Formation of Titanium Oxide Layers Decorated by Gold Nanoparticles on the Surface of Ti6Al4V Alloy

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Abstract

Titanium and titanium alloys have been mostly used as biomaterials especially for dental implants due to their great combination of high mechanical strength and high corrosion rate. However, one of the most important drawbacks is the insufficient osseointegration. Therefore, the main purpose of this study is to improve the surface properties of Ti6Al4V by anodic oxidation and gold decoration. Initially, the surface of the alloy was anodized to thicken TiO2 layer. Subsequently, gold nanoparticles were produced using Turkevich method. Gold decoration on the oxidized surface were achieved by immersion of the alloy in gold solution after the oxidized alloy surfaces were activated by APTES solution. As a result of surface treatment highly rough surface containing thick oxide layer composed of 20 nm gold nanoparticles in addition to silane groups. In-vitro tests displayed no apatite formation in 20 days. Therefore, further tuning is needed on the surface in terms of oxide layer and gold nanoparticles.

1. Introduction

Metals are the one of the class of biomaterial that is commonly used in load bearing applications due to their relatively high strength and high endurance limit. Among the metallic class of materials titanium is mostly preferred due to its high corrosion resistance, non-toxic properties, good mechanical property and high biocompatibility compare to well-known stainless steel and Co-Cr alloys. However, as rest of the metallic biomaterials, titanium surface needs to be surface modify to enhance bone attachment on the surface thereby decreasing the healing time after surgery operation. Titanium and its alloys are generally used in medical implants such as knee, hip joint and dental implants [1]. The need for dental implants have been increased due to growth of elderly population. Generally dental implants’ success has been tried to be increased by designing its structure and surface modification. After machining the desired shape, the surface is change by physical and chemical methods. Physical methods such as physical vapor deposition (PVD), thermal spraying, ion implantation and deposition and chemical methods which are chemical vapor deposition (CVD), sol-gel coating, electrochemical treatment (anodic oxidation) are usually employed. Physical methods such as grinding, and texture formation are applied to increase surface roughness. On the other hand, chemical methods such as double etching by various acids produce oxide layer in addition to increased surface roughness [2]. However, because of acid residue left on the surface even after cleaning, the use of such techniques is still questionable. Therefore, the surface of titanium alloy should be modified or coated with a layer having high biocompatibility.

In this study, the aim is the improving of biocompatibility of Ti6Al4V alloy, by some surface treatments. Initially, anodic oxidation is carried out to form titanium oxide layer on which gold nanoparticles were decorated after they have been produced by Turkevich method [3]. The resultant surface layer was characterized by SEM, XPS and TEM. Mineralization tests were conducted for 5,10,20 days in simulated body fluid (SBF).
2. Materials and methods

2.1. Materials

Ti₆Al₄V alloy bar (supplied from ACNIS International, France) was used as starting sample. Before surface treatments, specimens were ground with grinding papers. Then, they were cleaned by acetone, alcohol and deionized water respectively.

2.2. Oxidation

Anodization was applied to obtain thick layer of titanium oxide. Ground and cleaned samples were anodized at 120V in deionized water for 3 minutes until blue color was obtained. All anodizing experiments were conductors in a titanium anodizer (Painful Pleasures, USA).

2.3. Surface Treatment with APTES Solution

Oxidized surfaces were treated with %2 3-Aminopropyltriethoxysilane (APTMS). Silane groups were attached to surfaces by immersing the samples in APTMS for 1 hour at 37 °C. Then, surface activated samples were kept at 120°C for 1 hour.

2.4. Production of GNp’s and their attachment on the surface

1 mole Chloroauric acid HAuCl₄ is added to 18ml deionized water and stirred until the solution boils, which takes approximately 15min. Then, the solution was reduced by adding of 1 mole Trisodium citrate (Na₃C₆H₅O₇) and stirred until color turns into red [3]. Afterwards, silanized alloys were immersed in the gold solution obtained by Turkevich methods for 1 hour which is followed by washing in deionized water.

2.5. Simulated Body Fluid (SBF) Test

To investigate apatite formation abilities of surfaces the samples were kept in SBF for 5, 10, 20 days at a temperature and pH value of 37 °C and 7.42, respectively.

3. Result and Discussion

3.1. Starting Oxidized Surface

Figure 1 shows 3D-AFM image of the surface after anodization. Sample was observed the contain scratches which were left from grinding operation.

Figure 1. AFM image showing 3D topography of anodized surface.

3.2. Synthesized Gold Nanoparticles

As a result of using Turkevich method spherical gold nanoparticles were obtained, figure 2(a). The size distribution was highly uniform and particles had around 20 nm average particle size. Although most of the particles were highly spherical hexagonal shaped gold nanoparticles were observed 2(b).

Figure 2. TEM image of produced gold nanoparticles.

Figure 3. UV-visible spectra of gold solution.

UV-vis spectra (figure3) taken from gold solution displayed an absorption peak at around 520 nm which is equivalent to 20 nm particle size.
Manufactured gold nanoparticles were highly crystalline and defect free as shown in figure 4.

Figure 4. High resolution TEM pictures of gold nanoparticles.

3.3. Gold Decorated Surfaces

After immersion of the samples in gold solution, gold nanoparticles were stuck on APTMS modified surface well; however, their distribution was not homogeneous (figure 5.).

Figure 5. SEM image of gold decorated titanium alloy surface (inlet: TEM image of gold nanoparticles)

Attachment of gold nanoparticles was also verified by XPS results shown in figure 6. Additionally, surface of the sample was become rich in carbon and nitrogen probably due to treatment with APTMS solution.

Figure 6. XPS result of sample that gold coated.

3.4. SBF Test

After keeping the samples in SBF, unexpectedly neither appetite formation nor any change was observed in 20 days as shown in figure 7. Further SBF tests should be conducted for longer durations to ensure mineralization abilities of surfaces. Additionally, further purification of gold solution may be needed just before decoration on gold nanoparticles on surface.

Figure 7. SEM results of gold coated in SBF 5, 10, 20 days respectively.

4. Conclusion

- Manufactured gold nanoparticles were highly spherical and highly crystalline.
- UV-vis spectra displayed absorption peak at 520 nm which was equivalent to 20 nm average particle size.
- Gold nanoparticles covered the whole surface, but their distribution was not homogeneous.
- No apatite formation was observed in 20 days probably due to insufficient immersion time in SBF.
References


