Flexible, high-strength titanium nanowire for scaffold biomimetic periodontal membrane

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Abstract
A layer of micro-sized periodontal membrane can buffer most chewing forces to protect the interface between the natural tooth root and alveolar bone. Artificial dental implants usually direct contact onto the alveolar bone without a buffer layer, which increases the risk of surface damage. The main purpose of this work was the bionic design of a flexible layer of nanowire scaffold on a titanium implant surface according to the function of the periodontal membrane. Millions of nanowires were woven into a superhydrophilic layer of porous scaffold. The evolution of mechanical properties displayed that the biomimetic nanowire scaffold could absorb a maximum of about 1.59 KJ energy per square centimeter by low-speed impact. The minimum tensile strength of one nanowire was 2 GPa. A biomimetic flexible periodontal membrane connection functioning between the natural tooth root and alveolar bone has great potential value for developing advanced artificial dental implants for dental restorations.

1 | INTRODUCTION

Tooth loss is a common phenomenon worldwide. For example, in China, more than 800 million people suffer from tooth loss [1]. Since ancient times, various implant materials have been used to repair the spaces left by lost teeth; however, most have been unable to satisfy the complex oral environment. In the middle of the last century, Branemark and Schroeder [2–4] found that animal bone tissue could bind closely with titanium metal. Oral implantology has developed rapidly and matured. Dental implants have become a first choice for repairing missing teeth because they have an appearance and function comparable to natural teeth.

Two parts make up the artificial implant tooth. One is the supporting implant part that is inserted into alveolar bone tissue by operation. The other part is the dental prosthesis that is revealed in the mouth. The metal titanium has been used for clinical dental implants for quite some time because of its great biocompatibility [5–7]. Oftentimes, however, dental implants become loose and lead to failure after a few years [8–13]. There are many reasons for the lost efficacy of oral dental implants, and they usually can be categorized as either biological or mechanical complications [8, 9, 14]. Biological complications are mainly caused by implant surgery (i.e. bleeding, nerve injury, and so on) [8, 9, 15, 16], whereas mechanical complications mainly refer to fracture of the implant [14, 17]. There are two main types of fracture in implants. Unscientific designs cause one type of fracture for individual patients due to a lack of accuracy [8, 9, 18, 19]. This kind of
fracture can be reduced by improving the accuracy for each patient. Another type of fracture is caused by fretting damage (i.e. fretting wear and fretting fatigue) between the implants and the bone tissue [18–20]. Zhou et al. [10] simulated 10, 100, 1000, 10,000, and 100,000 cycles of tangential and radial fretting on titanium to show the process of fracture from fretting. Their work revealed that fretting could cause the fracture of the implant, so effective protection from fretting was seen as an important way to reduce implant failure.

Because of the complex oral environment and multidirectional chewing force, the design of ideal dental implant surfaces is absolutely related to the connection between the natural tooth and the alveolar bone [10]. The periodontal membrane, also known as the periodontal ligament, is the connective tissue between the tooth root and alveolar bone that buffers the occlusal force caused by food being chewed from different directions [21]. The periodontal membrane contains bundles of fibres. One side of the membrane is buried in the alveolar bone, and the other is inserted into the surface of the tooth root to fix the root. The amazing natural biological connecting structure of the periodontal membrane almost eliminates the fretting damage on the interface between the natural tooth root and alveolar bone. The main purpose of this work is whether a type of flexible structure with a function similar to that of the periodontal membrane can be bionically designed.

Many researchers have worked on a titanium surface for dental implants. Jurczyk et al. [22] revealed that Ti–SiO2 scaffold could promote the speed of growth in bone tissue on the dental implant surface. Weiner et al. [23] revealed that bone tissue had better bonding on a textured dental implant surface. Nouri et al. [24] biomimetic designed hole texture surface to promote the bone tissue growth into the metal surface to form a cross-sectional area with titanium metal to increase the bonding strength between metal and bone tissue. Those works were important and improved the reliability of dental implants. However, so far, there was little work showing a designed connection can gain a buffer effect similar to that of the periodontal membrane between the natural tooth root and alveolar bone.

We have focussed on the surface texture on the dental implant surface, and the innovation point was that we controlled millions of high-strength nanowires to weave a layer of the porous structure to form a flexible cross-sectional area to realize the buffer function between the artificial dental implant and alveolar bone.

2 | MATERIALS AND METHODS

(1) In situ self-assembled nanowire scaffold on titanium surface. Medical-grade titanium substrates (size: 10 mm x 10 mm x 0.5 mm) were treated with acetone and deionized water at room temperature before synthesis. Then the titanium substrates were reacted with 1.0 mol/L NaOH solution at 230°C for 0.5, 1, 3, 6, and 12 h. Finally, the reacted titanium substrates were rinsed with deionized water and then dried.

(2) Characteristic inspection. The morphology of the nanowire scaffold was observed by scanning electron microscopy (SEM, Phenom G2, Netherlands) on the front, side, and oblique angle surfaces. The phase purity and crystalline structure of the nanowire scaffold were tested by X-ray diffraction (XRD, Cu Kz, λ = 1.5418 Å, D8 Advance, America) scanning from 20° to 70° at a speed of 5°/min. The hydrophilic and hydrophobic properties of the original and nanowire scaffold surfaces were tested by contact angle metre (Kino SL250, America). The natural tooth root and artificial implant were observed by oral X-light machine (Carestream Health Inc, NY) in the Department of Stomatoloy of Hangzhou First People's Hospital.

(3) Mechanical performance testing. A nanomechanical system tester (NST, Ti-Premiere, Hysitron Corp.) was employed for nanoindentation and scratch testing. For the nanoindentation test, a Berkovich diamond tip (half angle: 65.27, radius: 100 nm) with loads of 300, 400, 500, 600, and 1000 μN was pressed onto the nanowire scaffold; the process was repeated nine times for each load. For scratch testing, a conical diamond tip (radius: 5 μm) with loads of 300, 400, and 1000 μN was used to scratch (speed: 2 μm/s) the nanowire scaffold layer; the process was repeated nine times for each load.

3 | RESULTS

Figure 1a is an X-ray light photograph of a connection between the natural tooth root and alveolar bone. The photograph shows the membrane layer (marked by white points in Figure 1a) between the tooth root and alveolar bone called the periodontium. The periodontal membrane is the dense connective tissue between the tooth root and the alveolar bone. Based on the X-ray light photography, a schematic diagram of the periodontium connection between the tooth root and alveolar bone is drawn in Figure 1b. It contains bundles of fibres, with one side of the membrane buried in the alveolar bone and the other inserted into the tooth root's surface to fix the root and relieve the occlusal force caused by food chewing. While chewing forces $F_1$ on the tooth, the periodontium fibres tighten to relieve the chewing force (see Figure 1c). The tensional periodontium stopped the tooth root from a direct hit on the alveolar bone to protect both the root and alveolar bone surfaces when chewing food. Figure 1d is an X-ray light photograph of a connection between an artificial dental implant and alveolar bone, which at present is one of the most common ways to repair a missing tooth in the clinic. The photograph shows the direct connection between the implants and alveolar bone. There is no buffer layer between the artificial dental implant and alveolar bone. Based on the X-ray light photography, a schematic diagram of the dental implant alveolar bone connection is drawn in Figure 1e. The metal layer
is shown in direct contact with the alveolar bone surface. With chewing forces on the artificial tooth, the metal implant directly hits the alveolar bone without any buffering protection. Based on the function of flexible buffer protection from the periodontal membrane between the natural tooth root and alveolar bone, a biomimetic flexible nanowire scaffold layer was designed to increase the buffering ability of artificial dental implants. The schematic diagram of an ideal flexible connection between an artificial implant and alveolar bone is shown in Figure 1f. As designed, there is a flexible nanowire scaffold layer between the metal layer and alveolar bone, Osteocyte growth in the nanowire scaffold was used to build a flexible transition buffer region with a function similar to that of the periodontal membrane.

Figure 2 shows SEM and XRD images of the original titanium surface and nanowire scaffold layer. As shown in Figure 2a, the original titanium surface was hydrophobic. After a hydrothermal reaction under 1 mol/L NaOH solution in 230°C for 12 h, the nanowire scaffold layer was grown on the titanium, now with a hydrophilic surface. Figure 2b is an SEM photograph of the nanowire scaffold layer with millions of nanowires woven into a layer of porous structure—the size of the microholes is around 16 μm (see Figure 2c). The thickness of the scaffold layer was about 30 μm (see Figure 2d). Figure 2e is an SEM image of the oblique (45°) view of the nanowire scaffold layer; the SEM photograph clearly shows the microholes woven by the nanowires. Figure 2f is powder XRD images of both the original titanium and the nanowire scaffold layer. The XRD pattern of the nanowire scaffold resembles a layer of hydrogen titanates [25, 26].

Were the nanowire scaffold thickness and microhole size inside the nanowire scaffold constant following the hydrothermal reaction? A systematic SEM observation of the nanowire scaffold on the side and front surfaces is shown in Figure 3. Both the nanowire scaffold thickness and the size of the microhole on the nanowire scaffold can be controlled by the reaction time. The thickness of the scaffold layer was close to ~90 μm for reaction times of 0.5 h (see Figure 3a) and 1 h (see Figure 3c). It was then increased to ~125 μm for reaction times of 3 h (see Figure 3e) and 6 h (see Figure 3g) and decreased to ~30 μm for a reaction time of 12 h (see Figure 3i). The size of the microholes on the nanowire scaffold was also related to the reaction time. For reaction times of 0.5 and 1 h, no microholes were evident in the scaffold. For the reaction time of 3 h, millions of nanowires were woven into microholes with a size of ~4 μm. The size of the microholes then increased to ~10 μm for 6 h and ~16 μm for 12 h.

Figure 4 shows flexibility and strength testing conducted with press loads of 300, 400, 500, and 1000 μN using a nanomechanical testing system. The nanowire scaffold layer had deformation to load at the normal direction and recovered after unloading (see Figure 4a, b, c & d). However, for the original titanium metal, there was no recovered deformation phenomenon after nanoindentation (see supporting information in Figure 5). One interesting phenomenon was that when the press load was set to 300 μN, the nanowire scaffold could carry 300 μN (see Figure 4a). When the press load was set to 400 μN, the nanowire scaffold could carry 400 μN (see Figure 4b). While the press load was set to 500 μN, the nanowire scaffold could carry 500 μN (see Figure 4c). But
when the press load was increased to 1000 μN (see Figure 4d), the nanowire scaffold only could carry a maximum of only 500 μN.

Figure 6 shows the tensile strength test in a tangential direction with press loads of 300, 400, and 1000 μN by nanotip using a nanomechanical testing system. As shown in Figure 6a, b & c, all the tangential forces dropped suddenly around 400 μN. The tensile elongation of the nanowires was 1000-2000 nm. The results implied that the tangential carrying capacity of the nanowire scaffold was around 400 μN.

4 | DISCUSSION

The phenomenon of the thickness of the nanowire scaffold layer increasing from 1 h to 3 h and then decreasing from 3 to 12 h can be explained as follows. For a reaction time less than 1 h, few nanowires were formed (see Figure 3b and d), so the thickness of the layers remained constant. For a reaction time from 1 to 3 h, the nanowires began to grow, leading to a fluffy surface that increased the thickness of the nanowire scaffold. From 3 to 12 h, some nanowires on the outermost surface began to fall off, which led to a decrease in the thickness; meanwhile, the microhole size increased from ~4 to ~16 μm.

Based on the function of the periodontal membrane between the natural tooth root and alveolar bone, some of the most important properties of the nanowire scaffold are mechanical, including flexibility and tensile capacity. The cyclic curves of force–shape deformation in Figure 4a, b, c & d show that the nanowires had hysteretic recovery capability after unloading. A schematic diagram of the deformation of the nanowire is shown in Figure 7a. The nanowire was compressed with a nanotip in the load process, and the nanowire then exhibited hysteretic recovery during unloading. An estimate of the future of energy absorption of the nanowire scaffold at loads of 300, 400, 500, 600, and 1000 μN can be obtained by the following formula:
loads layers μN; of nanomechan (a) system. (b) tests scaffold 400 (nanoindentation) FIGURE testing μN (d) Press (a)(b) microscopy FIGURE scaffold titanium Side (i)(j) times. (e)(f) electron h; 1 h; 12 h of scanning 3 different ire h; 3 3 surface (g)(h) area where implant, force solar buffering can, which is one of the most important indicators for the bionic buffering function of the periodontal membrane in vivo.

For the tensile capacity of the nanowires, based on the phenomenon of the tangential forces dropping suddenly around 400 μN for all setting forces, the tensile strength can be estimated by the following formula:

\[
F = kt
\]

\[
W = \int_0^t ksdt
\]

where \( F \) is the indentation force related to time (newton, N), the maximum value of \( F \) is 500 μN based on the nanoindentation experiment in Figure 4; \( k \) is a coefficient; \( dt \) is instantaneous time (seconds, s); \( W \) is the absorbed energy during nanoindentation (kilojoule, KJ); \( s \) is the displacement of the tip (centimeter, cm). The calculation results showed that the nanowire scaffold could absorb about 1.59 KJ energy per square centimeter at maximum (see Figure 7b). These data suggested that the nanowire scaffold had excellent impact buffering performance, which was one of the most important indicators for the bionic buffering function of the periodontal membrane in vivo.

On the other hand, the size of osteocyte was around 10 μm at the short axis [27, 28], smaller than the size of the microhole (∼16 μm) in the scaffold layer (see Figure 2e and e), which makes it possible for the osteocyte to be embedded in the scaffold layer (see schematic diagram in Figure 1f). Meanwhile, the diameter of the bone synapses is from 50 to 100 nm, close to our designed nanowire, which makes it possible for intertwining bone synapses and nanowires during growth to build a buffering layer between the artificial dental implant and alveolar bone (see schematic diagram in Figure 2f). With chewing force on the artificial tooth implant, the nanowires on the implant metal would tighten to relieve the chewing force, but
the tensional nanowires stopped the implant root from a direct hit on the alveolar bone to protect the implant root surface and the alveolar bone surface (see schematic diagram in Figure 7d). The high energy absorption of the flexible scaffold layer and the high tensile strength of the nanowires ensure the protection of the implant root and the alveolar bone surface from the impact of chewing force.

5 | CONCLUSION

Human biological tissues and organs have developed the ability to effectively reduce the degree of damage in loading environments through evolution [29]. For example, the periodontal membrane is a micro-sized layer that can cushion most chewing forces through micromotion [21] to reduce damage to the tooth root and alveolar bone surfaces from the impact of fretting. Fretting is a problem for most mechanical devices and artificial implants [10]; however, the attachment of the periodontal membrane between the natural tooth and alveolar bone allows for fretting to reduce tissue damage. The biomimetic function of the flexible connection in the human body has great potential value for developing advanced artificial implants with little impact from fretting damage during application in the human body.

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