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Perspective

Bioinspired Strategies for Functionalization of Mg-Based Stents

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Abstract: Magnesium alloys have attracted considerable interest as prospective biodegradable materials in cardiovascular stents because of their metal mechanical properties and biocompatibility. However, fast degradation and slow endothelialization results in the premature disintegration of mechanical integrity and the restenosis of implanted Mg-based stents, which is the primary hurdle limiting their predicted clinical applicability. The development of bioinspired strategies is a burgeoning area in cardiovascular stents' fields of research. Inspired by the unique features of lotus leaves, pitcher plants, healthy endothelial cells (ECs), marine mussels, and extracellular matrix, various bioinspired strategies have been developed to build innovative artificial materials with tremendous promise for medicinal applications. This perspective focuses on bioinspired strategies to provide innovative ideas for reducing corrosion resistance and accelerating endothelialization. The bioinspired strategies are envisaged to serve as a significant reference for future research on Mg-based medical devices.

Keywords: Mg-based stents; bioinspired surface design; corrosion resistance; pro-endothelialization

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1. Introduction

Magnesium is vital in the process of human metabolism, and the concentration of magnesium ions in the blood is around 0.70–1.10 mmol L^{-1} [1]. Magnesium can dissolve in blood plasma, which means that implanted magnesium can degrade during the healing process. At present, Mg alloys, such as AZ31, AZ91, AM50, ZK60, and WE43 [2,3], have been well established commercially and regarded as suitable materials for biomedical applications because of their potential benefits over bioresorbable polymers in terms of improved flexibility, stiffness, and processability [4–6]. For instance, Mg alloys are presently being researched as a promising material for cardiovascular stents owing to their increased radial strength and biodegradability [7]. In 2003, Heublein et al. [8] were the first to implant 20 stents fabricated of AE21 Mg alloy into the arteries of pigs to evaluate degradation following the endovascular implantation of customized Mg-based stents. In the absence of local damage, there was no inflammatory response or neointimal development. Furthermore, the mechanical integrity of Mg-based stents was lost between days 35 and 56. These advantages of biodegradability and unique mechanical properties would greatly assist health care, in part by eliminating the need for a second operation. Unfortunately, Mg-based stents degrade quickly after being placed in blood containing chloride ions because of low standard potential (−2.37 V) [9]. Rapid degrading behavior often results in adverse reactions, such as hydrogen gas and local alkalization [10,11], and even leads to stent failure owing to the premature loss of radial support. Therefore, improving the corrosion resistance and pro-endothelialization ability are of great significance in promoting the clinical application of Mg-based stents [12–14].

Nature has provided us with a plethora of ideas to help us overcome the challenges of magnesium alloys [9,15–18]. We can gain innovative ideas for improved medical gadgets

by examining the behaviors of natural creatures. For example, lotus leaves, with hierarchical micro- and nanostructures, provide a unique case for improving anticorrosion properties [19–21]. Pitcher plant, which forms a dynamic liquid layer, stimulates the design of liquid surfaces for long-term durability and corrosion resistance [22–24]. Healthy ECs, which maintain an extended and aligned morphology in natural blood arteries, have established a model for the regulation of ECs' morphology [25,26]. Marine mussels, which contain a high-adhesion protein, have emerged as one of the most extensively used strategies for functionalizing magnesium alloys' surfaces [27–29]. Hyaluronic acid, which is the most prominent component of the extracellular matrix, has been examined as a case to improve its functions [30–33], etc. We believe that bioinspired strategies could be used to create medical magnesium alloys with optimum qualities and improve their functioning for clinical applications. This review aims to highlight bioinspired strategies to improve corrosion resistance and accelerate endothelialization on Mg-based stents from methodological, structural, and functional perspectives (as shown in Figure 1).

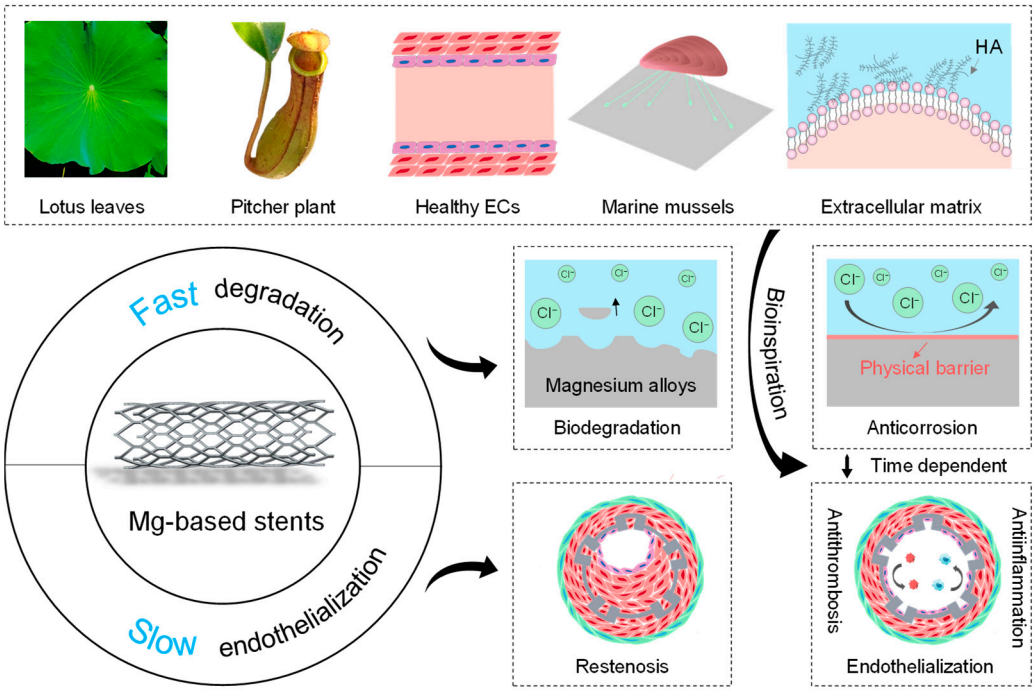

Figure 1. Schematic illustration of bioinspired strategies for Mg-based stents with enhanced corrosion resistance and promoted endothelialization.

2. Recent Bioinspired Strategies on Mg-Based Stents

As shown in Figure 2, the number of academic papers on Mg-based stents and bioinspired strategies studies has increased dramatically over the previous decade. The amount of research on bioinspired strategies studies has increased significantly over the last ten years, indicating that bioinspired strategies research has received a lot of attention. In contrast, publications on Mg-based stents increased continuously from 2012 to 2017, but the number of publications began to decline in 2018, indicating that certain obstacles in Mg-based stent development may exist. Typically, with the increase in bioinspired strategies studies, the number of publications on Mg-based stents has risen dramatically since 2020, suggesting that bioinspired strategies are a promising technique for the functionalization of Mg-based stents to address the existing issues. The limitations that hinder magnesium alloys in the direction of cardiovascular stents are their rapid degradation and delayed endothelialization. Bioinspired strategies could provide an alternative to make Mg-based stents with optimal properties and enhance their functionality for clinical applications. In the following sections, we will discuss the current advances in bioinspired strategies

on Mg-based stents in regulating degradation behavior and biofunction. A potential research direction is also concisely discussed to help guide bioinspired strategies and inspire further innovations.

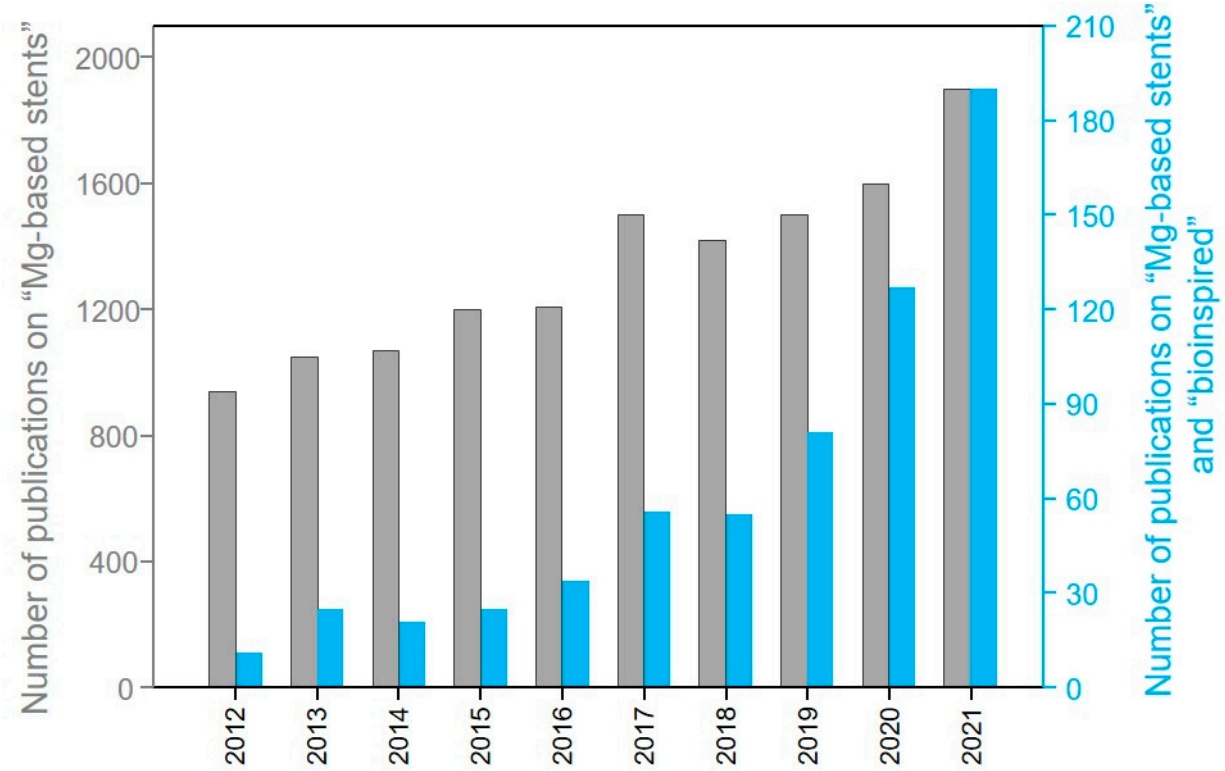

Figure 2. Publications relevant to Mg-based stents and bioinspired strategies research from 2012 to 2021. The information was collected from the Web of Science database with the search date 30 September 2022, and the keywords were "Mg-based stents", "Mg-based stents + bioinspired".

3. Bioinspired Strategies for Mg-Based Stents

3.1. Bioinspired Strategies to Reduce Corrosion

Because of its low standard potential (−2.37 V), Mg-based stents degrade quickly after being placed in the body [34,35]. The corrosion resistance of Mg-based stents has emerged as a major barrier to widespread clinical implementation. Bioinspired strategies can help increase the corrosion resistance of Mg-based stents [36]. Several protective physical barriers, including the bioinspired solid surface and bioinspired liquid surface, are used to form a protective layer to prevent the excessive and rapid deterioration of magnesium alloys [9,37,38].

The bioinspired solid surface has been commonly used to reduce the corrosion of Mg-based stents [21,39–41]. The bioinspired strategy is based on the perception that the solid surface can prevent Mg-based stents from coming into direct contact with the external aqueous solution [37]. This can significantly reduce the interaction between corrosive species and magnesium alloys, thereby exhibiting anticorrosion properties. One case is creating a lotus-leaf-inspired biomimetic structure to develop a superhydrophobic surface on magnesium alloys. The liquid on top of this bioinspired surface would be separated by trapped air in the small solid–liquid interfacial space on top of the protrusions. The air regions on the bioinspired surface cannot be replaced by corrosive species, and the "air" areas of the surface are deemed entirely non-wetting, increasing the corrosion resistance of magnesium alloys. Unfortunately, the bioinspired solid surface of superhydrophobization shows poor biocompatibility and abrasion resistance, and the air cushion is unstable, especially under long-term exposure. The relevant repair steps cannot be implemented spontaneously; once the bioinspired solid surface is physically and chemically damaged

during the process, its protective efficacy is greatly weakened or entirely fails, thereby resulting in the infiltration of corrosive ions and magnesium alloys' corrosion.

In comparison to the air cushion in the bioinspired solid surface of superhydrophobization, the bioinspired liquid surface is a new concept that has attracted widespread research interest [23,42,43]. Inspired by the Pitcher plant that can prevent the adhesion of insects by utilizing a layer of liquid to generate a low friction surface, the anticorrosion is achieved by generating a stable immobilized functional liquid overlayer to isolate magnesium alloys. When soaked in a sodium chloride solution, the bioinspired liquid surface preserved the capacity to resist additional corrosion for more than 20 days, outperforming the bioinspired solid surface in terms of corrosion inhibition [44]. The bioinspired liquid surface process "immobilizes" on structured magnesium alloys by using capillary force and van der Waals force [23,45,46]. Three criteria should be based on to construct the bioinspired liquid surface [9,47]: (1) the functional liquid must be stabilized on the surfaces of the magnesium alloys; (2) the functional liquid must wet the surfaces of the magnesium alloys preferentially over an aqueous solution; and (3) the functional liquid and aqueous solution must be immiscible. Furthermore, the bioinspired liquid surface can prevent the creation of flaws and repair possible damage due to its fluidity. It endows the surface with specific properties such as antibiotic adherence and antibacterial activity. The potential for bioinspired liquid surfaces in anticorrosion applications is expected to be the future research project in this area.

3.2. Bioinspired Strategies to Accelerate Endothelialization

Restenosis occurs with smooth muscle cell proliferation and extracellular matrix deposition after Mg-based stents implantation in animals or the human body [7,48,49]. Promoting the rapid endothelium of Mg-based stents is becoming a promising therapeutic strategy for avoiding thrombosis and intimal hyperplasia [50–52]. The resolution of the endothelium issue encountered by Mg-based stents would reduce the risk of in-stent restenosis. Here, we introduce two bioinspired strategies to promote rapid endothelialization: (1) constructing bioinspired micro-/nanoscale patterns on Mg-based medical devices; (2) providing bioinspired bioactive molecules for Mg-based medical devices.

One strategy for improving endothelialization is to create a bioinspired micro-/nanoscale design that mimics the natural endothelial arrangement to achieve optimal EC performance [53]. The bioinspired micro-/nanoscale patterns can effectively promote EC elongation and regulate EC response, thereby enabling the formation of the EC monolayer, which is comparable to the endothelium in natural blood arteries [54]. Bioinspired micro-/nanoscale design, such as plasma dry etching [55], reactive ion etching [56], polishing, and microblasting [50], have been used to create groove/ridge stripes [57], square or round micro-domains [58], and nanopillars patterns [59] that are beneficial for endothelialization. Furthermore, surface modification can be used to change the physical and chemical characteristics of magnesium alloy surfaces to reduce platelet adherence. However, it is challenging to generate a homogeneous directed microstructure on the surface of Mg-based stents with a complicated spatial structure using the bioinspired micro-/nanoscale design. Moreover, the above method for preparing bioinspired micro-/nanoscale patterns on magnesium alloys is time-consuming, and how to achieve long-term effective and precise regulation of in situ vascular intimal repair through the reasonable construction of the surface physical and chemical structure remains an important task.

A second strategy is to introduce the bioinspired bioactive molecule, including polydopamine (PDA) [60–62], hyaluronic acid (HA) [30–33], chitosan (CS) [63], heparin [64], vascular endothelial growth factor (VEGF) [65], stem cell homing factor (SDF-1α) [66,67], Arg-Glu-Asp-Val (REDV) [68], and other representative bioactive molecules. Bioinspired bioactive surfaces are more prominent than bioinspired inorganic structure surfaces in the field of implanted Mg-based stents due to their degradation ability, biocompatibility, and modulation of cell behavior (e.g., adhesion, proliferation, and differentiation). The bioinspired bioactive surfaces can be created via bioactive molecular interactions be-

tween functional groups and Mg-based stents surfaces, such as electrostatic interactions or intermolecular forces. For instance, PDA, which was inspired by mussels' feet with a high-adhesion protein, has emerged as one of the most widely employed techniques for functionalizing the surfaces of magnesium alloys [62]. The bioinspired PDA surface is beneficial in enhancing the attachment, proliferation, and viability of ECs. To repel platelet and prevent thrombosis, the bioinspired PDA surface can be employed as a surface reaction site on magnesium alloy substrates for subsequent surface-mediated processes. One case is that a designed, bioinspired, multifunctional surface based on PDA and HA can promote reendothelialization and improve blood compatibility both in vitro and in vivo [33,69]. The advantage of the bioinspired bioactive surface is that biochemical attachment is fast and rapid endothelialization is also achieved. The above bioinspired strategy is widely employed in the development of bioactive coatings on Mg-based stents and is becoming a viable method for accelerating the endothelialization of stents. Furthermore, this can be utilized for Mg-based stents with an extending multifunction as antithrombosis and antiinflammation performance [70], which may open up new avenues for the development of medical Mg alloys.

4. Conclusions and Prospect

Bioinspired strategies for the functionalization of Mg-based stents were presented in this perspective. The disadvantages of Mg-based stents include their rapid degradation and insufficient endothelialization after implantation. Bioinspired strategies for Mg-based stents can increase not just the corrosion resistance but also their biocompatibility. For instance, bioinspired strategies would exhibit slow degradation by constructing a bioinspired physical barrier to prevent exposure of Mg-based stents to the ambient atmosphere and achieve fast endothelialization after implantation to tackle restenosis problems. However, the obstacle encountered by the current bioinspired strategies of Mg-based stents is how to guide or coordinate with the biodegradation and the functions of biological cells to ensure the time-ordered biological requirements. The Mg-based stents with biological multifunction that are time-ordered would be a subject of future work. Therefore, a thorough understanding of the time-ordered mechanism of bioinspired strategies for the biofunctions of Mg-based stents should be explored more. There is no doubt that bioinspired strategies take a broad range of collaborations in the fields of bioinspired materials, physical chemistry, biomedical engineering, mechanics, and clinics to motivate fundamental science and clinical applications. We hope this perspective will attract the attention of researchers in various fields, allowing them to contribute to the creation of bioinspired medical devices for the benefit of humanity.

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