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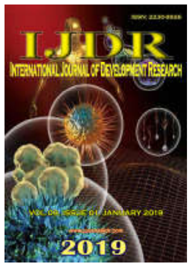

REVIEW ARTICLE OPEN ACCESS

NANOBIOMATERIALS IN RESTORATIVE AND ESTHETIC DENTISTRY: A REVIEW

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ABSTRACT

There are signs that we are in the midst of an explosion of new health-related technologies. In addition to specific advances in health research, traditional sciences and technology are undergoing significant changes that could have a farreaching impact on all aspects of scientific research, including health. Nanotechnology is defined as the design, characterization, production, and application of structures, devices, and systems by controlled manipulation of size and shape at the nanometer scale (atomic, molecular, and macromolecular scale) that produces structures, devices, and systems with at least one novel/superior characteristic or property.

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INTRODUCTION

Nanobiomaterials are materials with basic structural units, grains, particles, fibers, or other constituent components smaller than 100nm in at least one dimension, have evoked a great amount of attention for improving disease prevention ,diagnosis, and treatment. Nanoparticles (molecular units typically defined as having diameters of between 0.1 and 100 nm) of various composition represent the most widespread use of nanoscale units in dentistry. Nanoparticles and associated modifications of existing RBC systems have a considerable record of demonstrated clinical utility and widespread use. Nanohybrid RBCs are currently the most ubiquitous example of such technology.

Nanorods: Nanorods are of particular interest in a restorative context. Chen and colleagues have synthesized enamel-prism-like hydroxyapatite (HA) nanorods that have exhibited self assembly properties. Since nanorods are similar to the enamel rods that make up the basic crystalline structure of dental enamel, nanorods could contribute to a practical artificial approximation of such a naturally-occurring structure

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Sadat-Shojal *et al.* (2010) evaluated the hypothesis that the incorporation of fibrous hydroxyapatite nanoparticles with high crystallinity and high aspect ratio, synthesized by hydrothermal method, into an experimental ethanol-based one-bottle dentin adhesive, improves the mechanical properties of the adhesive layer, and accordingly increases the bond strength to dentin. Their results confirmed the high purity, high crystallinity, and high aspect ratio of synthesized HAp nanorods. The diametral tensile strength of nanorod containing adhesive system appeared to increase when 0.2-0.5wt.% HAp nanorods were incorporated. A similar trend was observed in the flexural test providing higher flexural strength at filler contents of 0.2-0.5wt.% while flexural modulus remained unchanged. The highest microshear bond strength was also obtained at 0.2wt.% filler content. The improved properties of the new adhesive system might be due to the high crystallinity and high aspect ratio of the nanorods. SEM observation of debonded surfaces revealed that most specimens showed an adhesive failure from the adhesive-dentin interface. Energy dispersive X-ray (EDX) mapping confirmed the uniform distribution of nanorods in the adhesive matrix. The colloidal stability studies indicated that synthesized hydroxyapatite nanorods have high colloidal stability in the dental adhesive solution. Indeed, the nanorods are well dispersed and protected from aggregation by their high surface charge confirmed by zeta potential measurement. Hydroxyapatite-based composites have shown promising bioactivity. However, the knowledge about the influence of the nano-sized HAp on the properties of the dental materials, especially dentin bonding adhesives, is yet insufficient. The nanorod containing adhesive system presented here might be considered to have practical applications in dental clinics. Chen *et al.* (2006)[i] investigated the conditions necessary to synthesize fluorapatite nanorods of different size, shape and composition for future use either directly or indirectly, that is by incorporation into dental materials, in the treatment and prevention of caries. By controlling the chemical conditions, nanorods of desirable chemical composition and dimension were produced. It can be used to mimic this natural anti-caries ability of teeth by developing new, effective anticaries materials using fluorapatite nanorods or nanowires. The advantage of these nanorods or nanowires is that the physico-chemical composition is the same as the hydroxyapatite crystals in the dental hard tissues. They also have the ability to release fluoride ions as the site specific pH drops which will help in preventing caries and aid in remineralisation.

Nanospheres: In a similar direction, such a potential transition to restorative systems that also mimic nanoscale processes already inherent in natural tooth development has also been explored. Specifically, nanosphere assembly in conjunction with calcium phosphate deposition and amelogenin nanochain assembly will be discussed in a restorative context (Fan *et al.*, 2007)[ii].

Nanotubes: Nanotubes of various types have been investigated for dental applications in a number of interesting directions. Titanium oxide nanotubes have been shown in vitro to accelerate the kinetics of HA formation, mainly in a context of bone- growth applications for dental implant coatings (Oh *et al.*, 2005)[iii]. More recently, modified single-walled carbon nanotubes (SWCNTs) have been shown to improve flexural strength of RBCs. These cylindrical carbon molecules have novel properties that make them potentially useful in many applications in nanotechnology, electronics, optics, dentistry and other fields of material sciences. They exhibit extra-ordinary strength , unique electrical properties and are efficient conductors of heat and electricity. These SWCNTs had silicon dioxide applied to them in conjunction with specialized organosilane bonding agents (Zhang *et al.*, 2008)[iv].

Nanofibers: Nanofibers and their uses for biomedical applications have been reviewed (Zhang *et al.*, 2005)[v]. More recently, nanofibers have been used to generate ceramics containing HA and fluor-HA (Kim and Kim, 2006)[vi]. Nanofibrillar silicate crystals have also been recently studied in the capacity of reinforcement of dental composites, specifically a combination of the widely-used 2,2'-bis-[4-(methacryloxypropoxy)-phenyl]-propane (Bis-GMA) with triethylene glycol dimethacrylate (TEGDMA) added as a thinning agent (Tian *et al.*, 2008)[vii]. Added in the correct proportions (Tian *et al.*, 2007)[viii] and with uniform distribution of the fibers/crystals, nanofibers were demonstrated to improve the physical properties of these composites.

Dendrimers and dendritic copolymers: Dendrimers and dendritic copolymers have been studied, albeit less extensively than other nanostructures, in relation to dental composite applications. Combinations of specific polymers to optimize efficacy of restorative applications have been reported (Viljanen *et al.*, 2006)[ix].

Restorative Dentistry using Nanocomposites: Evolution of direct RBC systems to the level of the nanofill composite has been recently reviewed by Puckett and colleagues (2007)[x]. The materials' physical properties have improved considerably (especially over the past five years). These changes have occurred in response to the persistent and daunting vitro and in vivo toxicity. Gold nanoparticles exploit their unique chemical and physical properties for transporting and unloading the pharmaceuticals. First, the gold core is essentially inert and non-toxic. A second advantage is their ease of synthesis; monodisperse nanoparticles can be formed with core sizes ranging from 1 nm to 150 nm. Further versatility is imparted by their ready functionalization, generally through thiol linkages (vide post). Moreover, their photophysical properties could trigger drug release at remote place (Ghosh *et al.*, 2008; Laurent *et al.*, 2008)

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Quantum Dots; Quantum dots seem to be very promising for a range of different applications, particularly in medical issues of polymerization shrinkage, and the dependable strength, microhardness, and associated wear resistance required in posterior occlusal applications. The ongoing challenge remains one of continuing to meet the esthetic demands of patients and clinicians.

Nanoparticles and microfills from the 1970s forward: In the early 1970s, Johnson and Johnson (Langhorne, PA, USA) introduced the composite, Adaptic (which contained a resin matrix filled with ground quartz particles). This material was shortly followed by 3M's composite, Concise™ (3M ESPE, St. Paul, MN, USA). Both quickly gained wide acceptance as anterior restoratives. Their main drawback was the surface discoloration that resulted from the coarse quartz particles they contained. (Michl, pers comm). These materials have also been used extensively for crown core buildups for more than 25 years. Since the beginning of the era of microfills in 1973 and their commercialization via the patent process in Germany and the following year in the United States, RBCs have been increasingly used in place of amalgam as the filler-matrix technologies have improved. Microfilled composites use silicon dioxide filler particles less than 100 nm in diameter in conjunction with prepolymerized organic fillers, aggregated by crushing them into larger filler particles. While this system produces consistently high-quality surface smoothness and has the longest clinical track record, these restorations lack the high strength needed to emulate amalgam (Christensen, 2009)[xi]. During this same period in which microfills were gaining popularity, nanomaterials were already available as titanium dioxide, aluminum oxide and silica oxide. These were used in dental products in small amounts (1%–5%) to improve powder flow. One of the nanosilica oxide products previously manufactured by Degussa in Germany (currently Dentsply International, York, PA, USA) was silanized with a methyl silan (Ox-50). This led to research attempts to fill the resin matrix with as much of the nanoparticle phase as possible, which resulted in the development of the restorative materials Isopast® and Heliomolar® by Ivoclar Vivadent (Schaan, Liechtenstein). This novel development was quickly emulated by 3M ESPE (Michl, pers comm). The progressive development of RBCs to date, including microfilled and nanofilled restoratives, has been recently reviewed by Christensen. Microfilled composites have the longest clinical track record, and provide a consistently smooth surface. However, microfills' lack of strength necessary for Class-I and -II occlusal applications has been a primary driver of the ongoing debate about progressive RBC use in applications typically – or perhaps traditionally – served by amalgam. The most commonly used RBCs currently comprise microhybrids and nanohybrids (virtually interchangeable terms). These materials use filler particles ranging from <100 nm to 600+ nm and have overcome most of the strength issue. Nanofills (such as Filtek™ Supreme Plus [3M ESPE] and Estelite® Sigma [Tokuyama America, Inc., Encinitas, CA, USA]) offer the combined advantage of less surface roughness than nanohybrids, with smoothness that approximates that of microfills, albeit with a much shorter clinical track record.

Esthetics of Nanocomposites: An early goal of nanocomposite development was the introduction of materials that possessed the strength to function under the stresses of Class I and Class II occlusal applications, while at least replicating the esthetic standards of hybrids and microfills. With this objective, Mitra and colleagues used bottom-up manufacturing design to produce a nanocomposite that contained a combination of nanomericparticle and nanocluster nanofillers that possessed physical properties comparable to hybrids and with esthetic properties comparable to microfills (Mitra *et al.*, 2003)[xii]. This formulation is currently used in Filtek™ SupremePlus nanocomposite (3M ESPE).

Nanocomposites have been reported for the past several years to offer desirable overall esthetics, function and biocompatibility for anterior restorations. A two-part series published in 2004 by Terry (2004a, 2004b)[xiii,xiv] provided initial clinical recognition of nanocomposites' role in the esthetic dentist's armamentarium. The series recaps the history of nanocomposite development and provides clinical guidance specifically for their use in anterior restorations. A case report by Milnar (2004)[xv] also illustrates predictable replication of esthetics via combined use of a direct nanofill and calorimetric analysis for shade selection. A study by Beun and colleagues (2007)[xvi] that primarily highlights the elastic strength of nanofills comments on their esthetic utility in anterior restorations as well. Favorable compatibility of nanofills with esthetic dentistry has also been reported by Ward (2005)[xvii]. However, larger-scale clinical colorimetric esthetic studies comparing nanocomposites with older-generation RBCs are lacking to date. Significant improvement in surface smoothness/polish retention have been reported for nanofills compared with conventional microfills (Jung *et al.*, 2007)[xviii]. Yap and colleagues (2004)[xix] reported that a nanomer-based RBC (Filtek™ Supreme Translucent) as significantly smoother than nanocluster-based RBCs (Filtek™ Supreme [dentin]). This is an interesting observation in view of a more recent study by Senawongse and Pongprueksa (2007)[xx], in which the same nanocluster RBC system produced the smoothest overall finish after polishing or brushing, measured by both scanning electron microscope (SEM) and surface roughness tester.

Conclusion

Nanobiomaterials faces many significant challenges in bringing its promises to fruition.There are larger social issues of public acceptance, ethics, regulation and human safety that must be addressed before molecular nanotechnology can enter the modern medical armamentarium. To end with 'How very small the very great are!'

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