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Full Length Article

A comprehensive study on electrophoretic deposition of a novel type of collagen and hexagonal boron nitride reinforced hydroxyapatite/chitosan biocomposite coating

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ABSTRACT

A novel family of Hydroxyapatite/Chitosan/Collagen/h-BN biocomposite coatings were successfully produced by electrophoretic deposition (EPD). A new type of polyelectrolyte consisting of water, ethanol and isopropyl alcohol was used for EPD process. Collagen (main ligament of human bone) and h-BN (a promising solid lubricant) has been used as supporting materials for biocomposite coatings. The effect of h-BN concentration in the EPD suspension has been investigated. Crystallographic, morphological, spectroscopical, corrosion protection performance, thermal behaviour, mechanical and tribological, topographical and *in-vitro* biocompatibility investigations have been carried out by XRD, FE-SEM, FTIR, Tafel extrapolation and EIS, TGA/DSC, nanoindentation and nanoscratch, SPM and 12-weeks of immersion into r-SBF, respectively. Corrosion protection performance and mechanical and tribological properties of the coatings have been improved with increase in h-BN concentration in deposition suspension up to 5 $g{\cdot}L^{-1}$ and worsen with further increase. The results are encouraging for in-vivo applications of HA/CTS/COL/h-BN biocomposite coatings.

1. Introduction

Bone fracture which is a most common bone defect can result in due to multiple traumas or natural ageing. Implantation to the fractured bone with temporary or permanent prostheses is seen as an inevitable treatment in many medical cases. For this reason demand for the bone substitutes in medical field is growing rapidly [1]. There are some alternatives currently using in orthopaedic surgery such as CoCrMo [2] and stainless steel [3] but the damage of such materials to the body is still a matter of debate [4,5]. Because of their suitable mechanical and anti-corrosion properties and also their feasible biocompatibility titanium and its alloys are considered as an excellent option for orthopaedic bone implantation applications [6,7].

Long-term performance of an implant material is a crucial issue in chirurgical field. Although Ti6Al4V is a good alternative for implantation, there are still remaining concerns due to periprosthetic bone loss such as osteolysis arising from wear and periprosthetic bone resorption arising from stress shielding effect. This type of complications cause to revision surgery in order to fix the applied implant [8–11]. There are lots of attempts to prevent wear and stress shielding related problems including pharmacological [12], engineering [13] and surgical [14].

Coating the implant surface with hydroxyapatite (HA) is thought to be the best alternative [15]. Since it constitutes the mineral proportion of mammalian bones. Although there are many studies and applications that regarding pure HA coating on metallic implants [16,17], the point reached is still quite far from the perfection of the natural bone. Natural bone is a nano-biocomposite and having unique properties owing to its hierarchical structure comprised of mineral (hydroxyapatite) and polymer (polysaccharides and collagen) contents. Due to its excellent osteoconductivity [18,19], usage of HA in orthopaedic and dentistry is becoming almost compulsory.

Various methods can be used for depositing HA coatings on metallic implant surfaces including pulsed laser deposition [20], micro-arc oxidation [21], plasma spraying [22], RF magnetron sputtering [23], ion beam assisted deposition [20] and electrophoretic deposition (EPD) [24]. Many disadvantages come together with the advantages of these techniques such as decomposition and formation of non-stoichiometric and amorphous HA coatings during processing [25]. Due to its low cost, ease of use, room temperature application, controllable parameters and various alternatives for both precursors (dissolved salts, suspensions,

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sols) and substrates electrophoretic deposition method draws more attention among them.

However, further high-temperature sintering which causes to decomposition of HA to tricalcium phosphate is needed after electrophoretic deposition of pure HA coating [23]. As a new strategy to tackle the unwanted decomposition problem and enhancement of biocompatibility while functionalizing HA coatings, electrophoretic deposition as a composite of organic and inorganic materials with HA is becoming a hot research topic [26]. The most popular choice in the production of HA composites is electrophoretic deposition of HA with chitosan. There are many studies entreating the electrophoretic deposition of HA/chitosan composites with other organic [21] or inorganic [24] compounds.

With its macromolecular structure of (1,4)-linked 2-amino-2-deoxy-β-glucan, massive positive charge and molecular weight, chitosan is a chitin derivative cationic natural polysaccharide. Due to its excellent biocompatibility, antibacterial property, biodegradability, flexibility, and low cost, chitosan has become a very popular material in biomedical field [27]. Chitosan has been a commonly used material in a large scale of biomedical applications including wound healing [25], drug delivery [28] and tissue engineering [27]. HA/chitosan coatings on metal implants were well studied in the literature [29–31]. Combining HA, chitosan and collagen for bone tissue repairing is a new and promising study area in biomedical field [32–34]. But there is not much work that this combination is used as a metallic implant coating.

In living tissues collagen serves as the main ligament and also for bone, it acts as a template for the crystallisation of HA onto it. Due to its incommensurable benefits such as perfect biocompatibility, acceptable biodegradability and suitable cellular resemblance, collagen has been used in many biomedical drug delivery [35], wound healing [36] and especially in tissue regeneration and recovery [37] applications. Due to its low mechanical properties, electrophoretically deposited HA/chitosan based composite coatings are needed to be reinforced with other mechanically strength ceramics. There are many studies carried out in the literature for this purpose such as reinforcing with carbon nanotubes (CNTs) [38], graphene [39] and halloysite nanotubes (HNTs) [40], etc.

Thanks to its graphite-like lamellar structure, hexagonal boron nitride (h-BN) is seen as the one of the most promising solid lubricant material in engineering. Not only the solid lubricating properties that make h-BN attractive, but also the properties such as thermal conductivity [41], low electrical conductivity [42], good thermal stability [43] and high corrosion resistance [44,45] make this material reliable for many applications. The potential biomedical use of h-BN in recent years has also begun to be a research topic [46].

In this study, ceramic and biopolymers were brought together in a similar way to the structure of the natural bone with biomimetic approach to achieve high wear resistance, high mechanical strength, high corrosion resistance and high biocompatibility. HA, which has high bioactivity and biocompatibility and is used in implant coatings and implantology in many places, has been used as a base material. h-BN, a solid lubricant with superior mechanical properties, was added to the HA matrix to obtain hardness and abrasion resistance. In addition to this, it is aimed to add extra lubrication and impact resistance by utilizing the viscoelasticity resulting from the gelatinization feature by adding the commonly used chitosan biopolymer in the biomedical field. Moreover, type 1 collagens have been added to the structure in order to benefit from their biocompatibility and elasticity. Thus, HA/ Chitosan/Collagen/h-BN biocomposite coatings with decent biocompatibility properties as well as high wear, mechanical and corrosion resistance, which are very important demands and requirements for possible region implants which are likely to be subjected to load and abrasion, have been fabricated via electrophoretic deposition technique for the first time in the literature.

2. Materials and methods

2.1. Materials

All chemicals were reagent grade and purchased from Merck excluding chitosan and collagen. Medium molecular weighted Chitosan with a degree of deacetylation of 85% and type-I collagen derived from calf skin were purchased from Sigma-Aldrich. All chemicals were used without further purification. Distilled water with a resistivity of 18 MΩ.cm was used to prepare all suspensions.

2.2. Fabrication of HA

Nano-sized HA particles were synthesised via an ultrasonically assisted wet chemical method. Calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) was used as Ca^{2+} source and dibasic ammonium phosphate ($(NH_4)_2HPO_4$) was used as phosphorous source. Equal volumes of 1.0 M $Ca(NO_3)_2{\cdot}4H_2O$ and 0.6 M $(NH_4)_2HPO_4$ solutions were prepared by dissolving the salts in distilled water. The temperatures of the solutions were adjusted to 70 °C, the pH of the solutions were adjusted to 10 with ammonia ($NH_3{\cdot}H_20$) solution. $(NH_4)_2HPO_4$ solution was very slowly added to calcium nitrate solution dropwise at a rate of 5 $ml{\cdot}min^{-1}$. Rapid precipitation of a white powder was seen while mixing the solutions. The pH of the final solution was adjusted to 11 by adding 2 M NaOH solution and subjected to subsequent ultrasonication. Ultrasonication was carried out by immersing an ultrasonic horn (Ultrasonic Processor 400 W; 24 kHz; 22 mm Titanium probe; model: Hielscher - UP400S). All solutions were aged for 24 h in order to bind the essential amount of OH^- ions to the main CaP molecules. Then, solutions were washed with deionized water to acquire neutrality and then washed with a mixture of ethanol-methanol. After ageing, the powders were filtered through filter paper, dried at 100 °C in a drying oven and then ground in a mortar.

2.3. Preparation of Ti6Al4V substrates

Commercially available cold-rolled Ti6Al4V sheets with 0.1mm thickness in 25 mm × 20 mm dimensions were used as substrate material. Before the EPD, substrates were etched using a hydrofluoric acid (HF) and nitric acid (HNO_3) solution in order to remove the naturally occurred protective oxide layer and then thoroughly polished with 600, 1200 and 2400 grade emery paper and rinsed with distilled water and acetone according to ASTM B600 standard [47].

2.4. Preparation of deposition suspensions and electrophoretic deposition

Two types of suspensions given in Table 1 were prepared for EPD of HA/chitosan/collagen/h-BN biocomposite coatings. For preparation of the suspension-I, 1.8 ml of acetic acid and 40 ml of distilled water mixed in a beaker. Chitosan and collagen completely dissolved in this solution and then 0.375 g of HA was added. For preparation of suspension-II, 10 ml of isopropyl alcohol and 50 ml of absolute ethanol and 0.5 g of HA and h-BN nanoparticles ranging from 0.35 to 0.55 g were added and mixed in a different beaker. Suspension I and II were agitated ultrasonically for 1 h and mixed. The final suspension was agitated ultrasonically for 1 h again and magnetically stirred for 24 h to obtain a fully stable suspension. The 24 h of ageing step is crucial for obtaining a stable suspension by the complete decomposition of polymer chains and the encapsulating the ceramic particles. Every deposition