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Review Article

Carbon-Reinforced Hydroxyapatite Nanocomposites: Mechanics, Interfacial Chemistry, And Bio-Performance In Bone Tissue Engineering

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ABSTRACT

Hydroxyapatite (HA; $Ca_{10}(PO_4)_6(OH)_2$) is an established bioceramic for bone regeneration owing to its chemical and crystallographic similarity to the mineral phase of native bone. However, its intrinsic brittleness, low flexural strength, and limited fatigue resistance restrict its application in mechanically demanding environments. Carbon nanostructures, particularly one-dimensional carbon nanotubes (SWCNTs and MWCNTs) and two-dimensional graphene-family materials (graphene, graphene oxide, and reduced graphene oxide), have therefore attracted considerable interest as reinforcing phases for HA-based nanocomposites. This review critically examines the relationships among carbon–HA interfacial chemistry, processing, microstructure, mechanical behavior, and biological performance. Particular attention is given to surface functionalization strategies, including covalent oxidation and non-covalent polymer modification, as well as low-temperature consolidation approaches aimed at improving dispersion and densification while limiting carbon degradation. The distinct toughening mechanisms associated with one-dimensional and two-dimensional carbon architectures, including crack bridging, pull-out, crack deflection, sheet wrapping, and grain-boundary effects, are comparatively evaluated. The review further examines how carbon surface chemistry, electrical conductivity, and carbon loading influence apatite formation, cellular responses, osteogenic activity, and potential electroactive applications. Finally, concentration-dependent cytotoxicity, reactive oxygen species generation, dispersion stability, and long-term biocompatibility are discussed to identify the processing and compositional parameters required for the safe and effective development of carbon-reinforced HA nanocomposites for bone tissue engineering.

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1. INTRODUCTION

Hydroxyapatite (HA; $Ca_{10}(PO_4)_6(OH)_2$) is one of the most widely investigated calcium phosphate ceramics for bone repair because of its chemical similarity to the mineral phase of native bone, as well as its bioactivity and osteoconductivity (Ahmed & Omer, 2024). However, its intrinsic brittleness, low fracture toughness ($K_{IC} \approx 0.8–1.2$ MPa·m$^{1/2}$), limited flexural strength, and poor fatigue resistance restrict its application in mechanically demanding bone defects (Fu et al., 2013; Sun et al., 2025). The relatively slow and composition-dependent dissolution of HA may also limit its ability to dynamically match bone remodeling, highlighting the need for HA-based materials with improved mechanical reliability and biological functionality.

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Carbon nanomaterials have emerged as promising reinforcing phases for addressing these limitations. One-dimensional (1D) carbon nanotubes, including single- and multi-walled CNTs, and two-dimensional (2D) graphene-family materials, including graphene, graphene oxide (GO), and reduced graphene oxide (rGO), exhibit high mechanical stiffness, large surface areas, and, in the case of selected carbon phases, electrical conductivity (Ashok Kumar et al., 2022; X. Gao et al., 2024). Their incorporation into HA can improve stress transfer and alter crack propagation through mechanisms such as crack bridging, nanotube pull-out, interfacial debonding, crack deflection, and increased fracture-path tortuosity. The distinct geometries of 1D and 2D carbon phases therefore provide different routes for controlling the mechanical response of HA nanocomposites (Solanke et al., 2025).

Several previous reviews have examined HA-based nanocomposites and, more specifically, the incorporation of carbon nanomaterials into calcium phosphate or HA matrices. These reviews have provided important foundations by summarizing the synthesis strategies, physicochemical characteristics, mechanical properties, and/or biological performance of carbon-containing HA composites (Doudkanlouy Milan et al., 2022). However, the existing literature remains fragmented in several respects. First, previous reviews have generally considered carbon nanotubes and graphene-family materials either collectively as carbon-based reinforcements or within broader reviews of HA nanocomposites, with limited systematic comparison of how their distinct one-dimensional and two-dimensional architectures govern interfacial interactions, stress transfer, crack evolution, and toughening mechanisms (Khalili et al., 2020; Siddiqui et al., 2018; H. Zhao et al., 2022). Second, the relationships among carbon surface chemistry, dispersion state, processing conditions, and HA–carbon interfacial bonding have not been sufficiently integrated with the resulting mechanical and biological responses (Akbulut et al., 2025; Awasthi et al., 2021; Siddiqui et al., 2018). Third, recent advances in low-temperature and rapid consolidation, surface functionalization, and the biological effects associated with carbon-induced surface and electrical properties have expanded the scope of this field but have not been comprehensively incorporated into earlier reviews (Niemczyk-Soczynska et al., 2020; Solanke et al., 2025; Yigit et al., 2026). Importantly, the potential benefits of carbon nanomaterials cannot be evaluated independently of their concentration, dispersion, surface chemistry, and processing history because these factors can simultaneously determine mechanical reinforcement, cellular responses, and potential cytotoxicity.

Nevertheless, achieving these benefits requires careful control of carbon–HA interactions, dispersion, and processing. Strong nanocarbon agglomeration and limited interfacial compatibility can reduce load transfer, while high-temperature ceramic processing may damage the carbon phase or promote undesirable grain growth (Feng et al., 2022; Y. D. Ravichandran & Kuo, 2026). Surface functionalization can improve wettability and interfacial bonding, whereas rapid, low-temperature consolidation techniques can facilitate densification while limiting thermal degradation (Abbas et al., 2026). Beyond mechanical reinforcement, carbon surface chemistry and electrical properties may influence apatite nucleation, cellular interactions, and osteogenic responses (Chebodaeva, 2025; B. Wang et al., 2023). However, these effects depend strongly on carbon type, surface chemistry, dispersion, and concentration, with excessive loading or poor dispersion potentially producing adverse biological responses.

Against this background, the present review provides an integrated and critical assessment of carbon-reinforced HA nanocomposites, with particular emphasis on (i) critically examining the interfacial chemistry and dispersion mechanisms governing carbon–HA compatibility; (ii) comparing the toughening mechanisms associated with 1D and 2D carbon architectures, including their effects on stress transfer and crack propagation; and (iii) evaluating the relationships between carbon surface characteristics, electrical properties, and cellular osteogenic responses. By integrating these previously separate dimensions, this review aims to provide a distinct mechanistic perspective for the rational design of mechanically reliable, biologically functional, and clinically relevant carbon-reinforced HA nanocomposites for bone tissue engineering.

2. HYDROXYAPATITE AS THE CERAMIC MATRIX

Hydroxyapatite (HA; $Ca_{10}(PO_4)_6(OH)_2$) is a calcium phosphate ceramic whose composition and structure resemble the inorganic mineral phase of bone. Stoichiometric HA has a theoretical Ca/P atomic ratio of 1.67 and generally crystallizes in the hexagonal crystal system (Beera et al., 2026). However, biological apatite is not strictly stoichiometric HA; it is poorly crystalline and contains various ionic substitutions, including carbonate, magnesium, sodium, and other trace species (dos Santos et al., 2025). Consequently, the structural and physicochemical properties of synthetic HA depend strongly on stoichiometry, crystallinity, lattice substitutions, particle morphology, and processing history (Vijayan et al., 2025).

2.1. Crystal Structure and Stoichiometry

The HA crystal structure consists of calcium and phosphate sublattices surrounding hydroxyl channels. In the ideal stoichiometric composition, ten Ca^{2+} ions balance six PO_4^{3-} groups and two OH^- groups. Deviations from this composition can produce calcium-

deficient or ion-substituted apatites with modified lattice parameters, crystallinity, solubility, and surface reactivity (Bohner et al., 2026). Such deviations are particularly relevant when HA is synthesized under aqueous or biological conditions, where the incorporation of carbonate and other ions can produce materials that differ substantially from highly crystalline stoichiometric HA (Kurzyk et al., 2023).

For carbon-reinforced HA, these structural characteristics are important because the crystallinity, grain size, and defect population of the ceramic matrix influence both its intrinsic mechanical response and its interaction with the carbon phase (Yigit et al., 2026). Thus, differences in HA composition and crystallographic state should be considered when comparing mechanical data reported for carbon/HA nanocomposites.

2.2. Surface Chemistry and Interfacial Reactivity

The surface of HA is chemically active and can interact with water, ions, proteins, and functional groups introduced by reinforcing phases. Surface calcium and phosphate species contribute to ion exchange and apatite-forming behavior, while hydroxyl groups and adsorbed species influence surface charge, wettability, and interfacial interactions (Martín-Santana et al., 2026). HA surface chemistry also depends strongly on crystallinity, stoichiometry, particle size, and the presence of substituted ions. Recent work emphasizes that HA should not be regarded simply as an inert crystalline phase; its surface provides a dynamically hydrated and reactive environment that can influence dissolution, ion exchange, and interactions with surrounding phases (Kothari et al., 2025; Omiyale & Ulasevich, 2026).

This surface reactivity is particularly important for carbon-reinforced HA. Pristine graphene and CNTs generally exhibit limited compatibility with hydrophilic ceramic matrices, which can promote agglomeration and weaken interfacial load transfer (Sharma, Miladinović, et al., 2026). In contrast, oxidation or other surface functionalization strategies can introduce oxygen-containing groups and improve wettability and interactions with HA (Niemczyk-Soczynska et al., 2020). The resulting carbon–HA interface therefore plays a critical role in determining dispersion, stress transfer, and ultimately mechanical reinforcement. This relationship underpins the interfacial chemistry discussed in Section 4.

2.3. Mechanical Properties

The principal limitation of dense HA as a structural biomaterial is its brittle mechanical response. Strong ionic bonding within the ceramic lattice provides relatively high compressive strength and stiffness, but the limited ability of the ceramic to accommodate localized deformation makes it highly susceptible to crack initiation and propagation (Ma et al., 2026). Reported mechanical properties vary considerably with density, porosity, grain size, crystallinity, stoichiometry, and processing conditions (Osuchukwu et al., 2021). For dense HA ceramics, reported flexural, compressive, and tensile strengths span broad ranges, while fracture toughness generally remains around or below approximately 1.2 $MPa \cdot m^{1/2}$ (Pazarlioglu & Salman, 2020).

Porosity is particularly influential because pores act as stress concentrators and reduce the effective load-bearing cross-section. Consequently, increasing porosity generally produces substantial reductions in strength and fracture resistance. Grain size and crystallinity also affect mechanical behavior, with dense, highly crystalline materials generally exhibiting higher strength than poorly consolidated or highly porous HA (Kanhed et al., 2017; D. Liu et al., 2017). These dependencies mean that direct comparisons of carbon-reinforced HA systems require consideration of not only carbon content but also matrix density and microstructure. Figure 1 illustrates the structural characteristics of hydroxyapatite, synthesis workflows, and interfacial mineralization mechanisms of hydroxyapatite–carbon nanocomposites.

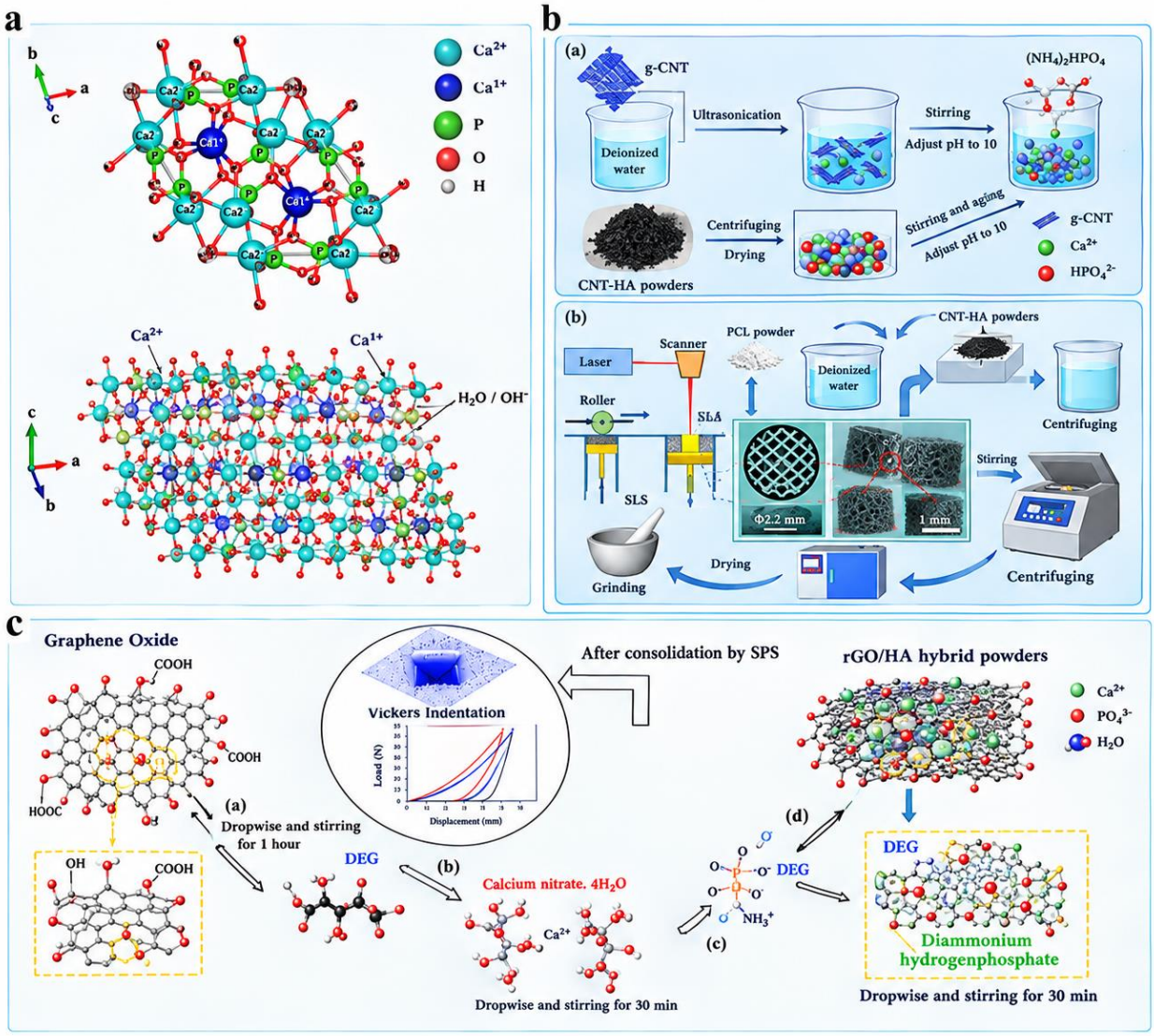


Figure 1. (a) Crystallographic structure of hydroxyapatite (HA) (Yacoubi et al., 2017), **(b)** Wet-chemical synthesis and additive manufacturing of carbon nanotube (CNT)/HA composites (Feng et al., 2022), **(c)** Interfacial mineralization mechanisms on functionalized graphene (Q. Zhang et al., 2015).

2.4. Limitations Relevant to Carbon Reinforcement

The mechanical limitations of HA arise from a fundamental mismatch between its ceramic behavior and the requirements of mechanically demanding bone environments. Although HA provides favorable bioactivity and chemical compatibility with bone mineral, its low fracture toughness and susceptibility to catastrophic crack propagation limit its reliability under tensile, impact, and cyclic loading (Budi et al., 2026). At the same time, increasing densification or crystallinity to improve mechanical strength can alter dissolution and surface reactivity. Thus, improving HA performance requires more than simply increasing its density; the microstructure, interface, and balance between mechanical stability and surface reactivity must also be controlled (Sriprapha et al., 2025).

These limitations provide the rationale for incorporating carbon nanomaterials into the HA matrix. Rather than functioning only as passive fillers, CNTs and graphene-family materials can interact with the ceramic at multiple length scales, potentially improving stress transfer and dissipating fracture energy through crack bridging, pull-out, deflection, and related mechanisms (Taghzouti, 2025). However, these benefits depend strongly on carbon morphology, dispersion, surface chemistry, interfacial bonding, and processing

conditions. Accordingly, the performance of carbon-reinforced HA is governed by the interaction between the intrinsic properties of the HA matrix and the characteristics of the carbon–HA interface, which forms the central focus of the following sections (Lawton et al., 2019). Here, Figure 2 expresses interfacial binding modeling, nanoscale morphology, and light-driven catalytic mechanisms of carbon-functionalized hydroxyapatite composites.

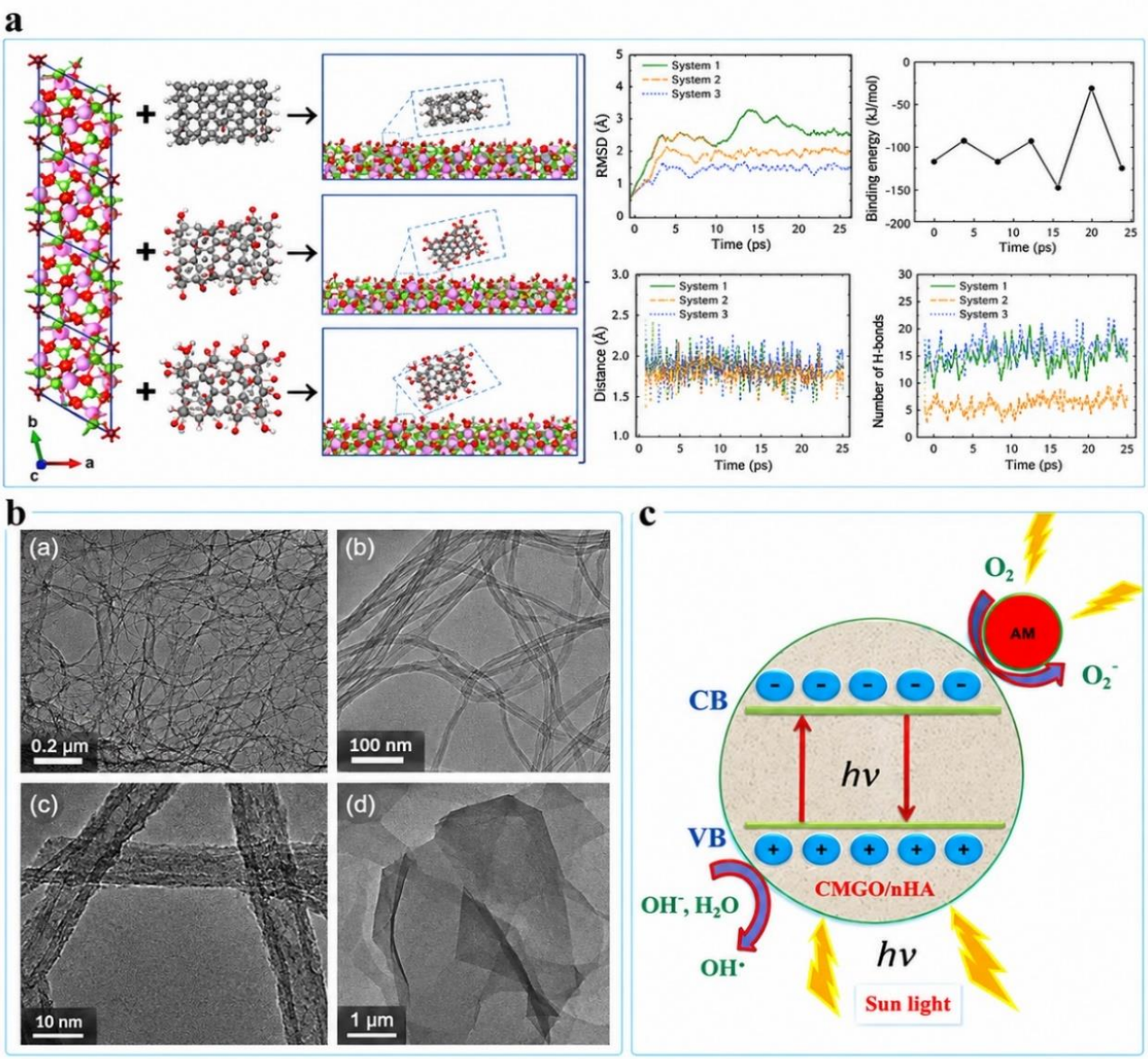


Figure 2. Interfacial molecular dynamics modeling, microstructural morphology, and photocatalytic mechanism of carbon nanomaterial–hydroxyapatite nanocomposites. **(a)** Molecular dynamics (MD) simulations showing the adsorption conFigureurations on carbon surfaces interacting with HA (Knupp et al., 2019), **(b)** TEM micrographs displaying the morphology of carbon nanotubes (CNTs) and graphene oxide sheets (Núñez et al., 2014), **(c)** proposed photocatalytic mechanism under solar irradiation over CMGO/nHA nanocomposites (Anirudhan et al., 2017).

3. CARBON NANOMATERIALS FOR HA REINFORCEMENT

Carbon nanomaterials have attracted considerable interest as reinforcing phases for hydroxyapatite because their high specific surface area, mechanical stiffness, and tunable surface chemistry provide opportunities to address the intrinsic brittleness of the ceramic matrix (Phogat & Awasthi, 2025). Among the various carbon allotropes investigated for HA composites, carbon nanotubes (CNTs) and graphene-family materials are particularly relevant because their nanoscale dimensions

enable interaction with HA grains and interfaces while requiring relatively low filler concentrations (Musharavati et al., 2023). Previous studies have demonstrated improvements in the mechanical and tribological performance of HA following incorporation of CNTs or graphene-based phases, although the magnitude and even the direction of these effects depend strongly on filler dispersion, surface chemistry, loading, and processing conditions (Sonekar & Rathod, 2022).

3.1. Carbon Nanotubes

Carbon nanotubes are cylindrical carbon nanostructures consisting of graphitic carbon walls and are commonly classified as single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) (Shoukat & Khan, 2021). Their high aspect ratio and intrinsic stiffness make them attractive for transferring load across regions of the relatively brittle HA matrix. Reported Young's modulus values for CNTs can reach several hundred gigapascals, although the effective properties of practical CNTs depend on diameter, number of walls, structural defects, chirality, and processing history (Sharma, Miladinović, et al., 2026).

In HA composites, the principal contribution of CNTs lies not simply in their intrinsic strength but in their ability to interact with and bridge developing cracks. Well-dispersed CNTs can promote crack bridging, interfacial debonding, nanotube pull-out, and associated energy dissipation, thereby increasing resistance to crack propagation (Siddiqui et al., 2018). CNTs can also influence HA grain growth and densification during consolidation. However, these benefits require efficient load transfer between the nanotubes and the ceramic matrix. Pristine CNTs possess relatively inert and hydrophobic graphitic surfaces, which can promote aggregation and limit their compatibility with the hydrophilic HA phase (Bocanegra-Bernal et al., 2025). Consequently, acid oxidation, polymer-assisted modification, and other functionalization approaches have frequently been employed to introduce reactive surface groups and improve dispersion and interfacial interactions (Vo et al., 2026).

The distinction between SWCNTs and MWCNTs can also influence composite behavior. SWCNTs have smaller diameters and potentially greater specific interfacial areas, whereas MWCNTs possess multilayered structures that provide greater structural robustness and distinct pull-out and load-transfer characteristics (Shar et al., 2023). However, the strong van der Waals interactions between SWCNTs and their tendency to form tightly bundled networks can make homogeneous dispersion particularly challenging. MWCNTs, with their larger diameters and multiple concentric walls, generally exhibit greater structural robustness and can facilitate effective crack bridging and pull-out during fracture (Hossain et al., 2025). Their lower specific surface area may reduce the available matrix–CNT interfacial area, but their greater structural stability can be advantageous during mixing and thermal consolidation (Sharma, Miladinović, et al., 2026). Thus, SWCNTs may be attractive when maximizing interfacial reinforcement at low loading is desired, whereas MWCNTs may be advantageous when robust crack bridging and processing tolerance are prioritized (Subah et al., 2026). Nevertheless, comparisons based solely on CNT type can be misleading because differences in purity, functionalization, aspect ratio, dispersion state, and processing conditions may have a greater influence on the final composite properties than the number of walls alone.

3.2. Graphene, Graphene Oxide, And Reduced Graphene Oxide

Graphene consists of an approximately atomically thin two-dimensional network of sp^2-bonded carbon atoms. Its combination of high in-plane stiffness, large specific surface area, and electrical conductivity makes it an attractive reinforcement for ceramic matrices (H. Singh et al., 2025). Graphene-based HA composites have been investigated in powder, coating, and scaffold forms, with reported improvements in mechanical properties attributed to mechanisms including crack deflection, crack bridging, sheet pull-out, and increased fracture-path tortuosity (M. Li et al., 2018).

Unlike pristine graphene, graphene oxide (GO) contains oxygen-containing functional groups, including hydroxyl, epoxy, and carboxyl groups, distributed across its basal plane and edges. These functionalities increase surface polarity and provide reactive sites for interactions with HA and other phases (Aliyev et al., 2019). Consequently, GO can offer advantages in aqueous dispersion and interfacial bonding compared with relatively non-polar graphene (Yoo et al., 2014). However, oxidation also disrupts the extended sp^2 carbon network and can reduce the intrinsic mechanical and electrical properties of the carbon phase. Reduced graphene oxide (rGO) partially restores the sp^2-conjugated structure through reduction, providing a balance between the surface reactivity of GO and the structural/electrical characteristics of graphene (Ismail et al., 2026). The extent of oxidation and reduction therefore becomes an important variable in determining the final composite behavior.

The interaction between HA and graphene-family materials can occur through physical adsorption, electrostatic interactions, hydrogen bonding, and interactions involving oxygenated surface groups and calcium-containing species. Such interactions influence the nucleation and distribution of HA, the quality of the carbon–ceramic interface, and the efficiency of stress transfer (Saini et al., 2026). Accordingly, graphene, GO,

and rGO should not be treated as interchangeable fillers even though they share a common carbon framework. Their different surface chemistries can produce substantially different dispersion, interfacial bonding, processing stability, and mechanical responses (Sedehi et al., 2023).

3.3. One-Dimensional Versus Two-Dimensional Carbon Architectures

The dimensionality of carbon reinforcement provides an important framework for understanding its interaction with HA. CNTs represent one-dimensional (1D) reinforcement, in which a high-aspect-ratio tubular structure provides discrete pathways for load transfer and crack bridging (Khan et al., 2026). Graphene and its derivatives represent two-dimensional (2D) reinforcement, in which extended nanosheets can interact with larger regions of the HA matrix and modify crack trajectories over comparatively broad interfacial areas (Dong et al., 2024). These geometric differences produce distinct reinforcement mechanisms rather than simply differences in filler size.

For CNTs, the effectiveness of reinforcement is strongly associated with nanotube continuity, aspect ratio, orientation, dispersion, and interfacial bonding. When sufficiently dispersed and bonded, CNTs can bridge cracks and dissipate fracture energy through interfacial sliding and pull-out (Sharma, Miladinović, et al., 2026). In contrast, graphene-based sheets can force propagating cracks to deviate from a relatively straight path, increasing crack-path tortuosity and the energy required for fracture. Sheet pull-out and interfacial separation can provide additional energy-dissipation mechanisms (Adhikesavan et al., 2026). Reported graphene/HA studies have associated mechanical improvements with combinations of these mechanisms, although their relative contributions vary with graphene loading, sheet size, defects, and processing conditions (Boyapati et al., 2023).

This distinction also highlights why carbon loading alone is insufficient to predict composite performance. At low or optimized concentrations, both CNTs and graphene-family materials can provide effective reinforcement when uniformly distributed and strongly coupled to the HA matrix. At excessive concentrations, however, nanocarbon agglomeration can introduce defects, increase porosity, interfere with HA grain rearrangement, and reduce effective load transfer (Abazari et al., 2023). Thus, the performance advantage of either 1D or 2D reinforcement ultimately depends on the interactions among carbon geometry, surface chemistry, dispersion, interfacial quality, and processing history. This interdependence provides the basis for examining carbon–HA interfacial chemistry and processing in the following sections. Here, Figure 3 illustrates the chemical modification pathways of graphene derivatives and the structural conFigureurations of 1D, 2D, and mixed-dimensional carbon nanostructures.

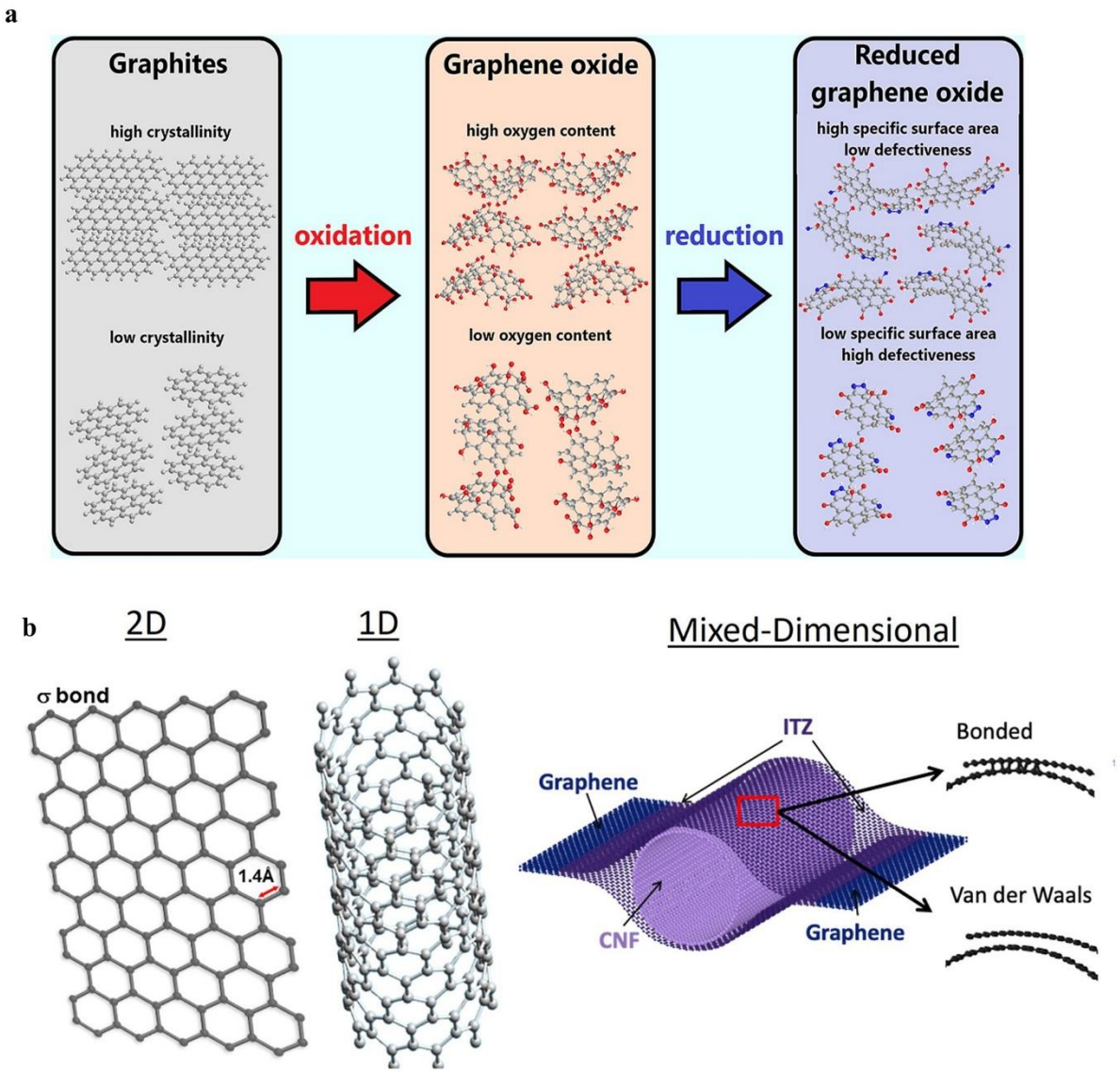


Figure 3. Oxidation–reduction pathways of graphene-family materials and structural dimensionality of carbon nanostructures. **a)** Chemical transformation of graphites into graphene oxide (GO) via oxidation and subsequent conversion to reduced graphene oxide (rGO) (Bychko et al., 2022); **b)** Structural classification of carbon reinforcements by dimensionality, comparing 2D planar graphene sheets, 1D cylindrical carbon nanotubes, and hybrid architectures showing interfacial transition zones (ITZ) and bonding interactions (Arshad et al., 2023).

4. CARBON–HA INTERFACIAL CHEMISTRY

The performance of carbon-reinforced hydroxyapatite (HA) nanocomposites is governed by not only the intrinsic properties of the carbon phase and ceramic matrix but also the quality of the carbon–HA interface. Because carbon nanomaterials and HA differ substantially in surface chemistry, polarity, morphology, and bonding characteristics, poor interfacial compatibility can limit stress transfer even when the reinforcement possesses exceptionally high intrinsic stiffness (Lawal, 2026; X. Zhao, Fan, et al., 2022). Conversely, a well-developed interface can promote homogeneous carbon distribution, regulate HA nucleation and grain growth, and provide effective pathways for transferring and dissipating mechanical stresses. Thus, interfacial chemistry represents a critical link between carbon structure, processing, microstructure, and mechanical performance.

4.1. Surface Chemistry of Carbon Nanomaterials

The surface chemistry of carbon nanomaterials varies strongly with their structural form and degree of functionalization. Pristine carbon nanotubes (CNTs) and graphene contain predominantly sp^2-hybridized carbon and relatively few chemically active surface groups. Their graphitic surfaces therefore exhibit limited interaction with the ionic and polar environment associated with HA (S. Ravichandran et al., 2026). This relatively inert character can contribute to aggregation, particularly during aqueous processing, reducing the effective interfacial area available for stress transfer.

Surface functionalization provides a means of modifying this behavior. Oxidative treatments of CNTs can introduce carboxyl, hydroxyl, and other oxygen-containing groups onto the nanotube surface. These groups increase surface polarity and can promote interactions with Ca^{2+} species during HA formation (Xia et al., 2019). In chemical precipitation routes, functionalized CNTs can therefore act as nucleation substrates, with calcium ions initially attracted to negatively charged surface groups followed by phosphate incorporation and HA precipitation. Experimental studies have shown that such functionalization can result in HA particles becoming attached to or deposited around CNT surfaces, strengthening the physical connection between the two phases (Eissa et al., 2026; Shin et al., 2011).

Graphene derivatives exhibit an even stronger dependence on surface chemistry. Graphene oxide (GO) contains hydroxyl, epoxy, carbonyl, and carboxyl groups distributed across its basal planes and edges. These oxygen-containing groups substantially increase its polarity and aqueous dispersibility compared with pristine graphene (Anjali et al., 2025). They can also provide sites for interaction with Ca^{2+} and subsequent HA nucleation. For example, negatively charged oxygen-containing groups on GO have been reported to attract Ca^{2+} ions, which can subsequently participate in the nucleation and growth of HA nanoparticles on the graphene surface (S. Singh et al., 2026).

Reduction of GO to reduced graphene oxide (rGO) partially restores the sp^2 carbon network while removing some of its oxygen-containing groups. Consequently, rGO generally exhibits intermediate surface chemistry between highly functionalized GO and pristine graphene (Guex et al., 2017). This distinction is important because greater restoration of the carbon network can improve the intrinsic properties of the carbon phase, whereas excessive removal of oxygen-containing groups may reduce the number of chemically active sites available for interaction with HA (Sindi, 2024). Therefore, graphene, GO, and rGO should be considered chemically distinct reinforcing phases rather than interchangeable forms of the same material.

4.2. Chemical and Physical Interactions With HA

The carbon–HA interface can involve several interaction mechanisms, including electrostatic attraction, coordination between surface functional groups and calcium species, hydrogen bonding, physical adsorption, and, depending on the surface structure and processing conditions, stronger chemical interactions (Awasthi et al., 2021). The relative contribution of each mechanism depends on the carbon material, degree of functionalization, HA surface termination, synthesis environment, and processing history.

For oxygen-functionalized carbon materials, interactions with Ca^{2+} provide one of the most frequently proposed mechanisms for interfacial attachment. The negatively charged carboxylate and other oxygen-containing groups can attract calcium species, generating localized regions favorable for phosphate adsorption and HA nucleation (Mambiri et al., 2024). In GO/HA systems, this mechanism can lead to the formation of HA nanoparticles directly attached to graphene sheets rather than as a separate ceramic phase. Such interfacial nucleation can influence HA particle size, orientation, and spatial distribution, thereby affecting the final composite microstructure (Qi et al., 2026).

These interactions are not limited to GO. Spectroscopic and nanoscale investigations of rGO/HA systems have indicated direct interactions between functional groups associated with HA phosphate species and residual oxygen-containing sites on rGO. These observations suggest that the interface may involve specific chemical interactions rather than merely mechanical contact between the two phases (Mambiri et al., 2024). Computational studies have further suggested that the strength of graphene/HA interactions depends on the crystallographic surface of HA, indicating that the atomic structure of the ceramic surface can influence interfacial adhesion (Y. Wang et al., 2022).

The distinction between chemical and physical contributions is particularly important when interpreting mechanical reinforcement. Stronger interfacial attraction can improve load transfer from HA to the carbon phase, but an excessively strong interface is not necessarily optimal for fracture toughness (Basirun et al., 2018). Some degree of controlled interfacial debonding or sliding can allow carbon nanotubes or graphene sheets to pull out or bridge developing cracks, thereby dissipating fracture energy (Fan et al., 2026). The optimal interface therefore represents a balance between sufficient adhesion for stress transfer and sufficient interfacial mobility to enable energy-dissipating mechanisms. Here, Figure 4 illustrates the chemical functionalization of carbon nanotubes (CNTs) and the synthesis pathways for CNT/graphene–hydroxyapatite (HA) composite coatings.

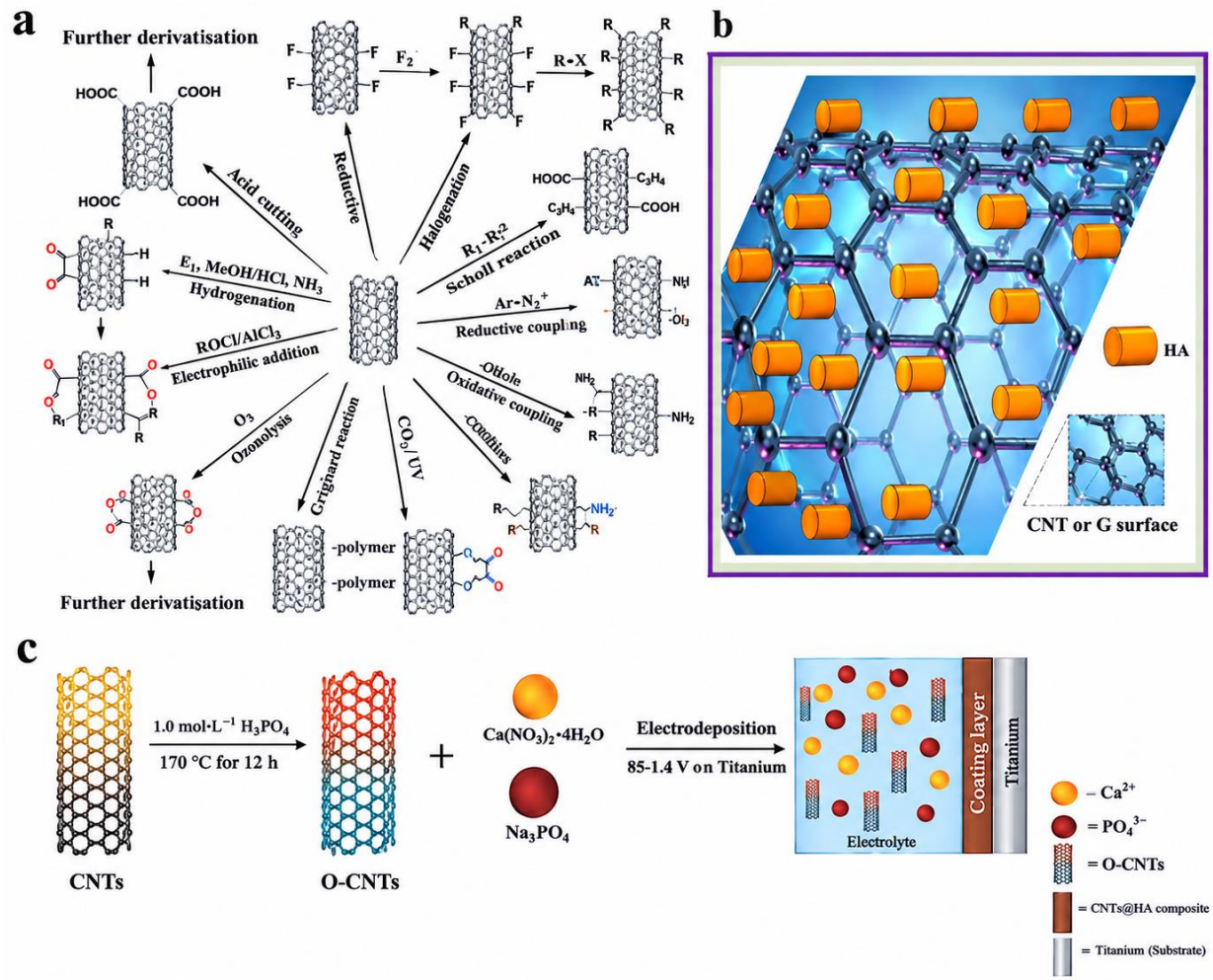


Figure 4. Overview of CNT modification and nanocomposite coating fabrication: **(a)** Covalent and non-covalent chemical functionalization routes for CNT (H.-C. Wu et al., 2010); **(b)** Schematic representation of hydroxyapatite (HA) nanoparticles decorated on CNT or graphene (G) surfaces (Kharisov et al., 2024); **(c)** Acid oxidation of CNTs and electrodeposition process of CNTs–HAP composites on a titanium substrate (Gopi et al., 2013).

4.3. Interfacial Bonding and Load Transfer

The primary mechanical function of the carbon–HA interface is to transfer stress from the relatively brittle ceramic matrix to the carbon reinforcement. Under external loading, insufficient interfacial adhesion can lead to premature debonding and limit the reinforcing contribution of the carbon phase. In contrast, well-dispersed reinforcement with effective interfacial bonding can carry part of the applied load and restrict local crack development (Kanhed et al., 2017).

For CNT-reinforced HA, the elongated geometry provides a favorable architecture for interfacial load transfer along the nanotube length. The efficiency of this mechanism depends on the nanotube aspect ratio, orientation, surface functionalization, and effective bonding area between CNTs and HA (Sharma, Miladinović, et al., 2026). When cracks encounter well-bonded nanotubes, several mechanisms may operate simultaneously, including crack bridging, nanotube pull-out, interfacial debonding, and frictional sliding. Experimental work on CNT/HA systems has associated strong CNT–HA bonding with more efficient load transfer and improved mechanical performance (H. Li et al., 2008).

Graphene-based reinforcement provides a different interfacial geometry. The large lateral dimensions of graphene sheets allow them to interact with relatively extensive regions of the HA matrix (Baghous et al., 2026). When sufficiently bonded to HA, these sheets can constrain local deformation and alter the trajectory of propagating cracks. Crack deflection around graphene sheets increases the effective fracture path, while crack bridging and sheet pull-out can contribute to additional

energy dissipation (L. Zhang et al., 2013). Experimental studies of GO/HA systems have linked the interfacial region to grain bridging and crack deflection, illustrating how surface chemistry and morphology can directly influence mechanical behavior (K. Cai et al., 2024).

The effectiveness of load transfer therefore cannot be predicted solely from the nominal carbon content. A small amount of well-dispersed carbon with an effective interface may provide greater reinforcement than a larger amount of poorly dispersed material. This consideration becomes particularly important at the nanoscale, where aggregation can substantially reduce the effective interfacial area and introduce pores or weak regions that act as stress concentrators. Here, Figure 5 illustrates the fabrication process and mechanical performance of in situ CNT-Col@HA composites as a function of CNT weight fraction.

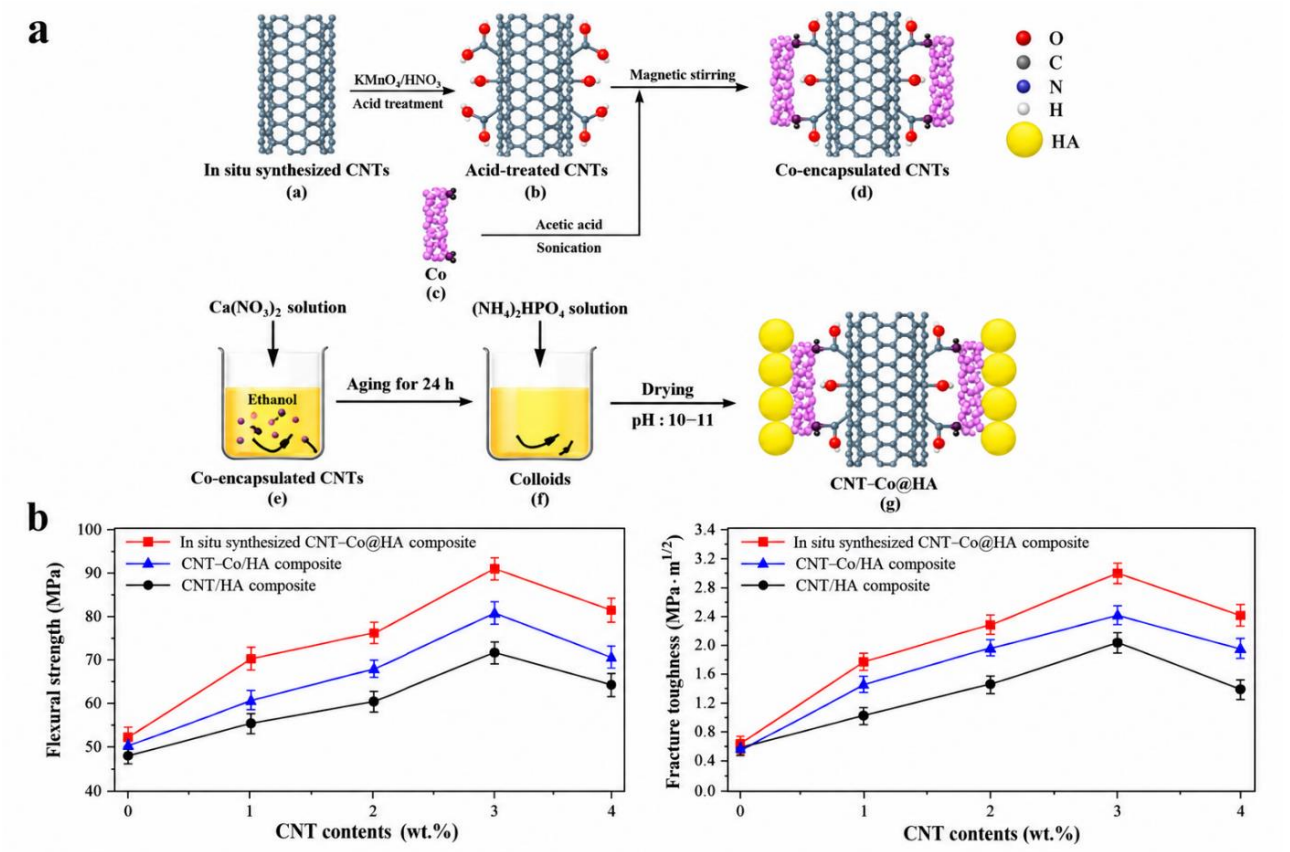


Figure 5. a) Schematic illustration of the step-wise fabrication process for in situ synthesized CNT-Col@HA composites, including CNT acid functionalization, collagen encapsulation, and hydroxyapatite mineralization; **b)** Influence of CNT loading (wt.%) on flexural strength (left) and fracture toughness (right) compared to binary and non-functionalized composite control groups (H. Li et al., 2020).

4.4. Role Of Functionalization in Dispersion and Interface Formation

Functionalization serves two closely related purposes: improving the dispersion of carbon nanomaterials and modifying their interactions with HA. For CNTs, oxidation can increase hydrophilicity and facilitate dispersion in aqueous precursor systems. The resulting functional groups can also provide sites for calcium adsorption and HA nucleation (Murjani et al., 2022). Consequently, functionalization can transform CNTs from relatively inert fillers into active substrates for ceramic growth.

For graphene-based materials, GO is particularly effective in aqueous systems because of its oxygen-rich surface. During HA synthesis, these functional groups can attract Ca^{2+} ions and facilitate heterogeneous nucleation, allowing HA nanoparticles to form directly on the graphene surface (S. Singh et al., 2026). This process can reduce the tendency of the ceramic and carbon phases to separate during subsequent processing. However, excessive oxidation is not necessarily advantageous because increased oxygen functionality

disrupts the continuous sp^2 carbon network and can reduce the intrinsic mechanical and electrical properties of the carbon phase (Hu et al., 2026).

The design of functionalization strategies should therefore be regarded as an optimization problem rather than simply an approach to maximizing surface reactivity. Excessive chemical treatment may introduce structural defects, shorten CNTs, damage graphene sheets, or alter their intrinsic properties (Sharma, Miladinović, et al., 2026). Conversely, insufficient functionalization may result in substantial aggregation and weak interfacial contact. The most effective surface modification is therefore one that provides adequate dispersion and affinity for HA while preserving sufficient structural integrity of the carbon reinforcement.

4.5. Interfacial Chemistry–Microstructure–Mechanical Relationships

The influence of interfacial chemistry extends beyond the interface itself because carbon–HA interactions can modify the development of the surrounding microstructure. During in situ or solution-based synthesis, functionalized carbon surfaces can act as heterogeneous nucleation sites (Figure 6), influencing HA particle size, morphology, orientation, and spatial distribution (Murphy et al., 2023). During subsequent consolidation, the resulting distribution affects grain growth, porosity, carbon segregation, and the continuity of the ceramic matrix. These microstructural features ultimately determine whether the carbon phase functions as an effective reinforcement or becomes a source of defects (Barzegar Eskandarkolaie et al., 2024).

Evidence from specific studies illustrates the importance of this processing–structure–property relationship. For example, the incorporation of approximately 3 wt% CNTs into HA has been reported to increase fracture toughness by more than 200%, demonstrating that relatively low carbon loading can produce substantial mechanical improvements when effective reinforcement and interfacial load transfer are achieved (Siddiqui et al., 2018). Conversely, increasing carbon content does not necessarily produce proportional improvements because excessive loading can promote agglomeration, porosity, and weak interfaces, thereby limiting stress transfer. Similarly, studies of graphene-family/HA systems have shown that improved dispersion and interfacial interactions can contribute to denser microstructures and enhanced mechanical performance, whereas poorly distributed carbon phases can act as defect sites (Sarkar & Roy, 2026; Sharma, Pradhan, et al., 2026).

A useful framework is therefore to consider the carbon–HA interface as part of a sequential processing–structure–property relationship: carbon architecture and surface chemistry → interfacial interactions → HA nucleation and dispersion → microstructural development → stress transfer and crack evolution → mechanical response. Within this framework, functionalization is not an isolated chemical modification but a tool for controlling the entire reinforcement pathway (Siddiqui et al., 2018). The optimal interface should provide sufficient adhesion to enable effective load transfer while retaining the capacity for controlled debonding, sliding, or pull-out when these mechanisms contribute to fracture-energy dissipation (Qi et al., 2026). This perspective also explains why mechanical comparisons among CNT-, graphene-, GO-, and rGO-reinforced HA systems remain difficult. Differences in carbon loading, functionalization, particle size, dispersion, synthesis route, consolidation temperature, porosity, and HA crystallinity can all modify the final interface and microstructure (Chakraborty et al., 2019). Consequently, reported mechanical improvements should be interpreted in relation to the complete processing–structure–interface history rather than attributed solely to the intrinsic properties of the carbon reinforcement. Here, Table 1 summarizes the key findings discussed in Section 4.

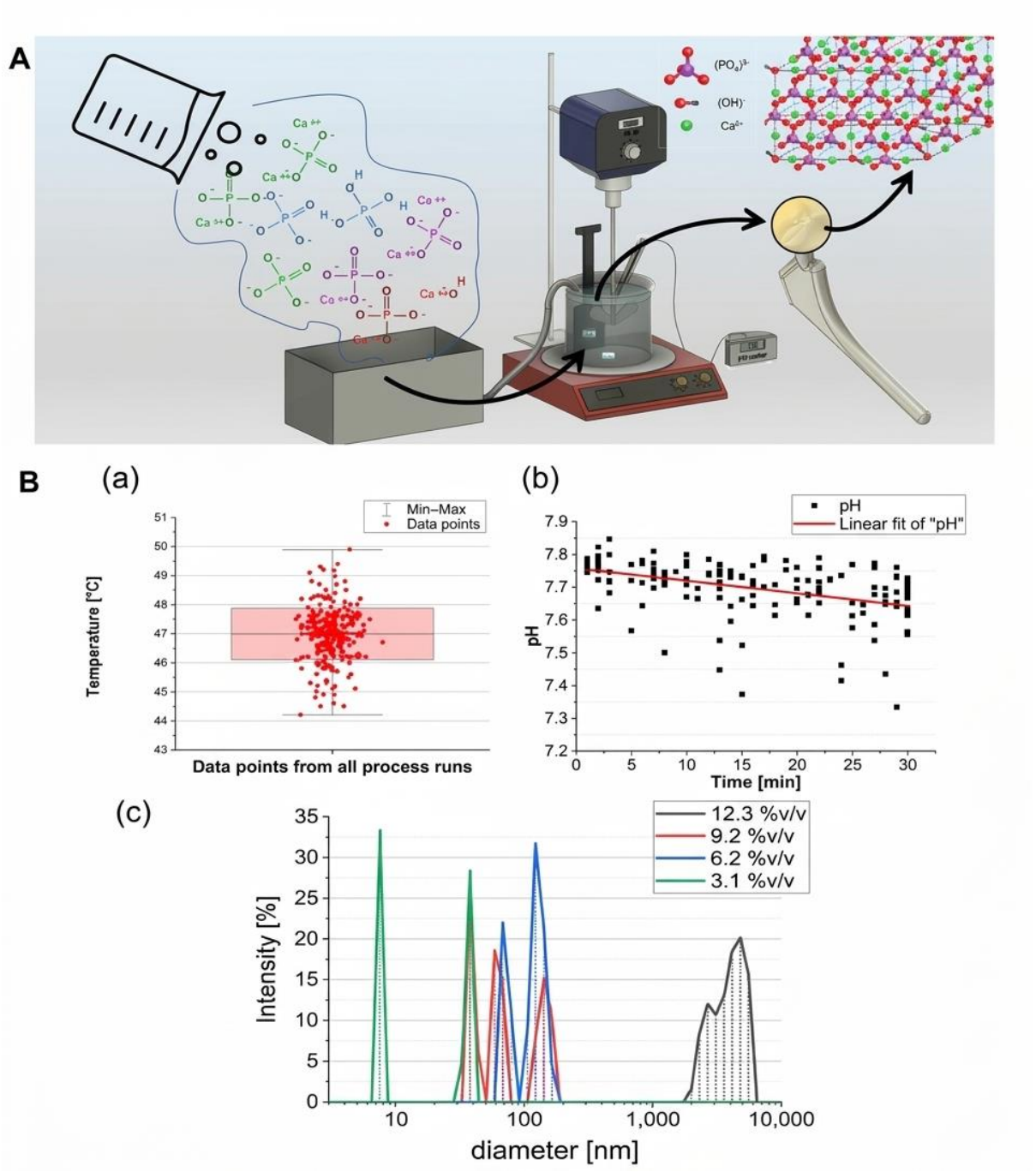


Figure 6. Experimental setup and process-parameter characterization during hydroxyapatite precipitation: (A) schematic of the synthesis procedure and (B) temperature distribution, pH evolution, and particle-size distributions at different solid concentrations (Murphy et al., 2023).

Table 1. Interfacial chemistry, microstructural effects, and reinforcement mechanisms in carbon-reinforced hydroxyapatite (HA) composites.

Carbon reinforcement	Surface characteristics	Interaction with HA	Effect on HA nucleation	Toughening mechanisms	Microstructural effects	Reference
CNTs	Predominantly sp^2-hybridized carbon; comparatively hydrophobic/inert surface	Relatively weak interaction with ionic/polar HA environment	Prone to aggregation during aqueous processing, reducing effective interfacial area	Load transfer along CNT length; crack bridging, and frictional sliding	Potential improvement in load-bearing capacity, crack bridging, and fracture-energy dissipation	(Sharma et al. 2026; H. Li et al. 2008)
Functionalized CNTs	Carboxyl, hydroxyl, and other oxygen-containing groups introduced by oxidation;	Ca^{2+} attraction with oxygen-containing groups; phosphate incorporation and HA precipitation	Functional groups act as nucleation sites and promote HA attachment around CNTs;	Efficient stress transfer; crack bridging, pull-out and controlled interfacial sliding	Improved interfacial contact, HA distribution and reinforcement efficiency	(Eissa et al. 2026; Shin et al. 2011; Murjani et al. 2022; Sharma et al. 2026)
Graphene	Predominantly sp^2 carbon; comparatively low density of chemically active groups	Relatively limited chemical interaction with HA compared with oxygen-functionalized graphene derivatives	Limited aqueous dispersibility; aggregation can reduce effective interfacial area	Large lateral surface enables extensive matrix interaction	Potential constraint of local deformation and increased fracture path	(S. Ravichandran et al. 2026; Baghous et al. 2026; L. Zhang et al. 2013)
Graphene oxide (GO)	Rich in hydroxyl, epoxy, carbonyl and carboxyl groups; highly polar	Strong interaction with Ca^{2+} through negatively charged oxygen-containing groups;	Promotes Ca^{2+} adsorption and direct nucleation of HA nanoparticles on graphene surface	Interfacial bonding, crack deflection, grain bridging and sheet pull-out	Improved HA dispersion, modified particle size enhanced interfacial reinforcement	(Anjali et al. 2025; S. Singh et al. 2026; K. Cai et al. 2024; Hu et al. 2026)
Reduced graphene oxide (rGO)	Partially restored sp^2 network with fewer oxygen-containing groups than GO;	Residual oxygen groups interact with HA phosphate species;	Intermediate surface reactivity and dispersion relative to GO and pristine graphene	Interfacial adhesion, crack bridging and controlled sliding	Balance between restored intrinsic carbon properties and remaining HA affinity	(Guex et al. 2017; Mambiri et al. 2024; Y. Wang et al. 2022; Sindi 2024)
Carbon–HA interface	Determined by carbon structure, functionalization, and HA surface termination	Electrostatic attraction, Ca^{2+} coordination, hydrogen bonding, and physical adsorption	Controls heterogeneous nucleation, HA particle size, morphology, and orientation	Stress transfer balanced with controlled deboning, and pull-out	Influences grain growth, porosity, carbon segregation, matrix continuity and crack evolution	(Awasthi et al. 2021; Basirun et al. 2018; Qi et al. 2026)

5. PROCESSING AND MICROSTRUCTURAL EVOLUTION

The mechanical performance of carbon-reinforced HA nanocomposites strongly depends on processing history because the fabrication route determines carbon dispersion, HA grain growth, porosity, interfacial integrity, and ultimately the efficiency of stress transfer. The high surface energy of nanoscale carbon materials promotes aggregation, while the thermal sensitivity of both HA and carbon phases imposes constraints on consolidation. Consequently, the nominal carbon content alone provides an incomplete description of the composite structure (F. Li et al., 2018; Yigit et al., 2026). A meaningful assessment of reinforcement requires consideration of the complete processing sequence, from powder preparation and dispersion to consolidation and post-processing.

5.1. Powder Mixing and Carbon Dispersion

Achieving a homogeneous distribution of the carbon phase is one of the first critical challenges in fabricating HA nanocomposites. CNTs tend to form entangled bundles because of strong van der Waals interactions between adjacent nanotubes, whereas graphene and its derivatives can restack because of π–π interactions and attractive forces between individual sheets (Sharma, Miladinović, et al., 2026). Such agglomeration reduces the effective surface area available for interaction with HA and produces local carbon-rich regions that can act as defects rather than reinforcing phases.

Several approaches have therefore been employed to improve carbon dispersion, including ultrasonication, mechanical mixing, ball milling, heteroaggregation, colloidal processing, and in situ precipitation of HA around carbon surfaces. Their effectiveness, however, depends on the specific carbon architecture (Sun & Gao, 2003). Prolonged or high-energy milling may improve powder homogeneity but can simultaneously damage CNTs or graphene sheets and introduce structural defects. Similarly, aggressive sonication can shorten nanotubes or fragment graphene sheets. Thus, dispersion should not be evaluated solely based on the absence of visible agglomerates; preservation of carbon structural integrity and maintenance of an effective aspect ratio or lateral dimension are also important (Y. Gao et al., 2025).

Surface functionalization provides an additional route to improving dispersion by increasing the affinity between carbon surfaces and the HA precursor environment. Oxygen-containing groups on oxidized CNTs and GO can improve interactions with aqueous media and facilitate the attachment of HA nanoparticles (Jin et al., 2026). However, functionalization and dispersion are interconnected with subsequent processing: a well-dispersed precursor can still develop carbon segregation during drying, compaction, or sintering (Sarkar & Roy, 2026). Spray drying, for example, has been used to produce composite agglomerates in which CNTs are distributed within HA-containing precursor particles before spark plasma sintering (SPS) consolidation. In one representative HA–CNT system, the resulting composite achieved approximately 96.5% of the theoretical density, compared with 94.9% for monolithic HA, while maintaining a fine-grained microstructure (Lahiri et al., 2010). This demonstrates that powder architecture before consolidation can be as important as the nominal reinforcement content.

5.2. Consolidation and the Competition Between Densification and Grain Growth

For dense HA-based composites, consolidation requires sufficient mass transport to eliminate pores while limiting excessive grain growth. Conventional pressureless sintering generally involves prolonged exposure to elevated temperatures, which can promote grain coarsening and, depending on the atmosphere and temperature, degradation of carbon reinforcements and decomposition of HA (Abbas et al., 2026). Grain growth is particularly important because the benefits associated with nanoscale HA can be lost even when the carbon phase itself remains structurally intact (Yigit et al., 2026).

Pressure-assisted techniques, including hot pressing, provide alternative routes for achieving high densification over shorter thermal cycles. SPS is particularly attractive for carbon-reinforced HA because rapid heating and simultaneous pressure application can facilitate densification while limiting the duration of high-temperature exposure. Reviews of HA–CNT systems have emphasized the ability of SPS to retain finer grain structures and reduce HA dissociation compared with prolonged conventional sintering treatments (Dujana et al., 2026; Sharma, Miladinović, et al., 2026). Nevertheless, SPS should not be regarded as a universally optimal processing method. Its advantages depend on the applied temperature, pressure, heating rate, holding time, atmosphere, powder condition, and carbon type (Özgün, 2026). Excessive temperatures can still promote HA decomposition or damage carbon phases, whereas insufficient temperature or pressure can leave residual porosity (Bertocco et al., 2025).

Microwave sintering offers another potentially useful route because volumetric heating can reduce processing time and thermal gradients while potentially limiting grain growth compared with prolonged conventional heating (Karayannis, 2016). It may therefore be attractive for rapid processing of fine-grained HA–carbon composites, although heating uniformity, electromagnetic coupling, sample geometry, and reproducibility can present important limitations (Ravi & Nozariasbmarz, 2026). Thus, microwave processing is particularly relevant when rapid heating and reduced

thermal exposure are desired, whereas SPS may be preferable when simultaneous pressure-assisted densification and tight control of porosity are required (Oghbaei & Mirzaee, 2010). No single consolidation technique is universally optimal. Conventional sintering offers advantages in terms of simplicity and scalability; hot pressing (HP) is suitable for controlled, high-density consolidation; SPS is preferred when rapid densification, fine-grained microstructures, and reduced thermal exposure are priorities; and microwave sintering is promising for rapid volumetric heating and reduced processing time (Kouhkanzadeh et al., 2020; Q. Wu et al., 2013). Selection should therefore be based on the desired balance among densification, grain-size retention, carbon preservation, phase stability, porosity, processing complexity, and scalability.

5.3. Carbon Stability During Thermal Processing

The thermal stability of the carbon phase is a particularly important consideration because the reinforcement cannot contribute effectively to mechanical performance if it is substantially oxidized, degraded, or structurally transformed during consolidation. The extent of carbon degradation depends strongly on temperature, atmosphere, exposure time, carbon architecture, and surface chemistry (Chousidis & Zeris, 2025).

This issue is particularly evident in conventional sintering under oxidizing conditions. Carbon fibers incorporated into HA have been reported to undergo oxidative damage during high-temperature processing, accompanied by deterioration of the reinforcing effect (Targońska et al., 2026). SPS processing under appropriately controlled conditions can substantially reduce this problem and enable retention of the carbon phase while also limiting HA decomposition. In a carbon-fiber/HA study, SPS produced refined microstructures and preserved the carbon reinforcement sufficiently to achieve a bending strength of 110.4 MPa and a fracture toughness of 2.41 MPa·m$^{1/2}$ at a carbon fiber content of 0.5 wt% (Kumar et al., 2005).

CNT-based systems provide a similar example. Raman characterization has confirmed the retention of graphitic carbon after SPS under selected processing conditions, while microstructural analysis has indicated that CNTs remained sufficiently intact to contribute to grain-boundary pinning and reinforcement (Pandey & Ganvir, 2026). A representative HA–CNT composite containing 4 wt% CNTs exhibited approximately 92% higher fracture toughness and a 25% higher elastic modulus than unreinforced HA under the reported processing conditions. However, these values should not be interpreted as universal effects of 4 wt% CNTs because they arise from a particular combination of dispersion, densification, grain size, interfacial characteristics, and SPS conditions (Lahiri et al., 2010).

5.4. Grain Growth, Grain-Boundary Effects, And Microstructural Refinement

Carbon nanomaterials can influence HA grain evolution during consolidation in addition to providing direct mechanical reinforcement. Well-dispersed CNTs, for example, can interact with grain boundaries and restrict their movement, thereby limiting grain growth (Adabavazeh et al., 2026). The resulting grain refinement can contribute to hardness, strength, and fracture resistance independently of CNT-mediated crack bridging or pull-out.

This distinction is important when interpreting the mechanical performance of carbon–HA composites. An increase in fracture toughness following carbon addition does not necessarily arise exclusively from the carbon phase carrying load across a propagating crack. The reinforcement may simultaneously alter HA grain size, grain-boundary characteristics, porosity, and crystallographic development (M. Wang et al., 2026). In SPS-processed HA–CNT composites, CNT addition has been associated with grain-boundary pinning and retention of a finer HA microstructure throughout the sintered body (Hachache et al., 2026).

Graphene-based reinforcements can produce similar microstructural effects, although their two-dimensional geometry introduces different dispersion and aggregation behavior. Graphene sheets can occupy grain boundaries or interfaces between HA particles, potentially restricting grain growth when uniformly distributed (Iqbal et al., 2024). However, restacked graphene or GO sheets can instead form weak intergranular regions and interfere with particle rearrangement and densification. Thus, the same carbon material may either refine or degrade the microstructure depending on its spatial distribution.

5.5. Porosity And Densification

Residual porosity represents one of the most important competing factors when interpreting mechanical data for HA nanocomposites. Pores reduce the effective load-bearing cross-sectional area and act as stress concentrators, making them particularly detrimental to tensile and flexural strength and fracture toughness (Nawang et al., 2019). Consequently, increasing carbon content can produce an apparent strengthening effect at one concentration but reduce mechanical properties at higher loadings if aggregation and pore formation become dominant (Mukherjee et al., 2014).

The relationship between carbon addition and densification is therefore non-monotonic and processing-dependent. Well-dispersed CNTs may facilitate densification during SPS through their thermal and electrical properties and by modifying particle-scale packing (Jia et al., 2024). In contrast, large CNT bundles or graphene stacks can hinder HA particle rearrangement

and create poorly bonded regions. Experimental observations of nanocarbon-reinforced systems demonstrate that differences in agglomeration can substantially influence the final mechanical response even when the reinforcement chemistry is similar (Baradaran et al., 2014; Núñez et al., 2014). For this reason, relative density should be reported alongside mechanical properties whenever possible. Comparing fracture toughness or strength between two carbon–HA systems without accounting for density, grain size, and porosity can lead to incorrect attribution of the observed improvement to the carbon reinforcement itself.

5.6. Processing–Structure–Property Relationship

The preceding considerations indicate that processing, interfacial characteristics, microstructure, and mechanical performance cannot be treated as independent variables. The processing route first determines the spatial distribution and structural integrity of the carbon phase; this distribution subsequently affects HA nucleation, grain growth, densification, and interfacial development. These microstructural characteristics then determine how efficiently the carbon phase contributes to load transfer, crack deflection, bridging, pull-out, and other energy-dissipation mechanisms (Y. Liu et al., 2013; M. Wang et al., 2026).

Accordingly, the mechanical response of a carbon-reinforced HA nanocomposite can be conceptually represented as follows:

Processing conditions → carbon dispersion and stability → HA densification and grain evolution → carbon–HA interface → defect structure → stress transfer and crack evolution → mechanical performance (Sharma, Miladinović, et al., 2026; Verma et al., 2026).

This sequence also explains why direct comparisons among published studies remain difficult. Nominally identical compositions can exhibit substantially different properties when prepared using different dispersion methods, levels of carbon functionalization, consolidation temperatures, pressures, atmospheres, or holding times (Azarniya et al., 2017). Integrated characterization is therefore essential for distinguishing genuine nanoscale reinforcement from improvements arising primarily from densification or microstructural refinement. This processing–microstructure relationship underpins the critical evaluation of the mechanical reinforcement mechanisms discussed in the following section. Here, Table 2 summarizes the key findings presented in Section 5.

Table 2. Effect of processing conditions on carbon dispersion, microstructure, densification, and mechanical performance of carbon-reinforced hydroxyapatite (HA) nanocomposites.

Processing parameter	Common approaches	Effect on carbon phase	Effect on HA	Effect on interface	Mechanical performance	Reference
Powder mixing & carbon dispersion	Mechanical mixing, ultrasonication, ball milling, hetero-aggregation, colloidal processing	Determines carbon distribution; excessive processing may damage CNTs/graphene	Uniform distribution improves HA–carbon contact; agglomerates create carbon-rich defects	Homogeneous dispersion increases effective interfacial area	Better load transfer and reinforcement efficiency; agglomeration can reduce performance	(Sharma et al. 2026; Sun & Gao 2003)
Ultrasonication	Controlled aqueous sonication	Breaks CNT bundles and improves dispersion; excessive sonication shortens CNTs or fragments graphene	More homogeneous precursor distribution	Greater surface exposure may improve HA attachment	Potential improvement in reinforcement efficiency	(Y. Gao et al. 2025)
Ball milling	Powder homogenization using ball milling	Can improve distribution, but excessive milling introduces structural defects	Improves powder homogeneity	Alters effective carbon surface and interface	Improves reinforcement through dispersion, but carbon damage may offset benefits	(Y. Gao et al. 2025)

Processing parameter	Common approaches	Effect on carbon phase	Effect on HA	Effect on interface	Mechanical performance	Reference
Surface functionalization	Oxidation of oxygen-containing groups	Increases hydrophilicity and precursor affinity	Promotes HA attachment and heterogeneous nucleation	Improves carbon–HA interaction	Improves load transfer and reinforcement efficiency	(Jin et al. 2026)
In situ HA precipitation	HA precipitation directly around carbon surfaces	Integrates carbon into growing HA phase	Promotes HA nucleation around carbon and more uniform phase distribution	Increases carbon–HA contact and reduces phase separation	Potentially improves stress transfer	(Jin et al. 2026)
Spray drying	Formation of composite agglomerates before consolidation	Promotes CNT distribution within HA-containing precursor particles	Can produce fine-grained, highly dense composites after SPS	Helps minimize carbon segregation during consolidation	HA–CNT system achieved 96.5% theoretical density vs. 94.9% for monolithic HA	(Lahiri et al. 2010)
Conventional pressureless sintering	Prolonged high-temperature exposure	Risk of carbon degradation	Grain coarsening and possible HA decomposition	Carbon degradation and porosity weaken the composite	Reduces toughness if excessive degradation occurs	(Abbas et al. 2026; Yigit et al. 2026)
Hot pressing	Elevated temperature + applied pressure	Shorter thermal exposure helps preserve carbon	Promotes densification and limits excessive grain growth	Improves particle contact and reduces porosity	Potentially improves mechanical properties	(Dujana et al. 2026; Sharma et al. 2026)
Spark plasma sintering (SPS)	Rapid heating + simultaneous pressure	Preserve carbon and limit thermal degradation	Rapid densification and finer HA grain structure	Reduced porosity and improved phase retention	Generally favorable for strength, modulus, and fracture toughness	(Dujana et al. 2026; Sharma et al. 2026)
SPS temperature	Controlled thermal cycle	Excessive temperature can damage carbon	Higher temperature promotes densification, but excessive temperature causes HA decomposition	Affects phase stability and defect formation	Improves strength, modulus, and fracture toughness	(Özgün 2026; Bertocco et al. 2025)

5.7. Electrical Conductivity and Functional Groups Influence Cellular Proliferation and Inflammatory Responses

Within carbon-reinforced hydroxyapatite (HA) nanocomposites, biological performance reflects the interplay between two distinct carbon-derived properties: the electrical conductivity of the percolating carbon phase and the specific oxygen-containing functional groups—hydroxyl, carboxyl, and epoxide—present on its surface (T. Zhang et al., 2015; H. Zhao et al., 2022). For cellular proliferation, conductive networks facilitate the delivery of applied electrical stimulation and support cell attachment, while these functional groups modulate surface wettability and protein–surface interactions, enhancing the adsorption of extracellular matrix proteins such as fibronectin and vitronectin and thereby promoting integrin-mediated adhesion (Saini et al., 2026; Trevisani et al., 2026). For stem-cell differentiation, studies on electroactive scaffolds have shown that electrical stimulation upregulates osteogenic markers such as Runx2, alkaline phosphatase, and osteocalcin, whereas the negatively charged, oxygen-rich surface of graphene oxide promotes calcium interactions and favorable binding of osteogenic proteins such as BMP-2, directing mesenchymal stem cells toward osteogenic differentiation (Kashte et al., 2024). Inflammatory responses, by contrast, depend less on conductivity than on surface chemistry and particle characteristics: carboxyl-functionalized carbons have been reported to alter macrophage reactive oxygen species production and pro-inflammatory signaling in some settings, while other reports have found that functionalization has little effect on cytokine release, indicating that immunological outcomes are context-dependent rather than uniformly beneficial or harmful (Canton et al., 2021; Xue et al., 2023). Because all three responses vary with carbon loading, lateral size, and dispersion quality, conductivity and functional-group density must be co-optimized rather than maximized independently.

6. MECHANICAL REINFORCEMENT: MECHANISMS AND EXPERIMENTAL EVIDENCE

The mechanical reinforcement of HA by carbon nanomaterials cannot be attributed to their high intrinsic stiffness alone. In a brittle ceramic matrix, reinforcement becomes effective only when the carbon phase is sufficiently well dispersed, appropriately bonded to the HA matrix, and retained during consolidation (Zafarrazzaghnia et al., 2026). Under these conditions, carbon nanomaterials can alter stress transfer, crack initiation, crack propagation, grain growth, and fracture-energy dissipation. However, the magnitude and even the direction of the mechanical response depend strongly on carbon type, loading, interfacial characteristics, porosity, grain structure, and processing conditions (Fan et al., 2026). Consequently, reported improvements should be interpreted in terms of the underlying fracture mechanisms rather than composition alone.

6.1. Crack Initiation and Propagation In HA

The intrinsic brittleness of HA makes crack initiation and propagation central to its mechanical limitations. Under mechanical loading, local flaws associated with pores, grain boundaries, processing defects, or microstructural heterogeneity can act as stress concentrators (Robert et al., 2026). Once a critical crack is initiated, the relatively limited capacity of the ceramic matrix for plastic deformation allows the crack to propagate with comparatively low energy dissipation.

Carbon reinforcement modifies this fracture process by introducing interfaces and mechanically distinct regions into the HA matrix. When a propagating crack encounters a well-dispersed carbon nanostructure, the crack may be deflected, bridged, arrested, or forced to follow a more tortuous path. These mechanisms increase the energy required for continued crack growth (Amirahmadi & Roy, 2026). However, carbon addition can also introduce new defects if the reinforcement is poorly dispersed. Carbon agglomerates, interfacial voids, and incomplete densification can become preferential sites for crack initiation and may therefore offset or reverse the expected strengthening effect (Fang et al., 2026).

The critical point is therefore that carbon reinforcement modifies the fracture pathway rather than simply increasing the nominal strength of the material. The effectiveness of this modification depends on whether the carbon–HA interface causes cracks to interact with the reinforcement in a controlled and energy-dissipating manner. Here, Figure 7 illustrates interfacial self-assembly and finite element modeling of crack growth dynamics in mesoporous hydroxyapatite-coated CNTs.

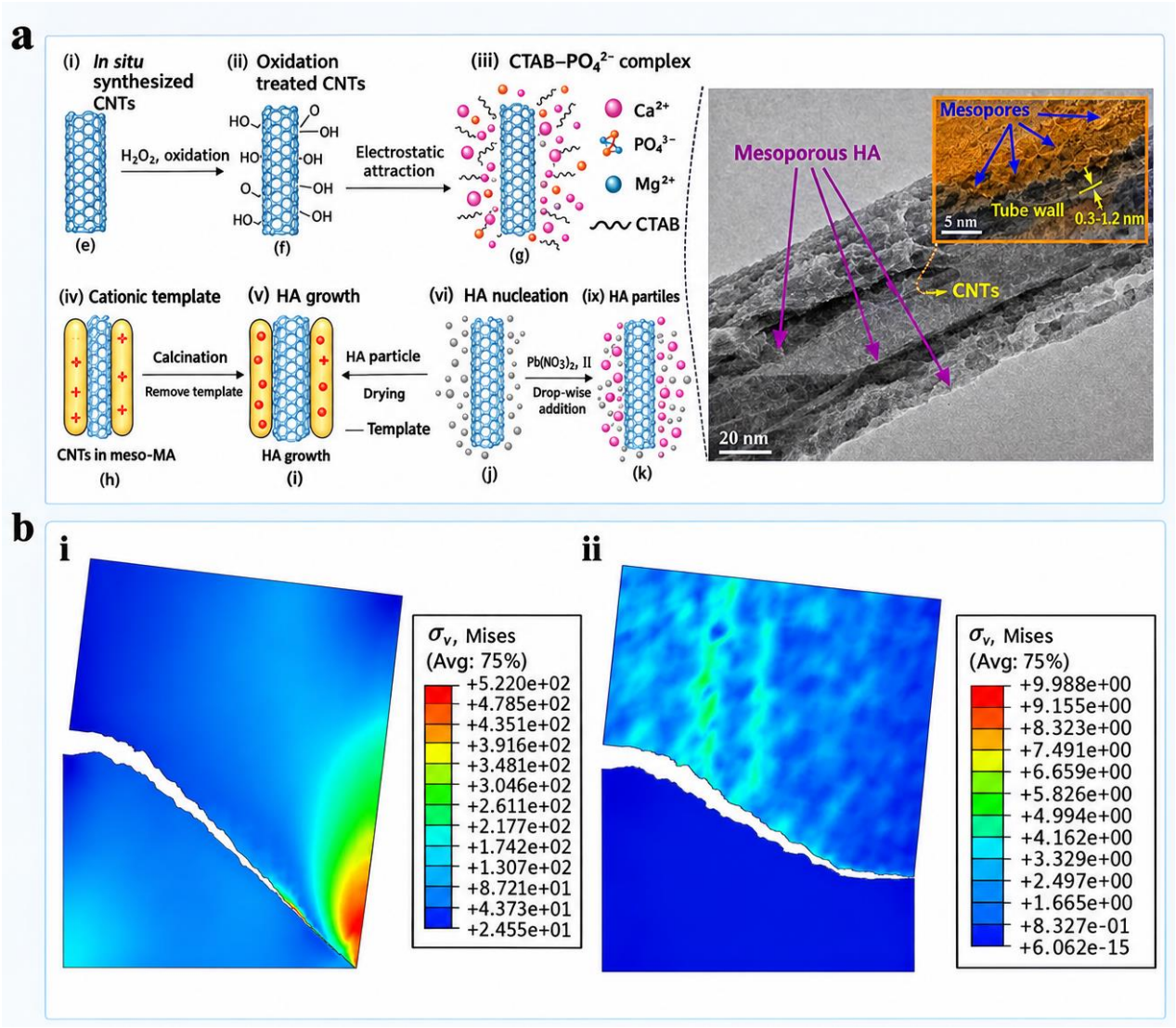


Figure 7. a) Schematic diagram of CTAB surfactant-assisted self-assembly and growth of mesoporous hydroxyapatite on CNTs (H. Li et al., 2017), **b)** Crack growth pattern in hydroxyapatite under shear loading: (i) non-porous, and (ii) porous plate (Prashant Singh et al., 2022).

6.2. CNT-Mediated Reinforcement

CNTs provide a one-dimensional reinforcement architecture with a high aspect ratio and the ability to interact with propagating cracks over an extended length. Several mechanisms can contribute to their reinforcing effect, including crack bridging, interfacial debonding, nanotube pull-out, frictional sliding, and load transfer from the HA matrix to the nanotubes (Alqurashi et al., 2026).

Crack bridging is particularly important when CNTs span crack surfaces after crack initiation. The nanotubes can sustain part of the applied load and reduce the effective driving force at the crack tip. If the CNT–HA interface is sufficiently strong, stress can be transferred efficiently to the nanotubes. At the same time, controlled interfacial debonding followed by nanotube sliding or pull-out can dissipate additional fracture energy (Eyidogan & Kirca, 2025). Reinforcement therefore depends on a balance in interfacial bonding: an interface that is too weak may debond prematurely without effective load transfer, whereas an excessively strong interface may suppress pull-out and reduce the contribution of frictional energy dissipation.

CNTs can also influence the HA matrix independently of direct crack bridging. Well-dispersed nanotubes located at grain boundaries may restrict grain-boundary migration and inhibit grain growth during sintering. The resulting grain refinement can contribute to increased hardness and strength, while the nanotubes

simultaneously participate in crack-related toughening mechanisms (Inam et al., 2010; Saberi et al., 2024). These effects are difficult to separate experimentally and should not automatically be attributed to CNT-mediated load transfer.

Experimental studies demonstrate that CNT addition can improve the mechanical performance of HA, but the reported magnitude of improvement varies considerably among systems. For example, an SPS-processed HA–CNT composite has been reported to exhibit substantially higher fracture toughness and elastic modulus than unreinforced HA, with these improvements associated with CNT reinforcement, grain refinement, and preservation of CNT structural integrity (Han et al., 2020; Lahiri et al., 2010). However, such improvements are strongly processing-dependent and should not be interpreted as universal performance characteristics of CNT/HA composites.

A further limitation is the tendency of CNTs to form bundles. Increasing CNT concentration does not necessarily enhance reinforcement because bundled nanotubes provide a smaller effective interfacial area and may introduce pores or weak interfaces (D. Zhao et al., 2024). Consequently, an optimal concentration generally exists for a given processing system, but this optimum cannot be generalized across different CNT types, functionalization strategies, aspect ratios, and fabrication routes.

6.3. Graphene-Mediated Reinforcement

Graphene and its derivatives provide a fundamentally different reinforcement geometry because their two-dimensional sheets can interact with relatively large regions of the HA matrix. Their contribution to fracture resistance can involve crack deflection, crack bridging, sheet pull-out, interfacial sliding, and increased crack-path tortuosity (Taghzouti, 2025).

Crack deflection is particularly relevant to graphene-reinforced ceramics. When a propagating crack encounters a graphene sheet with sufficient interfacial interaction, the crack may deviate from its original trajectory rather than propagate directly through the matrix. The resulting increase in fracture-path length requires additional energy for crack propagation. Graphene sheets can also bridge cracks and undergo interfacial sliding or pull-out, providing additional mechanisms for energy dissipation (A & M, 2024; Parente et al., 2026).

However, the large lateral dimensions of graphene do not automatically make it a more effective reinforcement than CNTs. Restacking can reduce the effective surface area and generate locally weak regions, while poorly dispersed sheets can interfere with HA particle packing and densification (X. Zhang et al., 2023). In addition, graphene sheets with insufficient interfacial adhesion may behave more like defects than reinforcing structures. Therefore, the mechanical advantages associated with the two-dimensional architecture can be realized only when sheet dispersion, interfacial quality, and matrix densification are simultaneously controlled (J. Zhang et al., 2025).

GO and rGO require further distinction. GO generally exhibits stronger chemical interactions with HA because of its oxygen-containing functional groups, which can promote HA nucleation and interfacial attachment (Taghzouti, 2025). However, disruption of the graphitic network during oxidation reduces its intrinsic structural properties relative to pristine graphene. rGO partially restores the graphitic network while retaining some oxygen-containing functional groups, providing a different balance between interfacial activity and intrinsic reinforcement capability (Ismail et al., 2026). Consequently, comparisons among graphene, GO, and rGO should account for both their structural differences and their different processing histories. Here, Figure 8 represents fabrication, morphological characterization, and mechanical testing of graphene oxide/hydroxyapatite composite scaffolds.

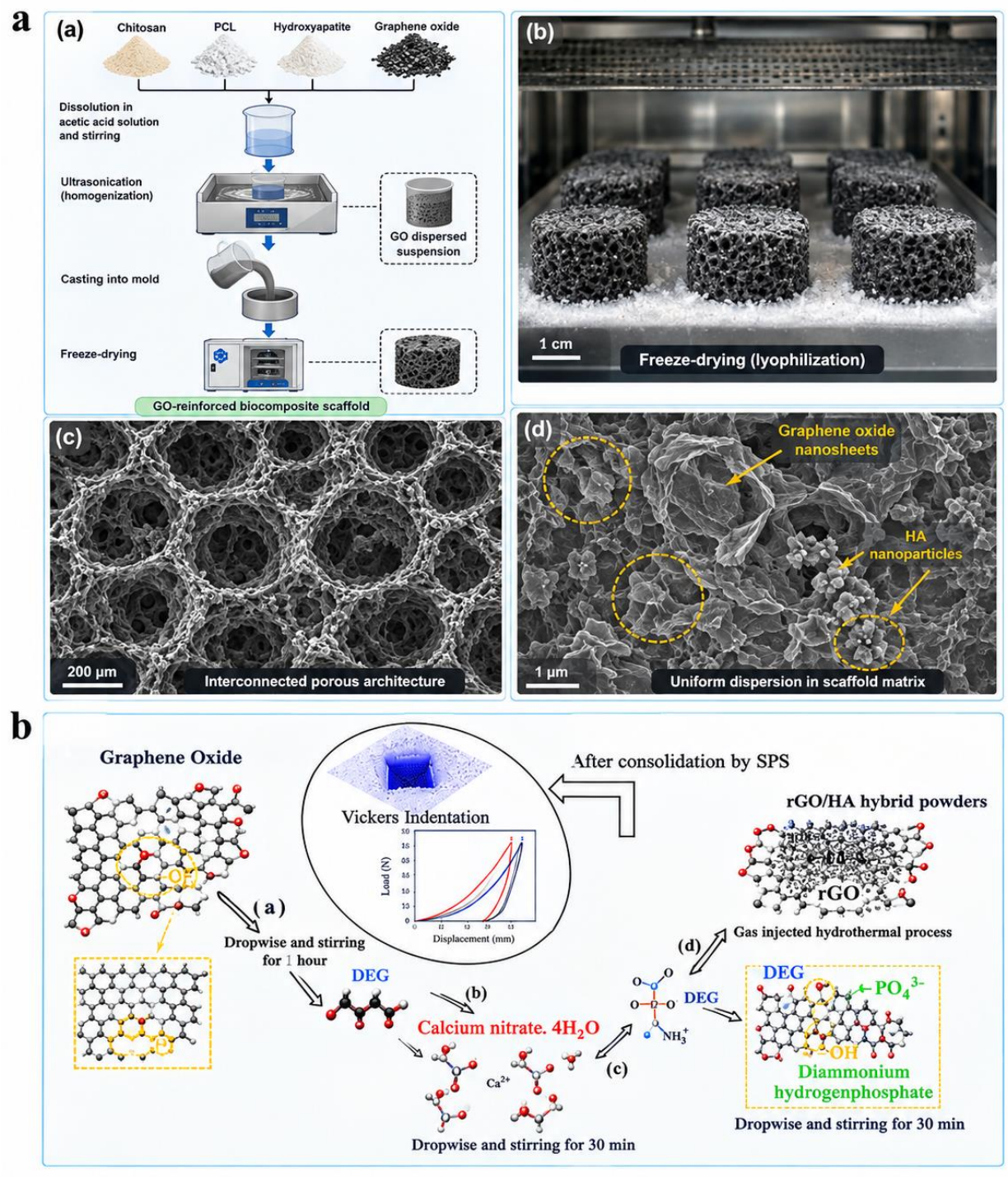


Figure 8. a) Fabrication and microstructural characterization of GO-reinforced biocomposite scaffolds; **i)** Workflow of the scaffold fabrication process; **ii)** freeze-drying stage; **iii)** SEM image of the interconnected porous architecture; **iv)** GO distribution within the scaffold matrix (Padhi & Choudhury, 2026); **b)** Reaction pathway for rGO/HA hybrid powder synthesis involving DEG surfactant, calcium nitrate tetrahydrate, and di-ammonium hydrogen phosphate via a gas-injected hydrothermal process (Nosrati et al., 2021).

6.4. Effect Of Carbon Loading And Dispersion

The relationship between carbon concentration and mechanical performance is typically nonlinear. At relatively low concentrations, introducing a well-dispersed carbon phase can increase the number of effective reinforcement sites while maintaining the continuity of the HA matrix (Sharma, Miladinović, et al., 2026). As the concentration increases, however, the likelihood of CNT bundling or graphene restacking rises, and the carbon phase may begin to interfere with HA particle rearrangement and densification (B. Liu et al., 2024).

This results in a competition between reinforcement and defect formation. Initially, increasing carbon content can improve crack bridging, load transfer, and grain refinement. Beyond a certain concentration, however, additional carbon may increase porosity, promote agglomeration, reduce interfacial contact, or disrupt the continuity of the HA matrix. The resulting deterioration in strength or toughness does not necessarily indicate that carbon itself is mechanically ineffective; rather, it suggests that the microstructural conditions required for effective reinforcement are no longer maintained (Akbulut et al., 2025; Qi et al., 2026).

Importantly, the optimal loading should not be expressed as a universal concentration. Reported optimal values differ because carbon type, aspect ratio, surface functionalization, particle size, HA morphology, consolidation method, and relative density vary among studies (del-Mazo-Barbara et al., 2024). A meaningful comparison should therefore relate carbon content to dispersion state, density, grain size, and interfacial characteristics rather than treating weight percentage as an independent descriptor of reinforcement efficiency.

6.5. Processing Microstructure Mechanical Relationships

The mechanical response of carbon-reinforced HA is ultimately determined by the interplay between processing and microstructure. Nominally identical CNT or graphene concentrations can produce substantially different mechanical properties depending on how the reinforcement is dispersed and consolidated (Pandey & Ganvir, 2026).

High densification generally improves strength by reducing stress-concentrating pores, while grain refinement can increase resistance to deformation and crack propagation. At the same time, excessive thermal exposure can promote HA grain growth and damage carbon structures, whereas inadequate consolidation can leave residual porosity (M. Wang et al., 2026). These competing effects explain why rapid, pressure-assisted techniques such as SPS are frequently investigated for carbon–HA systems. Nevertheless, SPS does not eliminate the fundamental processing trade-offs; inappropriate temperatures, pressures, or holding conditions can still lead to phase degradation, carbon damage, or incomplete densification (Abbas et al., 2026).

This processing dependence presents an important challenge when comparing published mechanical data. An apparent improvement in flexural strength, hardness, or fracture toughness may result from several simultaneous changes, including direct carbon reinforcement, grain refinement, increased density, reduced defect size, or improved interfacial bonding (J. Cai et al., 2026). Without corresponding microstructural characterization, it is difficult to determine which mechanism dominates. Therefore, mechanical testing should ideally be accompanied by measurements of relative density, grain-size analysis, phase characterization, carbon structural analysis, and fracture-surface examination.

6.6. Comparative Assessment Of 1D And 2D Carbon Reinforcement

CNTs and graphene-based materials should not be regarded simply as alternative fillers with different dimensions. Their distinct geometries give rise to different reinforcement mechanisms. CNTs provide elongated reinforcement pathways that are particularly well suited to crack bridging, axial load transfer, interfacial sliding, and pull-out. Graphene-based materials, in contrast, provide extended two-dimensional interfaces that can promote crack deflection, crack bridging, sheet pull-out, and increased crack-path tortuosity (Pandey & Ganvir, 2026; Parente et al., 2026).

This comparison also demonstrates why a simple question such as whether graphene or CNTs provide superior reinforcement is scientifically inadequate. CNTs may be advantageous when elongated bridging structures and pull-out mechanisms can be preserved, whereas graphene-based materials may be more effective when large interfacial areas and crack deflection are favored (Martínez-Gómez, 2026; Papageorgiou et al., 2020). The outcome depends on the combined effects of carbon geometry, surface chemistry, dispersion, loading, matrix grain structure, and consolidation conditions. Here, Figure 9 illustrates processing strategies, mechanical reinforcement mechanisms, and biofabrication workflows for carbon-reinforced hydroxyapatite biomaterials.

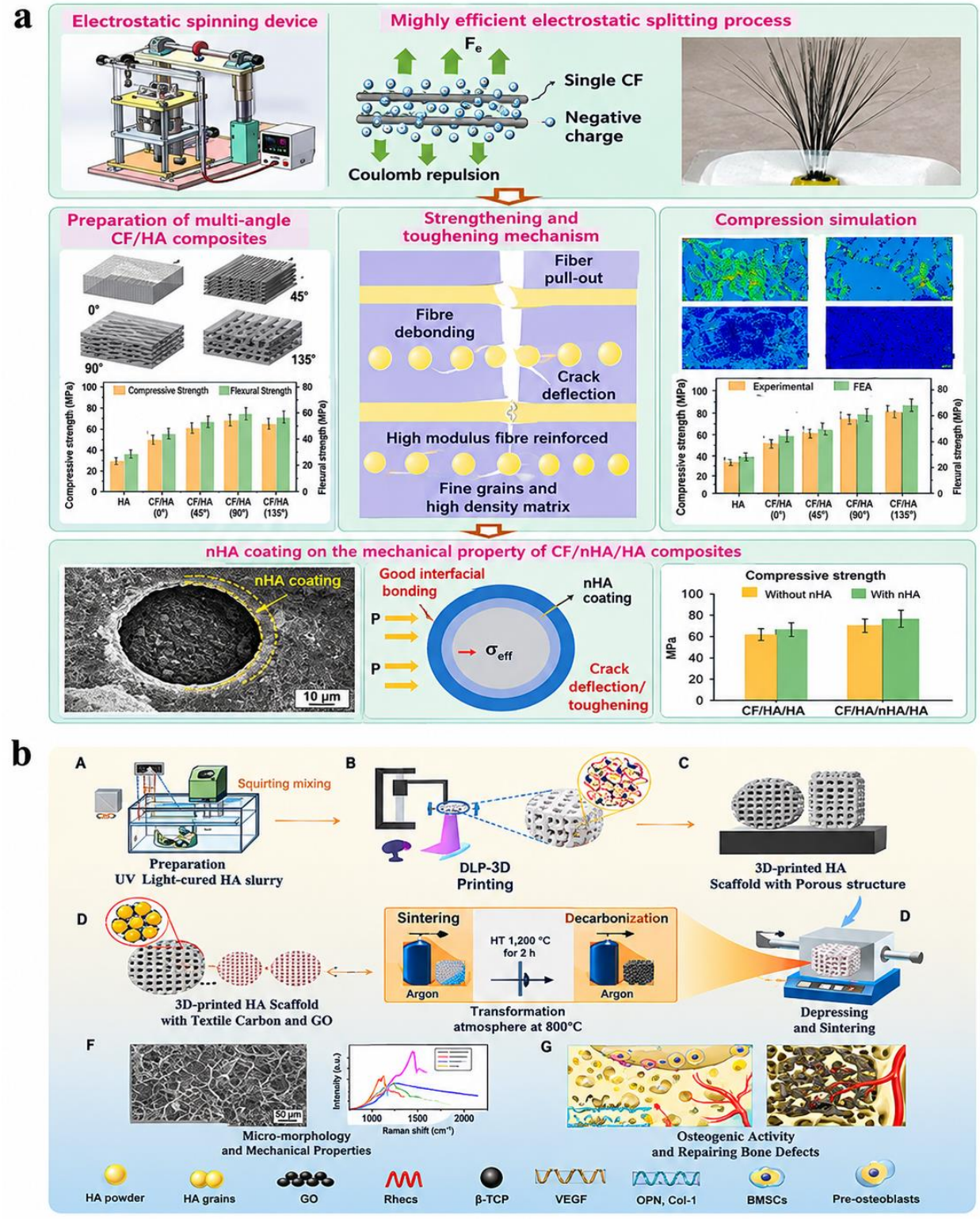


Figure 9. a) Electrostatic splitting process for single carbon fibers (CF), multi-angle orientation fabrication (CF/HA), strengthening/toughening mechanisms (X. Zhao, Liu, et al., 2022), **b)** Processing routes, strengthening mechanisms, DLP 3D printing, and osteogenic evaluation of carbon-reinforced hydroxyapatite composites (H. Zhao et al., 2025).

6.7. Critical Interpretation of Mechanical Performance

A recurring limitation in the literature is the tendency to attribute improvements in mechanical properties directly to the exceptional mechanical properties of carbon nanomaterials. Such an interpretation is incomplete because the intrinsic modulus or strength of an isolated CNT or graphene sheet does not directly translate into equivalent reinforcement in a ceramic composite (Estili & Sakka, 2014). Effective reinforcement requires efficient stress transfer across the interface, preservation of the structural integrity of the carbon phase, and a defect population that does not negate the benefits of reinforcement (Z. Wu et al., 2023).

Accordingly, the most convincing evidence for carbon-mediated reinforcement should demonstrate a consistent relationship among carbon distribution, interfacial quality, fracture behavior, and mechanical response (Lavagna et al., 2023). For example, an increase in fracture toughness accompanied by evidence of crack bridging or deflection provides stronger mechanistic support than an increase in toughness reported without corresponding microstructural or fractographic analysis (Zimmermann et al., 2010). Similarly, an increase in strength should be interpreted alongside relative density and grain size to distinguish direct reinforcement from improvements arising from densification or grain refinement.

The available evidence therefore supports a more nuanced interpretation: carbon nanomaterials can substantially modify the mechanical behavior of HA, but their effectiveness is conditional rather than intrinsic (Nezhad et al., 2021). The most effective reinforcement is achieved when carbon architecture, interfacial chemistry, dispersion, and consolidation are collectively optimized (Siddiqui et al., 2018). This conclusion shifts the design strategy from simply increasing carbon content toward engineering the carbon–HA interface and microstructure as an integrated, fracture-resistant architecture.

6.8. Fatigue Resistance and Cyclic Damage Tolerance

For bone tissue engineering applications, mechanical performance should be considered under repeated physiological loading rather than solely under monotonic loading conditions. Bone is continuously subjected to cyclic stresses during daily activities, making fatigue resistance and damage tolerance important determinants of long-term structural reliability (George et al., 2025; Seraji et al., 2024). This consideration is particularly relevant for HA-based ceramics, which are inherently brittle and sensitive to defects, porosity, and subcritical crack growth. Consequently, a material that exhibits high compressive strength or fracture toughness under monotonic loading may not necessarily maintain its mechanical integrity under prolonged cyclic loading (Jiang et al., 2017).

The fatigue behavior of HA is strongly influenced by its microstructure and defect population. Residual porosity, grain size, processing-induced flaws, and weak interfaces can act as preferential sites for crack initiation and subsequent propagation under cyclic loading (Rahimi Mamaghani & Parvin, 2026). In addition, aqueous physiological environments may promote subcritical crack growth through interactions between crack surfaces and the surrounding fluid, potentially reducing long-term fatigue resistance (Bajaj et al., 2008). Therefore, the fatigue performance of HA-based composites should be evaluated in relation to density, pore architecture, grain structure, and environmental conditions rather than treated as an intrinsic material property.

Carbon nanomaterials provide a potential strategy for improving cyclic damage tolerance because several of their established toughening mechanisms can also impede progressive crack growth. Well-dispersed CNTs and graphene-family materials may bridge developing cracks, deflect crack trajectories, and dissipate energy through controlled interfacial debonding, sliding, and pull-out (Vignesh et al., 2026). These mechanisms can reduce the effective driving force for crack propagation and potentially delay catastrophic failure. However, the presence of carbon does not inherently guarantee improved fatigue performance. Agglomerated CNTs or graphene sheets, weak carbon–HA interfaces, and processing-induced porosity may instead introduce stress concentrations and preferential crack-initiation sites (Szakács & Mészáros, 2018). Thus, the same carbon phase that reinforces optimized conditions may become detrimental when dispersion and interfacial quality are poorly controlled. Importantly, the optimal carbon content for maximizing strength or fracture toughness may not correspond to that required for optimal fatigue resistance (Y. Gao et al., 2025; Lahiri et al., 2010). Excessive carbon loading can increase agglomeration and porosity, whereas insufficient interfacial bonding may prevent effective stress transfer and stable crack-bridging or pull-out mechanisms during repeated loading.

7. CHALLENGES, DESIGN CONSIDERATIONS, AND FUTURE PERSPECTIVES

Despite substantial progress in carbon-reinforced HA nanocomposites, consistent relationships among carbon characteristics, interfacial chemistry, processing conditions, and mechanical performance have not yet been fully established. Reported improvements in strength, hardness, and fracture toughness vary considerably among studies, even for apparently similar carbon contents. This variability reflects differences in carbon morphology, functionalization, dispersion, HA

characteristics, consolidation routes, density, and mechanical testing conditions. Addressing these factors is essential for establishing reproducible structure–property relationships.

7.1. Dispersion and Interface Optimization

Carbon aggregation remains one of the principal limitations of nanoscale reinforcement. CNT bundling and graphene restacking reduce the effective reinforcement area and can introduce pores or weak interfacial regions. Surface functionalization can improve dispersion and affinity for HA, but excessive modification may damage the carbon structure and reduce its intrinsic reinforcing capability. Future studies should therefore focus on controlled functionalization that balances dispersion, interfacial bonding, and preservation of carbon structural integrity. More importantly, the interface should not be optimized solely for maximum adhesion. A mechanically effective interface must provide sufficient bonding for stress transfer while permitting controlled debonding, sliding, or pull-out when these mechanisms contribute to fracture-energy dissipation. This balance should be explicitly considered when designing carbon–HA interfaces.

7.2. Standardization Of Mechanical Evaluation

Direct comparisons among published studies remain difficult because mechanical properties are strongly influenced by density, specimen geometry, porosity, grain size, carbon distribution, and testing methodology. In particular, reported fracture toughness values can be highly sensitive to testing conFigureuration and specimen preparation. Consequently, mechanical improvements should not be reported solely as percentage increases relative to unreinforced HA. Future investigations should systematically report carbon loading and characteristics, together with relative density, porosity, HA grain size, phase composition, consolidation conditions, and relevant testing parameters. Fractographic evidence should also be incorporated to establish whether the proposed mechanisms, such as crack bridging, deflection, pull-out, or grain-boundary pinning, actually occur.

7.3. Moving From Composition Optimization To Architecture Design

The conventional strategy of identifying an “optimum carbon content” provides limited transferable information because the optimal concentration is highly dependent on processing and microstructure. A more useful approach is to design the composite architecture around the desired fracture mechanism. For CNTs, this requires control over aspect ratio, orientation, dispersion, and interfacial bonding. For graphene-based materials, sheet size, stacking behavior, surface chemistry, and spatial distribution become particularly important. Future work should therefore move toward controlling the location, orientation, and connectivity of carbon reinforcements rather than optimizing weight fraction alone. Such approaches could include hierarchical carbon architectures, controlled alignment, hybrid CNT–graphene reinforcement, and spatially graded carbon distributions. These strategies may provide multiple complementary toughening mechanisms while reducing the amount of carbon required to achieve a meaningful mechanical response.

7.4. Processing–Structure–Property Integration

A major research need is the development of processing strategies that simultaneously achieve high HA densification, limited grain growth, stable carbon structures, and reproducible interfaces. SPS and other pressure-assisted techniques provide useful processing windows, but their advantages remain strongly dependent on temperature, pressure, atmosphere, and holding time. Future studies should therefore treat processing as an integral part of reinforcement design rather than as a separate fabrication step. Combining advanced powder preparation, controlled surface functionalization, rapid consolidation, and multiscale characterization could help establish quantitative relationships between processing conditions and the resulting carbon–HA architecture.

7.5. From Laboratory Reinforcement to Reliable Biomaterial Design

Although mechanical reinforcement is an important objective, improved mechanical properties alone do not establish the suitability of a carbon–HA composite for bone-related applications. Carbon type, surface chemistry, residual processing species, degradation behavior, and biological responses may influence the overall performance of the material. Therefore, future development should avoid assuming that the mechanically strongest composition is necessarily the most suitable biomaterial. The more immediate scientific challenge is to identify carbon–HA architectures that provide reproducible mechanical reinforcement while maintaining the chemical and biological characteristics required for bone-contact applications. This requires coordinated evaluation rather than isolated optimization of mechanical properties.

7.6. Future Research Direction

The field is increasingly shifting from “carbon addition” toward “interface and architecture engineering.” Future research should prioritize four

interconnected objectives: (i) controlled carbon dispersion and surface chemistry, (ii) quantitative characterization of carbon–HA interfaces, (iii) processing strategies that preserve fine-grained and highly dense microstructures, and (iv) mechanistic validation of crack-interaction and energy-dissipation processes.

A particularly promising direction is the development of structure–property models that integrate carbon geometry, interfacial strength, dispersion state, grain size, porosity, and consolidation conditions. Such models could help distinguish the individual contributions of carbon reinforcement, grain refinement, and densification, thereby reducing the current dependence on empirical optimization. Ultimately, the next stage of carbon-reinforced HA research should focus less on demonstrating isolated increases in mechanical properties and more on establishing predictable relationships among carbon architecture, interfacial chemistry, processing, microstructure, and fracture behavior. Establishing these relationships will be essential for translating carbon nanomaterials from promising laboratory-scale additives into reliably engineered HA-based composite systems.

8. CONCLUSION

Carbon-reinforced hydroxyapatite (HA) nanocomposites offer a promising strategy for overcoming the mechanical limitations of HA while retaining its favorable biological characteristics. Their performance is governed not simply by carbon content but by the combined effects of carbon architecture, surface chemistry, dispersion, interfacial bonding, processing, and HA microstructure. CNTs and graphene-family materials provide distinct reinforcement and toughening mechanisms, including load transfer, crack bridging, pull-out, and crack deflection, which depend strongly on appropriate interfacial and microstructural conditions. Thus, carbon reinforcement should be regarded as an integrated structure–interface–processing–property–bioresponse engineering problem rather than a simple filler-addition strategy. Future research should focus on standardized characterization, quantitative optimization of carbon loading and dispersion, and deliberate carbon–HA interface engineering to establish predictable processing–structure–property relationships. Advanced processing and manufacturing strategies should also preserve carbon integrity while controlling HA microstructure and porosity, supported by systematic evaluation of long-term biological performance and in vivo safety. Ultimately, the rational design of carbon-reinforced HA should balance mechanical reliability, osteogenic functionality, biosafety, degradation behavior, and manufacturability, providing a clear pathway toward clinically relevant bone-repair applications.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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