Surface Modifications for Zirconia Dental Implants: A Review

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Zirconia-based bioceramic is a potential material for dental implants developed and introduced in dentistry 30 years ago. However, some limitations still exist for zirconia implants caused by several factors, such as manufacturing difficulties, low-temperature degradation (LTD), long-term stability, and clinical experience. Several studies validated that some subtle changes on the zirconia surface might significantly impact its mechanical properties and osseointegration. Thus, attention was paid to the effect of surface modification of zirconia implants. This review generally summarizes the surface modifications of zirconia implants to date classified as physical treatment, chemical treatment, and surface coating, aiming to give an overall perspective based on the current situation. In conclusion, surface modification is an effective and essential method for zirconia implant application. However, before clinical use, we need more knowledge about these modification methods.

Keywords: zirconia, ceramic, surface modification, dental implant, osseointegration

INTRODUCTION

Dental implant is a competitive and attractive treatment for replacing missing teeth. It reported that significant increase in dental implants in the United States from 0.7% in 1999 to 2000 to 5.7% in 2015 to 2016, and estimated implant prevalence could be as high as 23% by 2026 (1). The widespread application of dental implants relies on their high survival rate. A recent analysis indicated that a 10-year survival rate of the dental implant was 96.4% (2). Until now, titanium is still the priority choice of dental implant material, which has been used for almost 50 years. The shortcoming of titanium bothers practitioners and patients, such as allergic reactions, titanium deposits, discoloration of the mucosa, or unsatisfied aesthetic outcomes (3, 4). From this standpoint, an innovative type of implant material is urgently needed.

The first trial and the first generation of ceramic implants is aluminum oxide implant, which is proved to be osseointegrated (5). Whereas, the biomechanical properties of aluminum oxide implant, known as fracture toughness, are not satisfying, which consequently caused its unstable long-term survival rates, between 65 to 92% (6). Although aluminum oxide dental implant faces its failure and withdrawal from the market, it still provides a positive concept and direction: a metal-free material should be developed, such as ceramic material. Zirconia is a potential ceramic manufactured as a dental implant abutment since 1995 (7). It was recently thought to be a potential implant material attributed to its superior mechanical properties, outstanding biocompatibility, and ivory color (8, 9). Nevertheless, zirconia materials still need further evolutions on their fracture toughness (10).

It is known that morphology, chemical composition, and roughness are the three main factors affecting newly formed tissue quality and quantity (11). Surface modifications on implants were
proved to affect the osseointegration process and mechanical properties, used on titanium implants for over 25 years (12). Thus, particular attention was paid to exploring the surface modification benefits of zirconia. A recent study indicated that surface modification of zirconia might change its interfacial surface characteristics and advance biological performance (13). However, the exploration of surface modification on zirconia is still far from sufficient. This review summarizes zirconia’s primary and potential surface modification methods, classified as physical treatment, chemical treatment, and coating, giving an overall perspective of the present situation and providing available clues for future improvement.

THE UNIQUE PROPERTIES OF ZIRCONIA MATERIALS

Zirconia crystals are temperature-dependent, consisting of three phases: monoclinic crystal structure, tetragonal crystal structure, and cubic crystal structure (Figure 1). With the temperature increasing, zirconia changes its phase from a monoclinic structure to a tetragonal structure at around 1,170°C; then to a cubic structure at around 2,370°C; finally melts at 2,716°C (14). Phenomena termed Phase Transformation Toughening provides an excellent property to zirconia (15). In general, the tetragonal phase is a metastable state of zirconia at room temperature, which gets the micro-cracks process under stress. More concentrated stress will provoke a zirconia phase transformation from tetragonal to monoclinic with a consequent 4% volume expansion (16), finally stopping the micro-cracks propagation, recovering, and strengthening toughness (17).

Meanwhile, the phase transformation from tetragonal to monoclinic will accelerate Low-Temperature Degradation (LTD), also known as aging (18). LTD occurs in the presence of humid environments, such as water or body fluid, through a slow surface transformation from a metastable tetragonal phase to a stable monoclinic phase (19). In that case, zirconia will lose its Zr-O-Zr bond, leading to increasing monoclinic content. In addition, the forming micro-cracks in transforming regions make material lose strength (20), finally results in degradation.

For improving the defect of crystalline transformation, researchers find that small amounts of additional elements can stabilize the tetragonal or cubic phase of zirconia, such as yttria, magnesium, or ceria. Currently, yttria-stabilized tetragonal zirconia polycrystalline (Y-TZP) is the most common candidate for zirconia implants (21). Additionally, alumina toughened zirconia (ATZ), zirconia toughened alumina (ZTA), magnesium partially stabilized zirconia (Mg-PSZ), and ceria partially stabilized zirconia/alumina nanocomposite (Ce-TZP/Al2O3) were also reported as potential materials for dental implants (22).

PHYSICAL TREATMENT

Sandblasting
Sandblasting is an approach for obtaining optimal micro-roughness surfaces. The roughened surface shows a beneficial effect on two key indicators of osseointegration quality: bone-implant contact (BIC) and removal torque (RTQ), which reflects the amount of newly-form bone and the bond strength between implant and bone (23, 24). M. Gahlert. et al. (25) inserted zirconia implants with both machined and sandblasted surfaces into thirteen adult miniature pigs on the maxillae incisor area to test the different designs. The surface analysis showed that sandblasted zirconia implants had a higher surface roughness than machined zirconia implants. I. Mihatovia. et al. (26) investigated zirconia implants with three different surface roughness (Z1 < Z2 < Z3) in a dog model. Tissue biopsies after ten weeks of healing showed that the total BIC of three groups was significantly different as Z3(69.5%) > Z1(49.7%) > Z2(37.1%). It indicated that surface roughness plays a positive role in BIC. Another animal experiment compared machined zirconia surface with two kinds of porous zirconia surfaces verified that the RTQ value of the machined group showed significantly lower than all other types after six weeks healing period in rabbit tibia and femur (27). It demonstrated that zirconia with a rougher surface integrates more firmly in bone.

A study seeding human osteoblasts on 120 µm and 250 µm Al2O3 airborne particle abraded zirconia surfaces and machined surfaces proved that sandblasting surface before sintering could increase the initial osteoblasts cell adhesion up to 175%, compared with the machined samples. It also suggested that sandblasted zirconia implants can achieve higher stability in bone than machined zirconia implants and positively affect the interfacial shear strength (28). However, the mechanical forces formed during sandblasting will induce LTD (29). Even

![Figure 1](https://example.com/figure1.png)

**FIGURE 1** | Structure diagrams of the monoclinic phase crystal, tetragonal phase crystal, and cubic phase crystal of zirconia.
though LTD simulated by steam autoclave aging has few significant effects on the roughness, it still needs highlighting that the specimen preparation processing has a high impact on forming LTD (30). Also, sandblasting procedures will cause additional surface elemental composition due to inevitable alumina contamination (31).

**Laser**

Laser treatment is a fast, clean, contact-less, and easy-operating technique with high accuracy on material surfaces (32). The application of laser in dentistry began from the end of the 1990s on endodontic, periodontal, and oral surgery (33). Laser irradiation is verified to enhance surface roughness (34). It was reported that zirconia treated by femtosecond laser irradiation could create a consistent roughness on the interface between zirconia and resin cement and get higher early bond strength values (35). Fiber lasers, which can make 2 μm-wide grooves, were proved to produce adequate roughness on zirconia surfaces and increase new bone formation and mechanical strength on the bone-implant interface (36). Additionally, laser technologies positively affect wettability, acting as a critical determinant of cell adhesion, proliferation, and calcification, contributing to accelerating zirconia osseointegration (37, 38). Studies showed that laser treatment would not exhibit phase transformation to zirconia while improving mechanical properties (39, 40).

**Ultraviolet Light**

Creating a super-hydrophilic surface with a contact angle lower than 20° is the most attractive ultraviolet (UV) light treatment ability (41). High surface wettability contributes to improving integrations between soft tissue and dental implants (42). An animal study that placed UV-modified rough zirconia implant into rat femurs revealed the BIC increased by 1.7 folds after four weeks of healing compared with non-treated surfaces, and the amount of bone volume increased 13% at the same time (43). In addition, plenty of studies demonstrated that UV irradiation led to a significant improvement in initial cell adhesion, spreading, proliferation, and collagen release (44–46).

To investigate the effect of UV light on surface characteristics, Taskin Tuna, et al. (47) treated zirconia discs by UV light for 15 min and found the contact angles were changed from 56.4°–69° to 2.5°–14.1° after UV treatment. Taskin’s study elucidated that UV-treated samples showed a significant surface elemental composition change with a decrease of carbon by 43%~81% and an increase of oxygen by 19%–45%, which was thought to be the conversion factors of material hydrophobic to hydrophilic (48, 49). Meanwhile, an increase of the monoclinic crystalline was observed in this study. Conversely, another study demonstrated that no crystal phase transformation from tetragonal to monoclinic occurred. Thus, UV treatment could significantly reduce the aging of zirconia (50). However, crystalline transforming triggered by UV light is a controversial viewpoint, so that more efforts are needed for this promising strategy.

**CHEMICAL TREATMENT**

**Acid Etching**

Acid etching treatment of zirconia using hydrofluoric acid, nitric acid, or sulfuric acid is an efficient method to roughen any irregular surfaces homogenously without destroying material morphology (51, 52). Since acid etching could remove the additional residues caused by sandblasting, acid etching usually worked in conjunction with sandblasting, known as sandblasted, large grit, acid-etched (SLA) (53). SLA zirconia implant shows good BIC values for bone integration without interfering with osteoblasts proliferation and differentiation (55, 56). An animal study compared SLA, sandblasted alone, and alkali-etched sandblasting treatments showed that SLA-treated zirconia was related to the highest BIC rate, followed by sandblasting, while the alkali-etching sandblasted group created the lowest BIC rate (57). However, heat-treatment and acid-etching can decrease the flexural strength of zirconia, suggesting it may not be as effective as it is applied on titanium (58).

**Electrochemical Treatment**

Electrochemical treatments, such as electrochemical anodic oxidation, electrochemical deposition, or micro-arc electron, can make a composite coating or nanostructures on titanium surfaces and significantly improve osteointegration and antibacterial abilities (59). However, zirconia has a limitation in electrochemical application because of its non-conductive character. Liu et al. (60) introduced the electrochemical deoxidation (ECD) technique to improve zirconia surfaces, which removed oxygen from the solid metal oxides via molten salt electrolysis. It suggested that ECD treated zirconia showed well-arranged microporous, low contact angles, and a slight decrease in monoclinic phase content (∼4.4 wt%).

Based on the advantages of electrochemical technology, much effort has contributed to fabricate the nanostructures on zirconia (61–63). Among all methods, nanotubes are an emerging surface modification developed for drug delivery systems. The nanotube structure is related to well pore controllability, high surface area, stable chemical ability, mechanical rigidity, and excellent compatibility (64, 65). A study showed that electrochemical anodization could form a highly self-organized zirconia nanotube with a diameter of about 50 nm~130 nm, a length of 17 μm, and a high aspect ratio of more than 300 (66). It was verified that the nanotube structure on zirconia could be successfully obtained, but it cannot achieve an orderly arrangement due to the otherness between zirconia and other metals, such as different conductivities. Thus, the reaction condition of zirconia anodic oxidation technology needs to be explored furtherly (67). Guo et al. (68) soaked zirconia nanotubes into stimulated body fluids (SBF) for 20~30 days and found bone-like apatite could form on the surface of zirconia nanotubes, which indicates that zirconia nanotubes could exhibit favorable bioactivity. However, electrochemical treatment on zirconia is still limited in laboratory research and needs further investigation.
COATING

Calcium Phosphate Family
Calcium phosphate (Ca₃(PO₄)₂, CaP) is a biological apatite that favors zirconia stabilizing, stimulates bone repair, and accelerates cell attachment and proliferation (69). The calcium phosphate family includes several members with different crystallization, dissolution, and phase transformation processes which exhibit various properties (70). Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂, HA) is one of the most stable and least soluble calcium phosphate family members. HA is the primary mineral component of bones and has bioactive abilities to assist tissue response and enhance osseointegration (71). It was reported that zirconia enriched with HA showed more new bone formation than those free of HA (72). HA coating also significantly improves coating stability and bonding strength on zirconia (73).

However, the technology of calcium phosphate coating usually provides unsatisfied stability and weak bond strength to the base materials (74). Excess calcium ions even induce cubic phase zirconia which results in low mechanical strength (75). The thermal spraying coating method, such as plasma spraying, is usually used for calcium phosphate coating due to its high deposition rate and low cost. Nevertheless, it is not appropriate for complex morphology because of the high processing temperature and inhomogeneous thickness. Such inhomogeneous thickness can induce delamination and exfoliation, thus causes the premature failure of implants (76). The sol-gel method is developed to resist these drawbacks, which is proved to be an alternative low-temperature coating and results in a relatively homogeneous surface (77). Other advanced techniques are also introduced into calcium phosphate coating. For example, wet powder spraying (WPS) can accomplish complex curved surfaces with different thicknesses relying on its particular versatility (78). Aerosol deposition technique could produce a high-quality coating on the zirconia surface with controlled pore size and porosity (79).

Bioactive Glass
Bioactive glass is a composition system of Na₂O-CaO-SiO₂-P₂O₅, which was commercially trademarked as Bioglass 4555 (80). The bioactive properties make bioglass applicable as a coating material for dental implants. Bioglass positively interacts with the biological environment by forming a hydroxyapatite layer between the tissue and material (81). It was found that bioglass induced a rapid chemical combination and a faster apatite formation on bone tissue, which indicated that the healing period of dental implants might be reduced by using bioglass coatings (82).

Zirconia implant has a challenge in the bioglass coating due to its long-term stability. The insufficient mechanical properties will induce bioglass to be fragile (83). Moreover, bioglass is incompatible for thermal coating on zirconia because of its higher thermal expansion coefficient (TEC) (15-10⁻⁶ K⁻¹) than zirconia (10.8-12.5·10⁻⁶ K⁻¹) (84). During cooling, bioglass and zirconia or other metals will shrink in different degrees, making coating cracks. An ideal situation is that bioglass has a slightly lower TEC than the base material (85). A study proved that substituting the bioglass elements, such as replacing Na₃O with K₂O and replacing CaO with MgO, will efficiently decrease the TEC of bioglass (86). A. Kirsten et al. (87) added a tailored substitution of alkaline earth metals and alkaline metals into Bioglass 4555, showed that the TEC of the novel glass was slightly lower (11.58·10⁻⁶ K⁻¹) than that of the zirconia (11.67·10⁻⁶ K⁻¹). It might provide a possibility of applying bioglass coatings on zirconia surface modification.

Arginine-Glycine-Aspartate
Arginine-glycine-aspartate (Arg–Gly–Asp or RGD) tripeptides widely exist in adhesive proteins in the extracellular matrix, act as a significant factor in cell adhesion (88). Immobilizing these biomolecules such as RGD peptides on the material surface to promote the biological responses and biochemical properties is the so-called biomimetic surface modification, also known as biofunctionalization (89). RGD peptide can be successfully coated onto the zirconia surfaces as a stable and functional

| Surface modification                  | Effects on increasing bone formation                                                                 | References |
|--------------------------------------|-------------------------------------------------------------------------------------------------------|------------|
| Sandblasting/SLA                      | Roughen the surface;                                                                                  | (24–26, 28, 31) |
|                                      | Enhance bone apposition with high RTQ;                                                               |            |
|                                      | Improve cell adhesion, metabolic activity and proliferation.                                          |            |
| Laser                                | Roughen the surface;                                                                                  | (35–40)     |
|                                      | Increase zirconia bone strength;                                                                    |            |
|                                      | Improve cell viability.                                                                               |            |
| Ultraviolet light                    | Enhance bone-zirconia interface;                                                                     | (43–50)     |
|                                      | Improve surface hydrophobic;                                                                        |            |
|                                      | Improve surface wettability;                                                                        |            |
|                                      | Accelerate bone-zirconia integration;                                                                |            |
|                                      | Increase cell adhesion, spreading and proliferation;                                                  |            |
|                                      | Improve the soft tissue seal.                                                                        |            |
| Acid etching                         | Obtain better BIC.                                                                                   | (55, 57)    |
| Electrochemical treatment            | Fabricate micro/nano structures on zirconia;                                                          | (60–63, 65–68) |
| Calcium phosphate/                   | Improve surface wettability;                                                                        | (72–74, 79) |
| Hydroxyapatite coating               | Enhance zirconia osteogenesis ability.                                                                |            |
| Bioactive glass coating/scaffolds    | Improve bone-zirconia integration and reduce the healing time of zirconia dental implants.           | (87)        |
| RGD coating                          | Improve zirconia biocompatibility;                                                                  | (90–92)     |
|                                      | Increase cell adhesion;                                                                               |            |
|                                      | Accelerate osseointegration.                                                                        |            |
| PDA coating                          | Improve zirconia co-competability;                                                                  | (95–97)     |
|                                      | Enhance zirconia osteogenesis ability;                                                                |            |
|                                      | Decrease bacteria adhesion.                                                                         |            |

RTQ, removal torque; SLA, sandblasted, large grit, acid-etched; BIC, bone to implant contact; RGD, Arginine–glycine–aspartate; PDA, Polydopamine.
chemically attached coating (90). A study that grafted RGD-containing peptides onto zirconia validated that it can accelerate the osseointegration, improve the per-mucosal sealing, and incorporate to antimicrobial (91). Consistently, a study formed a hybrid nano/micro-scale zirconia surface by coating with RGD and magnesium ion (Mg+) revealed that it could improve the cell adhesion, spreading, and migration of osteoblasts and accelerate their mineralization (92).

**Polydopamine**

Polydopamine (PDA) is an essential component of marine mussel adhesion proteins, one of its unique abilities is attaching to organic and inorganic materials underwater (93). Since 2007, PDA adhesive coating has been widely applied on several material surfaces, including noble metals, oxides, semiconductors, synthetic polymers, and ceramics (94). A study suggested that PDA-coated zirconia performed better than uncoated zirconia on cell adhesion, spreading, and proliferation (95). Besides great adhesive ability, PDA coating enhances antimicrobial properties by reducing bacterial adhesion, which plays a positive role in peri-implant soft-tissue regeneration (96). Xu. et al coated a PDA-containing nanolayer on a 3D-plotted bio-ceramic scaffold and pointed out it was a viable and effective strategy to accelerate osteogenesis (97). Additionally, PDA can be used as a cross-linking. A recent study that treated zirconia with PDA coating showed that PDA improved the bond strength between the resin cement and zirconia surface (98). The manufacture of PDA coating is easy-going and multi-functional. PDA coating on zirconia should be a worthy exploration aspect by more researchers.

**DISCUSSION**

More and more researchers are devoted to investigating metal-free dental implants, especially zirconia, which is considered a competitive material for dental implants. However, the exploration of zirconia dental implants needs more effort. Surface modifications are introduced to improve zirconia properties. It effectively enhances bone osseointegration by adjusting surface roughness, morphology, hydrophilicity, chemical stability, and antibacterial resistance. The strategies for bone tissue engineering through surface modifications on zirconia-based materials in the review were summarized in Table 1. Sandblasting is a practical approach to obtain optimal micro-roughness surfaces. However, the formed mechanical forces during sandblasting will induce the LTD phenomenon. It would also slightly change the surface elemental composition due to inevitable alumina contamination. From that point, the acid etching method was introduced. For zirconia, acid etching and electrochemical treatments are less efficient than metals, and they are still under laboratory exploration. Contact-less physical treatments such as laser and UV are applied to surface modification, improving surface properties and cell viability. More recently, coatings are also introduced as surface treatments, which could enhance bioactivity, biocompatibility, or potential antibacterial properties of zirconia. However, it still faces a problem about the stabilities and application of these coatings. This review summarizes not all but most frequently used and potential techniques and gives general information on the usage of surface modification on zirconia, and it suggests surface modification would successfully improve the surface characteristic and compatibility of zirconia materials.

**AUTHOR CONTRIBUTIONS**

LS and GH contributed to the conception and design of the study. LS collected the articles, organized the database, and wrote the first draft of the manuscript. LS and GH wrote sections of the manuscript. All authors contributed to manuscript revision, read, and approved the submitted version.

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