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Zirconium ions integrated in 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) as a metalorganic-like complex coating on biodegradable magnesium for corrosion control

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ABSTRACT

In this study, a coating of ionic Zr integrated in 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) metalorganic-like complexes was applied on Mg for corrosion control. HEDP was first immobilized on alkaline pre-treated Mg followed by an alternating dip-coating process of Zr ions and HEDP to build a complex coating on Mg. This coating was demonstrated to be homogeneous, compact and with a metalorganic-like framework firmly anchored on Mg. This coating led to reduced corrosion current densities and remarkably suppressed long-term in vitro degradation of Mg in phosphate buffer saline (PBS). This complex coating showed promise for surface modification of Mg in biodegradable applications.

1. Introduction

Mg and its alloys have received much attention as potential components of biodegradable implants because of their easy biodegradation, biosafety, and suitable mechanical properties for bone fixation devices [1–3]. An active metal such as Mg can be readily corroded or degraded under physiological surroundings [4]. Compared with other metals, the Young's modulus of Mg is closer to that of cortical bone, minimizing the stress shielding effect between implants and the host tissue, and therefore favoring both bone growth and function naturally [1]. In addition, released Mg ions have been demonstrated to promote calcitonin gene-related polypeptide- α (CGRP)-mediated osteogenic differentiation, providing therapeutic value to this components in bone regeneration [5]. Therefore, Mg-based materials have been regarded as one of most promising candidates for biodegradable implants, particularly for internal bone fixation devices [6–8]. However, Mg suffers from rapid oxidation in physiological surroundings, and this remains to be the biggest challenge for the clinical use of this material [9,10]. Fast corrosion of Mg can cause premature mechanical failure of implants, leading to rapid accumulation of byproducts, evolved hydrogen, and

increased local pH, which can result in harmful side effects such as necrosis of the surrounding tissues [11,12]. Therefore, control of the corrosion rate of Mg is key for clinical biodegradable applications of this material [13].

One of the most effective strategies to control the corrosion rate of Mg lies in building a layer/coating on its surface. This layer/coating can serve as a protecting barrier between the surroundings and the Mg substrate [14]. Numerous efforts have been made to prepare a variety of coatings on Mg by a number of techniques [14–16] such as electron beam, plasma electrolytic oxidation (PEO), ion implantation, organic/polymeric coating [17], and composite coating [18], among others [19]. Among them, organic coatings have shown great potential for achieving both corrosion control and bio-compatibility/functional surface [20,21]. With regard to corrosion control, organic coatings present some advantages versus inorganic materials. Thus, when in contact with Mg matrices (anode), some inorganic phases act as a cathode, forming a galvanic corrosion cell that accelerates the dissolution of Mg [13]. This electrochemical behavior is not typically found in organic phases.

Phosphonic acids are regarded as one of the most promising organic

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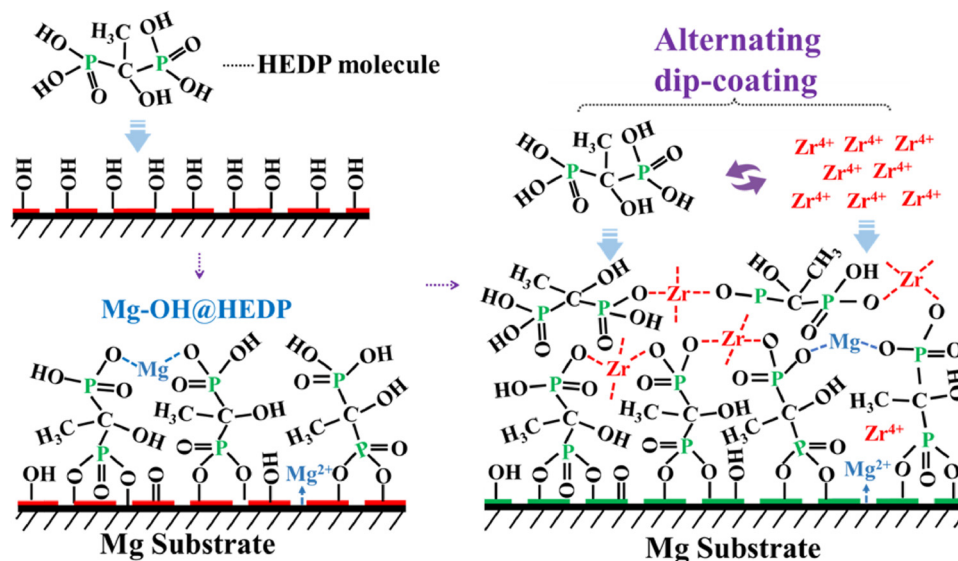
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coating materials for Mg [22]. First, the structure of phosphonic acids is similar to some chemical components of the cell membrane and bone, rendering them biomimetic characteristics. Second, these molecules can be immobilized on a solid surface by making use of their active phosphate groups. This can be done by a simple chemical reaction and subsequent self-assembly deposition, which takes place easily [23]. More importantly, phosphonic acids are powerful chelators of metallic ions, forming metal–organic complexes [24]. These complexes have been demonstrated to improve the quality of coating materials while showing great potential for improving bio-functionalization of metals (i.e., bio-metals) as loaded with drugs, among others [21,25].

In this study, a metal–organic complex coating was built on Mg using an alternating dip-coating method. This approach resulted in enhanced corrosion control and a potential biocompatible surface. We used herein a low molecular weight (206.3 g/mol) diphosphate such as 1-hydroxyethylidene-1, 1-diphosphonic acid (HEDP). HEDP has been widely used as water treatment agent, cosmetic component, and corrosion inhibitor, among other applications, and is considered a bio-safe material [26]. The HEDP molecule has two phosphate groups, making it a powerful chelator for metallic ions. In our previous work we demonstrated that HEDP can be chemically immobilized on alkaline pretreated Mg surfaces, resulting in an ultrathin HEDP film with good corrosion protection characteristics [23]. The Mg ions released during HEDP deposition could be spontaneously chelated by HEDP, and this could account for the good anti-corrosion characteristics of this material. These results motivated us to prepare coatings with different metallic ions, with the hope of further improving the quality of the HEDP coating and producing a new complex suitable for biomedical implant use. In this sense, we selected Zr ions because it has a strong chelating ability (four binding sites). More importantly Zr and its compounds have been demonstrated to have good biocompatibility, particularly for orthopedic regeneration [27].

The approach used for preparing a Mg coating containing Zr ions integrated in HEDP is illustrated in Scheme 1. Briefly, a conversion Mg(OH)₂ layer rich of hydroxyl (OH⁻) groups was formed on the Mg substrate by an alkaline pretreatment. In a subsequent step, HEDP molecules were surface-immobilized on the pretreated Mg by a dip coating method via reaction of the phosphate groups of HEDP with the OH⁻ groups on Mg. Thereafter, based on this layer, an alternating dip-coating process was carried out over the HEDP-anchored Mg with HEDP and Zr ion solutions. This dip-coating process achieved simultaneous self-assembly deposition of HEDP and chelation with Zr ions (note that

Mg ions from corrosion might participate as well). This complex coating preparation strategy involving surface-immobilization and alternating dip-coating processes is quite different compared to the Mg conversion construction coating strategies commonly investigated. The investigated conversion coating construction mechanism can be described as follows. The reactive reagents (e.g., anions (phosphate [28]) or negatively charged groups (phenols [29])) in dip coating solutions are combined with the in situ released Mg ions (resulting from the corrosion of the Mg substrate) and/or other cations to form a conversion coating on the micro-environmentally alkaline Mg surface. In this process, the corrosion of the Mg substrate is vital since it provides in situ Mg ions and alkaline micro-environment on the Mg surface, promoting deposition of the conversion coating on its surface [30]. In this case, dip coating solutions for conversion coatings are usually acidic [31]. Indeed, this strategy has demonstrated some positive results for constructing corrosion protective and functional conversion coatings on Mg surfaces [32], mostly to retard the initial corrosion process [28]. However, this strategy has limitations for constructing high quality conversion coatings on Mg having long-term corrosion protection properties. In addition, in some cases this strategy resulted in coatings presenting cracks after the deposition process since the formation of these coatings is based on the corrosion of the Mg substrate. In this study, the complex coating construction process is believed to involve a “in situ grows up and condense” process. To be specific, surface immobilization of HEDP molecules was first conducted on alkaline-pretreated Mg, followed by an alternating dip-coating process to allow the in situ growth and condensation of the coating with the help of additive metallic ions. This process may avoid severe corrosion of the Mg substrate, and therefore this strategy may provide high-quality coatings, especially for long-term degradation processes. Besides, the added Zr ions have four binding sites, and therefore this tetravalent metallic ion may have a stronger ability for combining with HEDP versus low valent metallic ions. Since it has four binding sites, Zr ion can provide more nucleation sites for the in situ growth of the coating material forming potentially a multiple bonded compound as compared to low valent ions. The as-formed coating might also suppress corrosion of the Mg substrate in the subsequent coating formation process. Meanwhile, this strategy may provide additional space, while allowing to use other high valent metallic ions for tailoring quality or other properties of the Mg coatings such as bio-functionality. Therefore, the strategy used herein was quite different as compared to current conversion coating constructing processes, and this strategy may be more promising for



Scheme 1. Schematic and rationale for the construction of Zr ions integrated HEDP coatings onto Mg surfaces by chemical immobilization, self-assembly deposition, and concurrently chelation.

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