabilized silver nanoparticles. Insert: HRTEM image of silver nanoparticles.

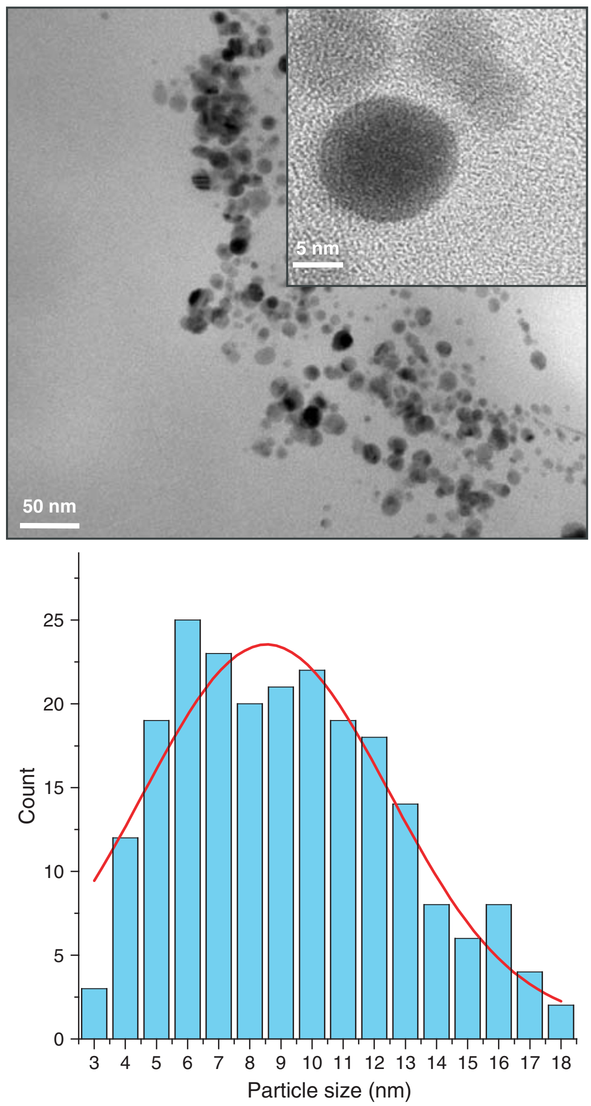

Fig. 4. Transmission electron micrograph image and particle size distribution histogram of polycarbonate films included silver nanoparticles. Insert: HRTEM image of silver nanoparticles in polycarbonate films.

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(cross section) and particle size distribution histogram of the polycarbonate film including 0.5 wt% of silver nanoparticles. The result shows that Ag nanoparticles exist in the center of polycarbonate film. Average particle size of the silver nanoparticles in the composite increased by about 2.5 nm compared with the initial silver nanoparticle. Antifungal effect of silver nanoparticles included in polycarbonate film was tested by coliform (*Escherichia coil* ATCC 25922). Colony-forming units (CFU) of the blank turned from 1.5×10^5 to 7.1×10^6 by incubation for 24 h. But CFU of the composite was 10 after the same treatment with the blank. This result showed that polycarbonate films included 0.5 wt% of silver nanoparticles had the activity of proved decrement coliform by 99.9999%. But, the mechanism of antifungal effect of silver nanoparticles is still not well known. In a previous report[19] on the antifungal effect of silver nanoparticles, it was shown that the interaction between silver nanoparticles and constituents of the cell wall arise structural changes in and damage to membranes, finally leading to cell death. We surmise that the antibacterial effect of silver nanoparticles is broadly similar to that of silver ion. Maybe silver ions originated by a bacterial cell in contact with silver nanoparticles, which restrain an enzyme for life-support, promoting the generation of reactive oxygen species and consequently damaging the cell.

The other samples such as silver nanoparticles of 1.0, 2.0, and 3.0 wt% were tested by the same method. Also, they had few or no CFU (<10), therefore the samples showed the same antifungal effects with 0.5 wt% of silver nanoparticles.

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4. CONCLUSION

We have described a novel and easy method for the preparation of silver nanoparticles well-dispersed in organic solvent. An average particle size of silver nanoparticles is 5.52 ± 1.55 nm with spherical shape. Silver nanoparticles were capped by 20 wt% dodecylamine. The synthesized silver nanoparticles and polycarbonate were mixing and molding to prepare new composites of various silver concentrations. And polycarbonate films containing silver nanoparticles were tested to investigate antifungal effect by film contact method. All silver nanoparticles dispersed on polymer display high antifungal effects.

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