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Preparation and characterization of hydroxyapatite coatings on human enamel by electrodeposition

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Abstract

Thin hydroxyapatite (HA) coatings, approximately from 1 μm to 10 μm in thickness, had been prepared on human enamel by electrodeposition with the current density of 0.5 mA/cm^2 at 55 °C in 1 h. They exhibited an acicular morphology and had a tight contact with the substrate by scanning electron microscope and transmission electron microscope observation. The comparison was made between the enamel specimens with HA coatings in this study and the sound enamel. In this comparison, while the Vickers micro-hardness showed a similar value, the antibacterial activities improved significantly after the formation of HA coatings. In conclusion, electrodeposition was proved to be an effective method for preparing HA coatings on human enamel and could be considered as a promising method to restore the initial enamel lesions in clinic.

Keywords: Electrochemistry; Hydroxyapatite (HA); Coatings; Enamel

1. Introduction

Enamel, the exterior coating of human teeth, was a biomineral with remarkable hardness and resistance to physical and biochemical attack. The major inorganic component of enamel was hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA) that was prone to dissolve under acid condition. In addition, the dissolution of HA would easily lead to the appearance of initial enamel lesion that was observed clinically as subsurface white spot lesions and had no obvious caries [1]. As patients had no obvious response when suffered from the outside cold or hot stimulation, the initial enamel lesions were easy to be ignored and would develop to the deep caries lesions. With the improvement of people's living standard, increasing attention was paid to the restoration of the initial enamel lesions in order to prevent the deep caries lesions.

In previous study, several methods had been developed to restore the initial enamel lesions. The conservative methods such as spreading the enamel surfaces with special medicine were reported. As fluoride could not only induce the growth of HA crystal, but also help to form the fluorapatite that had stronger stability, fluoride was introduced into a special medicine called fluoridated mouthrins [2]. However, the risks of fluorosis had also been reported [3]. Also, phosphoric acid polypeptide was introduced into the special medicine, as it could promote the remineralization of enamel, and played an important role in preventing caries and restoring the enamel lesions [4,5]. For well restoration of the initial enamel lesions, the teeth should be treated with these special medicines for quite a long duration, such as 1 h per day for successional 7 days. As a result, these methods were not suitable for clinical treatment. Neither was the method adopted by K. Yamagishi because of the low pH, though the rate of the restoration was rapid (within minutes) [6]. However, the results of the research by Yamagishi et al. shown that the HA nanocrystals seamlessly grew in the interface between the paste and tooth enamel, and arranged their (0001) face parallel to the tooth surface same as enamel apatite. In addition, this HA coatings could help to prevent reoccurrence of caries.

Consequently, some other techniques used for preparing HA coatings on the various substrates might be taken into

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consideration, such as hydrothermal technique [7], plasma spray method [8], sol–gel method [9], electrophoresis method [10], biomimetic method [11] and electrodeposition [12]. Among these techniques, the electrodeposition had exhibited much more interest as it could be carried out under a mild experimental condition, i.e. at relatively lower temperature and under atmospheric pressure. In addition, electrodeposition would possibly improve the bond strength of the substrate/coatings and also control the thickness, chemical composition and microstructure of the coatings. Although studies about depositing the HA coatings onto the metals, especially on titanium substrate, were well documented [12–16], there had been no report about preparing HA coating on the enamel surfaces by electrodeposition up to now. However, studies had been carried out to judge effectively whether teeth were carious through electrical resistance [17,18] and teeth were semiconductors that could be served as electrode. Therefore, there was a feasibility of preparing HA coatings on the surfaces of human enamel using electrodeposition technique.

As shown in the previous studies, the surfaces properties of human enamel would be changed, with the solubility and penetration increased significantly after being treated with 35–50% phosphorus for 20–60 s [19]. In addition, the treatment of 30% hydrogen peroxide might cause the alteration in the chemical structures of the teeth and result in the dissolution of HA crystals [20]. So in this article, the acid solution which was prepared by mixing aqueous solution of 30% hydrogen peroxide (H_2O_2) with 85% phosphoric acid (H_3PO_4) was used to produce the initial enamel lesions and change the performances of enamel surfaces. The detailed preparation and characterization of the HA coatings on the enamel surfaces by electrodeposition were described and a possible mechanism of HA crystallization was proposed. The aim of the study was to prove that electrodeposition was an effective method for preparing HA coatings on human enamel surfaces and restoring the initial enamel lesions.

2. Materials and methods

2.1. Preparation of enamel specimens

Six fresh human third molars extracted without visible evidence of caries were used in this study. They were stored in physiological solution after their roots and pulps were removed. Subsequently, they were made into slabs (5 mm length × 4 mm width × 3 mm height) using a low speed diamond saw (SYJ-150, Shenyang Kejing, China). In order to remove the bacterium speckle and pigment, the enamel surfaces of each specimen was mechanically polished using silicon carbide papers and 0.25 μm aluminium oxide powders. Then the specimens were washed with de-ionized water and dried in air.

2.2. Acid pretreatment

Initial enamel lesions were produced on human enamel using acid solution. The acid solution was prepared by mixing aqueous solution of 30% hydrogen peroxide (H_2O_2) with 85% phosphoric acid (H_3PO_4) at a volume ratio of 4:1. The specimens were then washed with de-ionized water and dried in air after immersed into this acid solution for 1 min.

2.3. Preparation of coatings by electrodeposition

After acid pretreatment, the enamel specimen was treated for 1 h with the current density of 0.5 mA/cm^2 at 55 °C. As shown in Fig. 1, it was performed with a two-electrode electrochemical cell at the open circuit potential in the electrolyte. The galvanostat was provided by Model 263A (EG&G Instruments, Inc, USA). A platinum plate was served as counter electrode and a slice of stainless steel as working electrode. The specimen of enamel was put entirely close to the stainless steel, and the enamel surfaces subjected to coatings faced to the counter electrode. To enhance the conductivity of the electrolyte, $NaNO_3$ was added and the electrolyte that contained 4.175×10^{-4} M Ca $(NO_3)_2$, 2.4×10^{-4} M $NH_4H_2PO_4$ and 0.1 M $NaNO_3$ was adjusted to pH 6.5 by NaOH at 55 °C.

2.4. Apparatus and methods

2.4.1. Contact angle and Vickers micro-hardness measurements

The contact angle was determined using a contact angle analyzer (Powereach JC2000A, Zhongchen Co., Shanghai, China) at room temperature. A distilled water droplet (1 μL) on the surfaces of specimen was observed using a video camera coupled to a light microscope, and the contact angle was determined automatically using image analysis software. The hardness of specimens at different state was measured using a HV-1000 Vickers micro-hardness tester (Shanghai Materials Tester Machine Co., China) with a load of 10 g for a dwell time of 30 s. In order to avoid the lag effect, each specimen was at least subjected to three measurements under the same testing condition.

Paired *t*-test was carried out to analyze the influence of acid pretreatment and formation of coatings on the contact angles as well as the Vickers micro-hardness of the specimens.

2.4.2. X-ray diffraction measurements

Crystal structures of the specimens' surfaces were characterized and analyzed by an X'Pert X-ray diffractometer (XRD, X'pert PRO, Panalytical, Netherlands) and attached software. XRD measurements were carried out using Cu Kα radiation

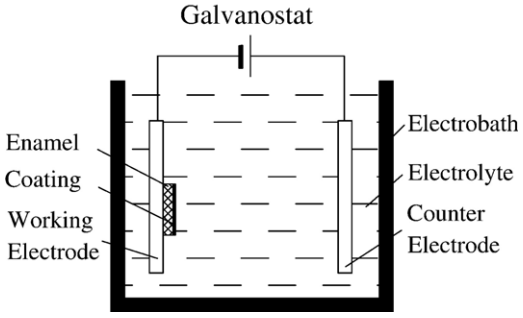

Fig. 1. The device of electrochemistry experiment.