# Water Glass Coating on Ti Substrate for improving Cell behaviors of Dental Implant

Solip Park[1], Sungsu Chun[1], Sooyoung Lim[1], Ekavianty Prajatelistia[1], Myunwhan Ahn[2], Dong Jun Yang[3], Hong-In Shin[4], Sukyoung Kim[1]

[1]School of Materials Science and Engineering, Yeungnam University, Gyeongsan, Korea

[2]Department of Orthopedics, College of Medicine, Yeungnam University, Daegu, Korea

[3]Megagen Implant, Gyeongsan, Gyeongbuk, Korea

[4]Department of Oral Pathology, School of Dentistry, Kyungpook National U. Daegu, Korea

sykim@ynu.ac.kr

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**Abstract.** Ti and its alloys are widely used as a material for orthopedic and dental implants since it shows outstanding corrosion resistance and good biocompatibility. However, they require a long period of time to bond with the surrounding living bone. In order to enhance early fixation and osseointegration with surrounding bone tissue in a human body, various coatings on Ti surface have been studied for many years. It is known the existence of functional groups such as Si-OH and Ti-OH on Ti surface accelerates the formation of HAp layer formation in SBF solution. Moreover, it has been well known that the collagen coating on Ti surface is effective for enhancing the initial cell attachment. But, the chemical coating of collagen on Ti surface is not easy.

In this study, water glass (WG) coating was conducted to form of silanol functional groups (Si-OH) on Ti surface and characterized with SEM and EDS for the examination of surface morphology and chemical composition, respectively. XPS and FT-IR are used to confirm the content of hydroxyl groups on Ti discs. The WG coated Ti discs were immersed in revised SBF solution to examine the ability of HAp formation. Also the cell test was performed to confirm the biocompatibility through cell attachment and proliferation. From SEM images, the WG coating layer was well adhered to the Ti substrate. The composition of WG coated layer was changed from sodium silicate to pure silica by the treatment of HCl solution via the ion-exchange. This result was confirmed by EDS analysis. From XPS and FT-IR results, the amount of hydroxyl group on Ti surface was depended to the vol% of WG and the number of WG coating. The higher vol% of WG and number of WG coating, the more hydroxyl groups exist on the Ti surface. It is expected that the hydroxyl groups on Ti surface will be strongly bonded with collagen. Thus, collagen coated Ti dental implants may be enhanced the cell behaviors..

## Introduction

Titanium metal and titanium alloys are commonly used as a material for orthopedic and dental implants since it shows outstanding corrosion resistance and good biocompatibility. However, they require a long period of time to bond with the surrounding living bone. In order to enhance early fixation and osseointegration with surrounding bone tissue in a human body, various coatings on Ti surface have been studied for many years. It is known the existence of functional groups such as Si-OH and Ti-OH on Ti surface accelerates the formation of bone-like HAp layer in SBF solution[1-3]. Moreover, it has been well known that the collagen coating on Ti surface is effective for enhancing the initial cell attachment[4]. But, the chemical coating of collagen on Ti surface is not easy because of chemical difference between collagen and Ti metal. It was suggested that the hydroxyl groups on Ti surface can be strongly bonded with collagen and collagen coated Ti dental implants may be enhanced the cell behaviors.

It is reported that titanium and titanium alloys which were exposed to NaOH aqueous solution and subjected to subsequent heat treatments form a bonelike apatite layer on their surfaces in a simulated

body fluid (SBF) solution with ion concentrations nearly equal to those found in human blood plasma. As in SBF, these NaOH and heat-treated metals form the apatite in the living body, and bond to bone through the apatite layer[10].

Sol-gel glass coating is a useful method for the preparation of a bioactive coating at relatively low temperature but the coatings are fragile. Water glass is well-known as an adhesive agent and simply adheres to substrates by heating at only 300 ℃. In addition, silica glass derived from water glass easily releases soluble silica in aqueous solution and contains numerous Si-OH groups, which was reported to induce HCA nucleation in a body fluid[5, 6].

In this study, water glass (WG) coating was conducted to form of silanol functional groups (Si-OH) on Ti surface. It is expected that the silanol functional groups on Ti surface will be strongly bonded with collagen. Thus, collagen coated Ti dental implants may be enhanced the cell behaviors.

## Materials and Methods

The preparation procedure of Ti substrate was shown in Fig. 1. Commercially pure Ti discs (grade 4) were polished using a series of SiC grit sandpapers. The polished samples were blasted using 250-300 μm HAp grit sizes and then washed in 1vol% of HCl aqueous solution to detach the impurities and residue of HAp on titanium disc surfaces for 2mins. The samples were cleaned in an ultrasonic bath to remove the impurities on titanium discs. The washed samples were etched in 5M NaOH solution for 24hrs and then cleaned in an ultrasonic bath. The washed samples were heat-treated at a rate of 5℃/min and kept at 600℃ for 1hrs. The heat-treated samples were coated with 10, 15 and 20 vol% water glass solution using spin coater at 5000rpm for 1min. The water glass coating were heat-treated at a rate of 0.5℃/min and kept at 300℃ for 2hrs. After heat treatment, the samples were etched in 0.1M HCl aqueous solution for 1hr in an ultrasonic bath glass to form Si-OH functional groups on titanium discs by etching out the $Na_2O$ of water glass.

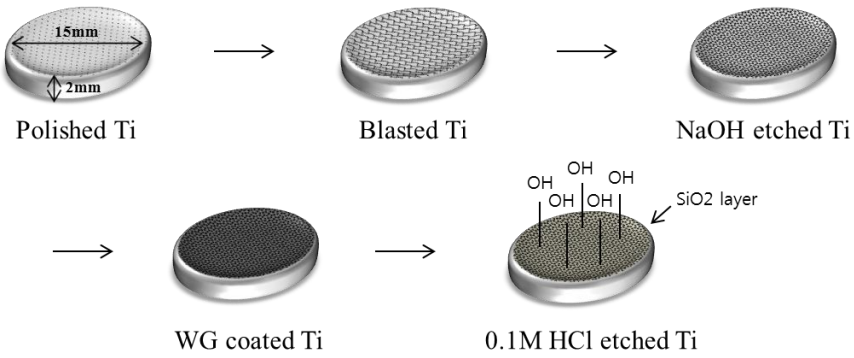


Fig. 1 Schematic diagram of preparation of Ti substrate

Si-OH functional groups were confirmed using XPS (X-ray photoelectron spectroscopy). The saturated vapor of trifluoroacetic anhydride (TFAA) was found to react with hydroxyl group on surface at 25℃ for several minutes[7]. The TFAA treatment on Ti substrate for XPS analysis was shown in Fig. 2.

The water glass coated on titanium discs were characterized with SEM and EDS for the examination of surface morphology and chemical composition, respectively. XPS and FT-IR are used to confirm the content of hydroxyl groups on Ti discs. The WG coated Ti discs were immersed in revised SBF solution to examine the ability of HAp formation. Also the cell test was performed to confirm the biocompatibility through cell attachment and proliferation.


Fig. 2 Experimental procedure of Ti surface treatment with TFAA treatment for XPS analysis

**Results and Discussion**

Fig. 3 shows FE-SEM pictures of the titanium disc surfaces after various treatments. From SEM examination, we confirmed that the NaOH etched-heat treated Ti substrates (NH) had a macro roughness from HAp blasting and micro roughness from 5M NaOH etching.The bioactive $SiO_2$ layer coated using water glass was found on as-coated with 10, 15 and 20 vol% of WG and heat-treated Ti substrate which is etched with 0.1M HCl. The WG coating layer was well attached on the Ti substrate and bioactive $SiO_2$ layer derived from water glass solution adhered to the titanium discs surface without bubbles and cracks between glass and titanium surface. As the vol% of water glass and the number of water glass coating were increased, the glassier surface on the specimen was observed.

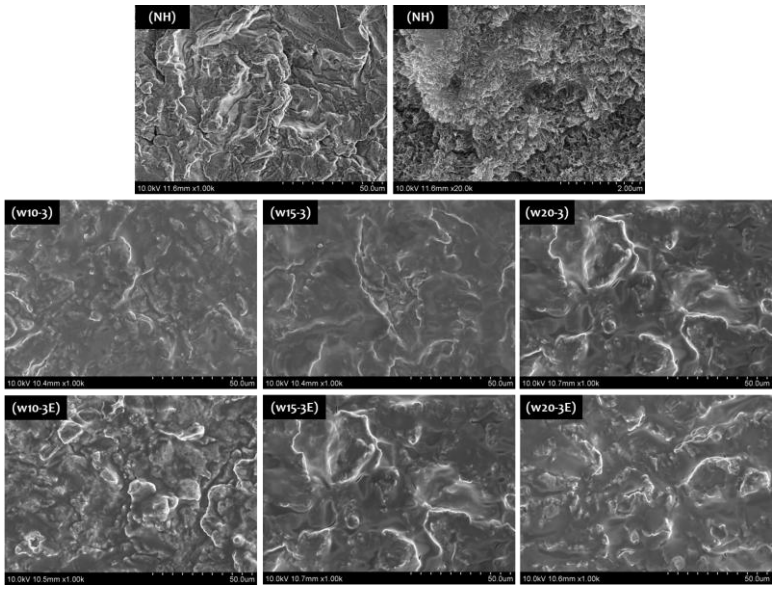


Fig. 3 SEM of NaOH etched-heat treated Ti (NH), as-coated with 10, 15 and 20 vol% of WG and heat-treated Ti ; [ non-etched (w10-3,w15-3, w20-3) and etched with 0.1M HCl (w10-3E, w15-3E, w-20-3E) ;
[These samples were treated with 3 times of WG coating in different concentration.]

The composition of WG coated layer was changed from sodium silicate to pure silica by the treatment of HCl solution via the ion-exchange. The silica layer was formed on the surface of titanium disc coated water glass through the heat-treatment 300˚C for 2h and the subsequent ion-exchange process using a diluted 0.1M HCl solution for 1hr in ultrasonic bath. The Na ions were found on 0.1M HCl untreated water glass coated titanium surface, but not found on 0.1M HCl treated surfaces. The composition of water glass coated layer on titanium discs was changed from sodium silicate to silica through the ion-exchange in the 0.1M HCl solution. The Si/Na ratio in as-coated samples and Si ion content in HCl treated samples were increased with the vol% of water glass and the number of water glass coating. This result is confirmed by EDS analysis in Fig. 4.

The Si/Na ratio same among each concentration of water glass (Fig. 4) must be similar. However, the Si/Na ratio was increased with the vol% of water glass and the number of water glass coating. The reason was that the Na ion have a property of evaporation of alkali content such as $Na_2O$. -알칼리의 휘발성 질

The Si/Ti ratio results were shown in Fig. 5. From the Si/Ti ratio results, $SiO_2$ coated layer became thicker with the increase of the concentration of WG and number of WG coating. It is expected that the higher Si/Ti ratio may formed the more hydroxyl groups on HCl treated samples.

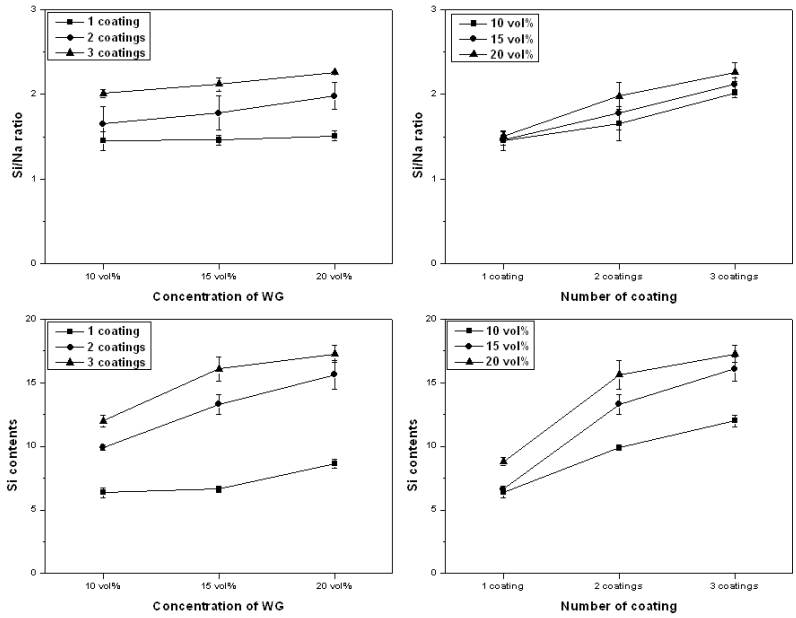


Fig. 4 Si/Na ratio of coated and then heat-treated Ti (above) and Si contents of heat-treated and then etched with 0.1M HCl (under)

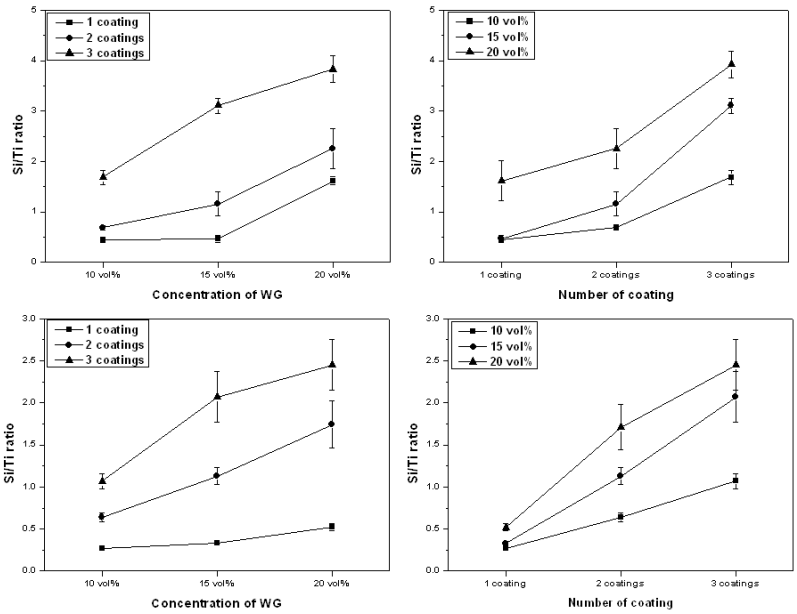


Fig. 5 Si/Ti ratio of coated and then heat-treated Ti (above) and heat-treated and then etched with 0.1M HCl (under)

We prepared XPS sample to confirm the amount of hydroxyl groups on 0.1M HCl treated sample, by using trifluoacetic anhydride (TFAA) treatment. Since between hydroxyl group on the 0.1M HCl treated-titanium disc and fluorine of TFAA were reacted, the amount of formation of Si-OH group could be confirmed by the fluorine peak in XPS data. XPS result showed that the fluorine contents in HCl treated samples were increased with the vol% of water glass and the number of water glass coating as shown in Fig. 6. This result indicates that the amount of hydroxyl group on water glass coated and then HCl treated samples

was depended to the vol% of water glass and the number of water glass coating. The higher vol% of WG and number of WG coating, the more hydroxyl groups exist on the Ti surface.

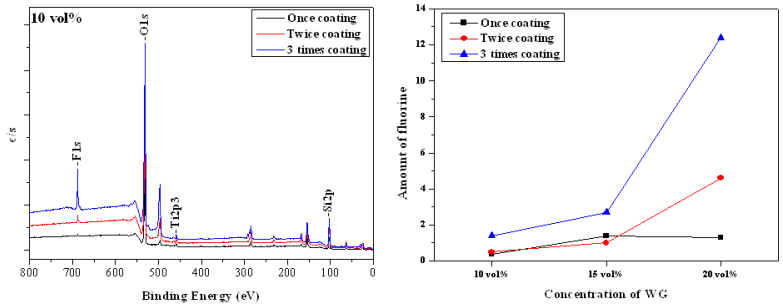


Fig. 6 XPS spectra of water glass coated Ti discs treated with 0.1M HCl and TFAA (left) and atomic % of fluorine on water glass coated, HCl treated and then TFAA treated Ti (right)

## Conclusions

The prepared Ti disc was well covered with water glass (WG) coating layer and surface of Ti discs were glassier with the increasing with the concentration of WG and the number of WG coating. The bioactive $SiO_2$ layer coated using water glass (WG) [Sodium silicate, $mNa_2O{\cdot}nSiO_2{\cdot}$ $(100\text{-}m\text{-}n)H_2O$ (m=9.0~10.0, n=28~ 30.0)] was found on Ti substrates. The chemical composition of WG coated layers was changed from sodium silicate to pure silica in the HCl solution via the ion-exchange. Si/Na ratio in as-coated samples and Si ion contents in HCl treated samples had the trends of increasing with the concentration of WG and the number of WG coating.

From the Si/Ti ratio results, $SiO_2$ coated layer became thicker with the increase of the concentration of WG and number of WG coating. It is expected that the higher Si/Ti ratio may formed the more hydroxyl groups on HCl treated samples.

The contents of hydroxyl groups on the samples were confirmed by trifluoacetic anhydride (TFAA) treatment using XPS. The amount of hydroxyl group on Ti surface was depended to the vol% of WG and the number of WG coating. The higher vol% of WG and number of WG coating, the more hydroxyl groups exist on the Ti surface.

Thus, it is expected that the hydroxyl groups on Ti surface by WG coating will be strongly bonded with collagen. The collagen coated Ti dental implants may be enhanced the cell behaviors.

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