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Nanotechnology in Dentistryn

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Abstract: *In the XXI century, application of nanostructures in oral medicine has become common. In oral medicine, using nanostructures for the treatment of dental caries constitutes a great challenge. There are extensive studies on the implementation of nanomaterials to dental composites in order to improve their properties, e.g., their adhesive strength. Moreover, nanostructures are helpful in dental implant applications as well as in maxillofacial surgery for accelerated healing, promoting osseointegration, and others. Dental personal care products are an important part of oral medicine where nanomaterials are increasingly used, e.g., toothpaste for hypersensitivity. Nowadays, nanoparticles such as macrocycles are used in different formulations for early cancer diagnosis in the oral area. Cancer of the oral cavity—human squamous carcinoma—is the sixth leading cause of death. Detection in the early stage offers the best chance at total cure. Along with diagnosis, macrocycles are used for photodynamic mechanism-based treatments, which possess many advantages, such as protecting healthy tissues and producing good cosmetic results. Application of nanostructures in medicine carries potential risks, like long-term influence of toxicity on body, which need to be studied further. The introduction and development of nanotechnologies and nanomaterials are no longer part of a hypothetical future, but an increasingly important element of today's medicine.*

Keywords: composites; nanoparticles; photodynamic therapy; photosensitizer; antibacterial nanoagents; nanotechnology; re-mineralization; caries; oral cancer; oral bacteria

I. INTRODUCTION

Nanostructures refer to objects that have at least one of their dimension in a three-dimensional space in the range of (1–100 nm), so called the nanoscale [**1**,**2**]. Due to their unique properties, i.e., high surface-to-volume ratios, and high compressive and flexural strength, scientists have researched different application methods and industries which would benefit from the use of these materials [**2**,**3**]. Currently, a dynamic development in the use of nanotechnology is observed in all areas of medicine. It is used, among others, in medical diagnostics (as markers for detection and identification of various diseases), cancer therapy (for targeted delivery of anti-cancer drugs), gene therapy (e.g., DNA or RNA nanovectors), treatment of infections (modifying the release of antibiotics or the antibacterial effect of molecules per se, e.g., nanosilver), tissue and organ regeneration (nanomaterials can be used to stimulate tissue growth and regeneration and to create biomaterials), medical imaging (as contrast agents in imaging techniques), photodynamic techniques (carriers of photosensitizing substances), in neuroscience and many others [**4**,**5**,**6**,**7**,**8**,**9**]. The use of nanotechnology is associated with many positive effects for a patient. In many cases, more effective treatment is possible because of its use. Thanks to the targeted drug delivery system,
it is possible to achieve higher concentrations of the drug at the site of action, while reducing the systemic side effects. The large share of nanotechnology in regenerative medicine also allows to achieve a significant reduction in convalescence time. Tissue reconstruction processes are accelerated due to the high biocompatibility of many new materials. All these aspects also lead to the development of individualized therapy based on precisely diagnosed needs of a patient [**4**,**5**,**6**].

A natural consequence of the development of nanomaterials and nanotechnologies in medicine is their entry into the field of dentistry and therapy of head and neck diseases. It is applied in the most basic areas related to oral personal care and also in advanced technologies related to bone reconstruction or cancer therapy. In the presented review, we discuss a wide spectrum of research in those areas. The industries of oral personal care products and medicine are the ones that have already benefited from the advantages of using nanomaterials. For instance, nanostructures found their role in improving dental prosthetics such as coating of the implants' surface or the implants themselves, leading to better biocompatibility and the process of osseointegration [**10**,**11**]. Nanoparticles can also be found in much more trivial products such as toothpastes for hypersensitivity, mouth washes, bleaching gels or even sports drinks [**5**,**6**]. Nanostructures such as nano-hydroxyapatite (*n*-HA), nano-carbonate apatite (*n*-CAP), nano-carbonate substituted hydroxyapatite (nano-CHA), nano-fluorohydroxyapatite (*n*-FA) and nano-sodium trimetaphosphate (TMP) are also used as innovative and functional dental care products. Moreover, when used in toothpastes, they can perform re-mineralizing and anti-caries functions, combat dentin hypersensitivity and prevent enamel erosion [**12**,**13**,**14**,**15**,**16**,**17**,**18**]

Other important areas of nanotechnology development in the field of dentistry include nanofillers in dental composites. Nanofillers are being studied to improve the mechanical properties and promote re-mineralization of tooth structures. Among other materials, glass ionomers modified using resin with nanofillers and agents releasing fluorine or calcium ions are used. Antibacterial nanofillers such as zinc nanooxide (*n*-ZnO) and silver nanoparticles (*n*-Ag) are used [**19**,**20**]. Clay, silica and carbon nanotubes are other nanofillers that are being studied for their impact on the mechanical properties and aesthetics of dental composites. This review indicates that extensive research is still needed to optimize the mechanical properties and cytotoxicity of dental composite materials. Another significant topic is the development of endodontic treatment, which focuses on the treatment of diseases of the dental pulp. One of the more dynamically developing areas of nanotechnology dealing with this topic is photodynamic antimicrobial chemotherapy (PACT). Already, PACT-based antimicrobial systems such as PAD™ and Helbo® have been introduced into dental practice. Ultrasonic irrigation with NaOCl is also being developed [**21**]

The effectiveness of PACT against periodontitis has been analyzed. This is a biofilm-related inflammatory periodontal disease and a major cause of tooth loss. It is primarily caused by a shift in the oral microflora towards Gram-negative pathogenic anaerobes. However, photodynamic therapy is not only limited to antibacterial but it is also used in anticancer applications. Porfimer sodium (Photofrin) and a hematoporphyrin derivative (HpD/Photofrin) have a particularly important place in the PDT of cancer, as well as the second-generation synthetic drug mTHPC (Foscan), which are used in the treatment of head and neck cancers. Photofrin has relatively poor tumor selectivity and limited absorption of red light while still being a well-penetrating drug. A new generation of chlorin photosensitizers (PSs) has been developed to improve selectivity, reduce exposure time and photosensitization. Derivatization of chlorin e6 (Photolon®) is becoming more and more popular in the treatment of superficial and deep lesions in the head and neck area, shortening the period of photosensitization after treatment [**22**,**23**]. Despite the enormous benefits of nanotechnology, knowledge about its use, even among surgeons, is relatively low. Some of the doctors use nanomaterials without even being aware of this fact [**24**]. This highlights the importance of disseminating knowledge about new treatment methods. The latest research presented in the review can expand knowledge in this area and it constitutes a handy compendium.

II. NANOSTRUCTURE OF TOOTH

Human teeth are built of tissues that constitute a hierarchical structure. The outer tissue of a tooth, the enamel, is a biocomposite that consists mainly of hydroxyapatite. High mineralization and its specific structure make enamel the hardest tissue of the human body (**Figure 1**) [**25**,**26**,**27**]. In enamel, hydroxyapatite forms crystallites with nanorod-like shape, having a vertical array. Such an alignment also results in anisotropic properties [**25**,**27**,**28**]. The enamel acts as an insulating barrier and protects the rest of the tooth from injuries due to physical, chemical or thermal forces [**29**].

The boundary between the enamel and dentine is called a dentin–enamel junction (DEJ). It is a place in which the orientations of the enamel and dentin nanostructures change [**25**]. The surface of the DEJ is formed in ridges, which probably increase the adhesion of enamel and dentine, and therefore, reduce shearing of the enamel while the tooth works [**30**]. Due to its unique mechanical properties, the junction can prevent traversing of cracks from enamel into dentin [**26**].

Dentin consists of hydroxyapatite and about 20–30% of collagen, which mainly contains the collagen-I fibrils. Therefore, the structure of dentin is mainly poly-crystalline and consists of plate-like crystallites. Thanks to that and the fixed orientation of collagen fibers (aligned perpendicularly to crystallites present in enamel), the dentin also possesses anisotropic properties [**25**,**26**,**28**,**31**,**32**]. Due to less mineralization and less brittle construction, dentine acts as a support for the enamel [**26**]. Plate-like crystallites of dentin tend to appear more likely near the junction [**25**]. Their orientation differs, depending on the region of dentin: near the junction, they are rather horizontally oriented, whereas near the pulp, their orientation tends to be vertical [**25**]. There are also suggestions that those crystallites are covered with some hydrated layer [**32**]. It appears that the hardness of the dentin is somewhere between the hardness of an enamel and a bone, although it still has an elastic property, preventing fracture of the tooth [**26**]. Dentin is considered to be the most abundant tissue in the human tooth, thus, its structure alterations may affect tooth fragility [**32**]

III. RESTORATIVE DENTISTRY (DENTAL MATERIALS)

One of the common disorders in the oral cavity is dental caries. Caries is caused by the acid demineralization process of the tooth's hard tissues—dentin and enamel. It leads to dental matrix destruction via acidic dissolving of hydroxyapatite. Bacterial flora of the oral cavity (*Streptococcus mutans*, *Streptococcus sanquis*, *Actinomyces* and *Lactobacillae*) is responsible for the decrease in pH. The microorganisms metabolize their primary energy source—simple sugars (i.e., glucose, which is delivered with food)—in the biochemistry pathways via lactic acid, which is the main agent of dental hard tissue disintegration. The other main factors for caries formation are diet and personal predisposition. Authors have mentioned over fifty factors responsible for caries development [**33**]. The symptom at the beginning of the process is a white spot on the surface of the tooth, which then turns into a darker color and finally becomes brown or black. The tooth tissue gradually softens and dissolves, turning into cavity [**33**]. After removing the destroyed surfaces from the soft material and bacteria as much as possible, the cavity is refilled with restorative materials. The new dental restorative materials should fulfill a few requirements: (i) lack of toxicity, (ii) inhibit bacterial growth, (iii) provide good separation of the oral environment and be placed beneath dental structures, (iv) repair destroyed tooth structures, (v) similar mechanical properties to dental structures, (vi) properties enabling tooth shape restoration, and (vii) aesthetic appearance [**34**]. Dental restorative materials can be divided according to chemical structures: (i) resin composite, (ii) polyacid-modified resin composite, (iii) glass ionomer types of cements and (iv) resin-modified glass ionomer cement. It can be also divided according to filler particles used: (i) macrofill, (ii) microfill, (iii) hybrid, (iv) midifill, (v) minifill and (vi) nanofill (**Figure 2**) [**35**,**36**].

Using nanofillers facilitates the incorporation of new intelligent tools into dental treatment protocols. Extensive research is performed to develop fillers, which can enhance the mechanical properties of a composite material such as shrinkage profile, flexural, tensile strength, microhardness, toughness, and resistance to wear. If all the aforementioned properties are not adequate, clinical use of composites become problematic. New intelligent composites possess the ability to re-mineralize dental structures and inhibit bacterial plaque growth, and they even exhibit some mechanical properties that are better than those of dentine or enamel [**20**].

The usage of restoration depends on its adhesion to tooth structures. Therefore, in clinical practice, there are two strategies: direct connection of restoration and tooth, or restoration through adhesive substances (bond) to achieve better adhesives' toughness. Researchers have studied the adhesion strength of nanofilled seals from resin-modified glass ionomer groups in comparison to non-nanofilled ones. Authors have concluded that the bonding mechanism of nano-modified seal to dentin/enamel is similar to non-nanofilled resin-modified glass ionomer. The mechanism is based on the formation of a polycarboxylate bond between the polycarboxylic acid of nano-modified seal and the calcium ions from hydroxyapatite (**Figure 3**) in a micro-mechanical interlocking way. It was expected that nanofilled glass ionomer would reveal higher bonding strength due to the reaction of the nanofilled particle with the dentin/enamel structures. Surprisingly, the strength of bonding was at the same magnitude for both types of glass ionomers [**37**,**38**].

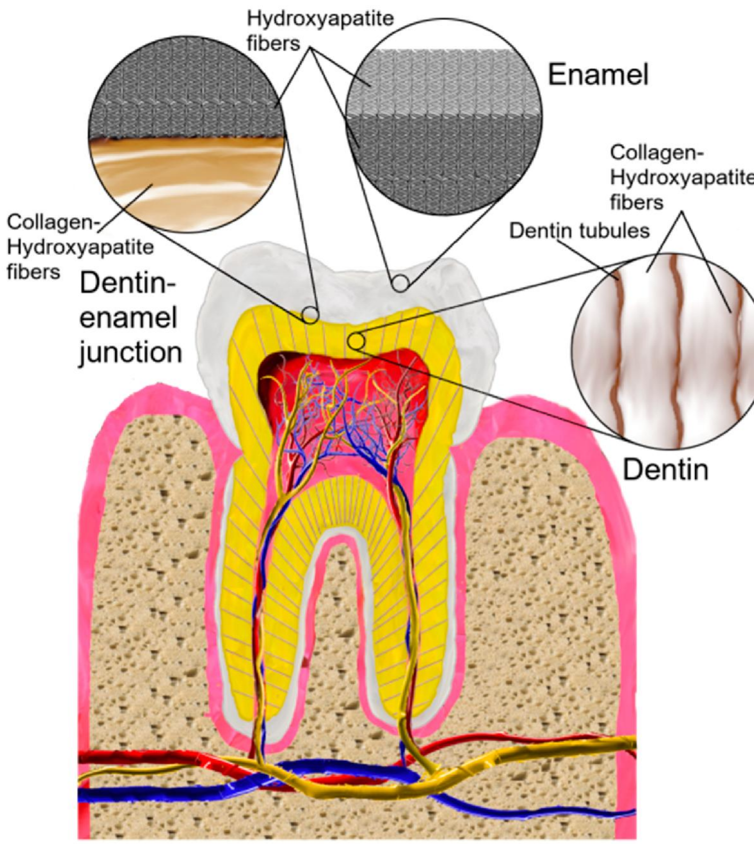

Figure 1. Nanostructure of a tooth.

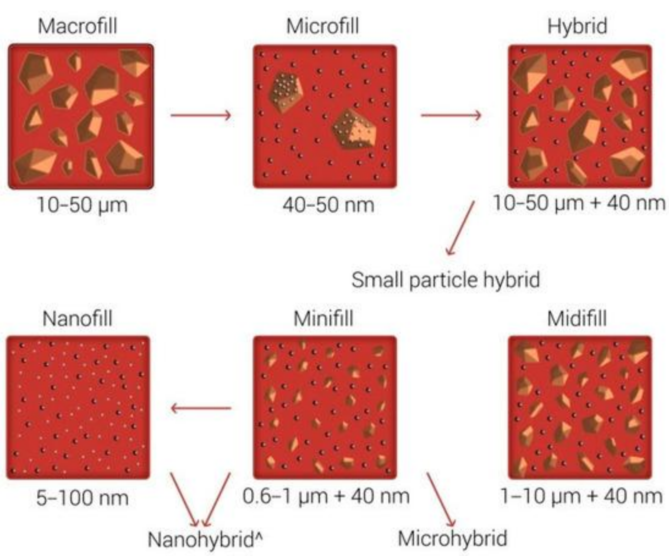

Figure 2. Division of dental composite fillers [**35**,**36**]. Adapted with permission from Ferracane, Dental Materials; published by Elsevier, 2011.

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Demineralization and re-mineralization processes of the tooth are physiological, but if the re-mineralization process is disrupted, the dental caries starts developing. To reduce and control the development of dental caries, fluoride or calcium ions-releasing agent was incorporated into dental practice for enhancing the re-mineralization process. In particular, re-mineralization functions are very important in the newly sealed tooth, especially on the surface between the filling and dentine [**20**]. Studies have been performed on the usability of nanoagents in re-mineralization of the aforementioned contact surface. It used nanosized (diameter about 100 nm) amorphous calcium phosphate fillers (ACPs) and silanized glass filler as co-fillers (diameter ca. 1.4 µm), and bisphenol glycidyl dimethacrylate (Bis-GMA) and triethylene glycol dimethacrylate (TEGMA) as the composite matrix. Authors have tested the different amounts of fillers and their impact on the mechanical properties and the release profiles of Ca^{2+} and PO_4^{3-} ions. The results indicate that a high ion release level was observed at a relatively low nanofill concentration in the composite. For ACP concentration in the range of 10 to 15%, increase in ion release was linear, but at 20% of ACP, an intense increase in ion relief was noticed. The release profile at different pH values was also checked; the results indicate that the highest release was observed at pH = 4 (very cariogenic environment for tooth). Mechanical properties such as flexural strength and elastic modulus before and after immersion in solutions of different pH have been studied. The authors concluded that after immersion, the ACP nanocomposite (10% ACP, 65% glass and 15% ACP, 60% glass) revealed a period flexural strength of 80–120 MPa, whereas the commercially available nanocomposite (Heliomolar, Ivoclar, Mississauga, ON, Canada) achieved a ca. value of 70 MPa. The elastic modulus test showed similar dependence to flexural strength. For the ACP nanocomposite, 10–13 GPa values were obtained in comparison to the reference of 7 GPa. Unfortunately, at the ACP concentration of 20%, dramatically decreased values of flexural strength and elastic modulus were noted. Obtained data suggest high potential usability of newly designed restorative material in prevention of secondary caries formation at the seal–tooth contact surface [**39**].

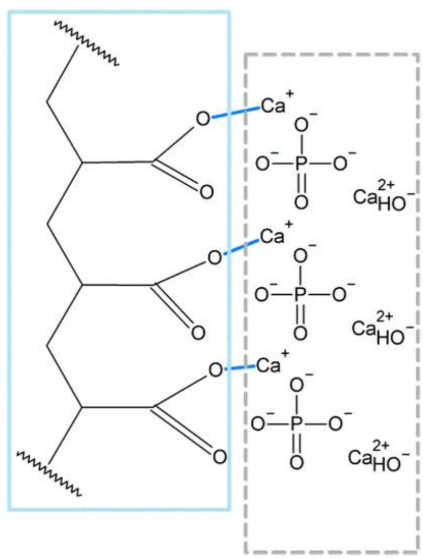

Figure 3. Binding of the polycarboxylate and hydroxyapatite.

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