

# Improvement of anti-tarnishing and anti-bacterial properties of silver by a waterborne polyurethane/silver nanocomposite coating

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Silver (Ag) objects tarnish when exposed to the human sweat or atmospheres polluted by sulphide. In this work, a waterborne and transparent polyurethane/Ag (WPU/Ag) nanocomposite was synthesised and applied on the surface of the Ag sample with enhanced anti-bacterial and also protection against the tarnishing in the corrosive solutions. Ag nanoparticle in the WPU/Ag was investigated by field-emission scanning electron microscopy and transmission electron microscopy. To study the anti-tarnishing behaviour of the Ag samples, the bare as well as the coated samples were immersed in corrosion solution of 0.35 wt% Na<sub>2</sub>S which is a simulating solution of the human sweat. The corrosion products were then studied with X-ray diffraction and energy-dispersive X-ray spectroscopy. The bare Ag surface was covered completely by a black layer after 60 min immersion in the corrosion solution. However, the presence of either waterborne polyurethane (WPU) or WPU/Ag coatings was remained on the surface and protected the substrate from tarnishing. Anti-bacterial properties of the samples were determined by disc diffusion and the minimum inhibitory concentration methods. Anti-bacterial effect of the Ag coated by WPU/Ag was greater than the bare substrate, whereas the WPU coating lost the anti-bacterial effect of the Ag substrate.

**1. Introduction:** Silver (Ag) has been used for thousands of years as a precious metal by humans in different applications such as handicrafts and archaeological objects in holy sites. Wide use of Ag owes to its shiny surface and also anti-microbial property. For example, Ag vessels were used for the storage of water because it was believed that this metal preserved their conditions [1]. However, the shiny surface of Ag tends to be tarnished when it is touched by human hand and therefore, is reacted with human sweat. Tarnishing is also possible by Ag reaction with atmospheric pollutant elements [2–5]. Often, the blackish film formed on the surface of Ag which is composed of Ag<sub>2</sub>S and AgCl [6–8]. Recently, different anti-tarnish methods have been proposed by the scientific community, none of which perfectly satisfy the requirements of the mentioned applications. One method for protection against tarnish would be the isolation of the Ag surface from corrosive medium by applying a coating layer. However, the coating itself should not alter the shiny appearance [9–11]. Moreover, the coating layer has to retain the anti-microbial properties of Ag.

Waterborne polyurethanes (WPUs) comprise an important polymer material which is widely used in industry as a bulk composite or as a base for the coating. This material is non-toxic, non-flammable, and do not pollute the air. WPU is a binary colloidal system in which polyurethane (PU) particles are dispersed in continuous aqueous media [12–14]. In recent years, the structures and properties of composite thin films consisting of nanosize metal particles dispersed in WPU matrices have been the subject of intense research for practical applications [15–17]. It is reported that Ag nanoparticles (nano Ag) possess the anti-microbial property and when they are dispersed into WPU matrix, the interaction between nano Ag and WPU brings the coating with required physical and chemical properties and also resistant to bacteria [18–27].

## 2. Experimental

**2.1 Materials:** A bullion of Ag with purity of about 99.95% was procured from the Iran Institute of Materials and Energy (MERC). Polyurethane dispersion and the diisocyanate salt were obtained from Arko Paint Co. Iran. Colloidal nano Ag was purchased from Apadana Co. Iran. Sodium chloride (NaCl), lactic acid, L-histidine

monohydrochloride monohydrate (C<sub>6</sub>H<sub>9</sub>O<sub>2</sub>N<sub>3</sub>·HCl·H<sub>2</sub>O), disodium hydrogen orthophosphate anhydrous (Na<sub>2</sub>HPO<sub>4</sub>) and sodium sulphide (Na<sub>2</sub>S) were obtained from Sigma-Aldrich. Bacterial strains of *Streptococcus mutans* (*S. mutans*) (ATCC 25175), *Staphylococcus epidermidis* (*S. epidermidis*) (ATCC 12228) and *E. coli* (ATCC 8739) as well as the standard strain for anti-microbial test were taken from Fungi and Bacteria Collection Center, Iran.

**2.2. Preparation of Ag substrate:** To prepare the Ag substrate, the bullion was rolled into a sheet with the thickness of 1 mm. The sheet was cut to 10 mm-diameter disc by a laser, after which the discs were wet polished with SiC paper to 600 grit.

**2.3. Preparation of WPU and WPU/Ag:** WPU dispersion was diluted to 10 wt% solid content by adding distilled water or colloidal nano Ag. Diisocyanate salt then was added so that the achieved concentration of the diisocyanate salt was 1 wt%. The mixture was then stirred for 30 min. Resulted mixture was either the suspension of WPU or the suspension of WPU/Ag. Concentration of nano Ag in the WPU/Ag was 80 ppm by adding a calculated amount of colloidal nano Ag into the system.

**2.4. Preparation of WPU and WPU/Ag thin films:** Before applying the film coating, it is necessary to remove grease or other fatty pollutants from the sample surface. Therefore, Ag discs were ultrasonically cleaned in analytical grade ethanol for 5 min prior to the coating. Samples were dipped into the suspensions of WPU or WPU/Ag for about 10 s. Thin films dried at 25°C temperature for 7 days. After drying, the film thickness was measured as about 10 µm.

**2.5. Preparation of corrosive media:** Corrosion behaviour of the samples was tested in a simulated solution for human sweat and wet atmosphere containing sulphide pollution. Formulation of artificial sweat was prepared according to the American Association of Textile Chemists and Colorists (AATCC Test Method 15- 2002) [28], with additional sodium sulphide as shown in Table 1.

**Table 1** Chemical composition of the corrosion solution

Chemical composition	Concentration, % (w/v)
L-histidine monohydrochloride monohydrate	0.025
sodium chloride	1.00
disodium hydrogen orthophosphate anhydrous	0.10
lactic acid (88%)	0.097
sodium sulphide	0.35

**2.6. Characterisation of WPU/Ag:** A transmission electron microscope (ZEISS, Germany) was used for studying the morphology and particle size of nano Ag in WPU matrix. A very thin coating film was prepared by dispersing a few drops of WPU/Ag on copper grids which was supported by carbon film and then dried at 60°C for 72 h. The microstructure of the WPU/Ag and dispersion of Ag into the WPU matrix were examined using a MIRA3TESCAN-XMU field-emission scanning electron microscope (FESEM) equipped with EDS analyser.

**2.7. Evaluation of tarnish resistance:** Degree of tarnish resistance of samples was determined by visual examination and the light reflectance measurements methods. The light reflectance of the corroded bare and coated samples was measured using a gloss meter (Konica, MG-268).

Chemical composition of the tarnished specimen was evaluated by EDS patterns. X-ray diffraction measurements were carried out with Philips Mode PW 3710 using Cu-K $\alpha$  ( $\lambda = 0.154$  nm) at 40 KV and 30 mA for surface phases identification after tarnishing.

**2.8. Evaluation of anti-bacterial activity:** Anti-bacterial properties of the samples were determined according to the disc diffusion and the minimum inhibitory concentration (MIC) methods.

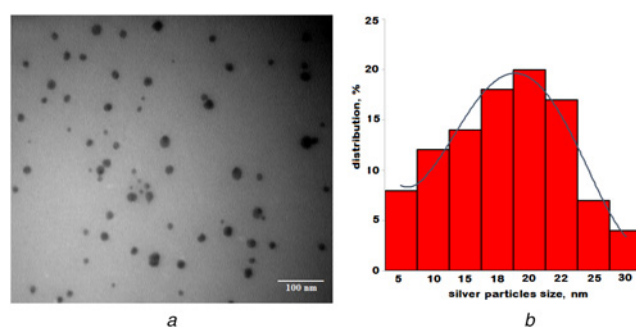
Disc diffusion method was used to appraise the anti-bacterial activity of the samples against *S. mutans* (ATCC 25175), *S. epidermidis* (ATCC 12228) and *E. coli* (ATCC 8739). This method was performed in Luria-Bertani (LB) medium solid agar Petri dish. Samples of the bare as well as the WPU or WPU/Ag coated ones, was situated on bacterial strain genteel agar plate. Agar plate was then incubated for 24 h at 37°C. Inhibition zone was monitored after incubation where the presence of bacterial growth inhibition halo around the samples was absorbed and their diameter in millimetres was measured.

For measurement of MIC, each bacterium culture [*S. mutans* (ATCC 25175), *S. epidermidis* (ATCC 12228) and *E. coli* (ATCC 8739)] was used for the anti-bacterial experiments. Bacteria was activated and then collected by centrifugation. Bacteria were diluted to  $2-5 \times 10^6$  colony forming units per millilitre (CFU/ml). After incubation in LB agar, mentioned samples were placed on agar. After further incubation at 37°C for 24 h, to establish the anti-bacterial activity of samples on the bacterial growth, the bacterial colonies were counted.

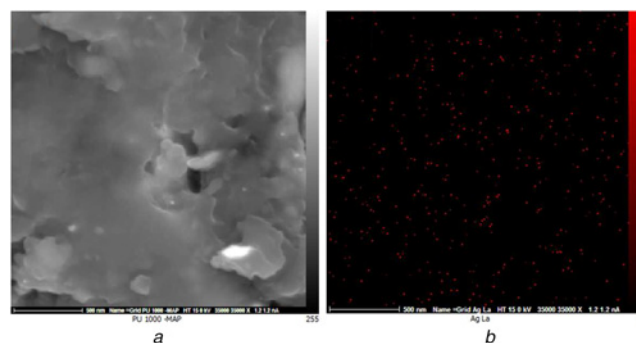
### 3. Results and discussions

**3.1 Characterisation of WPU/Ag thin film:** Transmission electron microscopy image and the resultant particle size distribution of nano Ag in the WPU/Ag are shown in Figs. 1a and b. Mean diameter and size distributions of nano Ag were obtained by measuring the diameter of all particles in the image. It was found that the particle size is <35 nm.

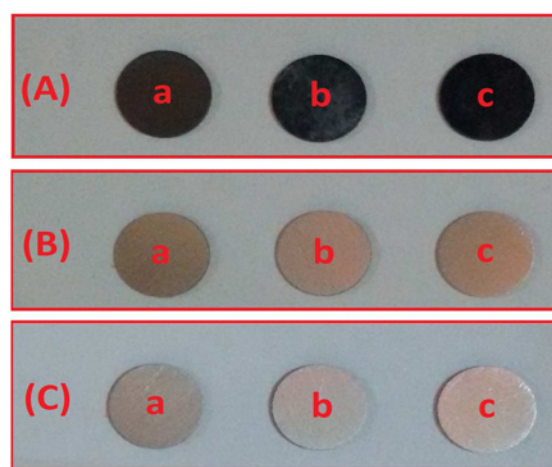
Fig. 2a shows the FESEM topography image of the as-coated WPU/Ag film. From dot-mapping results (Fig. 2b), it is evident that nano Ag is homogeneously dispersed in WPU matrix.



**Fig. 1** Image and the particle size distribution for nano Ag  
a Transmission electron microscopy image and  
b Particle size distribution for nano Ag synthesised in WPU matrix



**Fig. 2** FESEM topography image of the as-coated WPU/Ag film  
a FESEM image of WPU/Ag film and  
b Dot mapping EDS of Ag element, where red indicates the presence of Ag



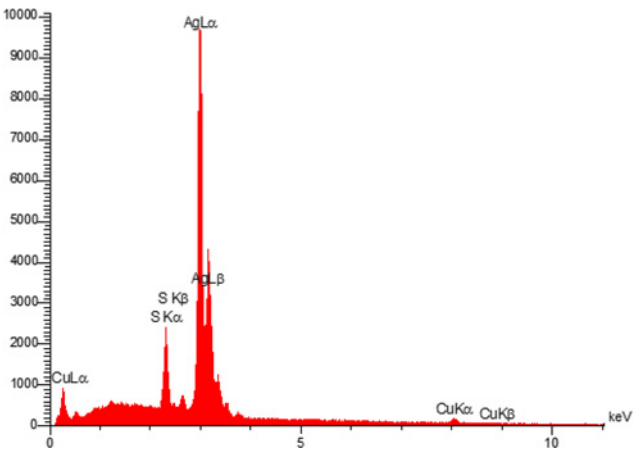
**Fig. 3** Surface states of the Ag (A) bare, (B) coated by WPU/Ag and (C) coated by WPU after  
a 20 min  
b 40 min and  
c 60 min immersion in the tarnishing solution

**3.2. Tarnishing behaviour:** Fig. 3 shows the visual appearance of the Ag samples after tarnishing process. The bare Ag surface was covered by a dark grey layer soon after it was immersed in the corrosion solution. It is shown that after 20 min immersion in the tarnishing solution the bare Ag sample was covered completely with black deposit (Fig. 3A). From this figure, it can be seen that although WPU coating imparted a high resistance to tarnishing, the WPU/Ag coating possessed more tarnishing resistance than WPU coating.

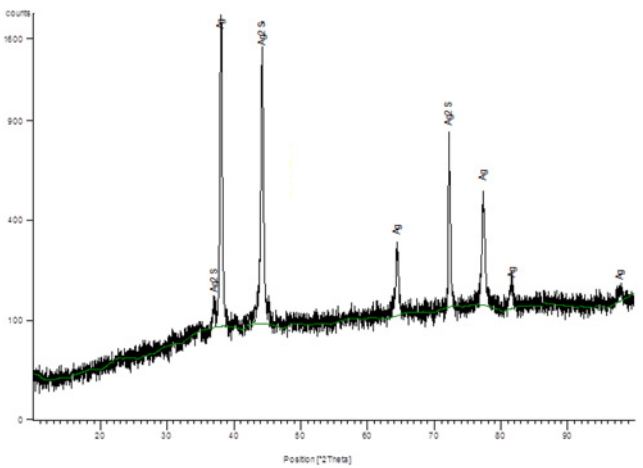
Degree of tarnishing was then determined quantitatively by reflectance measurements. Table 2 shows the loss of reflected

**Table 2** Reflectance change of Ag plates by different coating after 60 min immersion in the tarnishing solution. Values are average for three evaluations

Reflectance, %	Sample		
	Bare	WPU	WPU/Ag
initial reflectance (%)	95 ± 1	97 ± 1	95 ± 1
reflectance (%) after 10 min	66 ± 1.1	96 ± 0.8	94 ± 1
reflectance (%) after 20 min	45 ± 1.2	96 ± 1.5	94 ± 1.2
reflectance (%) after 30 min	32 ± 1	96 ± 1	93 ± 0.8
reflectance (%) after 40 min	27 ± 2	96 ± 1.6	93 ± 1
reflectance (%) after 50 min	25 ± 1.5	96 ± 1.5	93 ± 1.2
reflectance (%) after 60 min	24 ± 1	96 ± 1	92 ± 1.1



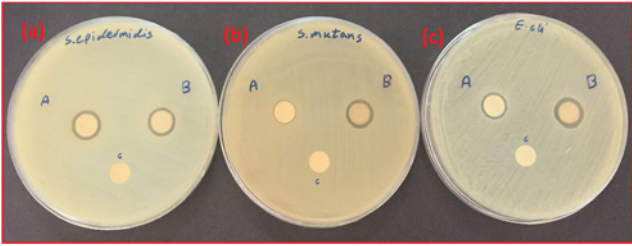
**Fig. 4** EDS pattern of the bare Ag surface after 60 min immersion in the tarnishing solution



**Fig. 5** XRD diffractogram of the bare Ag after 60 min immersion in the tarnishing solution

intensity for different specimen during tarnishing test. Light reflections before tarnishing test were almost the same for all three samples. After 10 min immersion in tarnishing solution, the light reflection of the bare sample was reduced to 66% where the other two were not changed. After 60 min immersion, the light reflection of the bare sample was reduced to about 25% which is almost 70% loss. However, the lost light reflection of the WPU/Ag and WPU after 60 min immersion in tarnishing solution was about 2 and 0.6%, respectively.

Fig. 4 shows the EDS patterns of the bare Ag surfaces. The chemical composition shows the presence of sulphur on the



**Fig. 6** Inhibition zone of the Ag (A) bare, (B) coated by WPU/Ag and (C) coated by WPU against a *S. epidermidis* (ATCC 12228) b *S. mutans* (ATCC 25175) and c *E. coli* (ATCC 8739) after incubated for 24 h at 37°C

**Table 3** Inhibition zone (mm) of the samples against each bacterial strain. Values are average for three evaluations

Sample	Bacteria		
	<i>S. mutans</i> ATCC 25175	<i>S. epidermidis</i> ATCC 12228	<i>E. coli</i> ATCC 8739
bare	0.2 ± 0.1	0.9 ± 0.2	1 ± 0.1
coated by WPU	0	0	0
coated by WPU/Ag	1 ± 0.2	1 ± 0.2	2 ± 0.3

surface of Ag sample after 60 min immersion in the tarnishing solution.

XRD diffractograms of the bare Ag after 60 min immersion in the tarnishing solution is shown in Fig. 5. It indicates the formation of Ag<sub>2</sub>S on the Ag surface. XRD peaks in the wide angle range of 2θ (0° < 2θ < 100°) ascertained that the peaks in 37.02°, 44.22° and 72.16° can be attributed to the Ag sulphide (Ref. Code 00-034-1160).

3.3. Measurement of anti-bacterial properties: Disc diffusion of the bare Ag sample and also coated samples with WPU and WPU/Ag against each bacterium strain after incubation for 24 h at 37°C are shown in Figs. 6a–c and quantified in Table 3. As expected, anti-bacterial effects of the samples are not the same. However, the bare Ag sample showed much better anti-bacterial effect than WPU in all three tests. On the other hand, WPU/Ag coating imparted the best effect compared with the other two samples. Inhibition zone of the Ag sample coated by WPU was about zero for all three bacterial strains. Ag nanoparticles in WPU/Ag coating improved the anti-bacterial effect of Ag.

More detailed research was conducted on the anti-bacterial effect of bare Ag and sample coated with WPU/Ag by MIC. MICs of the bare Ag and coated by WPU/Ag against *S. mutans*, *S. epidermidis* and *E. coli* are shown in Table 4. Percentage reduction in the bacteria was calculated by the following equation:

$$\% \text{ Bacterial reduction} = 100 [(B - A)/B] \quad (1)$$

where *A* is the CFU of bacteria recovered from the inoculated coated Ag by WPU/Ag incubated for 24 h, and *B* is the CFU of bacteria recovered from the inoculated bare Ag incubated for 24 h. These results indicate that the coated Ag by WPU/Ag increased the anti-bacterial activity of the Ag against those bacterial strains studied.

**4. Conclusion:** Ag samples coated by WPU and WPU/Ag imparted relatively high protection against tarnishing in the solution of artificial sweat with additional sodium sulphide. The degree of

**Table 4** Minimum inhibition concentrations of the samples against each bacterial strain

Type of bacteria	Sample	CFU/ml	%Bacterial reduction
<i>S. mutans</i>	coated by WPU/Ag	$3.1 \times 10^6$	36.73%
ATCC 25175	bare	$4.9 \times 10^6$	—
<i>S. epidermidis</i>	coated by WPU/Ag	$4.3 \times 10^6$	10.41%
ATCC 12228	bare	$4.8 \times 10^6$	—
<i>E. coli</i>	coated by WPU/Ag	$3.8 \times 10^6$	25.49%
ATCC 8739	bare	$5.1 \times 10^6$	—

tarnishing was determined by the light reflectance. Protection effectiveness of the WPU and WPU/Ag coatings were about 99 and 98%, respectively.

Interaction of bare and coated Ag with each bacterium culture of *S. mutans* (ATCC 25175), *S. epidermidis* (ATCC 12228) and *E. coli* (ATCC 8739) were determined. In this Letter, the methods used to detect anti-bacterial activity were the disc diffusion and the MIC methods. Results indicate that the WPU/Ag coating increased the anti-bacterial activity of bare Ag against each bacterial strain studied.

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