Silver-Hydroxyapatite Composite Coatings with Enhanced Antimicrobial Activities Through Heat Treatment

X. Zhang,[1] W. Chaimayo,[2] C. Yang,[1] J. Yao,[1] B. L. Miller,[2] and M. Z. Yates[1,3]

[1]Department of Chemical Engineering, University of Rochester
[2]Department of Dermatology, University of Rochester
[3]Laboratory for Laser Energetics, University of Rochester

Ceramic coatings find applications in corrosion protection, thermal insulation, altering wetting, electrical insulation, and enhancing chemical or biochemical surface properties. This study focuses on the electrochemical synthesis of nanoscale coatings of the ceramic hydroxyapatite (HA), a calcium phosphate with the stoichiometric formula $Ca_{10}(PO_4)_6(OH)_2$. The HA coating was synthesized from an aqueous electrolyte solution using a process called cathodic electrolytic deposition.[1] After forming the coating on a titanium cathode, a second cathodic electrochemical reaction was used to reduce silver ions from an electrolyte solution and deposit metallic silver nanoparticles onto the HA coating. The resulting silver-hydroxyapatite (Ag-HA) composite coating was investigated for its ability to kill bacteria. Coatings of HA on titanium find commercial application in dental and orthopedic implant applications, where the HA layer is known to enhance the rate of integration of metallic implants with surrounding bone tissue. One of the most serious complications of implant surgery is infection of the bone. The coatings show promise in lowering the chance of infection without the use of antibiotics that create antibiotic-resistant strains of bacteria.

Figure 1 shows electron microscopy images of the HA coating on titanium before and after electrochemical reduction of silver. The HA grows on the surface as nanoscale rod-shaped crystals, as seen in Fig. 1(a). The metallic silver nanoparticles can be seen in Fig. 1(b) as spherical nanoparticles that form preferentially on the tips of the HA nanocrystals. Although HA is known to be an electrically insulating material, our previous results show that HA can conduct electricity if the applied potential is high enough.[2] The fact that metallic silver forms on the tips of the HA indicates that electrons are passing through the HA crystals in

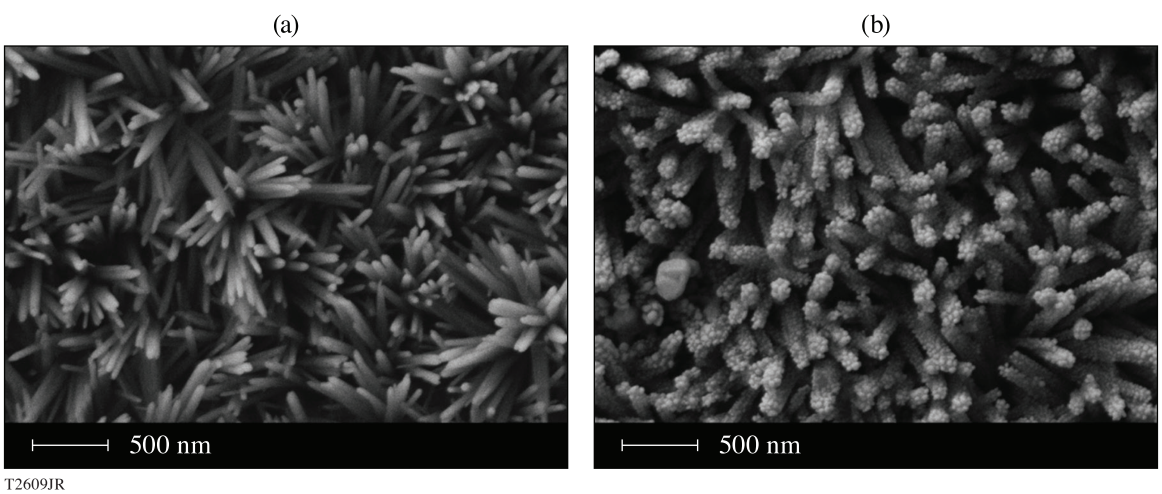

Figure 1
Scanning electron microscope (SEM) images of Ag-HA coating (a) before and (b) after electrochemical deposition of Ag nanoparticles.

order to electrochemically reduce silver cations (Ag^+) in solution to metallic silver (Ag^0). The HA crystal phase was confirmed with x-ray diffraction, and the metallic silver on the surface was confirmed with x-ray photoelectron spectroscopy.

Composite Ag-HA coatings, similar to those shown in Fig. 1, were found by our group to kill bacteria.[3] However, the effectiveness of the coating in killing bacteria varied significantly from sample to sample. The antibacterial activity of silver is related to the dissolution of silver ions into solution. It was postulated that the release of silver ions would be enhanced by the formation of silver oxide, which undergoes the following reactions:

$$Ag_2O + H_2O \longrightarrow 2AgOH \tag{1}$$

$$AgOH \longrightarrow Ag^+ + OH^- \tag{2}$$

To test this hypothesis, the Ag-HA coatings were heated in air at 170°C for 8 h to form an oxide layer. The formation of silver oxide on the surface after heating was confirmed using x-ray photoelectron spectroscopy. Next, the growth of *Escherichia coli* (*E. coli*) was monitored in the presence of HA and Ag-HA coatings before and after the heat treatment.

Light scattering was used to characterize the relative number of bacteria versus time, as shown in Fig. 2. The reported optical density is proportional to the number of bacteria in the sample. The results demonstrate that heat treatment enhances the antibacterial activity and reduces the variation in antibacterial activity from sample to sample. The results demonstrate a simple route to form coatings that may simultaneously enhance integration of implants with surrounding bone tissue while reducing the likelihood of post-surgical bone infection.

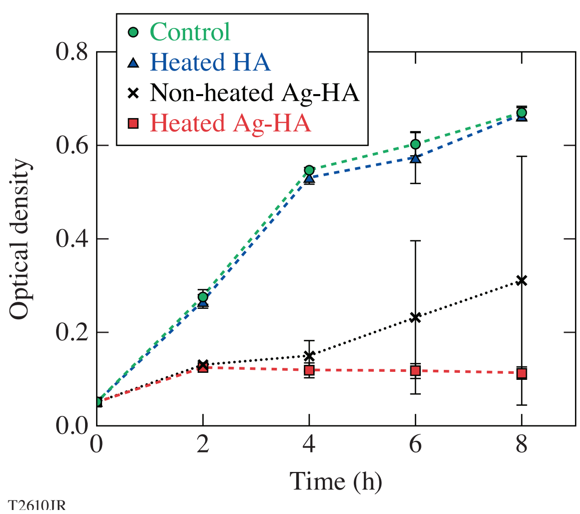

Figure 2
The growth of *E. coli* when exposed to HA and Ag-HA coatings measured by light scattering. Data points indicate the mean value, and error bars indicate standard deviation.

This material is based upon work supported by the Department of Energy National Nuclear Security Administration under Award Number DE-NA0003856, the University of Rochester, and the New York State Energy Research and Development Authority.

1. I. Zhitomirsky, Adv. Colloid Interface Sci. **97**, 279 (2002).
2. C. Fu *et al*., Chem. Mater. **27**, 1164 (2015).
3. C. Fu *et al*., Surf. Coat. Technol. **301**, 13 (2016).