

Self-assembly of nano-hydroxyapatite on multi-walled carbon nanotubes

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Abstract

Inspired by self-assembly of nano-hydroxyapatite (nHA) on collagen associated with the 67 nm periodic microstructure of collagen, we used multi-walled carbon nanotubes (MWCNTs) with approximately 40 nm bamboo periodic microstructure as a template for nHA deposition to form a nHA–MWCNT composite. The assembled apatite was analyzed by transmission electron microscopy and scanning electron microscopy. Defects that were analogous to edge dislocations along the carbon nanotubes' multi-walled surfaces were the nucleation sites for nHA after these defects had been functionalized principally into carboxylic groups. Spindle-shaped units consisting of an assembly of near parallel, fibril-like nHA polycrystals were formed and oriented at a certain angle to the long axis of the carbon nanotubes, unlike nHA–collagen in which the nHA is oriented along the longitudinal axis of the collagen molecule. One possible explanation for this difference is that there are more bonds for calcium chelation ($-\text{COOH}$, $>\text{C}=\text{O}$) on the collagen fibril surface than on the surface of MWCNTs. Spindle-shaped units that are detached from the MWCNT template are able to maintain the ordered parallel structure of the nHA polycrystal fibril. We have thus created a self-assembled hydroxyapatite on MWCNTs.

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1. Introduction

Various models have been designed to simulate the collagen mineralization process from the gene to the peptide level using a range of materials from natural extracellular matrix to synthetic polymers. Such investigations aim to

study the basic mechanisms of biomineralization. Moreover, insights and understanding of these mechanisms will enable better design and fabrication strategies for nanocomposites to be used for hard tissue (bone and teeth) repair and replacement [1–8]. Zhang focused on fabricating self-assembling peptides and protein nanofibers. He showed that surfactant-like peptides (~2 nm in size) could self-assemble into nanotubes with a diameter of ~30–50 nm, which then formed an interconnected network similar to that observed in carbon nanotubes [3]. Stupp and colleagues developed a peptide–amphiphile model to study the self-assembly and mineralization mechanisms.

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After cross-linking the peptide–amphiphile fibers, Stupp et al. were able to direct mineralization of hydroxyapatite (HA) to form a composite material in which the crystallographic *c*-axes of HA were aligned along the long axes of the fibers. This alignment is similar to that observed between collagen fibrils and HA crystals in natural bone [4]. However, this model does not simulate higher-level assembly. Because the micro–macro hierarchical structure is not modeled, it is not possible to infer realistic gross mechanical properties.

Since the discovery of fullerenes and carbon nanotubes, the unique structure-dependent electrical and mechanical properties of carbon structures have been the subject of extensive research [9]. Potential applications include nanodevices, nanosensors, ultra-high-strength engineering fibers, etc. To optimize the use of carbon nanotubes (CNTs) in these applications, a number of strategies have also been developed for the surface modification of CNTs by functional groups and functional-group-anchored nanoparticles [10–12]. It has demonstrated that open-ended single-walled carbon nanotubes (SWCNTs) can be solubilized in organic solvents, and can be further derivatized by the adsorption of hydroxystilbene fluorophore onto the carbon surface via ester coupling [12]. Mixed-monolayer-protected Au clusters can be strongly adsorbed onto the carbon surface. SWCNTs that are prepared via alumina-membrane synthesis and filled Pt/Ru nanoparticles can act as an electrocatalyst for methanol oxidation and oxygen reduction [13]. Han et al. reported a simple and effective method for preparing alkanethiolate monolayer-capped gold nanoparticles on multi-walled carbon nanotubes (MWCNTs) by molecularly mediated assembly [14]. In yet another demonstration of the self-assembly capability of CNTs, Rosca et al. [15] and Li et al. [16] showed that after prolonged nitric acid oxidation, the fragmented MWCNTs aligned themselves into areas of parallel nanotubes, and had the tendency to self-organize into aligned nanotube ribbons. There has also been a tremendous interest in taking advantage of the unique properties of CNTs for promising biological applications. MWCNTs are capable of being shaped into three-dimensional (3-D) architectures, giving rise to the possibility of using this material as a new form of scaffold for tissue engineering [17]. In view of the high surface area/volume ratio, structure periodicity and molecular affinity, we studied the feasibility of using MWCNTs as a template for the fabrication of assembled nano-hydroxyapatite (nHA). A comparison of the mechanism of mineralization of this template with the mineralization of collagen fibers may help develop a more rational design strategy for biomimetic materials for hard tissue repair. We hypothesize that the unique microstructure of certain MWCNTs with bamboo periodicity can direct the nano-sized apatite assembly via an aqueous solution reaction. The dislocations on the surface of these CNTs can serve as sites for nucleation of HA after the MWCNTs are functionalized by carboxyl groups or other groups for calcium chelation [15,18–20]. We also compare the mechanism of

in vitro mineralization of the collagen fibril unit with that of CNTs with and without carbonate. By studying the capability of CNTs to promote assembly and mineralization, it is possible to gain insights in new self-assembling mineralization systems.

2. Materials and methods

Non-carbonated nHA and carbonated nHA were prepared for comparative studies using MWCNTs and collagen as nucleation templates. MWCNTs with bamboo structures provided by Nanolab Inc. (USA) as shown in Fig. 1a were grown by chemical vapor deposition. They have a diameter of 20–40 nm, and an average length of 5.0 μm . The purification procedure for MWCNTs was as follows: First, MWCNTs were heated to approximately 773 K for 90 min under atmospheric conditions. Next, the cooled MWCNTs were transferred into a flask containing 6 M HCl and treated at 333 K for 2 h to remove residual metals and metal oxides. The acid solution was filtered using a polytetrafluoroethylene membrane filter with a pore size of 0.2 μm . The filtered cake was rinsed out with double-distilled water and subsequently dried at 333 K for 12 h.

The above-purified MWCNTs were added to 0.5 M acetic acid. Solutions of 0.5 M CaCl_2 and 0.5 M H_3PO_4 ($\text{Ca}/\text{P} = 1.66$) were gradually added through separate tube pumps and the mixture stirred for 1 h. The mixture was then separated into two equal portions. A solution of Na_2CO_3 (molar ratio of $\text{CO}_3^{2-}/\text{PO}_4^{3-} = 3$) was gradually added to one of these portions. Both portions were stirred for 30 min, and then titrated with sodium hydroxide to pH 9 at room temperature [21]. After aging the solution for 2 h, two types of materials, namely nHA/MWCNTs (nHAM) and nano-carbonated HA/MWCNTs (nCHAM) were harvested from each of the portions by centrifugation and freeze-drying.

The above process was repeated with type I atelocollagen gel (2 wt.%, Koken Company, Japan) to make nHA/collagen (nHAC) and nano-carbonated HA/collagen (nCHAC) in a similar manner.

X-ray diffraction (XRD) analysis was performed in a Rigaku/Multiflex diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation, in the 2θ range of 10° – 80° at a scan rate of 2°min^{-1} , with a sampling interval of 0.02° . Data were analyzed by the accompanying MDI JADE6 software [22]. The diffraction peak broadening due to small crystallites can be semi-quantitatively estimated from the Scherrer equation: $\beta_{1/2} = (K\lambda)/(D \cos \theta)$ [23]. $\beta_{1/2}$ is the full-width at half maximum in 2θ and this is automatically calculated by the MDI JADE6 software. K is a constant that we set to 1, λ is the X-ray wavelength in Angstroms, D is roughly the average crystallite size and the θ is the diffraction angle of the corresponding reflex.

A Raman spectrometer (Dilor Jobin Yvon Spex, Group Horiba) was also used to evaluate the samples.

The carbonated weight percentages were measured using thermogravimetric analysis (TGA) (Rigaku Thermoflex

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