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New Evaluation of Initial Growth Mechanisms of Hydroxyapatite on Self-assembled Collagen Nanofibrils by Using ToF-SIMS and AFM Techniques

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Bone is considered as hierarchically organized biocomposites of organic (collagen) and inorganic (hydroxyapatite) materials. The precise structural dependence between hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$) crystals and collagen fibril is critical to unique characteristics of bone. To meet those conditions and obtain optimal properties, it is essential to understand and control the initial growth mechanisms of hydroxyapatite at the molecular level, such as other nano-structured materials. In this study, collagen fibrils were prepared by adsorbing native type I collagen molecules onto hydrophobic surface. Hydrophobicity was introduced on the Si wafer surface by using PECVD (plasma enhanced chemical vapor deposition) method and cyclohexane as a precursor. Biomimetic nucleation and growth of HAp on the self-assembled collagen nanofibrils were occurred through incubation of the sample in SBF (simulated body fluid). Chemical and morphological evolution of HAp nanocrystals was investigated by surface-sensitive analytical techniques such as ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) and AFM (Atomic Force Microscopy) in the early growth stages (< 24 hrs). The very initial stages (< 12 hrs) of mineralization could be clearly demonstrated by ToF-SIMS chemical mapping of surface. In addition to ToF-SIMS and AFM measurement, scanning electron microscopy, energy dispersive spectroscopy and X-ray diffraction analysis were conducted to characterize the HAp layer in the late stages. This study is of great importance in the growth of real bone-like materials with a structure analogous to that of natural bones and the development of biomimetic nanomaterials.