

The role of monomer on size and facet of crystal silver nanoparticles obtained by plasma technology

Lizhen Yang, Qiang Chen^{*}, Lijun Sang, Zhengduo Wang, Zhongwei Liu

Laboratory of Plasma Physics and Materials, Beijing Institute of Graphic Communication, Beijing, 102600, China

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ABSTRACT

In this paper Ag/SiO_x nanocomposites are fabricated by inductively coupled plasma (ICP) assisted magnetron sputtering technology. During the deposition of matrix the monomer hexamethyldisiloxane (HMDSO) was flowed into the chamber for SiO_x deposition; Ar ions generated in plasma sputtered target to emit Ag nanoparticles. The role of processing parameters, ICP power and the deposition time, on the microstructures and properties of nanocomposites was then investigated in this work. Through FTIR, UV–Visible chemical structures of the nanocomposite Ag/SiO_x were characterized; the Ag status in the surface was analyzed by XPS; the morphology of the matrix was detected by AFM and SEM; and the Ag particle size and crystalline were measured by HRTEM and XRD, respectively. As an application the antibacterial behavior of Ag/SiO_x nanocomposites was also examined in this paper.

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1. Introduction

As well known [1,2] nano-Ag can much effectively prevent the bacteria adhesion by denaturing the adhered bacteria duo to nano-size Ag exhibition of strong toxicity. So the synthesis method of Ag nanoparticles is widely studied recently. Among these methods the magnetron sputtering (MS) technology was prior due to achieving the quick deposition rate. But the easy oxidation of both target and sputtered nano-Ag led to the deposition and collection processes performing in a relatively low pressure chamber [3]. Additionally, the aggregation of sputtered particles, when they nucleate on the surface, makes it difficult to obtain the small diameter particles (1–10 nm in diameter), not to mention the controllable orientation of the crystal nano-Ag [4].

The nano-Ag composites, simultaneously synthesizing organic/inorganic matrix with sputtered metal particles, might be the way not only to solve the oxidation of nano-Ag but also to control the nano-particle size. However, the combination of Ag target-and-electrode sputtering with the simultaneous polymerization of organic polyethylene oxide (PEO)/Ag nanocomposites in radio frequency (RF) plasma enhanced chemical vapor deposition (PECVD) [5] seemed inefficient due to the poisoned electrodes. The process demonstrated a limited deposition rate and a monotonic film.

In our previous work [6], with inductively coupled plasma (ICP) assisted MS, the diameter controllable nano-Ag particles were successfully synthesized in organic/Ag matrix. The nano-Ag sputtered and PEO polymerized were carried out simultaneously during the

matrix formation. Because the polymerized PEO totally encapsulated the nano-Ag particles when they were escaped from the target, the nano-Ag nucleated and grown into big clusters was avoided. We obtained the diameter of the controllable nano-Ag crystals in the Ag/PEO matrix by varying process parameters.

As a sequence work now we replace organic monomer ethylene oxide with hexamethyldisiloxane (HMDSO) for Ag/SiO_x nanocomposite deposition. One of the advantages of using SiO_x as the matrix is that silicon oxide does not remarkably decompose by ion bombardment, which poisons the target. The Ag target shall not be easily oxidized by the decomposed products as appeared in Ag/PEO fabrication. On the other hand, due to the relatively high energy in MS process the as-deposited SiO_x will be pure since the monomer HMDSO is nearly completely dissociated in the MS plasma.

So in this paper we present recent results about the nano-composite Ag/SiO_x. As comparison the previous Ag/PEO matrix was used. We conclude that the monomers absolutely dominated the nano-Ag diameter and crystal orientation. The reason is then explored in the paper.

2. Experiments

The Ag/SiO_x nanocomposite was deposited using ICP assisted direct current (DC) MS equipment as shown in Fig. 1. Herein Ar gas (99.99% in purity) flowing above the target was used to sputter Ag particles; and the volatile hexamethyldisiloxane (HMDSO) inletting below the substrate was used as monomer for SiO_x formation. After flowing into the chamber the monomer was consequently ionized, dissociated, fragmented and condensed by plasma. SiO_x radicals will be formed in gas phase and encapsulate the simultaneously

^{*} Corresponding author. Tel.: +86 10 6026 1109; fax: +86 10 6026 1108.
E-mail address: chenqiang@bigc.edu.cn (Q. Chen).

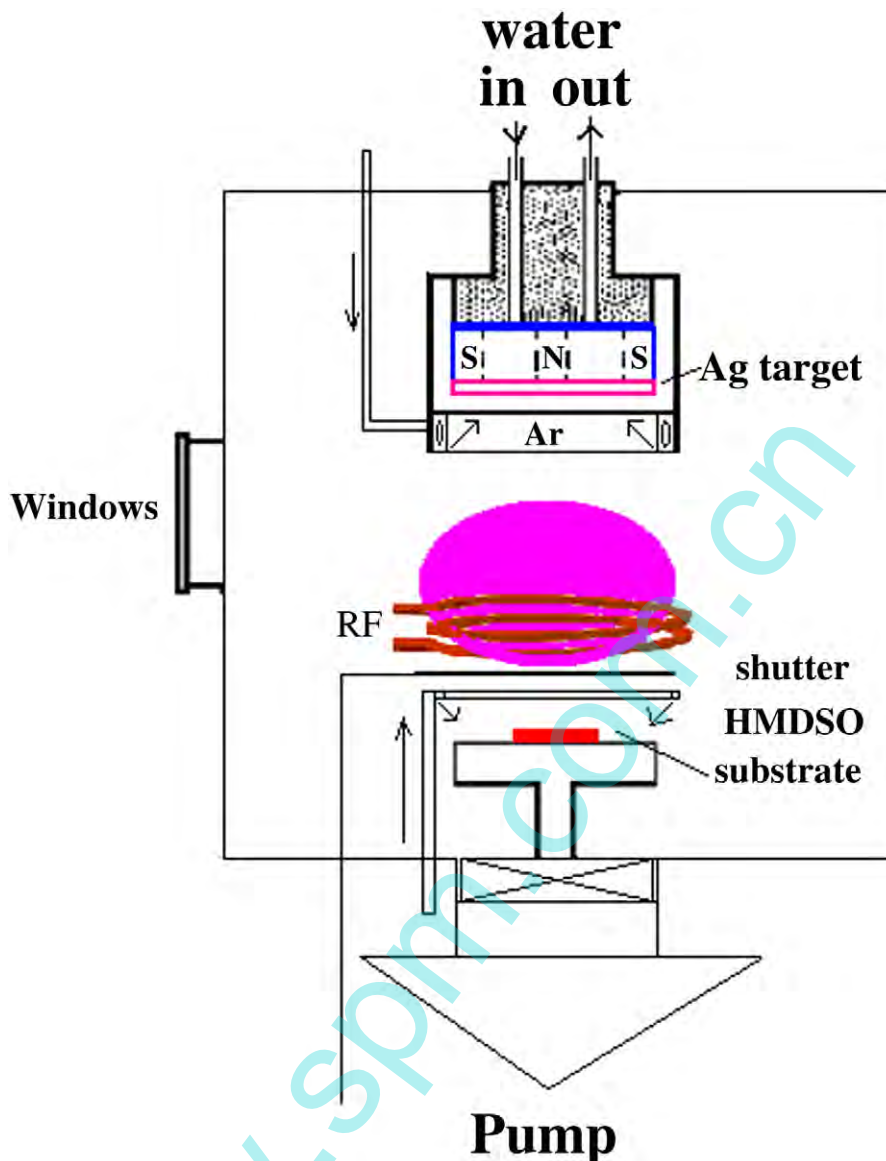


Fig. 1. Schematic diagram of the ICP assisted MS experimental setup.

sputtered Ag particles. The diffusion of clusters was then deposited on the substrate and formed the matrix lastly.

For different purposes, the substrates used in this experiment were glass, quartz slides, p-silicon, and copper mesh as well as KBr tablets. Before mounted on the holder the substrates were ultrasonically cleaned in ethanol, deionized water and acetone for 15 min, respectively (except KBr tablets and copper mesh), then dried up in N_2 gas. Based on the results in the Ag/PEO matrix deposition [6], the size of Ag particles depending on processing parameters was carried out. In SiO_x matrix fabrication the ICP power was varied from 10 to 30 W, and the deposition time was changed from 5 min to 30 min. The as-deposited nanocomposites were characterized by Fourier transform infrared spectroscopy (FTIR, FT-8400, SHIMADZ, Japan) and UV-visible absorption spectrum (HITACHI U-3010/3310) for chemical structures. The morphology was detected by atomic force microscopy (AFM, CSPM4000, Ben Yuan, China) and scanning electron microscopy (SEM). Transmission emission microscopy (TEM, JEM-200CX) was employed for the crystal analysis; and X-ray diffraction (XRD) as well as X-ray photoelectron spectroscopy (XPS) for nano-Ag crystalline and status on surfaces was carried out in a D/max-r A X-ray diffraction instrument and Al $K\alpha$ ion source, respectively.

3. Results and discussion

The influence of ICP input powers on the structure was carried out by varying the applied power from 10 W to 30 W when other processing parameters were fixed, i.e. 20 sccm of Ar flowing rate, 0.5 Pa of the operation pressure, and the ratio of monomer:Ar = 1:1.

Fig. 2(a) shows the FTIR spectrum of the as-deposited nanocomposites versus the ICP input powers. It is clearly observed that the Si–O–Si absorption peak at $\sim 1040\text{ cm}^{-1}$ for stretch vibration is appeared in the spectrum and the intensities are increased with the ICP input powers. Thus resulting that a relatively pure SiO_x can be synthesized in ICP assisted MS plasma.

From Fig. 2(b) the UV-visible spectrum one can see that the peaks at ca. 420 nm caused from nano-particle Ag surface plasmonic resonance are also significant and increased along with the ICP input powers. It implies that Ag sputtered from the target and encapsulated in the matrix improves the surface plasmonic resonance signal. The peak slightly shifted from 422 nm to 429 nm predicting the dependence of particle diameter or the Ag statue on applied powers [7]. The increase of peak intensity along with the ICP input power means that ICP plays an important role when nano-Ag was sputtered and grown on substrates.

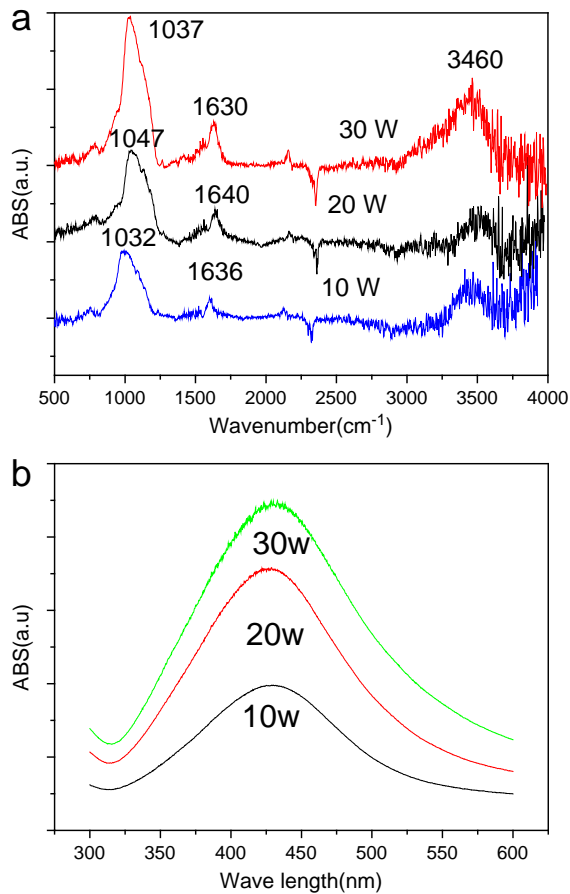


Fig. 2. The FTIR spectrum—a and the UV-visible—b versus ICP input power.

The comparison of AFM images in Fig. 3 provides us that the ICP source also dominated the film topology. The analysis of images indicates that a much compact surface can be formed in the high ICP plasma power condition: a regular array of particles is formed, and the size of the particle is quite uniform. The surface roughness of RMS=0.184 nm in 30 W ICP power deposited film instead of RMS=0.537 nm in 20 W ICP power deposited one suggests that the high power is beneficial for the uniform and compact matrix formation.

The SEM images in Fig. 4 confirm the film uniformity resulted in AFM. A uniform distribution of nanoparticles in the matrix is observed in Fig. 4(a) when the ICP power was 30 W. The Ag particles, in the range of 10 nm to 45 nm derived from Fig. 4(b), were totally encapsulated in the SiOx matrix. Comparing the size of 3–8 nm in diameter of the nano-Ag covered in polymerized PEO [6] the size of the nano-Ag particles is relatively large when the matrix SiOx was used.

Additionally, the high-resolution transmission electron microscopy (HRTEM) in Fig. 5 exhibits that nano-Ag particles grown by ICP assisted MS were still a single crystalline. The clear lattices are viewable in the figure (noted with a white arrow). As a result the crystal statues are remained after the SiOx encapsulation when they were sputtered from the target. From the high resolution image one can also obtain the sizes of particles actually having a big derivation: the small one was sized at ca. 2 nm, whereas the big ones were as large as 40 nm. It is quite different from the polymerized PEO covered nano-Ag, in which the sizes of the nano-Ag were in the narrow range of 3–8 nm, and distributed in relative uniformity.

In Fig. 6 the XRD pattern of the Ag/SiOx matrix clarifies the nano-Ag crystal formation. The visual peaks at 38.2°, 44.4°, 64.6°, and 77.6° correspond to Ag crystal facets of (111), (200), (220) and

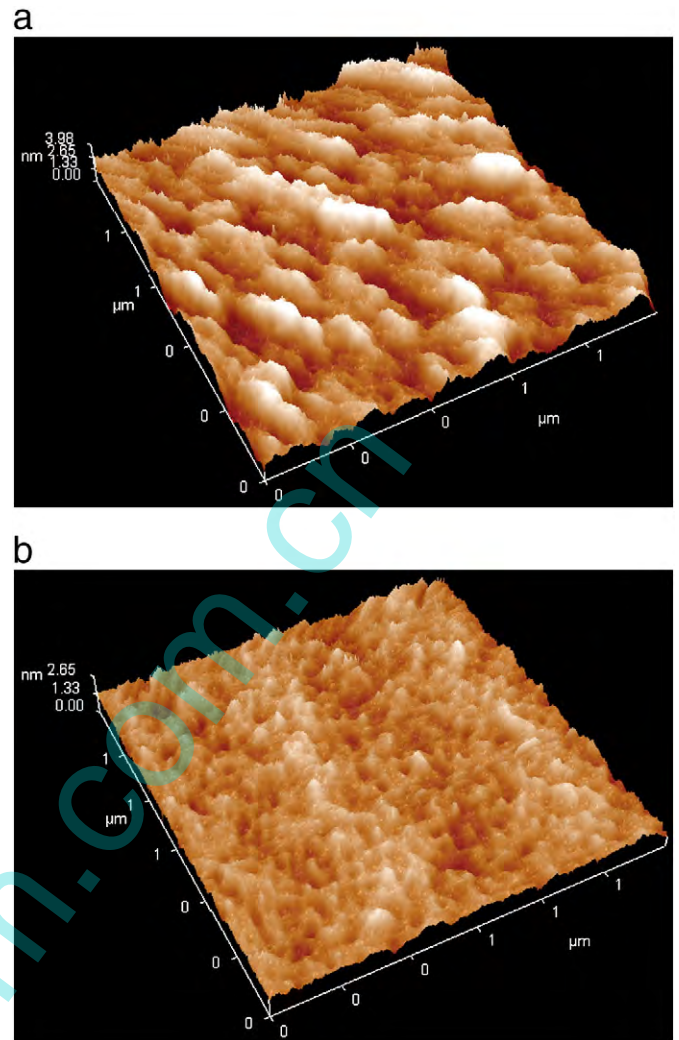


Fig. 3. The AFM images of the nanocomposite films deposited in ICP assisted MS when the ICP power was a—20 W; b—30 W.

(311), respectively. Compared with the standard XRD pattern of Ag (JCPDS cards 4-0783) [8], we found that the nano-Ag particles' growth in ICP assisted MS is face center cubic (FCC). Analyzing the pattern furthermore we find that particles are still preferential to (111) orientation growth like that we found in PEO encapsulated Ag particles [7], but the ratio of $I_{(111)}/I_{(200)}$ is low to 6.7, instead of 8.3 in PEO covered Ag matrix.

XPS had been used to investigate Ag particles on the surface. Fig. 7 shows the XPS spectra of the Ag nanocrystals deposited at the ICP power of 30 W. The peak of Ag 3d was deconvoluted in Gaussian into Ag 3d_{5/2} and 3d_{3/2} bonding energies (BE) at 368.5 eV and 374.3 eV, respectively, which clearly indicate that nano-Ag is existed at atomic status. A little bit of blue shift of the electron BE of Ag corresponded to the increase of an average domain size of Ag nanoparticles. The XPS spectrum confirms our above TEM results that the diameters of deposited Ag nano particles were increased in the SiOx matrix.

From Figs. 5, 6, and 7 we can deduce that crystal and the size of the nano-Ag synthesized by the encapsulation method depend on the matrix component. The chemical structure of the matrix dominating the nano-Ag crystalline might be relative to the induction of active groups on the crystal growth and the thermal diffusion. The polar group inducing behavior was found in chemical synthesis of nano-Ag

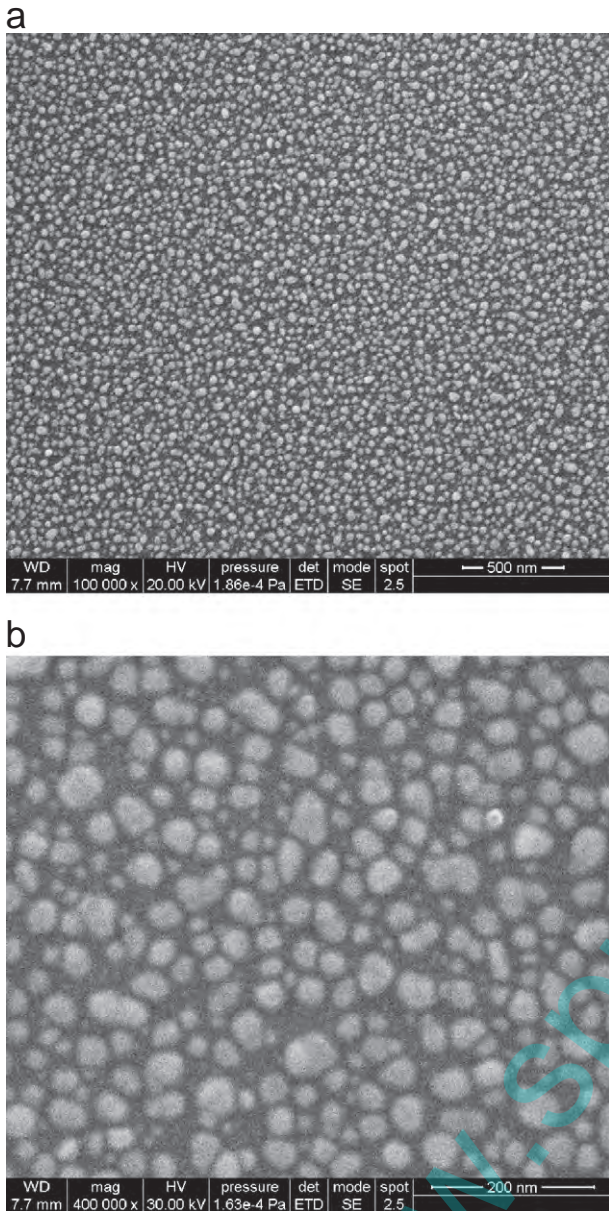


Fig. 4. The SEM topography images of nanocomposite Ag/SiOx when the ICP power was 30 W. a—the scale is 500 nm; b—the scale is 200 nm.

[9]. It was noticed that the lattice and the facet of nano-Ag, in particular (111) facet, can be induced growth by the special chemical materials. With poly(vinylpyrrolidone) as the preventive agent the orientation (111) of nano-Ag rods can be facily synthesized [9]. Then, we assume that the derivation of nano-Ag orientation covered in the PEO and SiOx matrix might also result from the different chemical structures because the deposition condition was identical in the matrix formations.

Besides the sputtered particle thermal diffusion, which is an essential momentum for the cluster formation, the different hydrophilicities of the PEO and SiOx matrix might also be one of the main factors. The water contact angle (WCA) of the as-polymerized PEO was lower than 20°, whereas the SiOx films demonstrated the WCA over 90°. It shall be investigated in detail in the future.

As one of the applications of the nano-Ag matrix the antibacterial behavior was examined by the foil method [10]. The bacteria of *Escherichia coli* (ATCC 25922) and *Staphylococcus aureus* (ATCC 6538) were used in this experiment as done in the Ag/PEO matrix test.

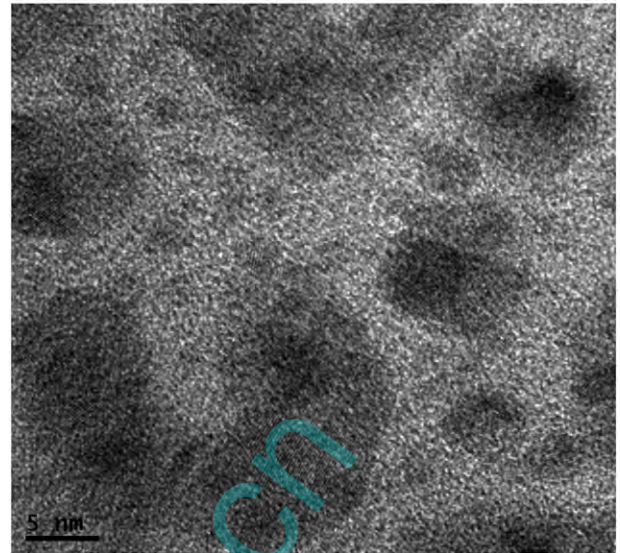


Fig. 5. HRTEM images of nanocomposite Ag/SiOx deposited by ICP enhanced MS (the scale is 5 nm).

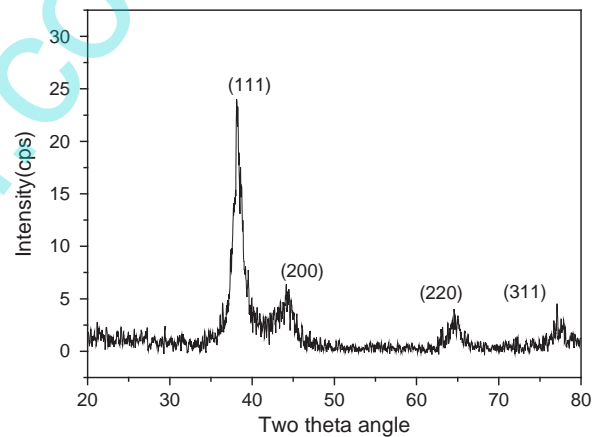


Fig. 6. XRD pattern of nanocomposite Ag/SiOx.

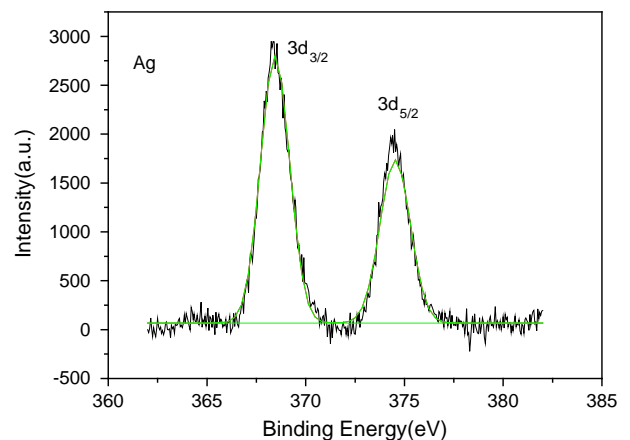


Fig. 7. XPS spectra of Ag 3d peaks when ICP was 30 W deposited SiOx embedded Ag nanoparticles (solid lines indicate the as-deposited and the dot lines are simulated in Gaussian mode).

Table 1
The calculation of anti-bactericidal rate of Ag/SiOx nanocomposites.

Sample	Item					
	The mold resistance of Ag/SiOx					
	<i>Escherichia coli</i>			<i>Staphylococcus aureus</i>		
	Average viable count (individual)		Antibacterial rate, 24 h (%)	Average viable count (individual)		Antibacterial rate, 24 h (%)
0 h	24 h		0 h	24 h		
Scan blank	328	338	100%	856	855	>80%
The sample received	0	0		150	147	

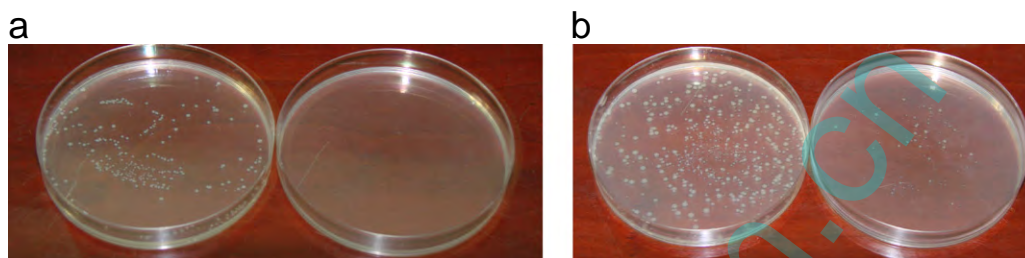


Fig. 8. The photos of anti-bacterial test of nanocomposite Ag/SiOx for 24 h (a—*Escherichia coli*; b—*Staphylococcus aureus*).

The efficiency of the anti-bacteria is calculated following the equation:

Anti – bacteria rate(24 h)

$$= \frac{\text{average viable count scan blank} - \text{average viable count sample received}}{\text{average viable count scan blank} - \text{average viable count sample received}}$$

From Table 1 and Fig. 8 we notice that the nanocomposite Ag/SiOx demonstrates a high efficiency in anti-bacterial behavior for both gene negative and positive bacterium. The matrix almost killed the total bacteria in the test period.

However, based on recent results we still think that it is impossible to distinguish the crucial role of efficient anti-bacteria behavior of the Ag/PEO or Ag/SiOx matrix played by the particle size or the orientation of Ag (111) facet, even though the diameter and the orientation in both matrices were significantly different. The possible reason is that the high concentration of nano-Ag in matrices killed the bacteria and masked the influences from the facet and the size. It is suggested the labeled nano-Ag with florescence sensor shall be proper to trace the immigration of particles in cells. Then it shall be convincing to explain the high efficient antibacterial behavior of nano-Ag matrix played by Ag particles not Ag ions, and to decide the role of size or orientation of nano-Ag. This purpose is under processing in our future work.

4. Conclusions

In this paper the ICP assisted MS method was employed again to prepare nanocomposite Ag/SiOx. It is found that the plasma process parameters influence nanocomposite Ag/SiOx structure and morphology as done in Ag/PEO. But compared to the results in the Ag/PEO matrix we find that the covering materials dominate the Ag particle

size and the facet orientation. We think that derivation of the nano-Ag in different matrices was caused from the active properties of the materials, like the surface polarity and chemical structure as well as thermal diffusion coefficient. Due to the high concentration of nano-Ag migrated from the matrix into the liquid for bacteria incubation, it is impossible to distinguish the role in the anti-bacteria behavior played by the particle size or their orientation until now.

Acknowledgments

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