

# Next-generation bone implants: multifunctional hydroxyapatite-CNT composites with embedded Ag/Cu nanoparticles

## Abstract

Bone-related disorders such as fractures, osteoporosis, and infections have accelerated the development of advanced materials for orthopaedic implants. Hydroxyapatite (HA), a bio-ceramic resembling the mineral phase of bone, offers excellent biocompatibility and osteoconductivity. However, its brittleness and poor fracture toughness limit its use in load-bearing applications. To overcome these limitations, this study presents a novel composite comprising hydroxyapatite reinforced with carbon nanotubes (CNTs) and silver/copper (Ag/Cu) nanoparticles. Functionalization of CNTs with carboxyl groups improves dispersion and bonding with the HA matrix, while Ag/Cu are incorporated via in-situ chemical reduction. The composite is densified using spark plasma sintering (SPS) to ensure structural integrity.

A comprehensive set of characterization techniques was employed: FTIR and Raman spectroscopy confirm chemical bonding and CNT integration; SEM and TEM reveal morphology, dispersion, and interfacial interactions; XRD verifies phase composition; mechanical testing assesses hardness and toughness; and EIS is utilized to evaluate real-time infection sensing capability through CNT-based conductivity changes. The resulting CNT-HA-Ag/Cu composite can have improved mechanical performance, antimicrobial resistance, and potential for biofilm detection. This multifunctional material addresses key challenges in orthopedic implant technology by combining mechanical resilience, infection control, and smart sensing. Future studies will explore in vivo biocompatibility and clinical application to establish its suitability as a next-generation implant material.

**Keywords:** hydroxyapatite composite, antimicrobial nanoparticles, orthopaedic implants, smart bio sensing materials

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**Abbreviations:** CNTs, carbon nanotubes; Ag/Cu, silver/copper; HA, hydroxyapatite; SPS, spark plasma sintering; CuNPs, copper nanoparticles; AgNPs, silver nanoparticles; MWCNTs, multi-walled carbon nanotubes; XRD, X-ray diffraction; SEM, scanning electron microscopy; TEM, transmission electron microscopy; EDS, energy dispersive X-ray spectroscopy; DSC, differential scanning calorimetry

## Introduction

Bone-related injuries and diseases, including fractures, osteoporosis, and bone infections, have driven significant advancements in biomedical implants over the past few decades. The global orthopedic implants market is projected to reach USD 66.2 billion by 2030, driven by aging populations, increasing sports injuries, and rising demand for minimally invasive surgeries.<sup>1</sup> Among various materials used in bone implant technology, metals (such as titanium and stainless steel), polymers (such as polyether ether ketone, PEEK), and ceramics (such as hydroxyapatite, HA) have been extensively studied.<sup>2</sup> While metallic implants exhibit superior mechanical strength, they suffer from corrosion, stress shielding, and poor bioactivity, often necessitating revision surgeries. Similarly, polymer-based implants are lightweight but lack mechanical integrity required for load-bearing applications.<sup>3</sup> Hydroxyapatite (HA), a calcium phosphate ceramic, is widely recognized for its biocompatibility and osteoconductive properties, making it a leading candidate for orthopedic applications.<sup>4</sup> However, its brittleness and weak fracture resistance limit its use in high-load-bearing scenarios. These mechanical limitations have motivated researchers to explore

reinforcement strategies, particularly with nanomaterials, to enhance its properties.<sup>5</sup> HA is structurally similar to the inorganic component of human bone and has been successfully used in orthopedic and dental applications for decades.<sup>6</sup> It promotes bone ingrowth, reducing the risk of implant rejection. Despite its biocompatibility, HA's low fracture toughness (~1 MPa√m) and poor wear resistance limit its practical use in high-stress environments.<sup>7</sup> Several studies have explored composite approaches, integrating HA with polymers, metals, and ceramics to improve its mechanical properties. The reinforcement of HA with nanoscale materials, particularly carbon-based nanostructures, has gained increasing interest due to their exceptional strength, conductivity, and surface functionalization capabilities. Among these, carbon nanotubes (CNTs) have demonstrated remarkable potential for improving the mechanical and functional properties of HA-based implants.<sup>8</sup> CNTs exhibit extraordinary mechanical strength (Young's modulus ~1 TPa) and electrical conductivity, making them attractive candidates for composite reinforcement in biomedical applications. The addition of CNTs into HA matrices has shown significant improvements in fracture toughness, mechanical resilience, and load-bearing capability. Furthermore, CNTs possess antimicrobial properties, preventing biofilm formation and reducing infection risks in implantable devices.<sup>9</sup>

Despite these advantages, direct integration of CNTs into HA has faced challenges related to dispersion, interfacial bonding, and potential cytotoxicity. To address these issues, functionalized CNTs (f-CNTs) with carboxyl (-COOH) or hydroxyl (-OH) groups have been explored to enhance their interaction with HA matrices.<sup>10</sup> Such modifications not only improve mechanical properties but also

allow for multifunctional applications, such as real-time infection sensing. Periprosthetic joint infections (PJIs) remain one of the most critical complications following orthopedic implant surgeries, with an incidence rate of 1-2%.<sup>11</sup> Bacterial colonization on implant surfaces can lead to biofilm formation, making infections resistant to conventional antibiotics and often necessitating implant removal.<sup>12</sup> *Staphylococcus aureus* and *Escherichia coli* are among the most common pathogens responsible for these infections. Traditional antimicrobial strategies, including systemic antibiotic delivery and local drug coatings, have shown limitations due to bacterial resistance and short-term efficacy. To combat these challenges, researchers have investigated nanomaterial-based antimicrobial strategies, particularly incorporating silver (Ag) and copper (Cu) nanoparticles into implant surfaces.<sup>13</sup> Silver and copper nanoparticles exhibit strong antimicrobial properties through multiple mechanisms, including reactive oxygen species (ROS) generation, disruption of bacterial membranes, and inhibition of DNA replication. Silver nanoparticles (AgNPs) have been widely integrated into medical devices due to their potent antibacterial effects, but concerns regarding cytotoxicity and environmental persistence remain.<sup>14</sup> Copper nanoparticles (CuNPs), on the other hand, have gained interest due to their cost-effectiveness and ability to kill antibiotic-resistant bacteria.<sup>15</sup> The incorporation of Ag/Cu nanoparticles into HA-CNT composites offers a dual advantage: improving mechanical strength while imparting long-term antimicrobial functionality. However, their uniform distribution within the composite matrix remains a key challenge.<sup>16</sup> This study aims to optimize the integration of these nanoparticles to develop a multifunctional bone implant material. An emerging approach in biomedical implants is the development of smart, self-monitoring materials capable of detecting early-stage infections. CNTs, due to their high electrical conductivity, can serve as electrochemical biosensors for real-time infection monitoring.<sup>17</sup> Bacterial adhesion and biofilm formation alter the electrical resistance of CNT networks, providing a quantifiable signal for early infection detection.<sup>18</sup>

Previous studies have demonstrated the use of electrochemical impedance spectroscopy (EIS) to monitor changes in impedance caused by bacterial colonization on implant surfaces.<sup>19</sup> However, limited research has explored the integration of CNT-based bioelectronic sensing within HA composites. This study aims to fill this gap by developing a CNT-reinforced HA-Ag/Cu composite that simultaneously enhances mechanical strength, provides antimicrobial resistance, and enables real-time biofilm detection.

## Objective and hypothesis

The primary objective of this study is to develop and characterize a HA-CNT composite embedded with silver and copper nanoparticles for orthopedic implant applications. The hypothesis is that functionalizing CNTs and integrating Ag/Cu nanoparticles into HA can synergistically enhance mechanical properties, provide antimicrobial activity, and enable real-time infection sensing, thus overcoming key limitations of current implant materials.

This perspective introduces a novel carbon nanotube-reinforced hydroxyapatite composite with embedded Silver/Copper nanoparticles, which can have enhanced mechanical properties and provide long-term antimicrobial functionality. While HA-CNT and HA-Ag/Cu composites have been separately explored, their synergistic integration into a multifunctional implant material has not been extensively studied. This study aims to bridge this gap by providing a holistic solution for the next generation of orthopedic implants. Research on HA composites reinforced with CNTs has advanced significantly in recent years.<sup>20-23</sup> Studies indicate that

CNT incorporation enhances mechanical properties, bioactivity, and antimicrobial resistance. However, dispersion issues and biocompatibility concerns remain challenges.<sup>24</sup> Additionally, the incorporation of Ag and Cu nanoparticles in HA-based implants has been explored for infection prevention, but their long-term stability needs further evaluation.<sup>25</sup> A critical gap remains in integrating CNTs with Ag/Cu nanoparticles to create a multifunctional implant capable of both real-time infection sensing and superior mechanical performance. This study aims to address this gap by developing an optimized HA-CNT-Ag/Cu composite with enhanced bioactivity and mechanical resilience.

## Materials and methods

### Synthesis of CNT-HA-Ag/Cu composite

#### Hydroxyapatite (HA) synthesis via hydrothermal method

The synthesis of HA will be carried out using a hydrothermal method to obtain high-purity and crystalline HA particles. A 0.5 M solution of calcium nitrate [ $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ] will be prepared in deionized water and continuously stirred. A 0.3 M solution of diammonium hydrogen phosphate [ $(\text{NH}_4)_2\text{HPO}_4$ ] will be added dropwise while maintaining a Ca/P molar ratio of 1.6, which is characteristic of stoichiometric HA.

#### pH adjustment

The pH of the solution will be adjusted to 10 using ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) to facilitate HA precipitation. The solution will then be transferred to a Teflon-lined autoclave and subjected to hydrothermal treatment at 180°C for 12 hours. The obtained precipitate will be washed multiple times with deionized water and ethanol to remove any residual ions and then dried at 100°C overnight. The dried powder will subsequently be calcined at 700°C for 2 hours to enhance crystallinity.

#### Functionalization of carbon nanotubes (CNTs)

To improve the dispersion and interfacial bonding of CNTs with HA, a chemical functionalization process will be employed using acid treatment. Multi-walled carbon nanotubes (MWCNTs) will be dispersed in a mixture of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and nitric acid ( $\text{HNO}_3$ ) in a 3:1 v/v ratio and sonicated for 4 hours at 40°C. The treated CNTs will be washed with deionized water until the pH reaches neutral (~7) and then dried at 80°C. The presence of -COOH groups will be confirmed using Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy.

#### In-situ reduction of Ag/Cu nanoparticles

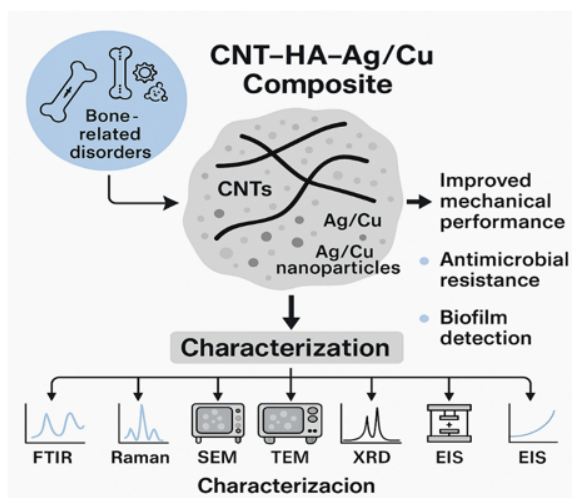
Silver and copper nanoparticles **will be incorporated** into the composite using an in-situ chemical reduction method. Aqueous solutions of silver nitrate ( $\text{AgNO}_3$ ) and copper sulfate ( $\text{CuSO}_4$ ) **will be prepared** separately. Functionalized CNTs and HA **will be dispersed** in deionized water using ultrasonication. Sodium borohydride ( $\text{NaBH}_4$ ) **will be used** as a reducing agent, **added dropwise** to facilitate  $\text{Ag}^+$  and  $\text{Cu}^{2+}$  reduction onto the HA-CNT surface. The composite **will be washed** to remove excess ions and **dried under vacuum** at 80°C.

#### Composite fabrication

The final composite can be fabricated using spark plasma sintering (SPS) process. The powder will be sintered at 900°C under 50 MPa pressure in a vacuum environment for rapid densification. The final composite product shall be obtained for characterizations and testing.

## Characterization techniques

A wide array of advanced characterization techniques (Figure 1) will be utilized to fully understand the structural, functional, and biological aspects of the CNT-HA-Ag/Cu composite. **Fourier Transform Infrared Spectroscopy (FTIR)** will be employed to identify key functional groups such as  $-OH$ ,  $-COOH$ , and phosphate vibrations, confirming chemical interactions among HA, CNTs, and Ag/Cu nanoparticles. This will validate surface modifications and ensure chemical compatibility crucial for biomedical use. **X-Ray Diffraction (XRD)** will determine the crystalline phases and structural integrity, revealing the presence of HA, metallic nanoparticles, and any secondary phases due to synthesis. High crystallinity will be directly linked to improved mechanical strength and bioactivity. **Scanning Electron Microscopy (SEM)** will offer detailed images of surface morphology, nanomaterial dispersion, and porosity-features that are vital for cell attachment, osteoconduction, and integration with native bone tissue. **Transmission Electron Microscopy (TEM)** will further aid in visualizing nanoparticle distribution, CNT alignment, and interface bonding at the nanoscale, allowing for a precise understanding of how these features influence the composite's strength and antimicrobial activity. **Raman Spectroscopy** will be essential for confirming CNT integration through D and G band analysis and observing any structural defects or bonding with HA, providing insight into the material's electronic and mechanical properties. Mechanical testing methods such as nanoindentation, tensile strength, and compressive tests will quantify hardness, elasticity, and fracture resistance-parameters essential for orthopedic load-bearing applications. **Electrochemical Impedance Spectroscopy (EIS)** will evaluate electrical conductivity, providing evidence of CNT networks for infection sensing. This technique is critical for enabling smart bioimplants that detect early biofilm formation. Additionally, **Energy Dispersive X-ray Spectroscopy (EDS)** coupled with SEM/TEM will confirm elemental composition and nanoparticle incorporation, while **Thermogravimetric Analysis (TGA)** and **Differential Scanning Calorimetry (DSC)** will offer insights into thermal stability and phase transitions. These comprehensive techniques together will provide a thorough understanding of the composite's performance in a biomedical context. **Antibacterial Assays** (Zone of inhibition, CFU counting) can confirm the antimicrobial efficacy of Ag/Cu nanoparticles against pathogens which ensures infection control post-implantation that is a major clinical concern.



**Figure 1** Comprehensive set of characterization techniques.

## Expected outcomes and comparative analysis

The CNT-HA-Ag/Cu composite is anticipated to significantly outperform conventional HA and HA-CNT materials in terms of mechanical strength, antimicrobial efficacy, and biosensing functionality. These properties are crucial for ensuring the durability and long-term safety of orthopedic implants. The following table summarizes a comparative analysis of the projected performance of the CNT-HA-Ag/Cu composite against established materials, based on reported literature benchmarks and expected outcomes from the proposed synthesis (Table 1).

**Table 1** Comparative analysis of HA-based composite materials

Property	Pure HA	HA + CNT	HA + CNT + Ag/Cu (This work)
Fracture toughness (MPa√m)	~1	~2	~2.8
Antimicrobial zone (mm)	~0	~5	~15
Sensing capability	None	Limited	Real-time via EIS

## Conclusion and future scope

The development of the CNT-HA-Ag/Cu composite marks a significant advancement in the field of biomedical implants, offering a multifunctional solution to several long-standing challenges. By integrating hydroxyapatite with carbon nanotubes and silver/copper nanoparticles, the composite combines bioactivity, mechanical strength, and antimicrobial functionality in a single platform. This approach not only enhances fracture toughness and load-bearing capacity but also provides long-term infection resistance-critical factors for orthopedic and dental implants. The functionalization of CNTs improves dispersion and interfacial bonding, while the in-situ reduction of Ag and Cu ensures uniform nanoparticle distribution. Importantly, the electrical conductivity of CNTs opens avenues for real-time infection monitoring, transforming passive implants into smart, responsive systems. Such innovations reduce the risk of implant failure, improve patient recovery, and minimize the need for revision surgeries. Characterization techniques like FTIR, XRD, SEM, TEM, and EIS confirm the structural, functional, and biosensing capabilities of the composite. This material aligns with the growing demand for advanced, multifunctional biomaterials in a market projected to expand rapidly. Its ability to integrate mechanical, antimicrobial, and sensing functions offers a holistic solution for next-generation implants. In the future, in vivo studies and biosafety assessments will be essential to translate this material into clinical practice. Additionally, the composite framework may be adapted for other tissue engineering and regenerative medicine applications. Overall, this work sets the foundation for developing intelligent, durable, and infection-resistant implants that meet the complex needs of modern medicine.

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## Conflicts of interest

The author declares that there are no conflicts of interest.

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