Antibacterial design for Preventing Peri-implantitis -Synthesis Silver Nanoparticles using Chitosan as scaffold-

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Abstract

The silver nanoparticles were synthesized on a bioactivated metallic glass surface using chitosan as a scaffold. The sphere shape nanoparticles 20 to 50 nm in radius were arranged uniformly on the surface. Some of the silver nanoparticles grew anisotropic by using citric acid and transformed their shape to triangular nanoplates. The silver nanoplates exposed {111} facet with the most densely packed surface which was expected to show an efficient bactericidal effect.

1. Introduction

Ti-based Bulk metallic glasses ($Ti_{40}Zr_{10}Cu_{36}Pd_{14}$) having a high corrosion resistance exhibited a lower Young modulus than that of conventional Ti alloy, and it is recognized as one of promising candidates for a new implant material[1)]. However, this material could not be joined directly to hard tissue due to its too high chemical stability. Our group conducted a Hydrothermal-Electrochemical process to Ti-based BMG at the temperature lower than its glass transition point and succeeded in modifying the surface to bioactive by forming titanate nanomesh layer[2)]. This surface layer was bioactive but seemed to be unfavorable due to the plaque breeding on their rough surface. The plaque could cause peri-implantitis after the operation, and therefore, an antibacterial property should be induced to the bioactive nanomesh layer on Ti-based BMG surface.

In this study, Ag nanoparticle, one of the representative antibacterial materials, was formed on bioactive nanomesh layer surface intermediated by chitosan layer. Chitosan is Crustacean-derived polymer and expected to be used in various bio applications due to its antibacterial and bioactive properties. It is also recognized as purifier since its chain can be coordinated and work as a chelate complex. In this study, biocompatible chitosan layer was used as a kind of adhesive agent of Ag particle on titanate nanomesh layer.

2. Experiment (or Theory)

Ti-based BMG substrates were treated by Hydrothermal-Electrochemical (HE) process and amorphous titanate nanomesh were formed on their surfaces. The chitosan was modified on nanomesh layer surfaces by dip coating process (CD). Ag particles are grown on chitosan layer by immersing in $AgNO_3$ aqueous solution (IS). The pH of solution is adjusted by adding NH_3, which make silver ions stable as $[Ag(NH_3)_2]^+$. It was also attempted to synthesize silver nanoplates in a solution containing 10 times more citric acid than $AgNO_3$.

3. Results and discussion

3.1 Sample after HE and CD

After HE treatment, a layer of amorphous sodium titanate with a nanomesh structure was formed on the metallic glass surface. A curtain like structure was observed on part of the mesh structure after CD treatment; The existence of functional groups of chitosan detected by FT-IR measurement (no figure) indicated that the nanomesh surface was coated with chitosan.

3.2 Sample after IS excluding citric acid

The pH of 10 mM $AgNO_3$ solution was adjusted to 7.8 by adding aq. ammonia, and the CD samples were immersed in this solution at 90 °C for 12 hours. Fig.1 shows SEM image in which the sodium titanate nanomesh structure and the aggregated nanospheres 20-50 nm in diameter were observed in SEM images. XPS measurement showed that these particles were not oxide or hydroxide but Ag metal. These Ag nanospheres were not produced by pyrolysis only but were synthesized by the functional groups of chitosan as reducing agent. FT-IR showed that some $-CH_2OH$ transformed to -COOH.

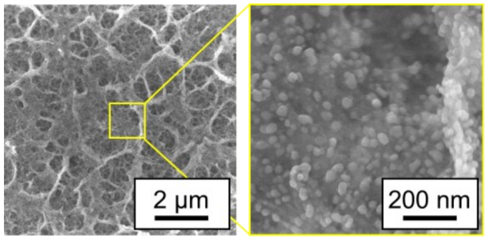

Fig.1 SEM image of sample prepared at 90 ºC (pH=7.80 $AgNO_3$ controlled by adding aq. ammonia)

3.3 Sample after IS including citric acid

The pH of solution including $AgNO_3$ and citric acid was adjusted to 8.5 by adding aq. ammonia. The CD samples were immersed in this solution at 90 °C for 24 hours. Fig.2 shows SEM image in which particles less than 200 nm were scattered around. There were several types of shapes for Ag nanoparticles like nanospheres, nanorods, and triangular nanoplates. This shape variation of Ag nanoparticles was caused by the anisotropic growth of crystals induced by citric acid attachment. It is supposed that the growth rate slowed down due to the stabilization of silver ions as ammine and citrate complexes.

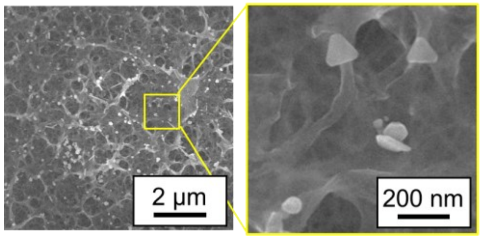

Fig.2 SEM image of sample prepared at 90 ºC (pH=8.50 $AgNO_3$ controlled by adding aq. Ammonia)

4. Conclusions (or Summary)

Ag nanoparticles were synthesized on titanate nanomesh layer intermediated by the chitosan layer. The triangular Ag nanoplates were obtained using citric acid, and it was expected to have high antibacterial effect.

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