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Quinone-rich polydopamine functionalization of yttria stabilized zirconia for apatite biomineralization: The effects of coating temperature

Norhidayu Muhamad Zain [a], Rafaqat Hussain [b], Mohammed Rafiq Abdul Kadir [a,*]

[a] Medical Devices & Technology Group, Faculty of Biosciences and Medical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[b] Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

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ABSTRACT

The use of yttria stabilized zirconia (YSZ) as biomedical implants is often offset by its bioinert nature that prevents its osseointegration to occur. Therefore, the functionalization of YSZ surface by polydopamine to facilitate the biomineralization of apatite layer on top of the coated film has incessantly been studied. In this study YSZ discs were first immersed in 2 mg/mL of stirred dopamine solution at coating temperatures between 25 and 80 °C. The specimens were then incubated for 7d in 1.5 SBF. The effect of coating temperature on the properties (chemical compositions and wettability) and the apatite mineralization on top of the generated films was investigated. It was found that at 50 °C, the specimen displayed the highest intensity of Ca 2p peak (1.55 ± 0.42 cps) with Ca/P ratio of 1.67 due to the presence of abundant quinone groups (C=O). However, the hydrophilicity (40.9 ± 01.7°) was greatly improved at 60 °C accompanied by the highest film thickness of 306 nm. Therefore, it was concluded that the presence of high intensity of quinone groups (C=O) in polydopamine film at elevated temperature affects the chelation of Ca^{2+} ions and thus enhance the growth of apatite layer on top of the functionalized YSZ surface.

1. Introduction

There has been enormous interest in recent decades in the development of biomedical materials for bone related clinical use due to the increasing demand for synthetic materials to replace and repair bone tissue loss due to injury or disease [1,2]. Inorganic materials in the form of ceramics are usually utilized for bone repair and reconstruction. Hench has classified bone-therapeutic ceramics as bioinert (e.g., alumina, zirconia), resorbable (e.g., tricalcium phosphate) and bioactive (e.g., hydroxyapatite, bioactive glasses, glass ceramics) [1,3].

The use of dense zirconia for orthopaedic purposes can be seen in the application of ball heads of hip replacements, dental implants and lumbar disc implants since it possesses excellent mechanical properties (high bending strength and fracture toughness) and good resistance to corrosion and wear [4–6]. However, the application of zirconia is offset by its bioinert nature and therefore it is not able to form a direct bond with the surrounding hard tissue [7]. Therefore various methods have been used to modify the bioinert surface so that it can be fully utilized and display good bioactivity.

Bioactivity refers to the interaction between the biomaterial and the cells, which can activate cells' specific response and behaviour. Mineralization and binding between the bone tissue and the implant is known to be the most reliable processes to increase bioactivity in bone repair and fixation. The bioactivity of a biomaterial can be evaluated through assessing the formation of apatite layer on the material surface upon incubation in simulated body fluid (SBF) solution.

Previous studies have shown that the mussels' unique ability to attach to a wide range of organic and inorganic marine surface might lie in the high concentration of DOPA and lysine amino acid group in the Mefp-5 protein found near the plaque-substrate interface [8–10]. Inspired by this property in mussels, polydopamine was prepared by polymerization of dopamine (a major pigment of melanin that act as neurotransmitter) to mimic the chemical compositions found in the plaque-substrate interface [8]. The presence of catechol moieties, OH^- and NH^{2-} in polydopamine can strongly bind Ca^{2+} ions onto the coated film, which later develops into hydroxyapatite and thus induce apatite mineralization in SBF [11]. Therefore, the polydopamine modification may improve the bioactivity of bioinert zirconia.

* Corresponding author. Tel.: +60 7 5558514; fax: +60 7 5558515.
E-mail address: rafiq@biomedical.utm.my (M.R. Abdul Kadir).

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Several studies have investigated the effect of temperature on the polymerization of dopamine and the thickness of polydopamine coating [12–14]. Dopamine molecule easily and quickly change to indolquinone molecule with the increase of reaction temperature and thus leading to a thicker deposited polydopamine layer on the surface of the substrate [14,15]. In this study we have investigated the chemical properties of polydopamine film deposited on the surface of YSZ at different temperatures (25 °C, 37 °C, 50 °C, 60 °C, 70 °C and 80 °C) and the apatite mineralization ability of the coated surfaces.

2. Materials and methods

2.1. Materials

Yttria-stabilized zirconia (8% Y), tris(hydroxymethyl)-aminomethane (TRIS) and 3-hydroxytyramine hydrochloride (dopamine hydrochloride) were obtained from NexTech Materials, Ltd. (Lewis Center, Ohio), Sigma–Aldrich (St. Louis, Missouri), and Acros Organics (Thermo Fisher Scientific, New Jersey), respectively. The 1.5× SBF solution with ion concentrations of Na^+, 213.0; K^+, 7.5; Mg^{2+}, 2.25; Ca^{2+}, 3.75; Cl^-, 221.7; HCO_3^-, 6.3; HPO_4^{2-}, 1.5; SO_4^{2-}, 0.75 mM was prepared according to the method of Kokubo and Takamada [16]. The YSZ suspension was prepared by dissolving YSZ powder into 10 mass% polyvinyl alcohol (PVA) aqueous solutions. The combined solution was filtered and dried at 80 °C for 24 h. The dried mixture was ground into powder and pressed using hydraulic press at 300 bar for 5 min to form discs. The YSZ discs were then subjected to heat treatment at 600 °C for 5 h and at 1400 °C for 5 h to obtain a dense structure. The dimension of each sintered YSZ disc was 11 mm in diameter and 1 mm in thickness.

2.2. Polydopamine grafting

The YSZ discs were sequentially ultrasonically treated using distilled water, acetone, and ethanol for 10 min and oven-dried at 40 °C for 2 h. The YSZ surface modification with dopamine was performed by simple immersion of the YSZ discs into a stirred dopamine hydrochloride solution (2 mg/mL in 10 mM Tris buffer, pH 8.5) for 24 h. The grafting temperature was held at 25 °C, 37 °C, 50 °C, 60 °C, 70 °C and 80 °C. The immersion resulted in the spontaneous deposition of polydopamine thin film on the surface of the substrates. The colour of the dopamine solution was subsequently changed from clear to pink and eventually to dark brown as the grafting time increased, which was attributed to the oxidation of dopamine. The coated YSZ discs were rinsed with distilled water and oven dried at 60 °C overnight. Six polydopamine coated YSZ (YP25, YP37, YP50, YP60, YP70 and YP80) were obtained and further incubated in 1.5 SBF to evaluate their biomineralization performance.

2.3. In-vitro biomineralization

In-vitro biomineralization tests were carried out in 1.5 SBF (pH 7.4) to monitor the formation of apatite. The specimens were immersed in 1.5 SBF at 37 °C for 7 days. The specimens were then washed using distilled water and oven dried overnight at 60 °C to furnish seven different specimens after biomineralization: (a) YSZH, (b) YP25H, (c) YP37H, (d) YP50H, and (e) YP60H, (f) YP70H and (g) YP80H (Fig. 1).

2.4. Surface characterization

2.4.1. X-ray photoelectron spectroscopy (XPS) analysis

The atomic composition of the bioactive surface was analyzed by using X-ray photoelectron spectroscopy, Kratos (XPS, Axis Ultra DLD, Shimadzu/Kratos Analytical, Japan) in a hybrid mode operating at 15 kV and 10 mA (150 W) with a monochromatic Al Kα source (1486.6 eV). The take off angle of 45° relative to the surface was used. During the measurements, ultralow vacuum (10^{-9} to 10^{-10} Torr) at analysis chamber was maintained. Survey spectra used for element identification and quantification were recorded in a range of 0–1200 eV with pass energy of 160 eV. High resolution scans were acquired for C 1s, O 1s, N 1s and Ca 2p regions with pass energy of 20 eV. Binding energies were calibrated to the C 1s hydrocarbon peak at 284.6 eV. The peak deconvolution processes were carried out by using CasaXPS (Casa Software Ltd., UK) software after the data was converted to VAMAS format. In this process, Gaussian and Lorentzian line shapes with ratio of 70:30 were used to deconvolve the acquired spectra after subtraction of a Shirley background for C 1s, O 1s, N 1s and Ca 2p peaks.

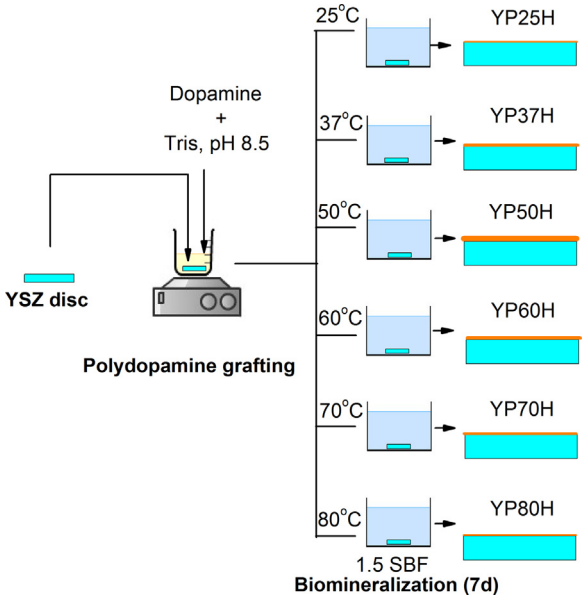

Fig. 1. Schematic illustration of the experimental procedure for the functionalization and biomineralization of the YSZ substrates.

2.4.2. FTIR-ATR analysis

The infrared spectra used to analyse the surface chemical functionality of biomineralized samples were obtained between 4000 and 400 cm^{-1} using Fourier transform-infrared attenuated total reflectance (FTIR-ATR, Thermo-Nicolet iS10) spectrophotometer.

2.4.3. Water contact angle analysis

Contact angle (CA) measurements were performed using video contact angle system (VCA-OPTIMA^{TM}, AST Products Inc, Billeria, MA, USA). The sessile drop method with 5 μL drop of distilled water as probing liquid was used and the dropping rate was set at 50 μL/min. The data from the same sample at five different positions was averaged to obtain the reported CA values.

2.4.4. FESEM and SEM analysis

The cross-section of coated YSZ specimens were characterized using a FE-SEM (SU8020, HITACHI) equipped with an energy dispersive X-ray spectrometer (EDX, INCA/350, Oxford) for chemical analysis. The images were taken at 10,000× and 40,000× magnifications using an accelerating voltage of 15 kV after the specimens were gold coated.

The topography and biomineralized specimens were studied using SEM (SEM, JEOL, JSM-6390) at an operating voltage of