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Characterization and analysis of fluoride calcium silicate composite interface in remineralization of dental enamel

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ABSTRACT

Tooth enamel is easily demineralization due to all kinds of food or drinking attacking, and fluoride calcium silicate (F−$CaSiO_4$) is widely used in demineralized enamel repair due to its good biocompatibility and bioactivity. In this study, F−$CaSiO_4$ as remineralized enamel reagent was used to repair acidic enamel by simulated tooth brushing. The surface morphology of F−$CaSiO_4$ was observed by scanning electron microscope (SEM) and atomic force microscope (AFM). Altrathin section samples were prepared by Dual-beam focused ion-beam (FIB) system for further observing the interface structure and crystalline by high resolution transmission electron microscopy (HRTEM) selected-area electron diffraction (SAED). Composition was evaluated by energy dispersion X-ray spectroscopy (EDX). The results indicated that F−$CaSiO_4$ can rapidly induce apatite formation for 24 h in human saliva and the mineralized layer's thickness was at 200–370 nm, and interface between mineralized layer and enamel matrix bonded well. This study indicated that F−$CaSiO_4$ may be a promising toothpaste additives/dentifrices as demineralized enamel restoration.

1. Introduction

Teeth withstand a range of physical and chemical processes such as chewing, carbonated drinks, whiten, *etc.* in the oral cavity environment, which led to enamel demineralization [1–4]. So remineralization of the enamel surface is necessary to repair the demineralized enamel with biomaterials. Since chemical composition of the enamel is mostly inorganic consisting primarily of 96 wt% hydroxyapatite (HAp) with less than 1 wt% organic [5–8], calcium-silicate based bioceramics (such as $CaSiO_4$, Ca_3SiO_3) with good bioactivity and biocompatibility were used to induce apatite formation [9–11]. This biomimetic way has been used for preparing so-called bone-like apatite [12]. At clinic, these types of biomaterials could deposite the bone-like apatite to improve the biological properties for widely restorative hard tissue application [13–19].

Fluoride is an essential trace element in tooth enamel, which exists in the form of fluoride hydroxyapatite (FHA) by fluoride ions filling hydroxyl vacancies in the c-axis columns or displacing hydroxyl ions [20]. This has the effect of lowering lattice energy and effectively stabilizing the crystal structure, which rendering it more difficult to dissolve at lower pH and more resistant to acidic erosion. Some study has been identified that fluoride toothpastes can repair demineralized enamel and occlude the dental tubules for dentine hypersensitivity [3,21–23]. This behavior is of crucial importance to the role of fluoride in dental caries prevention or control. But free released fluoride ions were difficult to control quantitatively leading to fluorosis of human body excessively or growth depression of teeth insufficiently [24–26]. So the aim of this study was to rapid restorative enamel using F−$CaSiO_4$ with controlled fluoride release rate.

However, a short period the formation of mineralized layer is too thin to prepare a sample to observe the remineralization-enamel interface [27–29]. In this paper, an equipment was used to prepare the sample and analyze the interface structure by TEM. Before, samples were grinded to a slice by grind machine and then ion milling by ultramicrotomy, the disadvantage was that some microfractures produced on the surface, and the interface integrity between mineralized layer and enamel matrix destroyed. So based on this, a new detected instrument, FIB was used to mill the cross-section of hard tissues in order

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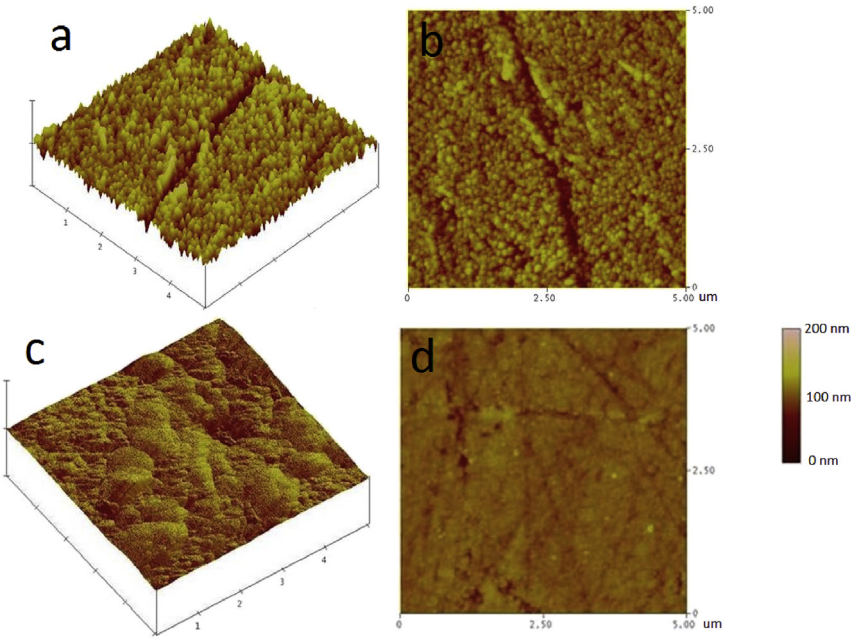

Fig. 1. AFM images of tooth samples etched (a), and its magnification image (b); Brushed with F—$CaSiO_4$ paste and soaked in natural saliva for 24 h (c), and its magnification image (d).

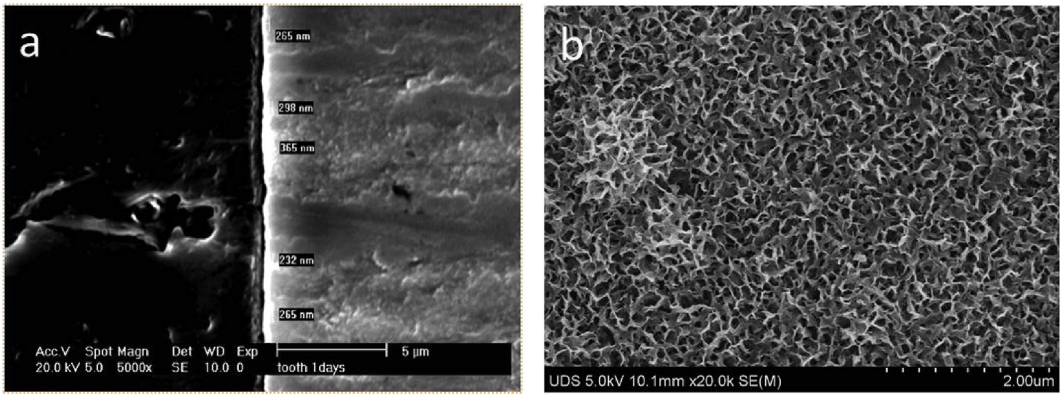

Fig. 2. SEM images of tooth samples of cross-section (a), and mineralized layer is 200–370 nm thickness. And surface morphology of mineralized layer in natural saliva for 24 h (b).

to observe their ultrastructure without detectable damage beyond 10 nm.

AFM has been used to study the surface structural mineralization. Compared to SEM, it has some advantage including no sample preparation or fixation, and capacity for direct quantification of image features. While, AFM is an extremely useful technique for probing surface topography and growth mechanisms, it cannot provide any information about the chemical composition and microstructure [30]. So TEM and corresponding EDX were used to observe the interface bonding between mineralized layer and enamel matrix and chemical composition and the crystal growth process.

This paper was conceived to further extend previous applied research on the influence of enamel remineralization ability using F—$CaSiO_4$ in human natural saliva to simulate oral microenvironment. Interface structure between mineralized layer and enamel matrix was analyzed and observed for further the treatment of enamel demineralization and cavities prevention.

2. Material and methods

2.1. Enamel samples preparation

Calcium silicate containing fluoride ions was prepared [26]. Briefly, 1000 mL of 0.4 mol $Ca(NO_3)_2$ solution was stirred at room temperature, and 1000 mL of 0.4 mol Na_2SiO_3 and NH_4F (12:1 M ratio) solution was added dropwise to $Ca(NO_3)_2$ solution over a period of 40–60 min forming a white precipitate. Then white precipitate was stirred for 24 h, washed 4 times with distilled water to remove the Na^+ and NO_3^- ions, and then washed twice with 100% ethanol to improve the dispersion characteristics. After washing, the remaining liquid was removed by vacuum filtration, and the precipitate was dried at 80 °C for 24 h. F—$CaSiO_3$ was obtained by sintering the powders at 800 °C. Enamel samples were prepared and then F—$CaSiO_4$ paste (L/P ratio of 1.2 mL g^{-1}) was brushed the enamel surface by toothbrush for 3 min and rinsed with running water. This treatment was repeated 3 times. Finally, the treated sample was placed in human saliva for 24 h at 36.5 °C, and observed the results. The healthy human saliva was collected from the same individual at the same time, then centrifuged and sterilized by γ radiation for 24 h and stored at 5 °C prior to use.