Nano-architecture on Carbon Nanotube Surface by Biomimetic Coating

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Calcium phosphate (Ca-P) coating on carbon nanotubes (CNTs) was done with a biomimetic coating method. The multi-walled CNTs (MWNTs) were immersed for 2 weeks in the simulated body fluid. Observation by scanning electron microscopy showed that needle shape of Ca-P crystallites at nano-scale levels were massively grown on MWNTs. Thus the nano-architecture of crystalline Ca-P on MWNT surface could be produced by simple method and the MWNT may be acting as core for initial crystallization.

Carbon nanotubes (CNTs) have been attracting considerable attention because of their unique physical properties and potential for a variety of applications.[1] The modifications of carbon nanotubes have been extensively investigated because of their relevance in electrical, mechanical and biological applications.[2] Immobilization of various biological species such as DNA,[3] protein,[4] enzyme,[5] poly- and mono-saccharide,[6] and others[7] on CNTs has also been examined in past studies. For biomedical applications, new modification methods to give biocompatibility are needed for achievement of various required designs. Here we developed a biomineralization method to produce the architecture of crystalline Ca-P at nano-scale levels on the surface of MWNTs, where crystalline Ca-P is easily formed for the vertical direction of a CNT axis.

Biomineralization is a natural process in human being and animals resulting in the formation of bones and teeth. The so-called biomimetic coating technique was employed to produce the Ca-P coating over implant surfaces. Ca-P solution such as simulated body fluid (SBF) has been frequently used for the biomimetic Ca-P coating to increase the bioactivity and successfully applied to implant materials for some special dental and orthopedic cases.[8]

We designed and built the crystalline Ca-P on the surface of MWNTs in a revised SBF. The MWNTs used in this study were obtained from two different sources: m-MWNTs (produced by MTR Co., Ltd., Ohio, U.S.A.) and n-MWNTs (NanoLab Inc., Brighton, MA). Typical scanning electron microscopy (SEM) images are shown in Figure 1. The crystalline Ca-P were grown by immersing the MWNTs in a revised SBF (the composition is NaCl (14.4 mM), KCl (2.0 mM), $CaCl_2$ (1.13 mM), $MgCl_2$ (0.29 mM), K_2HPO_4 (1.0 mM), KH_2PO_4 (1.0 mM) containing NaF (1.2 mM), and the pH was adjusted to 7.2 using KOH) at 37 °C for 2 weeks. After separation by centrifugation, the formation of Ca-P on the MWNTs surface was investigated by SEM.

After immersion of m-MWNTs (straight shape, about 300 nm in diameter), Figure 2a shows Ca-P embedded in the aggregated m-MWNTs. On the outer m-MWNTs of the aggregate comparatively homogeneous nucleation of Ca-P crystallite occurred and on the inner m-MWNTs heterogeneous nucleation was observed. Surface states of the aggregate show the complete coverage with the Ca-P crystals. The images reveal that the Ca-P crystals are cluster of needles. The needles of Ca-P crystals originate radially from a common center on the surface of a m-MWNT (Figure 2b).

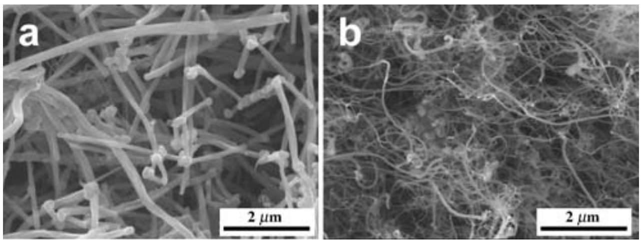

Figure 1. SEM images of purified MWNTs. (a) m-MWNTs produced by MTR Co., Ltd. and (b) n-MWNTs produced by NanoLab Inc.

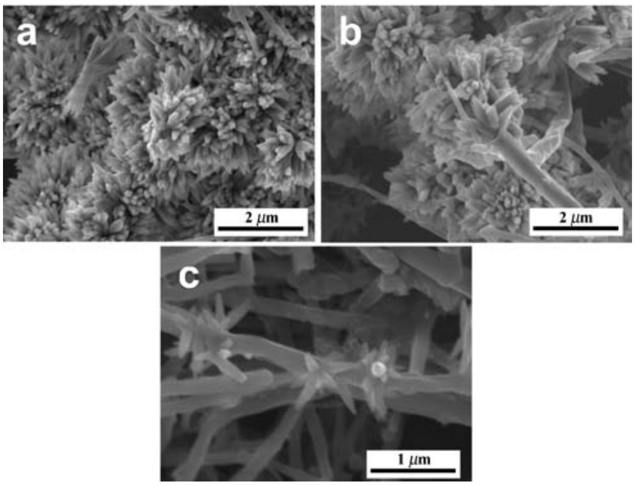

Figure 2. SEM images. (a) Needle-like shape of crystalline Ca-P grown on the aggregated m-MWNTs. (b) Crystalline Ca-P grown radially on a m-MWNT core. (c) Smaller crystalline Ca-P grown radially on a m-MWNT core of the inner m-MWNTs of the aggregate.

Although the majority of crystal size deposited of about 200 nm in diameter and 500 nm in length appeared surrounding the aggregated m-MWNTs, smaller crystals (about 150 nm in diameter) at the middle point of the nanotube were observed on the inner m-MWNTs of the aggregate (Figure 2c).

Figure 3a shows Ca-P embedded in the aggregated n-MWNTs after immersion of n-MWNTs (curled shape, about 30 nm in diameter). In a similar manner as m-MWNTs, on the outer n-MWNTs of the aggregate comparatively homogeneous nucleation of Ca-P crystallite occurred and on the inner n-MWNTs heterogeneous nucleation was observed. Ca-P crystals

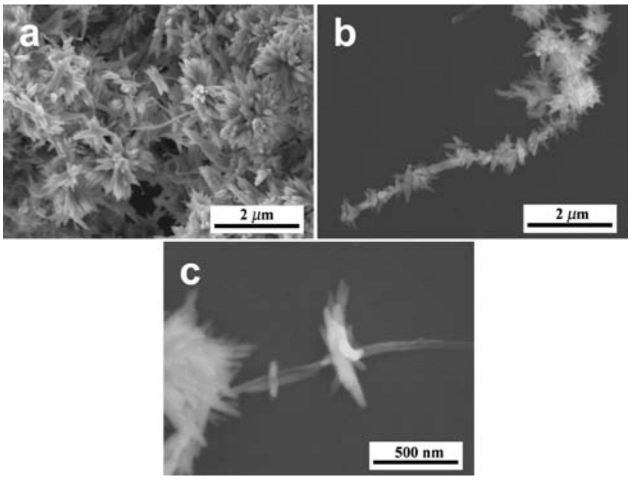

Figure 3. SEM images. (a) Needle-like shape of crystalline Ca-P grown on the aggregated n-MWNTs. (b) Barbed wire-shape of crystalline Ca-P on a n-MWNT core. (c) Crystalline Ca-P grown radially on a n-MWNT core.

show the complete coverage over the aggregate of n-MWNTs. The images reveal that the Ca-P crystals form the cluster of spherules consisting of needles. Acicular crystallites grown with about 150 nm in diameter form bloom-shape morphology. The barbed wire-like shaped feature was observed around a single n-MWNT (Figure 3b). The needles of Ca-P crystals originate radially on the surface of a n-MWNT. A SEM image at higher magnification clearly shows the crystals originating radially from a common center in the middle of a n-MWNT (Figure 3c). Thus these MWNTs may be acting as core for initial crystallization of Ca-P.

Although the mechanism of Ca-P formation on MWNTs is still poorly understood, we have demonstrated the crystalline Ca-P coating on the surface of MWNTs is achieved as a result. MWNTs with the defined surface morphology could be useful as biomaterials for scaffolds and as the manufacture of devices for biosensors. Our nano-architecture method can pave the way for the development of CNTs biomedical applications and improve bioaffinity when nanotubes are used as scaffolds in biomaterials.

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