

A Review on Carbon-Based Nanoporous Materials and Their Applications in Conservative Dentistry

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ABSTRACT

The evolution of nanotechnology and the development of various nanomaterials has resulted in greatly improved clinical applications. Carbon-based nanoporous materials have recently become an attractive choice for numerous dental applications. Carbon-based nanoporous materials possess outstanding physicochemical properties, which, in turn, depend on the nature of the nanocomposite, functional groups, synthesis technique, and purification method. Carbon-based nanoporous materials have a wide range of dental applications due to their outstanding physicochemical properties, mechanical properties, biocompatibility, antimicrobial activity, and physical properties such as shape, size, and elasticity. Furthermore, these carbon-based nanomaterials, primarily carbon nanotubes, graphene, and graphene oxide, have a wide range of dental applications due to their ease of functionalization and combination with other materials. The current review provides an overview of innovative carbon-based nanoporous materials in the dental field, particularly for conservative dentistry. The synthesis methods, structures, and properties of carbon-based nanoporous materials are discussed. Finally, the challenges and future prospects for carbon-based nanoporous materials are discussed.

Keywords: Nanoporous materials, carbon nanotubes, graphene, graphene oxide, graphene quantum dots, dentistry.

1. Introduction

Carbon is a ubiquitous component that exists in different forms and structures, resulting in a wide range of applications in the dental field in particular. Different carbon allotropes can be synthesized by varying the combinations of sp, sp², and sp³ hybridization, and several carbon nanostructures are currently available. Because carbon nanostructures are primarily composed of sp² hybridized carbon atoms structured in a hexagonal lattice, they can have various structures, patterns, and properties [1].

Carbon nanostructures could be categorized into zero, one, two, or three-dimensional. Zero-dimension carbon nanostructures involve fullerenes, carbon dots, and graphene quantum dots. Single-dimensional (1D) carbon nanostructures include nanotubes and nanofibers. Recently generated double-dimensional (2D) carbon nanostructures have several intriguing properties. Graphene is a well-known 2D nanostructure. Finally, triple-dimensional (3D) graphene superstructures and hybrid nanotube-graphene nanomaterials are mainly composed of single and double-dimensional structures [2].

Carbon nanotubes (CNTs) are hollow, cylindrical structures made of a hexagonal network of carbon atoms that range in size from a few nanometers to a few microns. Carbon nanotubes are now widely used in dentistry due to their mechanical properties. In this regard, they are promising candidates for use as reinforcement for dental materials, scaffolding, and targeted drug delivery systems. Nanotubes with a single wall are referred to as single-wall carbon nanotubes (SWCNT), whereas those with multiple walls are referred to as multi-wall carbon nanotubes (MWCNT) [3].

Carbon nanotubes' morphology, size, and arrangement influence their specialized applicability and adaptability. As a result of their enhanced carrying capacity and ability to interface with cellular membranes, MWCNTs have emerged as potential candidates for delivery systems. Furthermore, their superior mechanical properties indicate that they could be used as dental materials fillers. The addition of MWCNT to PMMA cement improved mechanical properties without affecting thermal properties. Goyal et al. investigated the effect of multi-walled carbon nanotubes (MWCNTs) in reinforced glass ionomer cements on their chemical, thermal, and mechanical properties as a posterior restorative material. The incorporation of 2% w/w MWCNTs improved the mechanical properties of the material, increasing its hardness from 2.19 MPa to 5.70 MPa. This composition also permitted higher wear pressures than the other two

compositions. The incorporation of carbon nanotubes in glass ionomer cement improved color stability [4].

Moreover, by adhering to the collagen fibers exposed from these surfaces, these materials demonstrated selective coating of the dentin and cementum surfaces. Carbon nanotubes added to a hydroxyapatite coating strengthen mechanical properties such as hardness and elastic modulus [5].

Nanofibers, like other nanomaterials, are attracting interest due to their possible applications in a variety of sectors, including catalysis, medicine, and dentistry. Several techniques of synthesis have been documented; however, electrospinning is the favored approach since it is inexpensive, simple, and relatively easy to scale. Chitosan and hydroxyapatite fibers are the most studied nanofiber/nanorod applications in dentistry [3].

Hydroxyapatite nano-rods/fibers were also identified as effective reinforcing materials for composite resins and polymers due to their excellent remineralization abilities. Hydroxyapatite nanorods can also exhibit antibacterial potential, such as when zinc particles have been embedded into the nanorods, permitting the material to load Zn^{2+} upon usage, resulting in inhibiting oral cavity bacteria [6].

2. Graphene and its derivatives

Of all the various nanomaterials, graphene is the strongest and thinnest. It is a potential two-dimensional (2D) carbon-based nanomaterial. Novoselov and Geim were awarded a Nobel Prize in 2010 as they were able to isolate the graphene in 2004 using mechanical exfoliation and adhesive tape. There are four different types of graphene-based materials: single-layer graphene, multiple-layered graphene, graphene oxide (GO), and reduced graphene oxide (rGO) [7]. Because of its superior physical properties, excellent electrical and thermal conductivity, and exceptional biocompatibility, graphene and its variants have aroused the interest of researchers in the medical and biological disciplines. Graphene and its variants have also generated considerable interest in the fields of dentistry and tissue engineering, resin additives, and teeth whitening.

2.1 Structure and Synthesis of graphene and its derivatives

Graphene is a two-dimensional carbon-based nanomaterial; it is considered to be the thinnest and strongest material. Graphene's primary derivatives are graphene oxide (GO) and reduced graphene oxide (rGO). Although the structures of graphene and its derivatives are similar, the differences in their functional groups could account for variations in their chemical and physical properties.

Novoselov and Geim isolated graphene for the first time in 2004 using a sticky tape mechanical exfoliation process. Graphene consists of sp² hybridized carbon atoms organized in a honeycombed lattice, and its structure is composed of six-membered rings stacked in parallel with no chemical groups on the surface [8].

Mechanical exfoliation yields graphene with high purity but low yield. Many synthesis methods have been investigated to increase graphene yield. There are two approaches to synthesizing graphene: down-up and top-down [9]. The Down-up strategy includes direct graphene synthesis from carbon materials via processes such as chemical vapor deposition, graphitization of carbon-containing substrates via high-temperature annealing, and solid-phase deposition. The top-down technique, on the other hand, includes micromechanical cleavage, chemical exfoliation of GO followed by reduction treatment, and liquid-phase exfoliation [9].

Liquid-phase exfoliation is an efficient method for producing graphene on an intimate scale. To reduce the van der Waals forces between the graphite layers, a graphite suspension in an organic solvent is created. The graphene is then stripped into graphene sheets using ultrasonic at a specific voltage. Following additional centrifugation, tremendous quantities of monolayer and multilayer graphene were produced [10]. Graphene is considered to be pristine yet very tiny, with an uncontrolled number of layers. Additionally, the usage of surfactants and organic solvents pollutes the environment.

Chemical Vapor Deposition (CVD) has been extensively utilized to produce monolayer or multiple-layer graphene at low cost, where a large area of monolayer graphene sheet is generated on the metal [9]. To create carbon on metal foils such as Cu, Ni, Fe, and Ru, methane, ethane, or propane is pyrolyzed at high temperatures. Therefore, the graphene layer is subsequently produced from free carbon atoms [10].

One of the most profitable approaches in the production of graphene-based products is **Chemical exfoliation**. The Hummers process, which combines sulfuric acid, potassium permanganate, and sodium nitrate with graphite in water and stirs or uses an ultrasonic reaction, is used to create graphene oxide (GO). The GO is then maintained at 1,000°C to exfoliate it. Reducing agents reduces GO to rGO. Ultimately, heat or chemical treatments are used to transform rGO into graphene. However, it is extremely difficult to remove every oxygen-containing molecule from the GO. Extended periods of processing and potentially hazardous fumes [10].

2.2 Structure and Synthesis of Graphene Oxide

Natural graphene undergoes oxidation to generate graphite oxide, which is then ultrasonically exfoliated to yield GO, which is then reduced to create rGO. Chemical reduction of GO with green reducing agents is ecologically sound, producing highly dispersible and biocompatible compounds. Natural reagents and environmentally conscious ways to reduce GO are currently gaining popularity. Many natural antioxidants have been used to reduce GO, including amino acids, organic acids, and vitamins. Similarly, polyphenols attack the carbonyl and hydroxyl groups nucleophilically while releasing a water molecule. GO can be effectively converted to rGO through this reduction method [11].

3. Compatibility of Graphene-Based Materials

To advance the implementation of graphene-based materials in dentistry, the biocompatibility and cytotoxicity of graphene-based materials must be evaluated. Numerous studies have been conducted to assess the cytotoxicity of graphene and its derivatives. Concentrations, surface functionalization, and other variables have already been influenced [12].

Numerous studies have proven that graphene and its derivatives have a dependent dosage effect on biocompatibility as well as toxicity. Multiple research investigations discovered that toxicity to fibroblast cells was limited when the concentration of GO was less than 20 g/ml. The cytotoxicity increased when the concentration was increased to 50 g/ml.

4. Antibacterial effect

Graphene-based materials are capable of causing physical damage to microorganisms by penetrating and cutting the cell membrane, wrapping cells, inducing mechanical stress, and

extracting phospholipids from lipid membranes. This significantly reduces the number of gram-positive and gram-negative bacteria. It promotes oxidative stress through the generation of reactive oxygen species and the transfer of charge events [13]. It is worth mentioning that Graphene nanosheets may also have an impact on bacterial membranes by creating a gap through which Van Der Waals pressures and graphene's hydrophobic properties dissolve phospholipids from the membrane's lipid layers [10].

It was previously reported that graphene antibacterial effectiveness against both Gram-positive and Gram-negative bacteria is also dose-dependent. While high GO concentrations inhibit Gram-positive and Gram-negative bacteria biofilms, low GO concentrations can increase their growth, resulting in an entirely unexpected response [12].

5. Graphene-based materials applications in conservative dentistry

5.1 Resin and cement

When considering graphene's role in restorative dentistry, keep in mind that the most commonly used materials are resins, cement, and adhesives. Initially, polymeric materials were used, which are prone to the formation of biofilms, which cause dental restorative failure and bacterial adherence.

Graphene nanoplates (GNPs) have been employed as a nanofiller in commercial dental adhesives to counteract the porous nature of the oral cavity, which enables organisms to thrive. Ultimately, the graphene nanocomposite prevents the growth of *S. mutans*. GNP is grey, which is not suitable for use in dentistry, but it works effectively without influencing the standard adhesion qualities of the dental adhesion [14].

By establishing hybrid metal Zinc Oxide Nanorods (ZnO-NRs) on the GNPs to improve their antibacterial qualities, the color of the GNPs was changed to make them look more realistic in the oral cavity. Even when used in tiny amounts, the resulting Zinc Oxide Nanorods Graphene Nanoplatelets (ZNGs) have been demonstrated to be effective against *S. mutans*. Moreover, when their biomass and exopolysaccharide synthesis are investigated, ZNGs are shown to be a barrier to biofilm. Consequently, as ZNGs inhibit the growth of *S. mutans*, they are a practical option for controlling dental caries [15].

Graphene sheets loaded with gold nanoparticles have been employed as a nanofiller for various dental nanocomposites on a BisGMA/tri ethylene glycol dimethacrylate matrix utilizing a catalytic chemical vapor deposition process over an Au/MgO catalyst. The graphene-gold nanocomposites show promise as another viable filler for dental nanocomposites because the large number of nanoparticles serves as a strengthening effect that could improve both the chemical and physical characteristics of the adhesive [14].

Furthermore, GO improves the performance of adhesives and silane primers. Bond strength and durability are improved with GO-enriched adhesive. Khan et al. concluded that silane primers reinforced with GO improve the shear bond strength between resin composites and zirconia [16].

Chen W et al. discovered that graphene quantum dots (GQDs) and carbodiimide work synergistically to improve adhesion durability and inhibit hydrolysis of collagen fibers. GQDs, in particular, cross-linked collagen noncovalently and significantly reduced collagenase activity but with a limited and unstable ability to inhibit collagen enzymatic hydrolysis. When combined with carbodiimide, GQDs may covalently link to collagen fibers, thereby increasing the anti-enzymatic hydrolysis capacity of collagen fibers while decreasing collagenase activity [17].

Glass ionomer cement incorporating fluorinated graphene is exactly efficient at inhibiting bacterial growth while improving cement mechanical characteristics. This has further advantages since it enhances microhardness while lowering the friction coefficient, thus offering compressive strength. When coupled with the appropriate materials, graphene's potential involvement with resins, cement, and adhesives seems promising [18]. As a result, graphene-based compounds are appropriate fillers for adhesives, cement, and silane primers.

5.2 PMMA

GO was added to PMMA to improve its mechanical properties due to the outstanding mechanical action of graphene and its derivatives [19]. The mechanical characteristics and hydrophilic capabilities of PMMA containing graphene-silver nanoparticles (Gr-Ag) were investigated by Bacali et al. [20]. The compression parameters, bending, and tensile strength of the Gr-Ag fillers were significantly higher than those of the pure PMMA group, indicating that the incorporation of Gr-Ag improved the mechanical characteristics of PMMA resin.

Furthermore, Bacali et al. explored the antimicrobial capabilities of Graphene silver-modified PMMA. They reported that Gr-Ag-modified groups inhibited Gram-negative strains, including *S. aureus*, *E. coli*, and *Streptococcus mutans*. Therefore, graphene-based materials could serve as an appropriate filler to enhance PMMA's physical, mechanical, and antimicrobial qualities [20].

5.3 Teeth whitening

Hydrogen peroxide (H_2O_2) is commonly used for a lengthy period of in-office whitening. The bleaching process is carried out by reaching deep into the teeth. However, the relatively elevated H_2O_2 concentrations induced sensitivity and irritation to gingiva. As a result, several enhanced ways have been developed to accelerate the tooth decay process. Su et al. demonstrated a nanocomposite containing cobalt (Co), tetraphenyl porphyrin (TPP), and rGO. When compared to H_2O_2 alone, it demonstrated enhanced tooth-whitening power when discolored with pigments, betel nuts, and tea [21].

Furthermore, H_2O_2 triggers an active free radical to possess an unusually short lifetime. H_2O_2 must first influence the teeth and rapidly form active free radicals to be able to achieve an effective bleaching action. The Co/TPP/rGO nanocomposite, on the other hand, may be used as a catalyst that attains additional reactions between the discoloration molecules and H_2O_2 , thereby speeding up the bleaching process. Finally, graphene-based nanomaterials are viable tooth-whitening catalysts.

5.4 Bacterial Detection

In the present day, bacterial infections are a constant source of concern due to numerous bacteria that have developed resistance to several commonly prescribed medications. To mitigate this, other approaches to combating bacterial infections have been investigated, such as graphene complexes with specific features such as sharp edges capable of puncturing the bacteria or chemical releases of reactive oxygen species to kill the bacteria. However, if bacterial infections are detected late, these remedies are rendered nearly useless. As a result, it is crucial to identify these bacterial species at an early stage.

Further investigation on graphene to serve as a bacterial biosensor has been conducted. These biosensors can be applied to tooth enamel to detect the presence of harmful bacteria and thus prevent the onset of an infection. Graphene is an excellent candidate for this matter due to its

many properties, including high thermal conductivity, an intrinsically high surface-to-volume ratio, and chemical inertness. The sensors work on the principle that when different bacterial species adhere to the surface of graphene, the conductivity changes. It has been discovered that different bacteria, as well as different growth/adhesion patterns, can result in different conductivity changes, allowing for specific bacteria detection. [12].

Mannoor et al. created the first graphene nano-sensors on tooth enamel. They established a graphene sensing element with a wireless readout coil attached to silk fibroin, which they then applied to tooth enamel. Self-assembling Anti-Microbial Peptide (AMP) graphene peptides onto graphene delivered specific biological recognition. The detection and wireless remote monitoring of *H. pylori* in saliva was successfully carried out using an AMP-modified graphene nanosensor that revealed an intimate relationship between peptides and bacteria. They concluded that graphene is a good candidate for use as a biosensor for early detection of bacteria [22].

5.5 Prevention of Enamel and Dentin Demineralization

Graphene and its derivatives can inhibit cariogenic bacteria and prevent tooth demineralization. Thus, it can be considered a promising nanomaterial that can prevent dental caries. Graphene and GO directly inhibit cariogenic bacteria while subsequently enhancing the antibacterial properties of metallic nanomaterials such as silver, copper, and zinc oxide nanoparticles [12]. In vitro, graphene nanoplatelets, glass ionomers loaded with fluoridated graphene, graphene nanoparticles, and graphene nanosheets have all been shown to significantly restrict the adherence and growth of *S. mutans* [10].

Graphene and its derivatives inhibit cariogenic pathogens and biofilm formation primarily by causing mechanical damage to the bacterial cell wall of the nanostructured materials, altering the biofilm architecture, and impairing extracellular polysaccharide matrix production and distribution [23].

Many researchers are now working on developing novel bonding agents to avoid enamel demineralization caused by oral bacteria. Because of Graphene's strong antibacterial activity, Lee and his colleagues incorporated GO into a bioactive glass (BAG). As GO concentrations increased, so did the duration of anti-demineralization of the GO group. Furthermore, antibacterial activity was higher in GO-containing groups after 24 and 48 hours. The anti-demineralization mechanism of the composites could be attributed to the synergistic effect of GO's antibacterial activity and

BAG's ion-releasing function. Therefore, GO has the potential to contribute to avoiding enamel demineralization.

Several studies have combined GO with modern technology to discover its antimicrobial impact. When ionically linked to cationic polymers, GO may efficiently transfer nucleic acids, enhancing gene uptake and protecting nucleic acids from the lysosomal path. Antisense *vicR* (*AsvicR*) RNA has been shown to suppress virulence gene transcription, thereby preventing biofilm formation in *S. mutans*. Using interacting GO-polyethyleneimine (PEI) complexes in conjunction with an *AsvicR*-expressing plasmid. Wu S et al. established a method for GO plasmid transformation. They revealed that the *AsvicR*-expressing plasmid could be effectively transported into *S. mutans* cells through GOPEI complexes, as well as a decrease in the virulence-associated glycosyl transferase gene (*gtf* BCD) expression caused by *AsvicR*. GO and *AsvicR* have been shown to significantly reduce biofilm formation and EPS production [24].

6. Challenges and future prospective

Due to their biocompatibility, excellent mechanical properties, and antimicrobial capabilities, graphene-based materials, a prospective contender for dentistry materials, have been extensively used in dental research. They have many applications, such as fillers in adhesives, cement, and resin composites, as well as in novel fields, including enamel and dentin demineralization prevention, an oral biomarker detection biosensor, and fungus growth suppression. The biosensor could identify bacterial and viral indicators, medications, and cancer markers. Before graphene's application in dentistry can be marketed, particular challenges must first be overcome.

The ambiguity of its *in vitro* and *in vivo* cytotoxicity, as well as its possible mechanisms, is a severe issue in clinical use. Several studies revealed inconsistent results on the cytotoxicity and potential risks of graphene-based materials. Cytotoxicity is affected by many factors, including concentrations, surface functionalization, graphene family, and synthesis processes [25].

Reactive Oxidative Stress (ROS) plays a significant role in cytotoxicity mechanisms. In terms of synthetic methods, graphene sheets synthesized via CVD methods are biocompatible and cytotoxic. However, as graphene degrades in solution, cell cytotoxicity may increase, possibly due

to accumulation or sharp-edge penetration into the cells. As a result, more research into long-term biocompatibility in vivo is needed [25].

Despite many investigations emphasizing the antimicrobial impact of graphene-based materials on a single strain of bacteria or monoclonal biofilm, none of them has demonstrated an antimicrobial effect on mature polymicrobial biofilms. Based on the aforementioned constraints, there is still a long way to go before the ultimate clinical use of graphene-based materials in the dental field.

7. Conclusion

Nano-porous materials are very promising materials due to their physicochemical and mechanical properties. Their incorporation into various dental materials is predicted to expand their use in the dental field. With the use of functionalized nanoporous materials, this breakthrough could lead to the development of new materials for caries prevention. Further studies, especially Clinical Trials, still need to be conducted, but these findings indicate that nano-porous materials are a step forward in Conservative Dentistry.

- **Conflict of Interest**

The authors declare no conflict of interest.

8. References

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