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A Rapid Synthesis of Silver Nanoparticles Using a Radical Initiator under UV Light and Evaluation of Their Antibacterial Activities[1]

Armin Mohmedi-Kartalai[a], Mansour Ghaffari-Moghaddam[a], Alireza Samzadeh-Kermani[a], Majid Zand Karimi[b], Mohammad Reza Sharifmoghadam[c], Mostafa Khajeh[a], Hassan Eslahi[a], Ashkan Keshavarzi[d], Mitra Mohammadi[e], and Mousa Bohlooli[f]

[a] *Department of Chemistry, Faculty of Science, University of Zabol, Zabol, Iran*
e-mail: mansghaffari@uoz.ac.ir

[b] *School of Pharmacy, Zabol University of Medical Science, Zabol, Iran*

[c] *Department of Biology, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran*

[d] *Otto-Schott-Institut, Jena University, Fraunhoferstr. 6, 07743 Jena, Germany*

[e] *Department of Environmental Science, Kheradgerayan Motahar Institute of Higher Education, Mashhad, Iran*

[f] *Department of Biology, Faculty of Science, University of Zabol, Zabol, Iran*

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Abstract—In this study the silver nanoparticles (AgNPs) were synthesized by reduction of silver ions using benzoin as a radical initiator under UV light. Polyvinyl alcohol (PVA) was used as a stabilizing agent. The AgNPs were characterized with UV-Vis spectrophotometry, X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and FT-IR. The results exhibited the spherical shape of nanoparticles with size of 20-30 nm. The synthesized AgNPs were evaluated for their antibacterial activities against the Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Escherichia coli*) bacteria. Two types of bacteria were effectively inhibited by synthesized AgNPs.

Keywords: polymer-matrix composites, nano-structures, initiator, electron microscopy, antibacterial activity

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INTRODUCTION

AgNPs belong to a special group of materials with many applications in various fields such as dentistry, clothing, catalysis, mirrors, optics, photography, electronics, and food industry. Due to such potentials many methods of synthesis of AgNPs have been developed. Such methods should control the size of AgNPs. Efficient synthesis of small particles without bulking was favorable [1, 2]. The most important methods for synthesis of AgNPs are follows: chemical reduction [3, 4], optical reduction [5], hydrogel method [6], micelles [7], gamma irradiation [8], sol-gel [9] and biosynthetic methods [10–12].

Polymers such as polyvinyl alcohol (PVA) are always the first choice for nanoparticles synthesis. PVA is water soluble, biocompatible, biodegradeable, and it has a lot of medical applications [13, 14]. Due to the advantages it can be used for preparation of AgNPs in PVA solution [15], nanospherical Ag_2S/PVA and nanoneedles of CuS/PVA composites [16], and also impregnation of bacterial cellulose gels in PVA solution [17].

Generally, Ag ions and Ag-based compounds are antimicrobial agents which can deactivate several microorganisms including and various bacteria [18-21]. The action of AgNPs against microbes is not fully understood. It has been reported that AgNPs can cause cell lysis or inhibit cell transduction [22].

The aim of this work was synthesys of the AgNPs using chemical reduction of Ag^+ in the presence of benzoin as a radical initiator under UV irradiation. Antibacterial activity of the synthesized AgNPs was evaluated against *Staphylococcus aureus* (Gram positive) and *Escherichia coli* (Gram negative) by

[1] The text was submitted by the authors in English.

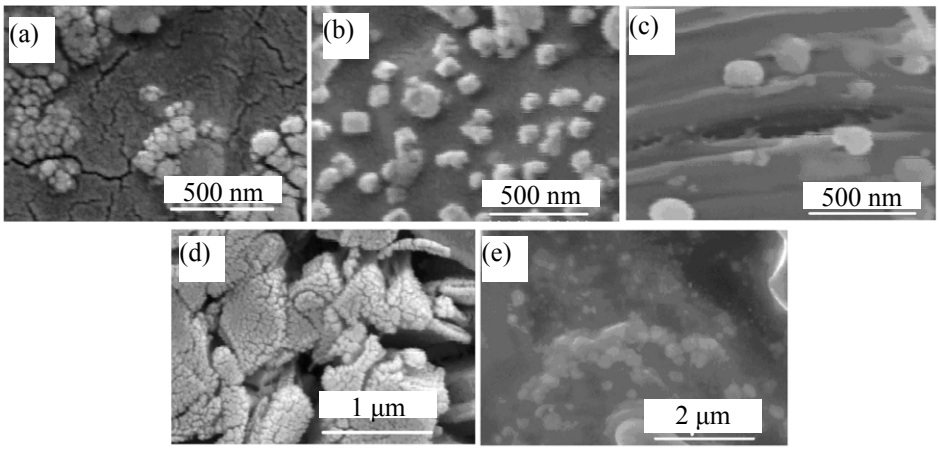

Fig. 1. The FESEM images of nanocomposites at concentrations of silver nanoparticles, %: (a) 1.5 (b) 2.5, (c) 5, (d) 10, and (e) 0.

using the agar disc diffusion method. To the best of our knowledge, this is the first report of Ag/PVA nanocomposite synthesys involing benzoin as a radical initiator.

Generally, metal nanoparticles are synthesized with noble metals silver, platinum, gold, tin, cupper, and titanium. Due to a combination of valuable properties silver is the most widely used metal among those [23–29]. Nanoparticles have a distinctive tendency to form aggregates exceeding nano-scale for this reason it is important to retard this tendency. Using polymers is the most applicable method to stabilize nanoparticles in preparation of Ag nanocomposites [30, 31].

UV-Vis spectrophotometry. A broad peak in the range 400–450 nm in UV-Vis spectra was characteristic for the synthesized AgNPs [32]. For optimization of the reaction it was carried out with different ratio $AgNO_3$: Benzoin (1 : 1, 1 : 2, 1 : 3, 1 : 4, 1 : 5, and 1 : 6) and various irradiation times (1, 3, 5, and 8 min). The corresponding ratio of 1 : 2 and irradiation time 1 min were determined as optimum ones.

XRD analysis. The presence of crystalline silver nanoparticles in nanocomposites was confirmed by the XRD analysis. The stabilized Ag crystalline structures had sharp and intense peaks around 2θ degrees of 38, 44, 64, and 78 with [111], [200], [220] and [311] diffractions, respectively [33]. There was a broad peak appearing at 2θ values in the range of 23°–28° related with the polymeric stabilizer chains. For all synthesized nanocomposites, the particle size of Ag was calculated by the Scherrer equation [Eq. (1)]:

$$D = \frac{0.94\lambda}{\beta\cos\theta}, \qquad (1)$$

where D is the average crystallite size, θ is the diffraction angle, β is the full width at half maximum (FWHM), and λ is the X-ray wavelength [34–36].

The average particles size of AgNPs was found to be in the range of 20–30 nm for all synthesized nanocomposites in this study. However, the spontaneous irreversible aggregation and growth of synthesized nanoparticles took place in the course of the process. Actually the average particles size reported corresponded to the product that contained agglomerates.

FESEM analysis. The surface morphology of nanoparticles of the Ag/PVA nanocomposites as well as the desirable nanoparticle coating by stabilizing matrix (PVA) were characterized by the FESEM analysis (Fig. 1). These images illustrated that nanoparticles were coated successfully by the polymer. They also show the haphazard distribution of Ag nanoparticles in the matrix. All reported in this paper particle sizes were derived from the XRD data.

In FT-IR spectra the strong broad band at 3200–3500 cm^{-1} was assigned to the O–H stretching vibrations that indicated its involvement in the formation of a complex with metal particles. The bands of 668 cm^{-1} and 851cm^{-1} were attributed to the out of plain vibration of O–H and C–H bonds influenced by silver concentration [37].

Antibacterial activity. The antibacterial activity of all nanocomposites was examined using *Staph. aureus* and *E. coli*. and exhibited the inhibition zones formed in the samples. The diameter of the inhibition zones 8, 12, 13, 9, and 0 mm, and 11, 13, 15, 13, and 0 mm were measured against *E. coli* and *Staph. aureus*, respectively (see the table). The mechanisms of action

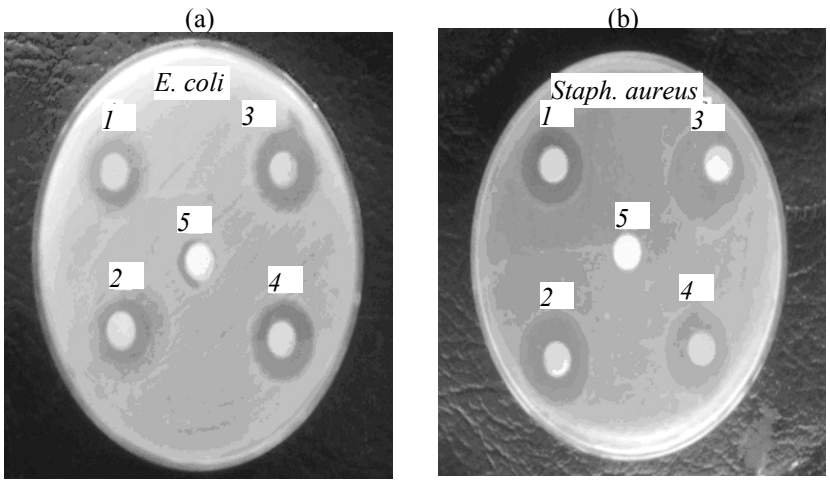

Fig. 2. Antibacterial activity of different nanocomposites against pathogenic strains, (a) *E. coli* and (b) *Staph. aureus* with various silver nanoparticles concentrations, %: (*1*) 1.5, (*2*) 2.5, (*3*) 5, (*4*) 10, and (*5*) 0.

of silver nanoparticles on bacterial cells are complicated [38–40]. The Ag/PVA nanocomposite *3* with 5% Ag nanoparticle exhibited the highest antibacterial activity against both types of bacteria (Fig. 2).

EXPERIMENTAL

Chemicals. All analytical grade chemicals were purchased from Merck (Darmstadt, Germany).

Microorganisms. The antibacterial activity of the synthesized AgNPs were evaluated using two different bacterial strains including Staphylococcus aureus (*Staph. aureus*) and Escherichia coli (*E. coli*). All bacterial strains were obtained from the School of Pharmacy, Zabol University of Medical Science, Zabol, Iran.

Techniques. UV-Vis measurements were accumulated with the UV-2100 double beam (UV-Vis spectrophotometer, Rayleigh, China) at room temperature. The FT-IR spectra were accumulated by the Bruker (Tensor 27, Germany). The XRD analysis was conducted by using CuK_α radiation on a Philips diffractometer (PW1800, Netherlands). The FESEM images were taken by scanning electron microscope (Hitachi S4160, Japan).

Synthesis of Ag/PVA nanocomposite. In the typical synthesis PVA (0.4 g) was dissolved in distilled water (20 mL) and acetic acid (0.3 mL, 0.35 M) to produce a clear solution followed by silver nitrate (one of the following 0, 1.5, 2.5, 5 or 10 % w/w), benzoin (0.002 g), and DMF (5 mL) addition. The resulting mixture was illuminated with ultraviolet light from a 1200 W UV lamp for 1 min at 60–80°C. Finally, the nanocomposite formed was dried in an electric oven at 40˚C for 72 h.

Antibacterial assay. The antibacterial activity of the Ag/PVA nanocomposites was tested against two pathogenic organisms, *Escherichia coli* (ATCC 1103) and *Staphylococcus aureus* (ATCC 9144) using the disc diffusion procedure based on the method described by Hwang and Ma [41]. The Muller-Hinton Agar (MHA) powder was used as a culture medium for bacterial growth. Agar, 19 g, was dissolved in 500 mL of distilled water and the transparent brown solution was achieved by boiling the solution. The MHA medium was sterilized (at 120°C and pressure of 15 atm) for 15 min in an autoclave, then cooled to 45°C in a water bath and poured into a sterilized petri dishes. A single colony of each test strain was grown overnight in Muller-Hinton liquid medium on a rotary shaker (200 rpm) at 35°C. The inocula were prepared

Average inhibition zones obtained from various nanocomposites at concentrations of silver nanoparticle, %: (*1*) 1.5, (*2*) 2.5, (*3*) 5, (*4*) 10, and (*5*) 0

Samples	Average inhibition zones, mm	
	E- coli	*Staph.aureus*
1	8	11
2	12	13
3	13	15
4	9	13
5	0	0

by diluting overnight cultures with 0.9% NaCl to a 0.5 McFarland standard and were applied to the plates along with the standard and prepared disks containing 10 μL of different concentration samples. After incubation at 37°C for 24 h the zones of inhibition were measured in mm. The size of those zones exhibited the efficiency of nanocomposites. The results of antibacterial activity were classified as no activity (inhibition zone <5 mm), weak activity (5 mm), moderate activity (6–12 mm), or strong activity (>13 mm) [41].

CONCLUSIONS

In this study Ag nanoparticles were synthesized by the reduction method using UV irradiation in the presence of benzoin as a radical initiator. PVA was applied for coating and stabilizing Ag nanoparticles. The particle size was measured by XRD analysis in the range of 20-30 nm. The FESEM results exhibited high efficiency of polymer in nanoparticle coating. Ag/PVA nanocomposites exhibited antibacterial properties against gram positive (*Staph. aureus)* and gram negative (*E-Coli*) bacteria. In comparison to the other methods, this procedure was fast, very simple, and cost efficient.

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