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Apatite formation on carbon nanotubes

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Abstract

Apatite coating on carbon nanotubes (CNTs) was done with a biomimetic coating method. The multi-walled CNTs (MWNTs) of curled shape with about 30 nm in diameter were immersed for 2 weeks in the simulated body fluid. Observation by scanning electron microscopy (SEM) showed the formation of apatite on the MWNTs surface. The clusters of spherules consisting of needle-shaped apatite crystallites were massively grown on the aggregated MWNTs. The crystallites of 100 nm in width and 200–500 nm in length were grown perpendicularly to the longitudinal direction and radially originating from a common center of a single MWNT. Thus, the architecture of crystalline apatite at nano-scale levels could be produced by simple method and the MWNT may be acting as core for initial crystallization of apatite.

Keywords: Carbon nanotubes; Biomimetic coating; Apatite

1. Introduction

Carbon nanotubes (CNTs) have been attracting considerable attention because of their unique physical properties and potential for a variety of applications. The modifications of CNTs have been extensively investigated because of their relevance in electrical, mechanical and biological applications [1–8]. Immobilization of various functional molecules on CNT has also been examined in past studies [9–12]. For biomedical applications, new modification methods to give biocompatibility are needed for achievement of various required designs [13,14].

Biomineralization is a natural process in human being and animals, resulting in the formation of bones and teeth. Ca–P solution, such as the simulated body fluid (SBF), has been frequently used for the biomimetic Ca–P coating to increase the bioactivity, and has been successfully applied to implant materials for some special dental and medical cases [15–17].

Here we developed a biomineralization method to produce the architecture of apatite crystallites at nano-scale levels on the surface of MWNTs.

2. Experiment

The MWNTs used in this study were obtained from NanoLab (Brighton, MA, USA). The MWNTs of curled shape with about 30 nm in diameter were produced by the chemical vapor deposition (CVD) method. The raw MWNTs were refluxed in 6 N HCl solution and then washed thoroughly with deionized water and completely dried. Typical SEM (HITACHI S-4000) images of purified MWNTs are shown in Fig. 1.

The MWNTs material was dispersed in calcium phosphate solutions at a concentration of 10 mg/l by ultrasonication for 10 min. Then, the apatite crystallites were grown by immersing the MWNTs at 37 °C for various periods up to 2 weeks. The composition of the calcium phosphate solutions is as follows.

Revised SBF (R-SBF): NaCl (866 mg/l), $CaCl_2$ (125 mg/l), K_2HPO_4 (803 mg/l), KH_2PO_4 (326 mg/l), KCl (625 mg/l), $MgCl_2$ (59 mg/l) containing NaF (22 mg/l) and the pH was adjusted to 7.2 using KOH and no precipitation was observed in the solution during the experimental period.
Dulbecco's phosphate-buffered saline (PBS(+)): NaCl (8000 mg/l), $CaCl_2$ (100 mg/l), KH_2PO_4 (200 mg/l), Na_2HPO_4 (1150 mg/l), KCl (200 mg/l), $MgCl_2$ (47 mg/l) containing NaF (22 mg/l) and the pH was adjusted to 7.4 using KOH

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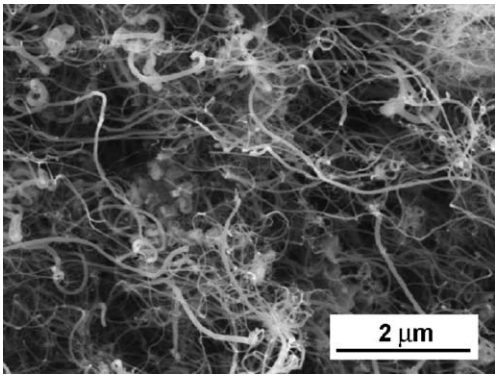

Fig. 1. SEM images of purified MWNTs.

and no precipitation was observed in the solution during the experimental period.

Standard SBF (S-SBF): NaCl (7996 mg/l), $CaCl_2$ (278 mg/l), K_2HPO_4 (174 mg/l), KCl (244 mg/l), $NaHCO_3$ (350 mg/l), $MgCl_2$ (143 mg/l), Na_2SO_4 (71 mg/l), $(CH_2OH)_3CNH_2$ (6057 mg/l), 1 M HCl (40 ml) containing NaF (22 mg/l) and the pH was adjusted to 7.4 using KOH.

Finally, the resultant MWNTs were separated from the suspension by filtration, gently washed with deionized water to remove impurities, and then dried at 60 °C for 6 h. In order to study the effects of immersing time-course on apatite growth, they were immersed for 6 h, 1 day, 2 days, and 2 weeks. To compare the influence of the substrates, we also use a square piece of carbon plate ($10 \times 10 \times 1$ mm^3) (Nirako, Japan) instead of MWNTs.

The formation of apatite on the MWNTs surface was investigated by SEM after coating with carbon. Transmission infrared spectra were performed by the KBr method using a fourier transmission infrared spectrometer (FT-IR, JASCO FT/IR-300E) in the wave number region 400–4000 cm^{-1} collected at resolutions of 4 cm^{-1}. Commercial hydroxyapatite (Seikagaku Corp.) was used as a control.

3. Results and discussion

3.1. Apatite formation in R-SBF

Zhao and Gao recently reported that hydroxyapatite nanoparticles decorated on the sodium dodecyl sulfate (SDS) adsorbed MWNTs by an in situ synthetic method with calcium nitrate, $Ca(NO_3)_2$, and ammonium secondary phosphate, $(NH_4)_2HPO_4$ [18]. In contrast, our strategy for the apatite formation consists of biomimetic coating on the surface of MWNTs in the calcium phosphate solutions such as a SBF.

To optimize this strategy, we first studied the apatite formation on MWNTs in R-SBF. After immersion for 2 weeks, the MWNTs apparently became the gray in the solution. SEM images show the massive growth of the clusters of apatite crystallites with a needle-like shape on the aggregated MWNTs (Fig. 2A). Acicularly grown crystallites with about 150 nm in diameter form the bloom-shape morphology. A further detailed observation clearly showed that the crystallites of 100 nm in width and 200–500 nm in length were grown radially originating from a common center in the middle of a single MWNT and perpendicularly to the longitudinal direction of MWNT. In part, there exist bowknot-like bundles with their two ends fanning out while the middle part tying together [19]. Barbed wire-like-shaped feature in Fig. 2B was also observed.

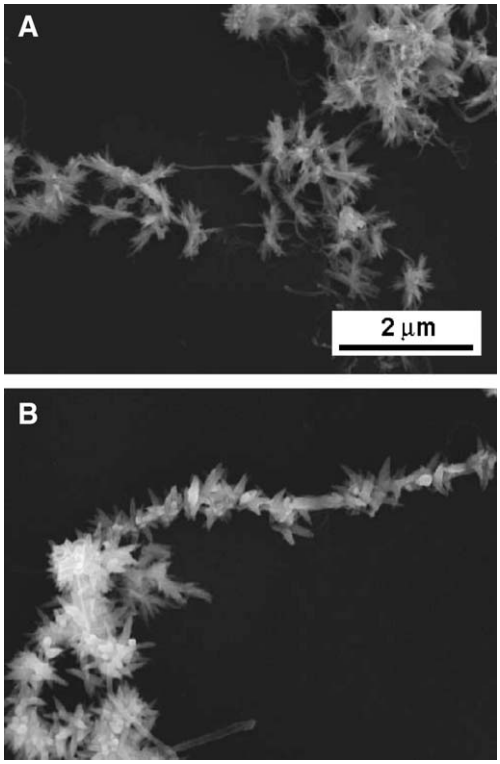

Fig. 2. SEM images of apatites: (A) needle crystallites grown radially on MWNT core; (B) barbed wire shape of crystallites on a MWNT core.

From these results, the needle-like apatite crystallites were directly grown starting from the surface of MWNT. Thus, the MWNT may be acting as core for initial crystallization of the apatites. However, in this condition, the reproducibility of sizes and shapes of apatites formed on MWNTs was poor because R-SBF was highly supersaturated and was difficult to handle.

Fig. 3 shows the infrared transmission spectra of the apatite/MWNTs after immersion in R-SBF for 2 weeks. Compared with the spectrum of commercial hydroxyapatite as a control, very similar peaks at around 3440, 1099, 1040, 966, 607 and 569 cm^{-1} on the spectrum were observed. The bands at 3440

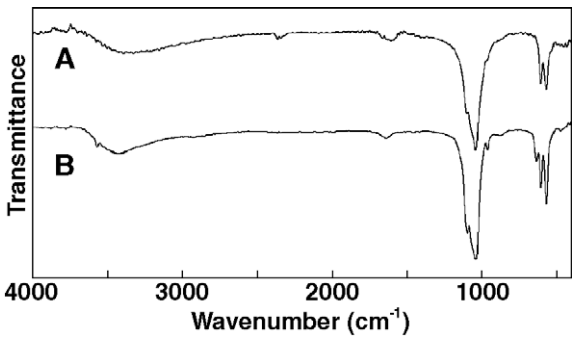

Fig. 3. FT-IR spectra of the apatite/MWNTs after immersion in R-SBF for 2 weeks (A) and hydroxyapatite as a control (B).