



Schottky barrier dependent antimicrobial efficacy of silver nanoparticles



Manle Wang^{a,b}, Huiliang Cao^{b,*}, Fanhao Meng^b, Xiaobing Zhao^c, Yunxia Ping^{a,*}, Xiaoying Lü^d, Xuanyong Liu^{b,*}

^a School of Materials Engineering, Shanghai University of Engineering Science, Shanghai 201620, PR China

^b State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China

^c School of Materials Science and Engineering, Changzhou University, Changzhou 213164, PR China

^d State Key Laboratory of Bioelectronics, School of Biological Science and Medical Engineering, Southeast University, Nanjing 210096, PR China

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ABSTRACT

The antimicrobial efficacy of silver nanoparticles (Ag NPs) modified material was generally governed by the dose of the particles or their capability to release silver ions. Here, it was found that Ag NPs acted against microbes by cooperating with tantalum oxide (TAO) in a Schottky barrier dependent manner. Size tunable Ag NPs were in situ fabricated and immobilized on TAO coating by a silver plasma immersion ion implantation process (Ag PIII). The antibacterial efficacy of these Ag NPs was reversely dependent on their size, that is large particles (~ 20 nm) were more efficiency than small ones (~ 10 nm) in defeating the invasion by bacteria. The result is consistent with the prediction of Schottky-Mott theory, which rectified the electron transfer nature across the interfaces between Ag NPs and the TAO substrate.

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1. Introduction

Silver nanoparticles (Ag NPs), serving as a disinfection drug, are currently integrated into various metal oxide semiconductors (MOS), including titanium oxide [1–3], zinc oxide [4], niobium oxide [5], tantalum oxide [6]. Under the illumination of light, the Ag NPs/MOS hybrids can disrupt bacterial cells more rapidly and efficiently because Ag NPs can act as electron traps, which facilitate the separation of photo-generated electron (e^-)/hole (h^+) pairs in MOS [7]. However, in the absence of photons, it was generally concluded that the antibacterial efficacy of these composites was governed by Ag NPs themselves or their capability to release silver ions [1–3]. Recently, the bactericidal activity of hybrid Ag/TiO₂ particles in the dark was found greater than either bare titania or pure silver particles, suggesting that the heterostructure may produce a synergistic effect independent of light illumination [8]. Even so, the mechanism involved has yet to be revealed.

On the other hand, tantalum oxide (TAO), because of its excellent compatibility to bio-systems, was widely explored for

biomedical applications [9], but its antibacterial property needs to be improved [6]. Accordingly, in the present study, Ag NPs were in situ fabricated and immobilized on a TAO coating by using the silver plasma immersion ion implantation process (Ag PIII). The results demonstrated that the TAO-supported Ag NPs had strong antibacterial activity in the dark independent of silver release.

2. Materials and methods

The tantalum oxide (TAO) coatings were fabricated by a plasma spraying technique (APS-2000, Switzerland). Powders of Ta₂O₅ were used to deposit the tantalum oxide layers onto commercial pure titanium (10 mm square plates with a thickness of 1 mm). The spraying parameters were similar as our previous report [10]. The as-sprayed TAO coatings were further treated by a silver plasma immersion ion implantation process (Ag PIII), thus, size tunable Ag NPs were in situ fabricated and immobilized on TAO coatings by Ag PIII at 30 kV for 0.5 h (designated as Ag 0.5 h), 1.0 h (designated as Ag 1.0 h), and 1.5 h (designated as Ag 1.5 h). The Ag PIII procedure was detailed in our previous study [10]. In order to evaluate the kinetics of silver release in Ag PIII groups, the samples were incubated for up to 28 days in 10 ml of physiological saline (0.9% NaCl, pH 7.4) at 37 °C without stirring, and the amounts of silver in the resulted solutions were determined by inductively

* Corresponding authors.

E-mail addresses: hlc@mail.sic.ac.cn (H. Cao), xyping@sues.edu.cn (Y. Ping), xyliu@mail.sic.ac.cn (X. Liu).

coupled plasma optical emission spectrometry (ICP-OES).

The antibacterial activities of the samples were evaluated by using strains of *Escherichia coli* (*E. coli*, ATCC 25922). The samples were sterilized in an autoclave at 121 °C for 40 min. The bacterial cells at a concentration of $\sim 1.0 \times 10^6$ cfu/ml were seeded onto the samples to a density of 0.06 ml/cm², and incubated at 37 °C for 24 h. The adherent bacteria were further dehydrated following the details described before [11], and observed by scanning electron microscopy (SEM). And the reduction rates were calculated according to the low magnification SEM images.

3. Results and discussion

The surface morphology of the TAO coatings, being treated by Ag PIII, was observed by SEM. The as-sprayed TAO coating was very rough on the micro-scale (Fig. 1A) but smooth on the nano-scale (the insert in Fig. 1A). After Ag PIII, nanoparticles were precipitated homogeneously on all the sample groups (Fig. 1B, C and D), but their size and distribution were different among the groups. There were about 4.05×10^9 particles per square centimeter on Ag-1.5h, while that on Ag-0.5h and Ag-1.0h were 6.76×10^9 and 8.31×10^9 , respectively. Only one group (with a mean diameter of ~ 10 nm, Fig. 1E and F) of particles can be classified on Ag-0.5h and Ag-1.0h, whereas there were two groups (with a mean diameter of ~ 20 nm and ~ 30 nm, Fig. 1G) on Ag-1.5h. Moreover, the X-ray photoelectron spectroscopy (XPS) spectra (Fig. 1H) evidenced that the chemical states of silver on all groups were about the same. And the Ag 3d doublet at 374.20 eV (Ag 3d3/2) and 368.19 eV (Ag 3d5/2) can be assigned to metallic silver [12].

E. coli cells were introduced onto the samples to evaluate their antimicrobial efficacy. Large amount of microbial cells were observed on the TAO control (Fig. 2A), while that on PIII-treated TAO was reduced apparently (Fig. 2B, C, and D), with the Ag-1.5h group ranked the best (The reduction rates for Ag-0.5h, Ag-1.0h, and Ag-1.5h were approximately 74%, 69%, and 99% respectively). In addition, abundant of intercellular tubes (which were important to bacterial communication [13]) can be detected among the microbes on the TAO group (arrowed in Fig. 2A), while cytosolic content leakage and cell lysis were prevalent on the Ag PIII treated

groups (arrowed in Fig. 2B, C, and D). This result indicated that the immobilized Ag NPs acted against bacteria by interrupting their inter-communication and disrupting the integrity of the bacterial cell envelopes. Moreover, the Ag PIII groups released minimal of silver, indicating that bactericidal action of these Ag NPs was independent of silver release.

Therefore, it was proposed that the antibacterial activity of the Ag PIII groups was related to the behavior at the interfaces of Ag NPs and the TAO substrate. The electron transfer nature across the interfaces of Ag NPs and TAO was monitored by photoluminescence (PL) spectra. Decreased PL signal was detected on all the Ag PIII groups as compared with that of the TAO control (Fig. 3), indicating that the Ag NPs served as efficient traps for electrons. In addition, the PL signal of Ag-1.5h was much weaker than that of Ag-0.5h and Ag-1.0h (Fig. 3), suggesting that large Ag NPs were better than small ones in trapping electrons. This interface behavior of Ag NPs and TAO can be explained by the Schottky-Mott theory [14], in which the Schottky barrier height (ϕ), is the difference between the work-function of silver (~ 4.26 eV [16]) and electron affinity of tantalum oxide (~ 3.3 eV [17]). And the maximum amount of electrons trapped by a silver particle, Q_{Ag} is given by [15],

$$Q_{Ag} = \frac{2\pi\epsilon_0\epsilon_v}{e} \cdot D_{Ag} \cdot \phi \quad (1)$$

where e is electron charge, ϵ_0 is the static dielectric constant of TAO (~ 25 [18]), ϵ_v is the vacuum permittivity, and D_{Ag} is the diameter of the silver particle. Accordingly, the amount of electrons trapped by Ag NPs with diameters of 10 nm and 20 nm was about 740 and 1280, respectively. This prediction is consistent with the profiles of PL spectra (Fig. 3), which demonstrated that large Ag NPs were more effective than small ones in decreasing the PL signal of TAO coating.

Eq. (1) well illustrates the direct effect of size on charging the silver particles, yet the point is that the bacteria were cultured on all groups in the dark, and there were no photo-generated electrons available for triggering toxic reactions to disrupt the adherent microbes. In fact, extracellular electron transport is an important procedure in bacteria by which they produce adenosine triphosphate (ATP), the energy for maintaining the metabolism and growth of microbes [19]. Accordingly, due to the Schottky

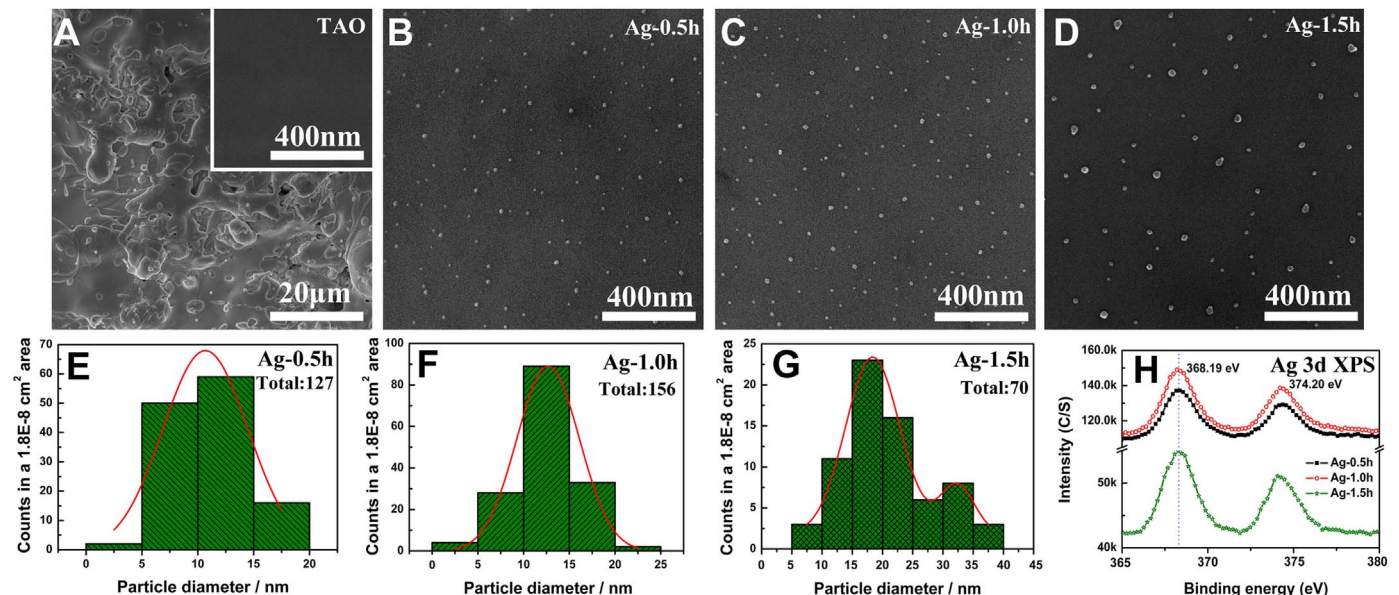


Fig. 1. Surface morphology of TAO (A), Ag-0.5h (B), Ag-1.0h (C), and Ag-1.5h (D) groups, and the size distribution profiles of the precipitated particles on Ag-0.5h (E), Ag-1.0h (F), and Ag-1.5h (G), and the XPS Ag 3d spectra of the Ag PIII treated groups (H).

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