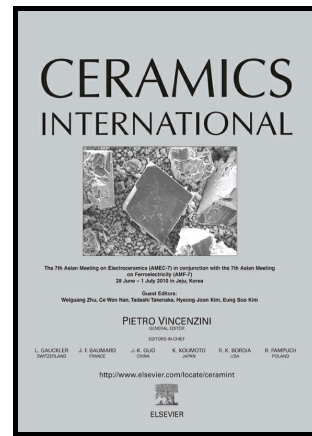


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**Synergistic reinforcement of surface modification on improving the bonding of  
veneering ceramics to zirconia**

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**Abstract**

Veneering ceramics should be strongly bonded to zirconia core in order to achieve successfully long-term clinical practice. Indeed, to pursue the high zirconia core–veneering ceramic bonding is still a concerned issue. In this regard, this study was to treat zirconia surface using a 3 wt%  $\text{Si}_3\text{N}_4$  solution in 4 M NaOH and to investigate the effect of soaking time (5, 10, and 20 days) on the surface properties of zirconia and shear bond strength between zirconia and veneering ceramics. The residual veneering ceramics on zirconia surfaces and failure modes were also examined after fracture. The results showed that the phase composition of zirconia before and after surface modification was not changed. The elemental mapping and depth profiling consistently revealed the soaking-time-dependent Si content on the zirconia surface. The surface roughness of zirconia was significantly ( $P < 0.05$ ) increased with the increasing soaking time. When zirconia was treated for 10 days, the shear bond strength value of 27.4 MPa was significantly ( $P < 0.05$ ) higher than the control (18.6 MPa), associated with greater remaining amounts of veneering ceramics on the zirconia surface. The failure mode of the treated zirconia was almost the mixed failure. On the basis of the data, surface modification using  $\text{Si}_3\text{N}_4$  in NaOH solution for zirconia core could be a simple and effective method for enhancing the veneering ceramic–zirconia bonding.

*Keywords:* zirconia; veneering ceramics; surface modification; silicon nitride; shear bond strength

## 1. Introduction

The high-strength zirconia ( $ZrO_2$ ) has been applied to fixed prosthodontics because of its unique properties, such as high resistance to wear and distortion, chemical stability, thermal stability, and biocompatibility [1–6]. Although metal–ceramic (MC) dental crowns have been widely used due to good mechanical properties, zirconia coping or framework constructed with other dental ceramics to form porcelain-fused-to-zirconia (PFZ) prostheses is also developed to replace the traditional MC prostheses [2,3,7,8]. To achieve successfully long-term clinical practice veneering ceramics should be strongly bonded to the  $ZrO_2$  core. However, according to several follow-up clinical studies [1,2], the failure rate of the veneer-core dental restorations is very high. Among the failure cases, 15–25% of them were caused by the detachment and crack of the veneer layer [1,2], implying the urgent need for novel routes to fabricate the dental restorations with higher durability by enhancing the bonding strength between zirconia core and ceramic veneers [9,10].

Apart from liner application [11] and ceramic veneer type [12,13], the core-veneer bonding is apparently influenced by the surface properties of the  $ZrO_2$  core [8,9,13,14]. For example, the increment in the surface area through sandblasting and mechanical grinding can enhance the mechanical interlocking between zirconia substrate and veneering ceramics to improve the bonding strength [8]. Unfortunately, the mechanical grinding and sandblasting process applied on the surface of zirconia can induce the occurrence of phase transformation from tetragonal to monolithic [10,15] and produce the micro-cracks into the zirconia [16]. The coexistence of tetragonal and monolithic phase on the surface of zirconia can jeopardize the mechanical stability between zirconia and veneering ceramics because of the difference in thermal expansion coefficient of the two phases, which leads to the

formation of internal stress in zirconia substrates [5,10,15].

Surface modifications other than sandblasting have been considered as candidate routes, including coating techniques [14,18] and hot etching soaking [5,10,19], to change surface morphology and chemistry of zirconia, which in turn might enhance the bonding of veneering ceramic to zirconia. Elsaka [10] reported that the hot etching soaking could be considered as alternative surface treatment to sandblasting for zirconia cores to avoid the tetragonal-monoclinic (t-m) phase transformation. Madani *et al.* [17] found that the silica-coating or aluminosilicate coating on zirconia not only improved the microtensile bond strength to veneering ceramic compared to the sandblasted group, but also it would not trigger the occurrence of the t-m phase transformation. Nevertheless, there have been few previous studies on the effect of the synergistic coating-hot etching techniques on the bonding of zirconia to veneering ceramic. In this study, attempts have been made to precipitate a roughened silica layer on the  $ZrO_2$  surfaces via soaking the specimens into a  $Si_3N_4$  solution in 4 M NaOH followed by heat treatment for changing surface characteristics of  $ZrO_2$ , thereby improving the  $ZrO_2$  core-veneering ceramic bonding. In addition to the microstructure, phase composition, roughness, and depth-profiling analysis of the treated  $ZrO_2$  surface, the shear bond strength of the surface modified zirconia and veneering ceramics was evaluated.

## 2. Materials and methods

### 2.1. Preparation of specimens

The commercially available pre-sintered yttrium stabilized zirconia blocks (VITA In Ceram YZ-55, Vita Zahnfabrik, Bad Sackingen, Germany) as core substrates were used to produce squared-shape specimens using a low speed cutting machine

(BUEHLER IsoMet, Lake Bluff, IL, USA). One surface of each specimen was polished with #800, #1000, and #1500 SiC abrasive papers by a grinder-polisher (BUEHLER), and then ultrasonically cleaned in distilled water for 20 min and air-dried. Zirconia specimens were sintered to 1530 °C at a rate of 17 °C /min and held for 2 h, and then cooled to room temperature at 17 °C/min according to the manufacture's recommendation. The final dimension of the zirconia specimens was 10 (length) × 5 (width) × 3 (thickness) mm<sup>3</sup>. A total of 40 specimens were then divided into 4 groups including a control and three experimental groups. Similar to the method proposed by Lung [14], in the experimental groups the zirconia specimens were soaked in a 4 M NaOH solution containing 3 wt% silicon nitride (Si<sub>3</sub>N<sub>4</sub>, 99% purity, Sky Spring nanomaterials Inc., Houston, TX, USA) at 60 °C for 5, 7 and 10 days. After that, specimens were heat-treated to 1400 °C at a heating rate of 10 °C/min and held for 2 h. In contrast, the control group was not soaked and heat-treated.

A liner of IPS e.max ZirLiner (Ivoclar Vivadent AG, Liechtenstein) with thickness of 0.1 mm was applied to the surface of each zirconia core, and then sintered by a furnace (Programat P310, Ivoclar Vivadent AG, Principality, Liechtenstein) according to the manufacturer's recommendations. Afterwards, a square-shaped wax pattern with dimension of 4 x 4 x 2 mm<sup>3</sup> was attached on the zirconia core with a liner. The wax pattern-attached zirconia core was invested by the phosphate bonded investment (Calibra express, Protechno, Spain) with a liquid/powder ratio of 0.25. The cast mold at 1 h after the start of mixing was put into a preheating furnace at 700 °C (Programat EP 5010, Ivoclar Vivadent AG, Liechtenstein), and then heated up to 900 °C at a rate of 60 °C/min for 15 min. The IPS e.max ZirPress fluorapatite glass-ceramic ingot (LT, Ivoclar Vivadent AG, Liechtenstein) was heated and pressed into the mold by pressing technique according

to the instruction of manufacturer. The mold was placed outside the furnace to cooling, when the temperature of the furnace was dropped to 700 °C. The investment was removed using sandblasting with alumina particle at pressure of 0.2 MPa, and the sprue was out from the specimen. The final dimension of heat-pressed ceramics was of 4 x 4 x 2 mm<sup>3</sup>.

## 2.2. Phase composition and morphology

The phase composition of zirconia with and without surface modification was detected at a scan rate of 2°/min using an X-ray diffractometer (XRD; Bruker D8 SSS, Madison, WI, USA) instrument equipped with CuK $\alpha$  radiation. The surface morphology of the specimens and interfacial morphology between the heat-pressed ceramics and zirconia substrate were examined using the field emission scanning electron microscope (SEM; JSM-6700F, JEOL, Tokyo, Japan).

## 2.3. Elements analysis

The Zr and Si element distribution on the Si<sub>3</sub>N<sub>4</sub>-treated surfaces was collected under a SEM quipped with an energy-dispersive X-ray spectroscopy (EDS) in the element mapping mode. To further characterize the chemical composition of the treated zirconia, a secondary neutral mass spectrometry (SNMS) system (INA-X, SPECS GmbH, Berlin, Germany) was used for the depth profiling of the specimens.

## 2.4. Surface roughness

The surface roughness values (Ra) of each specimen at three measuring locations were determined using a surface analyzer (Surfcom 50A, Tokyo Seimitsu, Tokyo, Japan) with a traverse length of 2.4 mm and a cut-off length of 0.8 mm. The five

specimens were examined for each group.

### 2.5. Shear bond strength

A universal testing machine (AG-1000E, Shimadzu, Kyoto, Japan) at a crosshead rate of 1.0 mm/min was employed to carry out the shear bond strength until specimens debonded. The ten specimens were measured for each condition. The shear bond strength (SBS) value of each specimen was calculated using the equation  $SBS \text{ (MPa)} = \text{load (N)} / \text{area (mm}^2\text{)}$ .

### 2.6. Fractured surface analysis

The fractured surface of zirconia after shear strength test was examined using optical microscope to evaluate the failure (adhesive, mixed, and cohesive) of specimens. Adhesive failure occurred along zirconia surface and cohesive failure was within veneering ceramic, while mixed mode was regarded as a combination of both adhesive and cohesive failures. Image analysis software (Image-Pro<sup>®</sup> Plus, MediaCybernetics, Inc., MD, USA) was used to measure remaining amounts of the veneering ceramics on zirconia surfaces.

### 2.7. Statistical analysis

One-way ANOVA statistical analysis, followed by the Scheffe's multiple comparison test, was used for evaluation of significant differences in surface roughness, shear bond strength, and the remaining amount of veneering ceramics on the zirconia surfaces. Statistical analysis was performed using SPSS 14.0 software (IBM, Armonk, NY, USA) for Windows. The significance was set as 0.05.



### 3. Results

#### 3.1. Phase composition

Fig. 1 shows the XRD patterns of  $\text{ZrO}_2$  specimens before and after surface modification for 5, 10, and 20 days. It could be observed that four characteristic peaks located at  $2\theta$  of  $30.2^\circ$ ,  $35.1^\circ$ ,  $50.2^\circ$ , and  $60.1^\circ$  were assigned to the tetragonal zirconia in the control [6]. There were no new characteristic peaks in the XRD patterns of treated specimens. Interestingly, the intensities of the tetragonal peaks of zirconia were reduced after surface modification, in particular for the 5-day sample.

#### 3.2. Morphology and chemical composition

As seen in Fig. 2, the SEM micrographs indicated that the surface morphology of specimens would be altered by tailoring the soaking time in  $\text{Si}_3\text{N}_4$  solution. In compared with the morphology of the control, it seems that a layer of amorphous material was occurred on the surface for the 5-day specimen, leading to the obscure image. Similarly, it was also on the 10-day specimen. Concerning the 20-day specimen, some of the crystal grain and grain boundary on the  $\text{ZrO}_2$  surface appreciably disappeared, as well as a roughened surface. On the other hand, the results of EDS/elemental mapping (Fig. 2) demonstrated the presence of Zr element as major components in the control group, in addition to O element (unshown). After surface modification, signals of Si emerged in the elemental mapping images. The enrichment of Si signal on the 5-day specimens was found in comparison with the other two specimens.

To have a further insight into composition, the SNMS depth profiles of specimens before and after surface modification were also examined, as shown in Fig. 3. It was reasonable to consider that the concentration of Zr and O elements on the surface of

the control reached the saturation (Fig. 3a). Depth profiling of the 5-day specimen showed the presence of Si on the surface with about 1  $\mu\text{m}$  depth (Fig. 3b), while the depth of the Si signal on the 10-day specimen surface was decreased to 0.5  $\mu\text{m}$  (Fig. 3c). By contrast, the presence of Si was also identified by SNMS for the 20-day specimen (Fig. 3d), but indicating a lower average depth compared to 5-day and 10-day treated zirconia.

### 3.3. Surface roughness

The surface roughness (Ra) values of various specimens are shown in Fig. 4. The results indicated that the Ra values of the surface modified specimens ranging from 0.20 to 0.40  $\mu\text{m}$  were higher than that of the control group (0.15  $\mu\text{m}$ ). It could be observed that the Ra value was increased with  $\text{Si}_3\text{N}_4$  soaking time, indicating a significant difference ( $P < 0.05$ ).

### 3.4. Cross-sectional structure

SEM backscattered electron micrographs of the cross-section of the ceramic-veneered zirconia indicated that the ceramic veneer layer was well attached to the zirconia regardless of treatment conditions (Fig. 5). A smooth surface and dense structure of the control can be also clearly seen. In contrast, the surface modified specimens showed rough surface and porous internal structures (5–10  $\mu\text{m}$  distance from the surface) of zirconia core with regard to the  $\text{Si}_3\text{N}_4$  soaking time. Of note, a looser superficial structure with a larger pore size ranging of 0.5–1.0  $\mu\text{m}$  could be obtained in the 20-day specimen.

### 3.5. Shear bond strength

Table 1 shows the mean shear bond strength values of veneering ceramic to treated zirconia cores. The results demonstrated that the bond strength values of all treated specimens were higher than that of the control. In addition, the strength of ceramic-veneered zirconia specimens would increase with increasing soaking time and reached the maximum value on 10 days, and then decreased. The bond strength of zirconia soaked in  $\text{Si}_3\text{N}_4$  for 10 and 20 days was significantly higher than that of the control ( $P < 0.05$ ). There was no significant difference between the shear strength of specimens soaked in  $\text{Si}_3\text{N}_4$  for 10 and 20 days.

### 3.6. Failure mode

To assess the failure modes, the de-bonded specimen on zirconia substrate were visualized after shear bond strength test, as shown in Fig. 6. The photographs pointed out a prominent trend, which the soaking time influenced the remaining amount of veneering ceramic on the zirconia core. In fact, four ceramic veneer layers out of the ten controls completely detached from the zirconia surfaces (Table 1), which could be attributed to the occurrence of adhesive fracture. For the other six control specimens, the ceramic veneer layers were partially detached from the substrates and some of the ceramic veneers still attached on the core, demonstrating a mixed failure mode. In the case of surface modified specimens, mixed mode of fracture was the most frequent, except one case that a fracture only took place at the veneering ceramics for the 10-day specimen.

To further analysis the fracture, the relative amount of remaining veneer ceramic on the zirconia side was determined by image analysis software after failure, as presented in Table 1. It can be clearly seen that significant differences ( $P < 0.05$ ) were found for the residue values among the test groups. Area fraction (%) analysis of

remaining ceramic on zirconia core surfaces after de-bonding revealed that mean amount of residual ceramic were 54.3, 70.0, and 67.7%, respectively, for the zirconia treated for 5, 10, and 20 days of soaking time in  $\text{Si}_3\text{N}_4$ , having a trend similar to the changes in shear bond strength. By contrast, the veneering ceramic was mostly delaminated for the control, leaving about 35% of the zirconia surface covered with ceramic.

#### 4. Discussion

The growing demand by patients for esthetic and metal-free restorations drives to develop all-ceramic restorations consisting of zirconia core and veneering ceramic. However, the core-ceramic bonding are prone to failure usually initiating from the crack and chip-off fractures of veneering ceramics [3,20,21]. In addition, the clinical failure of veneering ceramics is also attributed to the weak bonding between the zirconia coping and veneering porcelain [20]. Hence, to overcome delamination of ceramic-veneered zirconia restorations has attracted a great deal of attention. In this study, we utilized the synergistically efficacy of micromechanical and chemical bonding by using the  $\text{Si}_3\text{N}_4$  solution in NaOH at 60 °C followed by heat treatment to improve the surface properties of zirconia core. As reported in the roughness data, it was consistently elicited that the used methods produced a rougher surface of the zirconia core on a submicro scale than the control. Although zirconia reveals high corrosion resistance to acids and alkalis, the soaking in the hot acidic [10,22] or alkaline [14,22] solution induces the breakdown of the protected zirconium oxide layer and initiates the localized corrosion phenomena at the less arranged high energy grain boundaries [23]. The heat treatment is also responsible for the alternation of surface morphology. During the heat treatment, the precipitated silica would be

molten and then flow into the grain boundary or cover the surface of crystal grains [14], which led to the disappearance of partial zirconia crystal grain and grain boundary. These phenomena could be confirmed from the surface and cross-section micrographs that an irregular porous structure on the surface was found. The uneven surface topology was beneficial for enhancing the mechanical interlocking effect on the subsequently veneered ceramic, which corroborated the previous findings [5,10].

In addition to the micromechanical effect, it is necessary to explore the chemical effect by using the current methods. The XRD results demonstrated the peak intensities of highly crystalline zirconia on the treated specimens decreased possibly due to the formation of amorphous silica layer. In addition, it is worth noting the lack of the t-m phase transformation. Although there was no new characteristic peak appeared in the XRD patterns of surface modified specimens, Si element was detected by using EDS/mapping and SNMS. The two analyses indicated that the 5-day specimen had the greater Si content on the surface, while the 20-day specimen presented the lower value. The presence of Si on the zirconia surface may play an important role in promoting the formation of covalent bonds between the zirconia core, the liner, and the ceramic veneer layer. The formation of silica was attributed to hydrolysis of the used  $\text{Si}_3\text{N}_4$  component to colloidal silica under highly alkaline NaOH solvent, and then was transformed into silica layer via heat treatment at 1400 °C [14]. However, the precipitated amount of the Si component was decreased with prolonging soaking time. Although the detailed mechanism was not yet fully understood, it can be speculated that there was a competition between Si precipitation and NaOH over-etching at different treatment time. The mechanism of  $\text{Si}_3\text{N}_4$  modification-promoted bonding of veneering ceramic to the zirconia surface might be resulted from the synergistic effect of the enhanced surface microstructure and formed

reactive matter, as discussed later.

Regarding the ceramic-to-zirconia integration of zirconia-based restorations, the current study indicated that the control produced a worse zirconia-veneering ceramic bonding. Contrary to the control, all treated specimens had higher shear bond strength values. Among the treated specimens, the 10-day specimen revealed the highest value in shear strength (27.4 MPa), which was similar to that of silica glass coated zirconia proposed by Liu's group (24.4 MPa) [24]. Interestingly, the shear strength of the treated zirconia would be diminished when the soaking time was prolonged from 10 to 20 days, although there was no statistical difference. As aforementioned earlier, it is assumed that the etching of the concentrated NaOH solvent was continuously progressed during the soaking process. This possibly led to the formation of a precipitated silicate layer with different structure and thickness. As illustrated in SEM, the structure of the precipitated silica layer fabricated by soaking the specimens in  $\text{Si}_3\text{N}_4$  for 20 days was looser than that for 10 days. The highly porous/loose structure might be not beneficial for the bond strength.

Given that interfacial chemistry and related interfacial morphologies dominate the ceramic-ceramic bonding [24–26], in addition to interfacial morphologies, the formation of chemical bonding should play the indispensable role in the interfacial bond. In this study, the 5-day specimen had the greater Si content and penetration depth from the results of SNMS and SEM/mapping; however, its bond strength was the least among the treated groups. Similarly, the higher Si content and penetration depth on the zirconia surface were found in the 10-day specimen than the 20-day specimen. It is deduced that, when subjected to soaking in  $\text{Si}_3\text{N}_4$  for 10 days compared to 20 days, the excessive Si content/depth at the zirconia surface could lead to poor adhesion, which needs to further investigation. Surface conditioning of

zirconia with optimal silica coating could improve the bonding to veneering ceramics. Nevertheless, in this work, the similarity in the bond strengths between 10-day and 20-day specimens can be explained in terms of the compromise between surface structure and Si content/depth. Therefore, the surface properties (microstructure and Si content) of the zirconia and shear bond strength of the ceramic-veneered zirconia would be tailored by altering the  $\text{Si}_3\text{N}_4$  soaking time. In short, the 10-day specimen might have an appropriate microstructure and composition in favor of bonding as compared with the control.

The failure mode after fracture must be demonstrated in view of interfacial bond strength. In this study, the fracture visual examination of the veneering ceramic-debonded zirconia surfaces showed that the incidence rates of adhesive failure and mixed failure modes in the control group were 40% and 60%, respectively, and the average remaining amount of ceramic veneer was 35.0%. In contrast, all surface modified specimens were almost fractured in a mixed failure consisting of the interfacial area and the veneering ceramic part. Of note, the remaining amounts of veneering ceramics on the surface modified zirconia were 1.5–2.0 times higher than that of the control group. More importantly, the 10-day specimen had a remaining amount of about 70.0% veneering ceramics on the zirconia surface, implying that bond strength between zirconia and veneering ceramic was greater than the cohesive strength of the veneering ceramic. The fracture analysis also confirmed the 10-day specimen with the highest bond strength of the PFZ system. The results of failure mode analysis and the remaining amount of ceramic veneer consistently illustrated that surface modification proposed in this study promoted the shear bond strength of the ceramic-veneered zirconia. Concerning the limitations of this current study, the surface modification of zirconia by using 3 wt%  $\text{Si}_3\text{N}_4$  in 4 M NaOH solution for 10–

20 days and sequential heat treatment at 1400 °C can effectively introduce the silica species into the zirconia core and change the surface morphology, which could improve the veneering ceramic bonding to the zirconia core as compared with the control. However, to reduce the soaking time may be another work by virtue of optimization in Si concentration, Si components, and treatment temperature before the practice application.

## 5. Conclusions

Within the design of this study, it was found that the morphology of zirconia could be altered from smooth topology to a rough surface with a roughness in a range of 0.15 to 0.40  $\mu\text{m}$  after soaking in 3 wt%  $\text{Si}_3\text{N}_4$ -containing NaOH solution. The amorphous silica layer can be successfully precipitated on the surface of the zirconia core without t-m phase transformation and silica content and penetration depth on the zirconia surface decreased with the increasing soaking time. The shear bond strength of the 10-day modified specimen was 27.4 MPa, which was significant higher than the control (18.6 MPa). Further investigations into the fatigue behavior and long-term storage are needed to elucidate the clinical performance of the all-ceramic restorative system treated by the current methods.

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**Figure legends**

Fig. 1. XRD patterns of zirconia surfaces under surface modification with  $\text{Si}_3\text{N}_4$  in NaOH solution for the different soaking time.

Fig. 2. SEM morphologies and elemental mapping of Zr and Si elements of zirconia surfaces under surface modification with  $\text{Si}_3\text{N}_4$  in NaOH solution for the different soaking time.

Fig. 3. SNMS depth profiles of zirconia surfaces under  $\text{Si}_3\text{N}_4$  treatments before (a) and after 5 days (b), 10 days (c), and 20 days (d).

Fig. 4. The surface roughness values of the zirconia core before and after soaking in  $\text{Si}_3\text{N}_4$  for different time points. The same letter on the bar is not significant differences ( $P > 0.05$ ).

Fig. 5. Cross-sectional SEM micrographs of the veneering ceramic-treated zirconia specimens when the zirconia substrates were subjected to different soaking time.

Fig. 6. Fracture images of the ceramic-veneered specimens on the zirconia surfaces treated for different time points after shear test. The arrow indicates the remaining veneering ceramic.

Table 1

Mean shear bond strength values, the amount of the remaining veneering ceramic on the zirconia core, and failure modes of veneer to core in term of different soaking time on zirconia surfaces.

Soaking time (day)	Bond strength (MPa)	Amount of remaining veneer	Failure mode		
			Adhesive	Mixed	Cohesive
Control	18.6 ± 3.3 <sup>a</sup>	35.0 ± 34.9 <sup>a</sup>	4/10	6/10	-
5	20.5 ± 2.8 <sup>a,b</sup>	54.3 ± 11.2 <sup>a,b</sup>	-	10/10	-
10	27.4 ± 4.1 <sup>c</sup>	70.0 ± 15.9 <sup>b</sup>	-	9/10	1/10
20	23.6 ± 2.1 <sup>b,c</sup>	67.7 ± 19.9 <sup>b</sup>	-	10/10	-

Mean values followed by the same superscript letter in the same column are not significantly different ( $P > 0.05$ ) according to Scheffe's multiple comparisons.

Number of samples is ten in each subgroup.

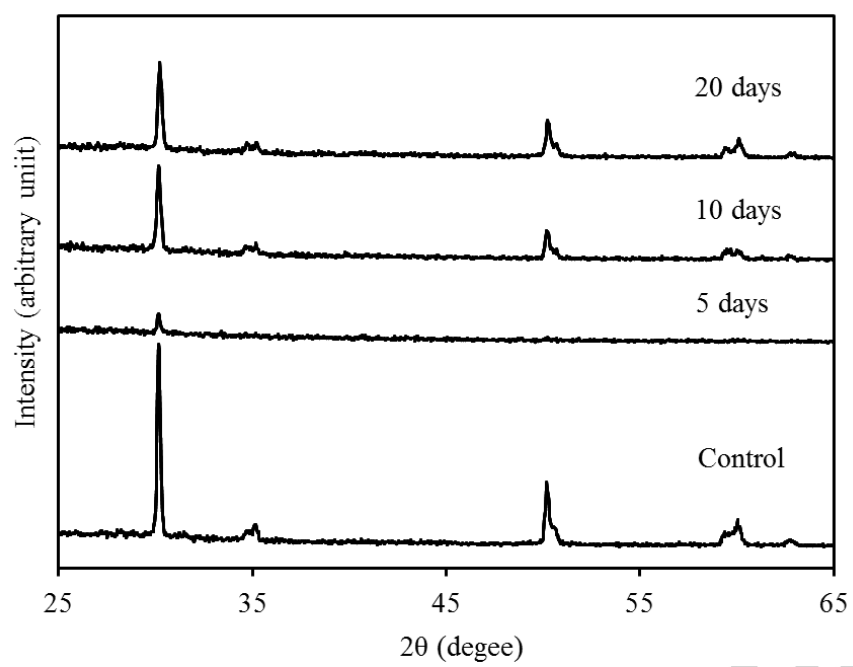


Fig. 1.

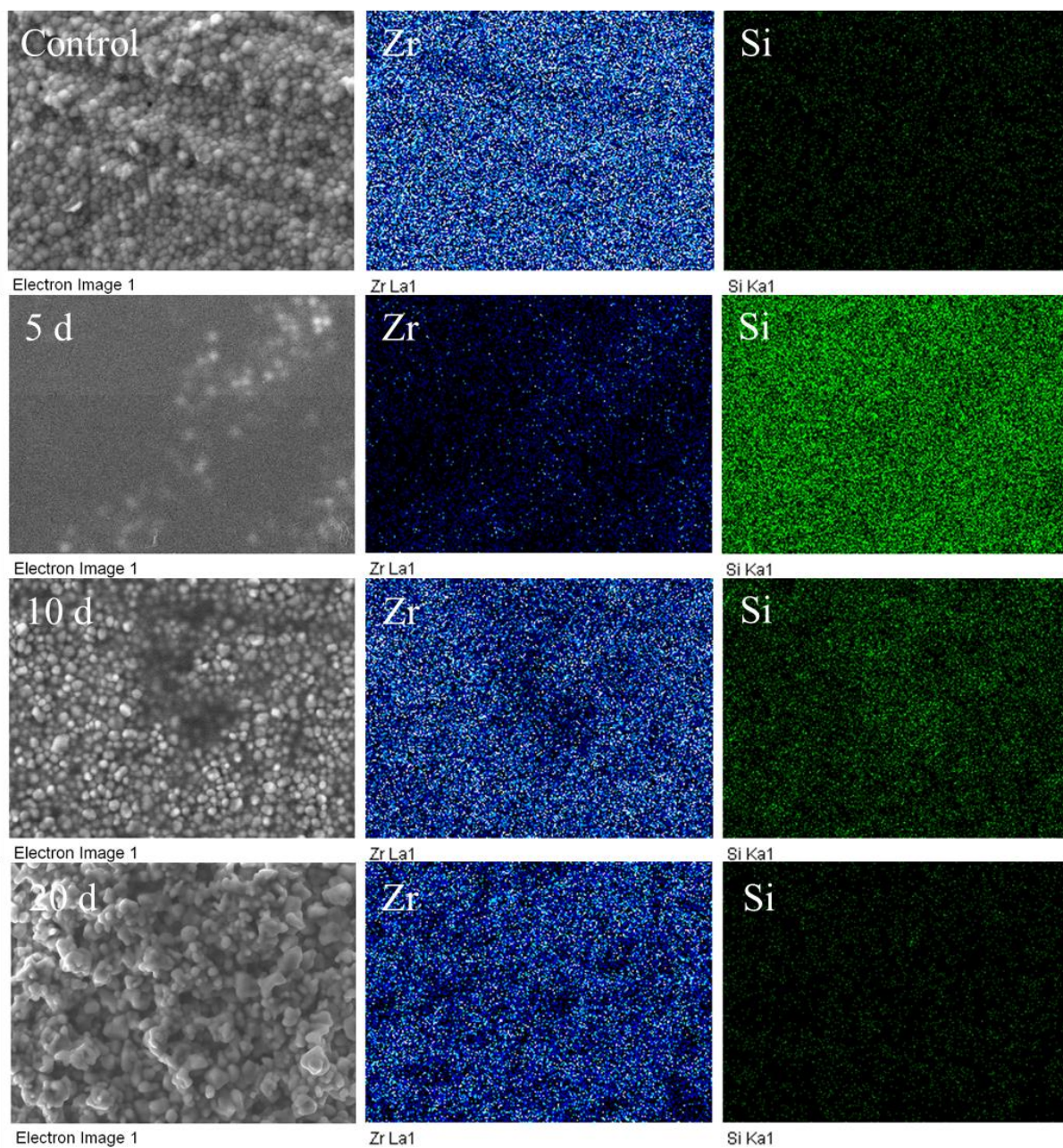


Fig. 2.



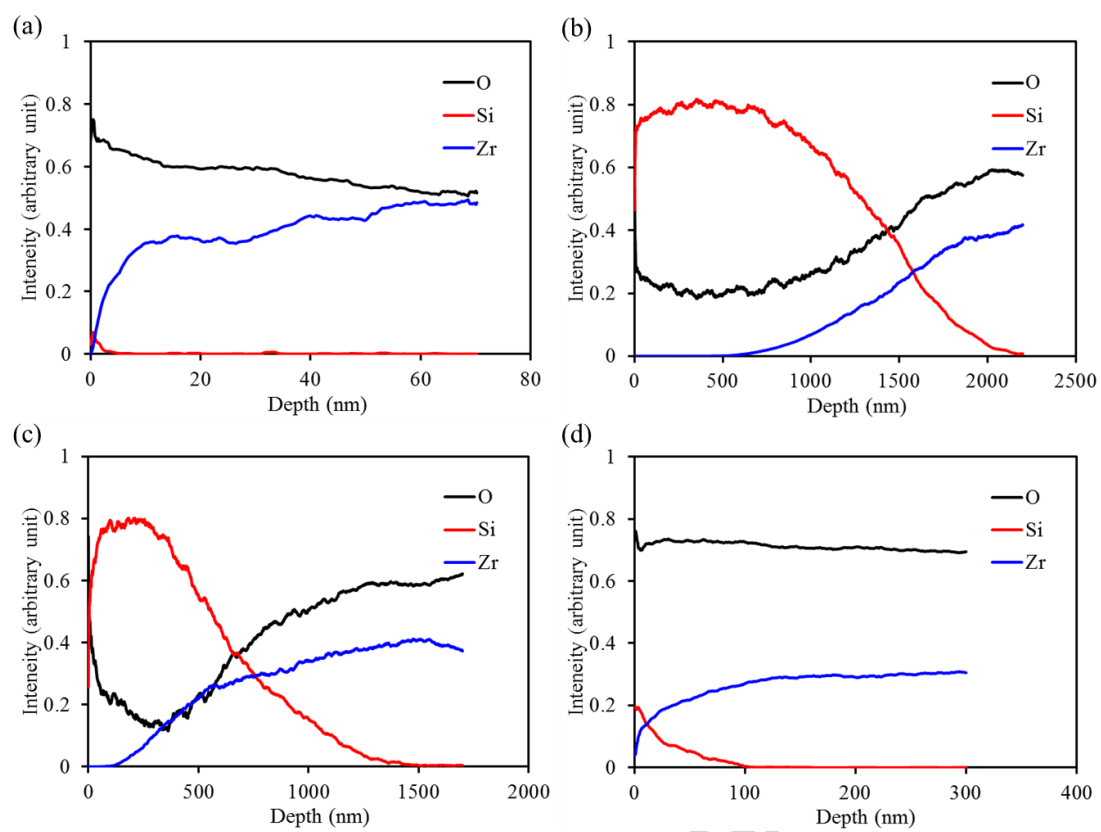


Fig. 3.

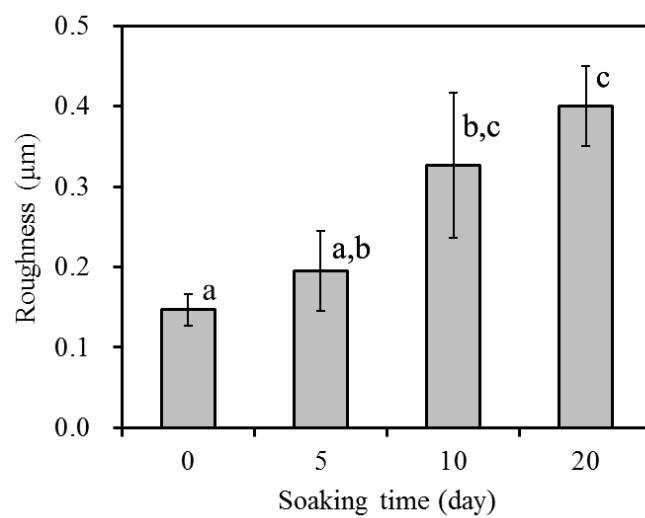


Fig. 4.

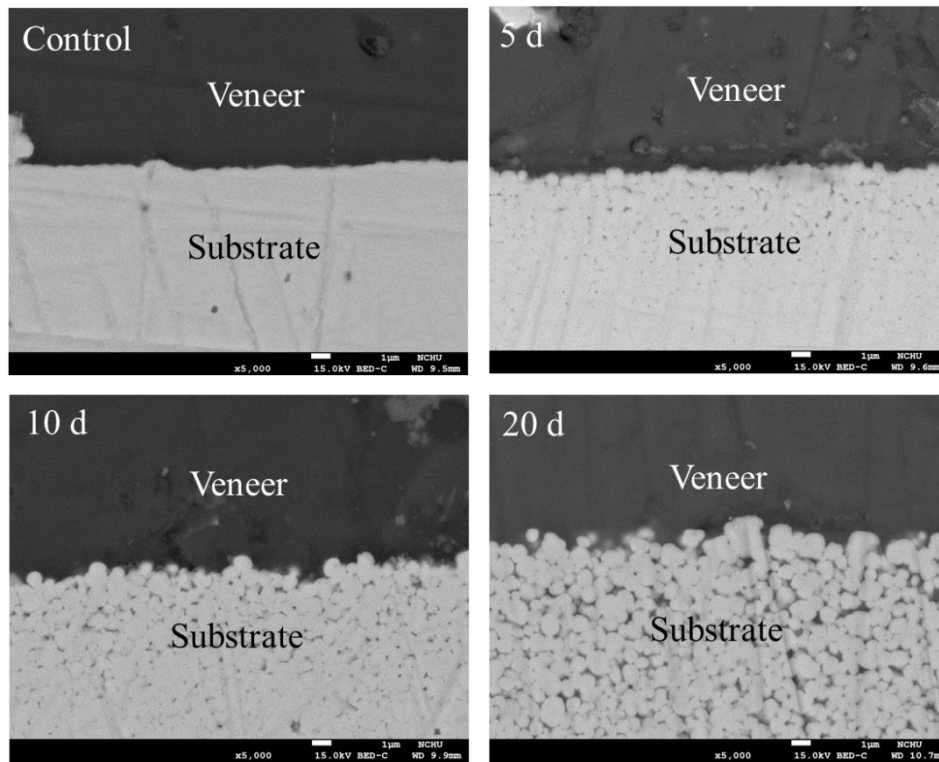


Fig. 5.

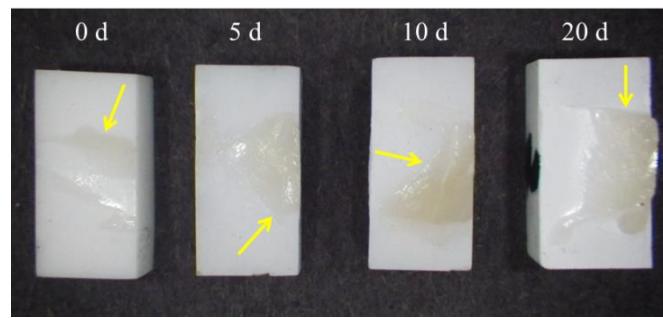


Fig. 6.

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