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Nano-Zirconia Synthesis Methods and their Pioneering Applications in Dentistry

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ABSTRACT

Nano-zirconia, also known as nanocrystalline zirconia or zirconia nanoparticles, is a versatile material with numerous applications in various fields, including catalysis, sensors, energy storage, and biomedical engineering. This review manuscript explores the synthesis methods of nano-zirconia, focusing on the sol-gel method, precipitation method, hydrothermal method, flame spray pyrolysis, and template-assisted synthesis. Each method is discussed in detail, highlighting its advantages and disadvantages. The selection of a synthesis approach depends on factors such as desired properties, scalability, cost, and equipment availability. Furthermore, the study examines specific dental applications where nano-zirconia materials find utility. In dental implantology, nano-zirconia implants have shown promising results in terms of osseointegration, with comparable or superior performance to titanium implants. Surface modifications, such as bioactive coatings, have been explored to enhance osseointegration and long-term success. Additionally, nano-zirconia ceramics have been utilized in dental prostheses, such as crowns, due to their biocompatibility and exceptional strength. Studies have evaluated the mechanical properties and translucency of different zirconia compositions for dental restorations. Moreover, improvements in the sol-gel process have led to the development of zirconia-silica glass ceramics with enhanced aesthetics and corrosion resistance. Lastly, the impact of professional tooth cleaning on zirconia dental prostheses has been investigated, providing insights into surface properties and bacterial adherence. Overall, nano-zirconia materials offer great potential in various dental applications, and their synthesis methods can be tailored to obtain desired properties for specific uses. Further research and optimization are required to fully explore and exploit the capabilities of nano-zirconia in dental settings.

Keywords: Nanoparticles, Zirconia**,** Dentistry, Nanotechnology, Synthesis.

1. INTRODUCTION

The ability to modify or alter the properties of materials employing strong tools in several technical applications has become a reality since the emergence of nanotechnology over the past few years (Omorogbe et al., 2020; Omorogbe et al., 2017; Ifijen et al., 2022a; Ifijen et al., 2022b; Ifijen et al., 2022c; Omorogbe et al., 2019). Because of the growing interest in these applications among

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researchers, several different kinds of nanomaterials and nanodevices have made excellent advancements (Ifijen and Ikhuoria, 2019; Ifijen and Ikhuoria, 2020; Ifijen et al., 2018a; Ifijen et al., 2019a; Ifijen et al., 2019b; Ifijen et al., 2020a; Omorogbe et al., 2017). Due to the significant advancement brought about by their debut, these sorts of materials have garnered a lot of interest in the field of dentistry (Ifijen et al., 2022d; Ifijen et al., 2018b; Ikhuoria et al., 2020; Ifijen et al., 2020; Ifijen and Maliki, 2022; Jonathan et al., 2022; Ozak and Ozkan, 2013).

Speaking, looking good, maintaining oral and general health, and living a quality life all depend on teeth. Oral illnesses such caries, pulpitis, and periodontal disease affect a huge majority of people and some of them can cause functional and aesthetic problems with teeth (Simón and Mira, 2015). Thus, there is a pressing demand, although it remains difficult to restore or regenerate the complex and dynamic dental anatomical system (Lin et al., 2018; Dong et al., 2018). To address this, many dental materials are researched and created for use in reconstructing the curve, color, shape, and functionality of teeth. Dental materials have significantly advanced over the last few decades, enabling more individualized dental treatments. Implants and ceramic crowns are the two most often used materials in dental restorations and prosthetics (Sailer et al., 2015).

To correct tooth flaws, ceramic fused metal and all-ceramic crowns are frequently employed. All-ceramic materials are chosen over ceramic fused metal restorations due to their natural color, wear resistance, biocompatibility, and aesthetics (Pjetursson et al., 2015). The most common implant used in clinics today is titanium (Giavaresi et al., 2003; Song et al., 2019), while ZrO_2 implants have recently gained a lot of interest (Hu et al., 2019). Studies conducted in vitro and in vivo have shown that ZrO_2 implants had comparable or even better osseointegration than Ti implants (Gautam et al., 2016). Supreme purity ZrO_2 is a common material in the dental industry. It is a type of biomaterial with good natural white color, high toughness, excellent strength, consistent chemical properties, and good corrosion resistance, and it can be used to make high-performance ceramic materials, particularly biocompatible implant materials (Gad et al., 2016). In addition, the high strength of ZrO_2 shows that it is challenging to synthesize and absorb. It is permissible to insert tiny blocks of micro/nano ZrO_2 to address the problems.

Nano-ZrO_2 offers additional application possibilities, such as filling with nanopowders, coating with nanopowders, sintering raw materials, and others (Hu et al., 2019). ZrO_2 nanopowders are utilized to improve the mechanical and bionic properties of dental ceramics and tissue engineering scaffolds. Recent studies have shown that the combination of ZrO_2

nanopowders can significantly improve the flexural strength, fracture toughness, and shear bond strength of a material (Lu et al., 2012; Gad et al., 2016). In a totally different situation, nano-ZrO_2 can be used to generate a strong porous coating on solid surfaces to create a nanostructured surface using a method of modification that could increase biocompatibility. For instance, nano-ZrO_2 coating on Ti implants or nano porous ZrO_2 implants can speed up the osseointegration process (Aboushelib et al., 2013). It is believed that bioactivation and surface treatment hasten the creation of new bone. This review delves into the diverse synthesis methods employed for nano-zirconia, encompassing sol-gel, precipitation, hydrothermal, flame spray pyrolysis, and template-assisted synthesis. Each technique is meticulously examined, elucidating their unique strengths and limitations. Moreover, the study specifically homes in on the invaluable dental applications of nano-zirconia materials, spanning dental implants, surface modifications like bioactive coatings, and dental prostheses such as crowns.

2. THE SYNTHESIS OF NANO-ZIRCONIA

Nano-zirconia, also known as nanocrystalline zirconia or zirconia nanoparticles, is a fascinating material with various applications in fields such as catalysis, sensors, energy storage, and biomedical engineering. Several synthesis approaches have been developed to produce nano-zirconia with controlled particle size, morphology, and properties. In this discussion, we will explore some of the commonly used methods for synthesizing nano-zirconia, providing a detailed analysis of each approach.

2.1. Sol-Gel Method

The sol-gel method is a widely employed technique for the synthesis of nano-zirconia due to its simplicity, versatility, and ability to control the particle size. The process starts with the formation of a stable sol, which involves the hydrolysis and condensation of zirconium alkoxide precursors (such as zirconium propoxide or zirconium n-propoxide) in a solvent (Catauro and Ciprioti, 2021). This step leads to the formation of zirconia nuclei. Subsequently, the sol undergoes aging and drying to promote particle growth and obtain a solid gel. Finally, the gel is calcined to remove the organic constituents and obtain the desired nanostructured zirconia (Esposito, 2019).

The sol-gel method offers several advantages, including low-temperature processing, control over particle size, and the ability to incorporate dopants (Catauro and Ciprioti, 2021). The properties of the resulting nano-zirconia can be further modified by adjusting the precursor concentration, pH, temperature, and aging time (Esposito, 2019). However, challenges associated with this method include gel shrinkage, agglomeration during drying, and the need for careful control of the reaction conditions.

2.2. Precipitation Method

The precipitation method involves the precipitation of zirconium salts from a precursor solution, followed by subsequent thermal treatment to obtain nano-zirconia particles (Kumari et al., 2022). The most commonly used zirconium salts include zirconium oxychloride ($ZrOCl_2$) and zirconium sulfate ($Zr(SO_4)_2$) (Wang et al., 2006). In this method, the zirconium salt solution is mixed with a precipitating agent, such as ammonia or sodium hydroxide, under controlled conditions (Arshad et al., 2022). The resulting precipitate is washed, dried, and calcined to obtain nanostructured zirconia.

The precipitation method offers simplicity, scalability, and relatively low cost compared to other techniques (Kumari et al., 2022). However, it may result in a broad particle size distribution and poor control over particle morphology. Additional steps, such as post-treatment or surface modification, may be required to improve the properties of the synthesized nano-zirconia.

2.3. Hydrothermal Method

The hydrothermal method involves the synthesis of nano-zirconia under high-pressure and high-temperature conditions in an aqueous environment (Behbahani et al., 2012). Typically, zirconium salts are dissolved in a water-based solution, and a hydrothermal reactor is used to control the reaction parameters. The hydrothermal process promotes the formation of nano-sized particles by providing a favorable environment for nucleation and growth (Bumajdad et al., 2018). After the reaction, the obtained product is washed, dried, and calcined to obtain nanostructured zirconia.

The hydrothermal method offers advantages such as the ability to control particle size, enhanced crystallinity, and improved homogeneity (Behbahani et al., 2012). The reaction conditions, such as temperature, pressure, pH, and reaction time, can be optimized to obtain desired nano-zirconia properties. However, the hydrothermal method requires specialized equipment, and the process parameters need careful optimization to prevent the formation of undesired phases or agglomeration (Behbahani et al., 2012).

2.4. Flame Spray Pyrolysis

Flame spray pyrolysis (FSP) is a versatile aerosol-based technique for the synthesis of nanostructured materials, including zirconia nanoparticles (Strobela and Pratsinis, 2007). In FSP, a precursor solution containing zirconium compounds is atomized into fine droplets and then sprayed into a high-temperature flame (Teoh et al., 2010). The droplets undergo rapid evaporation and pyrolysis, leading to the formation of nano-sized zirconia particles (Pokhrel and Mädler, 2020). The particles are subsequently collected, cooled, and optionally subjected to post-treatment processes.

FSP offers several advantages, such as high production rates, narrow particle size distribution, and control over particle morphology (Strobela and Pratsinis, 2007). The process parameters, including precursor concentration, feed rate, temperature, and residence time, can be adjusted to obtain the desired nano-zirconia characteristics (Teoh et al., 2010). However, FSP requires advanced equipment and safety measures due to the involvement of high-temperature flames and potentially hazardous precursor materials.

2.5. Template-Assisted Synthesis

Template-assisted synthesis involves the use of a template or sacrificial material to guide the formation of nano-zirconia (Kaplin et al., 2020). Various templates, such as polymers, surfactants, or biological materials, can be utilized (Zha et al., 2023). The zirconia precursor solution is introduced onto or into the template, allowing the formation of nanostructured zirconia following subsequent removal of the template material (Li et al., 2021). This can be achieved through processes like calcination, solvent extraction, or thermal degradation.

Template-assisted synthesis offers control over particle size, morphology, and pore structure by manipulating the properties of the template material (Kaplin et al., 2020). It enables the creation of unique nano-zirconia structures such as hollow spheres, fibers, or mesoporous materials (Li et al., 2021). However, the template removal step can be challenging and may require additional processing steps to obtain the desired nano-zirconia product.

In general, several synthesis approaches are available for producing nano-zirconia with tailored properties. The sol-gel method, precipitation method, hydrothermal method, flame spray pyrolysis, and template-assisted synthesis are some of the commonly used techniques. Each method has its own advantages and limitations, and the selection depends on factors such as desired properties, scalability, cost, and equipment availability. Through careful optimization of the synthesis parameters, researchers can obtain nanostructured zirconia materials suitable for a wide range of applications. Table 1 presents a tabular depiction of the pros and cons associated with various synthesis methods utilized for nano-zirconia (Arshad et al., 2022; Tran et al., 2022; Bumajdad et al., 2018; Behbahani et al., 2012; Hasan et al., 2022).

Table 1. Tabular representation of the advantages and disadvantages of each synthesis approach for nano-zirconia (Note that the advantages and disadvantages mentioned in the table are general and may vary depending on specific experimental conditions and requirements).

Technique	***Advantages***	***Disadvantages***
Sol-Gel Method	1. Provides control over the size and morphology of nanoparticles.	1. Requires careful control of the reaction conditions to achieve desired properties.
	2. Offers the possibility of doping zirconia with other materials for enhanced properties.	2. Long processing time due to the multi-step nature of the process.
	3. Can produce high-purity nanoparticles with good crystallinity.	3. Typically requires the use of organic solvents, which may pose environmental and health risks.
Precipitation Method	1. Simple and cost-effective technique.	1. Lack of control over particle size and morphology, resulting in a wide size distribution.
	2. Scalable for large-scale production.	2. Typically requires post-synthesis treatments, such as calcination, to improve crystallinity.
	3. Relatively fast synthesis process.	3. Limited control over the phase composition and purity of the resulting nanoparticles.
Hydrothermal Method	1. Allows synthesis of highly crystalline nanoparticles with controlled size and shape.	1. Requires high-pressure and high-temperature conditions, which may limit scalability.
	2. Provides uniform and narrow size distribution of nanoparticles.	2. Long synthesis times, ranging from hours to days, depending on the desired properties.
	3. Can produce nanoparticles with excellent chemical and thermal stability.	3. Limited control over the phase composition, which may result in the formation of unwanted phases.
Flame Spray Pyrolysis	1. Rapid and continuous synthesis process.	1. Requires specialized equipment and expertise, making it less accessible for some researchers.
	2. Enables the synthesis of nanoparticles with high purity and controlled size.	2. May require additional post-synthesis treatments to enhance crystallinity and remove impurities.
	3. Offers the ability to scale up production.	3. Flame temperature and feedstock composition need to be carefully controlled to obtain desired properties.
Template-Assisted Synthesis	1. Allows precise control over nanoparticle size, shape, and arrangement.	1. Requires the fabrication of suitable templates, which can be time-consuming and costly.
	2. Offers the possibility of creating complex nanostructures with hierarchical architectures.	2. Limited to the types of templates that can be used, which may restrict the design flexibility.
	3. Can produce nanoparticles with tailored properties for specific applications.	3. Template removal can be challenging and may affect the final properties of the synthesized nanoparticles.

3. APPLICATION OF NANO-ZRO_2 AS DENTAL IMPLANTS

3.1. Enhancing Osseointegration with Bioactive Hybrid Zirconia Implant Surfaces

Dental implants made of titanium and its alloys have become the standard of care for replacing missing teeth due to their mechanical strength and biocompatibility (Osman and Swain, 2015; Yan et al., 2015). However, the osseointegration, or the bonding between the implant and the bone tissue, achieved with titanium implants may not always meet the demands of the stresses placed on them. This has led to the exploration of surface modifications to enhance the process of bone regeneration and improve osseointegration (Roehling et al., 2015). Nano-zirconia (ZrO_2) has emerged as a promising material or coating for dental implants due to its favorable properties. Zirconia exhibits excellent chemical stability, biocompatibility, fracture resistance, and flexural strength, making it a suitable choice for implant applications. Researchers have conducted significant studies comparing the osseointegration of ZrO_2 implants to that of titanium implants, and the results have shown comparable or even superior performance of ZrO_2 implants in terms of bone integration (Apratim et al., 2015; Rasouli et al., 2018).

Mostafa and Aboushelib (2018) assessed the effects of novel bioactive hybrid zirconia implant surfaces on osseointegration in a rabbit model. The researchers aimed to improve the osseointegration of implants by utilizing bioactive-hybrid surfaces. Specialized zirconia implants were manufactured according to specific guidelines, creating a nano-porous surface using the selective infiltration etching (SIE) approach. Surface porosities were filled with either platelet-rich plasma or nano-hydroxy apatite particles, while uncoated surfaces served as the control. Characterization techniques such as mercury porosimetry, XRD analysis, SEM, and EDX analysis were employed to study the surface properties of the new implant surfaces. After the femur heads of rabbits had healed, histomorphometric analysis was performed to determine the percentage of bone-to-implant contact (BIC%). The results showed that the bioactive-hybrid surface and PRP-coated surface exhibited significantly higher BIC% (79.8 ± 3% and 71 ± 6%, respectively) compared to the control group (49 ± 8%). This improvement in osseointegration was statistically significant, as demonstrated by the analysis ($F = 14.6$, $P < 0.001$) (Fig 1). The selective infiltration etching technique successfully created a surface with interconnected porosities on the zirconia implants. The application of the bioactive coatings led to a decrease in total porosity percentage as observed through mercury porosimetry. XRD analysis revealed the presence of a hexagonal crystal structure of nano-hydroxy apatite (HA) in conjunction with the tetragonal crystal phase of zirconia.

Generally, the study demonstrated that zirconia implants with a bioactive hybrid surface showed improved osseointegration compared to the control group. This research highlights the potential of nanotechnology and surface modifications in enhancing the performance of dental implants, particularly in terms of bone integration and long-term success.

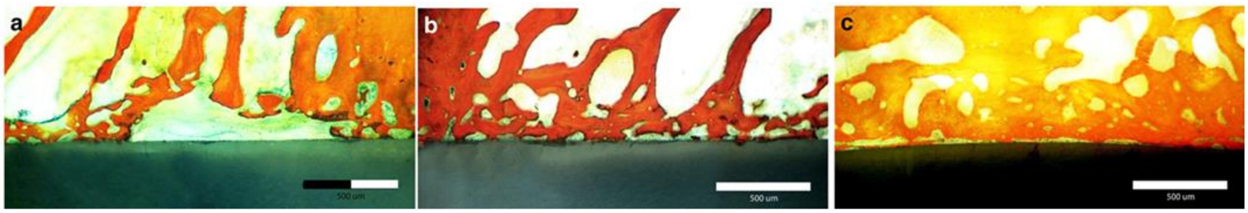

Figure 1. (a) Stained histomorphometric section demonstrating bone implant contact of uncoated zirconia implant. (b) Stained histomorphometric section demonstrating bone implant contact of HA–hybrid–zirconia surface. (c) Stained histomorphometric section demonstrating bone implant contact of PRP–hybrid–zirconia surface (Mostafa and Aboushelib, 2018) (Scale 500µm).

3.2. Assessment of Yttria-based and Ceria-based Nano-zirconia for Dental Prostheses

Porcelain-fused-to-metal (PFM) crowns have been a popular choice for dental restoration in esthetic dental treatments for many years (Sailer et al., 2015). These crowns consist of a metal framework with a layer of porcelain fused to the exterior, providing both strength and an esthetically pleasing appearance. However, in some cases, prolonged placement of dental prostheses in the oral cavity can lead to metal allergies caused by the eluate from the metal frame. This has prompted the development of new techniques and materials for tooth repair (Nakazawa et al., 2018). One of the alternatives to PFM crowns is the use of zirconia ceramics in dental prostheses. Zirconia is a type of ceramic material known for its excellent biocompatibility and exceptional strength. It is made from zirconium dioxide and has become increasingly popular in dental practice, particularly in cosmetic dentistry (Alqutaibi et al., 2022).

The biocompatibility of zirconia ceramics makes them well-suited for use in the oral cavity. When placed as dental prostheses, they exhibit minimal adverse reactions or allergies in patients. This is particularly important for individuals who have a known metal allergy or are sensitive to the eluate from metal frameworks (Bapat et al., 2022). Zirconia ceramics also offer exceptional strength and durability, making them suitable for use in dental restorations. Their high flexural strength and resistance to fracture make zirconia crowns a reliable option for restoring damaged or missing teeth. Additionally, zirconia ceramics have a natural tooth-like appearance, which contributes to their frequent use in cosmetic dentistry (Permatasari et al., 2012).

In recent years, advancements in dental technology and materials have further improved the esthetic properties of zirconia ceramics (Catauro et al., 2021; Cheng et al., 2019). Various shades and translucencies are available, allowing dentists to achieve highly esthetic results that closely mimic natural teeth. This makes zirconia crowns an attractive option for patients seeking both functional and aesthetically pleasing dental restorations (Cheng et al., 2019). Despite the many advantages of zirconia ceramics, it's worth noting that each dental material has its own set of considerations and limitations. The choice of the most appropriate material for dental restoration depends on various factors, including the patient's specific needs, the location of the restoration, and the dentist's professional judgment (Hu et al., 2019).

For example, the suitability of yttria-based zirconia and ceria-based nano-zirconia for usage in dentistry was assessed by Tanaka et al. (2019). The sintering density, crystalline phases, structure, translucency, bending strength, fracture toughness, and impact toughness of zirconia powders of various compositions are assessed mechanically. Additionally, sintered materials that mimic a single crown coping presuming a molar tooth were used in a fracture strength test. Sample TZ (yttria-based zirconia) with 0.26 wt% alumina showed the greatest results among the other zirconia samples in the flexural strength test, with biaxial flexure strength of 1384 MPa and three-point bending strength of 1278 MPa. The most fracture-resistant sample was MA (ceria-based composite zirconia), measuring 12.1 MPa/m1/2 for the SEPB method and 21.3 MPa/m1/2 for the IF method. The yttria-based zirconia sample ZS exhibited the lowest bending strength and fracture toughness, but its high translucency and white hue made it ideal for use as a full-crown prosthesis for short spans. Sample MA (ceria-based composite zirconia) did not display translucency, but it can be applied to long-span bridges due to its superior fracture toughness and flexural strength.

Due to their adequate mechanical qualities and attractive aesthetics, ceramics and glass ceramics are frequently utilized as dental materials. Although all-ceramic materials like zirconia and alumina have outstanding mechanical capabilities, their opaque nature makes them less aesthetically pleasing and makes it more challenging to match the color of the adjacent teeth than translucent glass ceramics like lithium disilicates. To create zirconia-silica glass ceramics with characteristics suitable for dental applications, Persson et al. (2012) improved the sol-gel process. The material's characteristics were contrasted with those of the commercially available lithium disilicate, IPS e.max® CAD. It was discovered that the zirconia-silica glass ceramic was translucent, had an excellent corrosion resistance, and had a transmittance of above 70%. With the appropriate heat treatment, a higher fracture toughness was attained for the zirconia-silica glass ceramic, which also showed a little lower elastic modulus but higher hardness than the lithium disilicate. The material used in this study demonstrated promising findings for usage in dental applications, however the production process is delicate, and it would be challenging to generate large specimen sizes.

Dental prosthesis made of zirconia (3Y-TZP) are often utilized in clinical dentistry. Nonetheless, research into the impact of professional tooth cleaning with ultrasonic scaling on 3Y-TZP dental prosthesis, particularly when combined with low-temperature deterioration (LTD), is still developing. In respect to bacterial adherence on the treated surface, Nakazawa et al. (2018) assessed the impact of ultrasonic scaling and LTD on the surface properties of 3Y-TZP. 4 4 2 mm 3Y-TZP specimens were polished, autoclaved at 134^{o}C for 100 hours to induce LTD, and then exposed to 10 rounds of ultrasonic scaling using a steel scaler tip for 1 minute each. By using optical interferometry, X-ray diffraction analysis, contact angle measurement, and the nano-indentation technique, researchers were able to determine the surface roughness, crystalline structure, wettability, and hardness of the material. Subsequently, an assessment of bacterial adhesion to the treated 3Y-TZP surface was conducted, employing Streptococcus mitis and S. oralis. According to the findings, the polished 3Y-TZP surface's Sa value (surface roughness parameter) increased significantly from 1.6 nm to 117 nm because of the combination of ultrasonic scaling and LTD. LTD had an impact on the crystalline structure, causing a phase transition from the tetragonal to the monoclinic phase and lowering the surface hardness and contact angle. These modifications to the surface properties did not, however, affect bacterial adhesion. The *S. mitis* and *S. oralis* formed on the specimens after 3 and 6 hours of incubation are depicted in representative confocal laser scanning microscopy (CLSM) pictures in figures 2A and 2B, respectively. S. mitis and *S. oralis* SYTO9 (green) and propidium iodide (PI) (red), respectively, were used to label both living and dead bacterial cells. Bacterial cells were seen to be linked and spherical. Both *S-mitis* and *S. oralis* significantly increased their biofilm coverage over the course of the incubation period ($p < 0.01$, Figs 2C and 2D). However, there was no discernible difference in biofilm coverage between the untreated (UT) specimen and the specimen that was subjected to LTD followed by US using a steel tip (LTD-US-S) at any given time point ($p > 0.05$). The majority of the bacterial cells were exclusively stained with SYTO9, and only a tiny percentage of the bacteria were also stained with PI (Fig 2E), demonstrating that the biofilm was primarily made up of live bacteria. The current investigation reveals that, despite mild surface roughening, ultrasonic scaling may be suitable for debridement of 3Y-TZP dental prosthesis because it did not promote bacterial adherence even when used in conjunction with LTD.

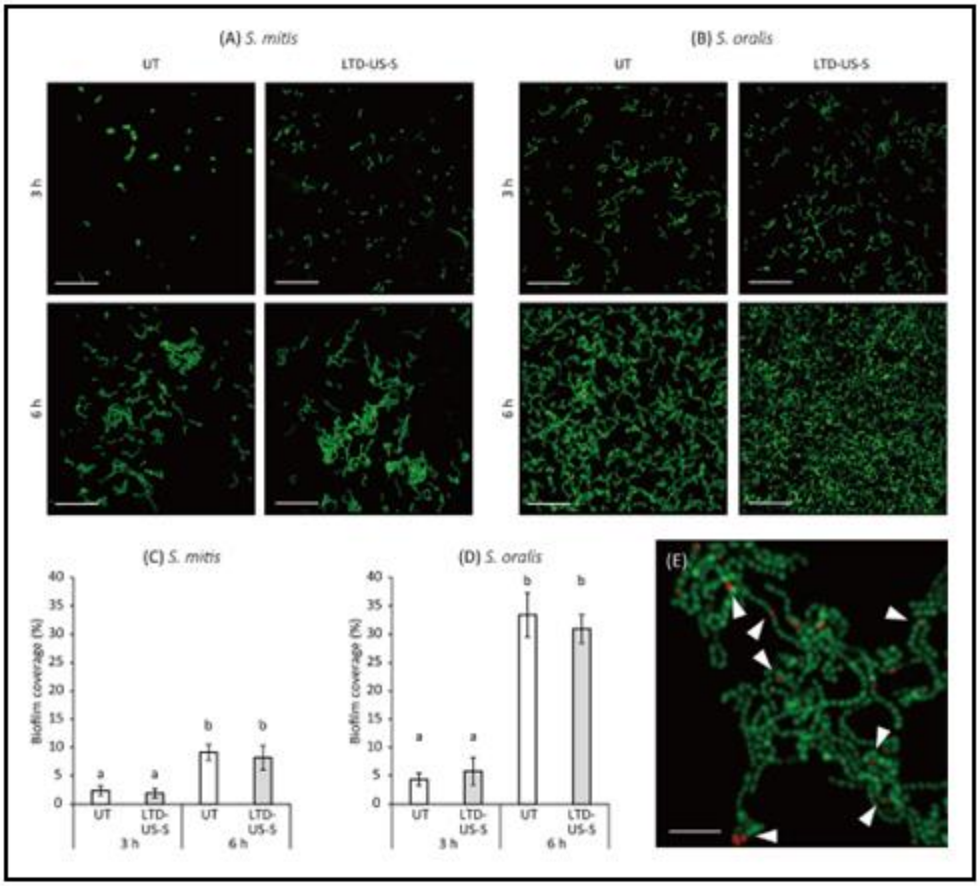

Figure 2. Microscopic analysis of *S. mitis* and *S. oralis* grown on zirconia (3Y-TZP) specimens subjected to low temperature degradation (LTD) and ultrasonic scaling (US). (A and B) Representative confocal laser scanning microscope (CLSM) images of S. mitis and S. *oralis*. Living and dead bacterial cells were stained with SYTO9 (green) and propidium iodide (PI) (red), respectively. The merged images were mostly composed of bacterial cells stained with SYTO9. (C and D) Change in biofilm coverage (%) by S. *mitis* and S. *oralis* on the observed area (Nakazawa et al., 2018).

In a nutshell, zirconia ceramics have emerged as a popular alternative to porcelain-fused-to-metal crowns for tooth repair in esthetic dental treatments. Their exceptional biocompatibility, strength, and esthetic properties have made them a frequent choice in dental practice, particularly in cosmetic dentistry. However, it's important for dentists to carefully evaluate each patient's unique situation and consider all relevant factors when selecting the most appropriate material for dental restorations.

3.3. The Influence of Nano-Zirconia Nanoparticles on the Wear Resistance of Dental Resin Composites and Denture Bases

The wear resistance of dental resin composites is impacted by multiple factors, with roughness and hardness playing crucial roles in determining their durability and performance (Azmy et al., 2022). Surface roughness in dental resin composites refers to the presence of irregularities or micro-features on the surface, which can be influenced by factors like filler particle size and distribution, polymerization shrinkage, and finishing and polishing techniques (Ghinea et al., 2011). A smoother surface tends to exhibit better wear resistance by reducing frictional forces, minimizing plaque and bacteria accumulation, and decreasing the likelihood of surface degradation. On the other hand, hardness represents a material's ability to resist indentation or scratching. In dental resin composites, hardness is influenced by the composition and degree of resin matrix polymerization, as well as the type, size, and concentration of filler particles (Elbishari et al., 2020). Higher hardness values generally indicate improved wear resistance due to the material's enhanced ability to withstand mechanical forces and resist abrasive wear (Vargova et al., 2022).

In addition to roughness and hardness, several other factors can affect the wear resistance of dental resin composites (Vargova et al., 2022). These include the type and quality of resin matrix and filler materials, the ratio of resin to filler, the curing process, the presence of additives or modifiers, and the oral environment in which the material is placed. Dental professionals should consider these factors when selecting and using dental resin composites to ensure optimal wear resistance and longevity of dental restorations (Tsujimoto et al., 2018). For example, in a study conducted by Rodriguez and Casanova in 2018, they investigated the use of different types of silica nanoparticles as reinforcement agents in dental resin composites. Specifically, they examined silica nanoparticles, silica nanoclusters, and silica-zirconia nanoparticles. To create spherical nanoclusters, the researchers employed a spray drying technique using aqueous dispersions of the nanoparticles (as depicted in Fig 3). They used atomic force microscopy (AFM) to measure the roughness of the composite surfaces and nanoindentation to assess their nanohardness. The study findings revealed that the roughness measurements obtained with silica nanoparticles were smaller compared to those of silica and silica-zirconia nanoclusters (138.1 ± 36.6 nm vs. 116.2 ± 32.2 nm, respectively). However, when it came to nanohardness, the measurements obtained for all the composite materials were comparable. The nanohardness values were found to be 0.24 ± 0.01 GPa for silica nanoparticles, 0.25 ± 0.04 GPa for silica nanoclusters, and 0.22 ± 0.02 GPa for silica-zirconia nanoclusters. Based on the results of this study, it can be concluded that the roughness of the final dental resin composite material is influenced by the particle size. Smaller silica nanoparticles resulted in lower roughness values. On the other hand, the concentration of the reinforcement materials, rather than the type of nanoparticles used, was identified as the primary determinant of nanohardness. In this case, the nanohardness values of the composites were similar regardless of the type of nanoparticles incorporated. These findings provide valuable insights into optimizing the wear resistance performance of dental resin composites. By carefully selecting the appropriate particle size and concentration of reinforcement materials, it is possible to control the roughness and hardness properties of the composite, thereby enhancing its durability and longevity in clinical applications.

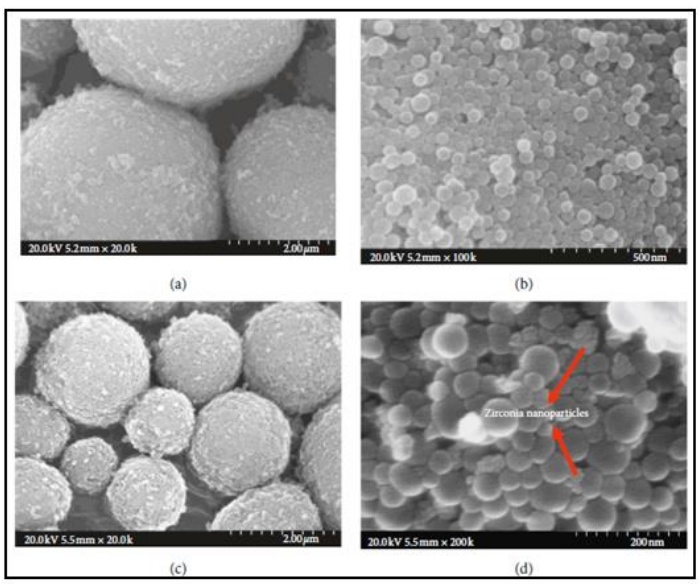

Figure 3. SEM micrographs of (a) silica nanoparticle nanoclusters, (b) surface of silica nanoclusters, (c) silica-zirconia nanoclusters, and (d) surface of silica-zirconia nanoclusters (Rodrguez and Casanova, 2018).

In a different study, Zidan et al. (2020) evaluated the tensile bond strength (TBS) between anterior acrylic teeth and denture bases made of high-impact heat-cured acrylic resin (HI PMMA) that were impregnated with zirconia nanoparticles. A total of 30 specimens were fabricated, each containing a set of six upper anterior teeth. The denture bases were reinforced with different weight concentrations of zirconia nanoparticles, ranging from 0% (control) to 10%. TBS was tested according to the British standard BS EN ISO 22112:2017. The results of the study showed that the TBS values between the anterior teeth (central and lateral incisors and canine) and the HI-PMMA denture base groups containing 7 wt.% and 10 wt.% of zirconia nanoparticles were significantly lower compared to the control group and the other nanocomposite groups. The TBS values for HI PMMA with 1.5 wt.%, 3 wt.%, and 5 wt.% of zirconia showed slightly lower values than the control group, but these differences were not significant. The failure modes observed between the teeth and denture base nanocomposites were predominantly cohesive fractures, which were considered clinically acceptable according to the standard. Based on these findings, it can be concluded that the addition of zirconia nanoparticles to HI PMMA denture base at high concentrations (7 wt.% and 10 wt.%) significantly affected the tensile bond strength between the anterior teeth and the denture base. However, lower concentrations of zirconia nanoparticles (1.5 wt.%, 3 wt.%, and 5 wt.%) did not have a significant impact on the tensile bond strength. These results suggest that the incorporation of zirconia nanoparticles at appropriate concentrations could be a potential strategy for improving the mechanical properties of denture bases used in dentistry. Further research is warranted to optimize the concentration of zirconia nanoparticles and explore their long-term effects on the performance and durability of denture prostheses.

3.4. Enhancing Mechanical Properties of Ceramics for Tooth Fragment Reattachment: Nano-ZrO_2 Modification of Resin Cement

The issue of poor mechanical properties in ceramics used for reattaching fractured tooth fragments with self-adhesive resin cement is an important consideration in restorative dentistry (Persson et al., 2012). The successful reattachment of fractured tooth fragments requires a durable bond between the ceramic and the tooth structure, ensuring long-term stability and functionality. Ceramics are commonly used in dental restorations due to their excellent aesthetic properties and biocompatibility (Nakazawa et al., 2018). However, they are inherently brittle materials with lower tensile strength compared to other restorative materials like metals or composite resins. This brittleness can lead to chipping or fracture of the ceramic restoration over time, especially in high-stress areas such as the posterior teeth.

One approach to addressing the issue of poor mechanical properties is to modify the ceramic material itself (Lu et al., 2012). Researchers have focused on improving the strength and fracture toughness of ceramics by incorporating reinforcing agents such as zirconia or alumina nanoparticles. These reinforcements can enhance the material's resistance to crack propagation and improve its overall mechanical properties (Lu et al., 2012; Gautam et al., 2016). Additionally, advances in ceramic processing techniques, such as hot isostatic pressing or microwave sintering, can also enhance the strength and reliability of ceramic restorations (Gautam et al., 2016).

Another important aspect is the choice of the resin cement used for bonding the ceramic fragment to the tooth structure. Self-adhesive resin cements are commonly used because they simplify the bonding procedure by eliminating the need for separate etching, priming, or bonding steps (Behbahani et al., 2012). However, they may have lower bond strengths compared to resin cements that involve additional adhesive steps. To address this, researchers have investigated various surface treatments for ceramics, such as airborne-particle abrasion or laser etching, to enhance the bond strength between the ceramic and the self-adhesive resin cement (Persson et al., 2012). Furthermore, the clinical technique employed during the reattachment procedure plays a crucial role in ensuring a strong and durable bond (Nakazawa et al., 2018). Proper cleaning and preparation of the tooth surface and the ceramic fragment are essential for maximizing the bond strength. The use of adhesive systems or bonding agents specifically designed for ceramics can also improve the bonding effectiveness (Lu et al., 2012).

It is worth noting that the choice of restorative material should consider not only mechanical properties but also factors such as esthetics, biocompatibility, and clinical longevity. Dentists and dental researchers are continually striving to develop innovative materials and techniques that can overcome the limitations associated with ceramic restorations. Collaborations between material scientists, dental manufacturers, and clinicians are crucial in driving advancements in this field.

To address the issue of poor mechanical properties in ceramics used for reattaching fractured tooth fragments with self-adhesive resin cement, El-Kemary et al. (2021) synthesized zirconium dioxide nanoparticles (nano-ZrO_2) using the Coprecipitation approach. These nanoparticles were combined with commercially available RelyX™ Unicem self-adhesive universal resin cement (ARC) at various concentrations (1.0, 2.0, 3.0, and 5.0 wt%), resulting in nano-ZrO_2/ARC composites. The synthesized nano-ZrO_2 and nano-ZrO_2/ARC composites underwent characterization using techniques such as high-resolution transmission electron microscopy (HR-TEM), field-emission scanning electron microscopy, X-ray diffraction, and Fourier transform infrared spectroscopy. The HR-TEM analysis revealed that the nano-ZrO2 particles possessed a spherical shape (Fig 4a) with an approximate diameter of 12 nm. The interplanar distance was estimated to be 0.296 nm (Fig 4b). The selected area electron diffraction (SAED) pattern of the nano-ZrO_2 indicated its polycrystalline nature (Fig 4c). When observing the TEM images of the nano-ZrO_2/ARC composite, it was apparent that irregularly agglomerated nanoparticles were dispersed within the organic ARC matrix (Fig 4d, e), suggesting successful incorporation of the nano-ZrO_2 particles into the ARC matrix.

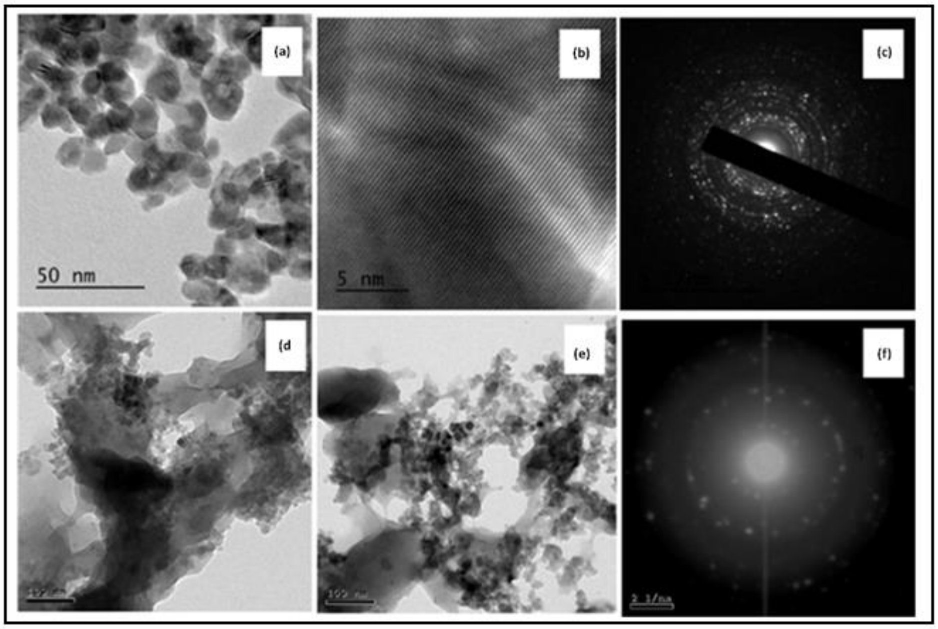

Figure 4 (a). Transmission electron microscope (TEM) image of nano-ZrO_2, (b) high-resolution transmission electron microscope (HR-TEM) image at high magnification, (c) selected area electron diffraction pattern (d and e) TEM image for nano-ZrO2/adhesive resin cement (ARC) and (F) diffraction pattern nano-ZrO_2/ARC, respectively (El-Kemary et al., 2021).

In figure 5(a), the viability of human lung fibroblasts (WI 38) was found to be high when exposed to ARC, with 85% viability compared to the control group. Notably, the addition of nano-ZrO_2 up to 3.0 wt% did not significantly reduce cell viability compared to ARC alone. However, at 5.0 wt% of nano-ZrO_2, the viability decreased to 65% ($p < 0.05$), indicating a significant impact on cell viability. Similar results were observed for normal human melanocytes (HBF-4) cells, as depicted in figure 5(b). The pure ARC exhibited 80% cell viability, while the inclusion of 5.0 wt% nano-ZrO_2 caused a notable decline of 50% in cell viability. Furthermore, the study evaluated the cytotoxicity of the nano-ZrO_2-modified resin cement by assessing cell death. The findings indicated that incorporating nano-ZrO_2 at concentrations up to 3.0 wt% did not induce significant cell death compared to the resin cement alone. Based on these results, the authors suggest that incorporating nano-ZrO_2 into resin cement could enhance its mechanical properties, making it more suitable for various dental procedures, including fragment tooth reattachment, as well as the cementation of dental crowns, bridges, and bands. This study provides valuable insights into the stability and potential applications of nano-ZrO_2-modified resin cement within the field of dentistry.

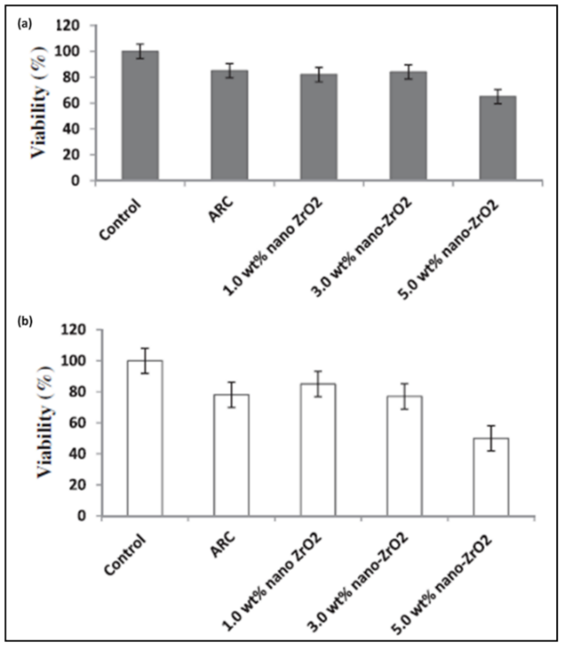

Figure 5. Biocompatibility assessment results of nano-ZrO_2, pure adhesive resin cement (ARC), their mixture at 1.0. 3.0, and 5.0 wt% compared to control consisting of only growth medium, (a) human lung fibroblasts (WI 38), (b) human melanocytes (HFB-4) cells were incubated for 3 days with either of them (El-Kemary et al*.*, 2021).

In general, addressing the issue of poor mechanical properties in ceramics used for reattaching fractured tooth fragments with self-adhesive resin cement involves multiple factors. Modifying the ceramic material, optimizing the resin cement, and employing appropriate clinical techniques can contribute to improving the bond strength and durability of ceramic restorations. Continued research and development efforts are needed to enhance the long-term success of these restorative techniques in dental practice.

3.5. Metakaolin-Zirconia-Apatite Composite: A Promising Material for Aesthetic and Durable Direct Composite Restorations

The Metakaolin-Zirconia-Apatite Composite is a novel material that shows great promise for use in aesthetic and durable direct composite restorations (Permatasari et al., 2012). This composite combines three key components: metakaolin, zirconia, and apatite. Metakaolin is a pozzolanic material derived from the calcination of kaolin clay. It possesses excellent mechanical properties and high reactivity, making it an ideal additive for dental composites (Apratim et al., 2015). Zirconia, a ceramic material, is known for its exceptional strength, durability, and biocompatibility. Apatite is a mineral that closely resembles the natural mineral components of teeth and bones, offering excellent aesthetic properties (Bapat et al., 2022).

By combining these three components, the Metakaolin-Zirconia-Apatite Composite exhibits a unique combination of strength, durability, and aesthetics. Metakaolin provides improved mechanical properties, such as enhanced fracture toughness and flexural strength, which are crucial for long-lasting dental restorations (Catauro and Ciprioti, 2021). The zirconia component adds durability, ensuring the restoration can withstand the stresses of everyday use. Additionally, the apatite component contributes to the composite's aesthetic appeal. Its resemblance to natural tooth structure helps achieve a seamless integration with the surrounding dentition, resulting in highly esthetic restorations (Hu et al., 2019; Schünemann et al., 2019). The use of the Metakaolin-Zirconia-Apatite Composite offers several advantages for direct composite restorations (Osman and Swain, 2015). It provides excellent bonding to tooth structure, reducing the risk of restoration failure. The composite's enhanced mechanical properties and durability increase its longevity, reducing the need for frequent repairs or replacements (Catauro and Ciprioti, 2021). Furthermore, the aesthetic properties of the composite allow for the creation of restorations that closely mimic the natural appearance of teeth (Apratim et al., 2015). This is particularly beneficial for anterior restorations, where the restoration's visual appeal is of utmost importance.

For instance, the Vickers hardness test was conducted by Permatasari et al. (2012) to evaluate the hardness of the metakaolin-zirconia-apatite nanocomposite, which exhibited excellent hardness reaching 37.5 Vickers hardness number (VHN). This indicates the high strength and durability of the composite material. Moreover, the scanning electron microscope characterization revealed that no shrinkage was observed at the interface between the teeth and the nanocomposite when used as a restoration material (Fig 6). This observation suggests that the nanocomposite effectively integrates with the teeth, resulting in a stable and secure restoration. Based on these findings, it can be concluded that the metakaolin-zirconia-apatite composite demonstrates favorable properties and interaction with the teeth when used for restoration applications. The composite exhibits high hardness and does not exhibit shrinkage at the tooth interface, indicating its suitability and effectiveness as a restoration material. These results highlight the potential of metakaolin-zirconia-apatite composite for improving the quality and longevity of dental restorations.

Essentially, the Metakaolin-Zirconia-Apatite Composite is a promising material for aesthetic and durable direct composite restorations. Its unique combination of metakaolin, zirconia, and apatite offers improved mechanical properties, durability, and excellent aesthetics, making it an attractive option for dental applications.

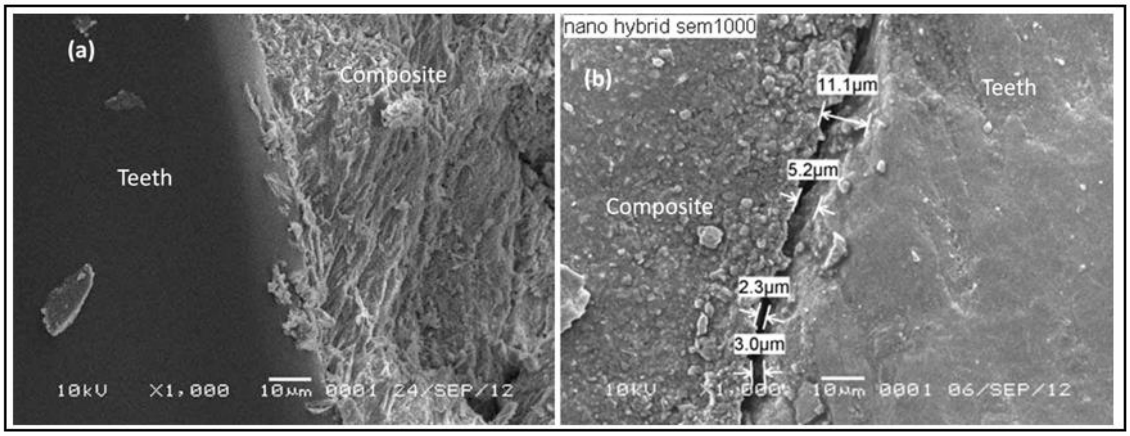

Figure 6. Interaction Between Teeth And (a) Metakaolin-Zirconia-Apatite Nanocomposite, (b) Commercial Nanohybrid Composite (Permatasari et al., 2012).

Nano-zirconia has various applications in dentistry, with its use extending to different dental procedures. It proves valuable in the creation of dental implant frameworks, offering exceptional biocompatibility, strength, and corrosion resistance (Osman and Swain, 2015). Furthermore, its natural tooth-colored appearance enhances the aesthetic appeal of dental implants (Shah et al., 2019). Nano-zirconia is also utilized in the fabrication of precise and long-lasting dental crowns and bridges, allowing for conservative restorations (Alqutaibi et al., 2022). When it comes to veneers, which are thin shells that improve tooth appearance, nano-zirconia demonstrates superior aesthetics and durability compared to traditional ceramics (Souza et al., 2018).

In dentures, nano-zirconia serves as a lightweight and biocompatible framework material, replacing traditional metal frameworks (Wettstein et al., 2008). This alternative enhances aesthetics and patient comfort. Orthodontic brackets made from nano-zirconia blend in with natural tooth color, providing improved aesthetics, strength, and durability (Papathanasiou et al., 2020). Incorporating nano-zirconia particles into dental composites enhances the mechanical properties of fillings, improving their strength and wear resistance (Azmy et al., 2022).

Root canal posts made of nano-zirconia offer high strength and biocompatibility, ensuring the stability and success of dental restorations (Bapat et al., 2022). In dental bone grafting, nano-zirconia acts as a scaffold material, supporting bone tissue growth and regeneration in areas of bone loss or defects (Polo-Corralesn et al., 2014; Silva et al., 2010).

These examples illustrate the versatility of nano-zirconia in dental applications. Its unique properties make it a promising material for various restorations and procedures, offering improved aesthetics, strength, and biocompatibility.

3.6. Exploring the Future Prospects of Dental Applications of Nano-Zirconia

The prospects of dental applications of nano-zirconia are highly promising, offering a multitude of advancements in the field of dentistry. Nano-zirconia, with its unique properties and versatility, holds great potential for further development and innovation. Here, we will discuss some robust aspects of the prospects in dental applications of nano-zirconia (Canullo et al., 2016; Ifijen et al., 2022; Barfeie et al., 2015; Cheng et al., 2019; Sreenivasalu et al., 2022; Bapat et al., 2022).

1. Enhanced Biocompatibility: Nano-zirconia has already demonstrated excellent biocompatibility, but ongoing research aims to further improve its interaction with the oral environment. Scientists are exploring surface modifications and coatings to enhance the biocompatibility of nano-zirconia implants and restorations, reducing the risk of adverse reactions, and improving long-term success rates.
2. Customized and Patient-Specific Restorations: The advent of additive manufacturing technologies, such as 3D printing, opens new possibilities for the fabrication of patient-specific dental restorations using nano-zirconia. This technology allows for the precise and efficient production of customized crowns, bridges, and other dental prostheses, tailored to each patient's unique oral anatomy, and needs.
3. Improved Strength and Durability: Nano-zirconia already exhibits exceptional strength and durability, but ongoing research focuses on further enhancing these properties. By optimizing the nanostructure and composition of zirconia, scientists aim to develop materials with even higher mechanical strength and wear resistance. This will result in longer-lasting restorations and implants that can withstand the demanding oral environment.
4. Advanced Aesthetics: The aesthetic properties of nano-zirconia restorations have already surpassed traditional materials. Ongoing research aims to refine and improve the aesthetic qualities of nano-zirconia, including color matching, translucency, and surface texture, to

achieve even more natural-looking and aesthetically pleasing results. This will contribute to patient satisfaction and acceptance of dental restorations.

5. Bioactive Surface Modifications: Researchers are exploring ways to modify the surface of nano-zirconia to promote better integration with the surrounding tissues. By incorporating bioactive substances, growth factors, or surface coatings with bioactive properties, nano-zirconia can stimulate bone regeneration and improve the osseointegration of implants. This could lead to enhanced success rates and faster healing times for dental implant procedures.
6. Therapeutic Applications: Nano-zirconia has the potential to be utilized in therapeutic applications within the field of dentistry. Researchers are investigating the possibility of incorporating antimicrobial agents or drug-delivery systems into nano-zirconia materials. This could enable targeted and controlled release of therapeutic substances, aiding in the treatment of oral infections, periodontal diseases, and other oral conditions.
7. Nanotechnology Integration: As nanotechnology continues to advance, the integration of nano-zirconia with other nanomaterials or nanoscale technologies holds great promise. This includes the development of nanocomposites with improved mechanical properties, the incorporation of nanoparticles for antimicrobial or regenerative purposes, and the utilization of nanosensors for real-time monitoring of oral health conditions.

Summarily, the prospects of dental applications of nano-zirconia are highly robust and hold great potential for significant advancements in the field of dentistry. With ongoing research and technological developments, we can expect to witness further improvements in biocompatibility, strength, durability, aesthetics, and therapeutic capabilities. Nano-zirconia has the potential to revolutionize dental treatments by providing customized, long-lasting, and aesthetically pleasing restorations, while also promoting improved oral health outcomes.

4. CONCLUSION AND RECOMMENDATION

Nano-zirconia materials offer great potential in various dental applications, including dental implantology and dental prostheses. The synthesis methods of nano-zirconia, such as the sol-gel method, precipitation method, hydrothermal method, flame spray pyrolysis, and template-assisted synthesis, have been explored in detail, highlighting their advantages and disadvantages. The selection of a synthesis approach depends on factors such as desired properties, scalability, cost, and equipment availability. Nano-zirconia implants have shown promising results in terms of osseointegration, comparable to or even superior to titanium implants. To enhance osseointegration and long-term success, surface modifications like bioactive coatings have been investigated. Nano-zirconia ceramics have also been utilized in dental prostheses, such as crowns, due to their biocompatibility and exceptional strength. The mechanical properties and translucency of different zirconia compositions for dental restorations have been evaluated. The sol-gel process has been improved to develop zirconia-silica glass ceramics with enhanced aesthetics and corrosion resistance. Additionally, studies have examined the impact of professional tooth cleaning on zirconia dental prostheses, providing insights into surface properties and bacterial adherence. Based on the findings presented, it is recommended to further research and optimize the capabilities of nano-zirconia in dental settings. Efforts should focus on refining synthesis methods to achieve tailored properties for specific dental applications. It is important to investigate the long-term performance and biocompatibility of nano-zirconia implants, comparing them to traditional titanium implants and exploring surface modifications to improve osseointegration. Further research should also be conducted to evaluate the mechanical properties, translucency, and aesthetics of different zirconia compositions for dental restorations. Advancements in materials and manufacturing techniques can lead to the development of high-quality zirconia-based dental prostheses with improved functionality and aesthetics. Additionally, understanding the impact of environmental factors and maintenance procedures, such as tooth cleaning, on zirconia dental prostheses is crucial. This knowledge can guide the development of improved surface properties and maintenance protocols to minimize bacterial adherence and ensure long-term durability. In summary, by investing in further research, optimization, and development of nano-zirconia materials, the full potential of these materials in dental applications can be realized, leading to advancements in implantology, dental prostheses, and related fields.

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6. CONFLICT OF INTERESTS

There is no conflict of interests.

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