Preparation and Properties of UV Irradiation Modified ZnO-HA Coating on the Biomedical Magnesium Alloys

Jin’e Sun¹*, Jie Liu², Zhanxiang Niu¹, Meizheng Chi¹, Xuecheng Peng¹, Yong Yang³ and Qihui Lin⁴
¹Tianjin College, Beijing University of Science and Technology, Tianjin 301800, People’s Republic of China
²Fourth Municipal Administration Co. LTD, Tianjin 300000, People’s Republic of China
³Equipment Bidding Center, Naval Armament Department, Beijing 100071, People’s Republic of China
⁴Beijing Electrical Engineering School, Beijing 100051, People’s Republic of China
*Corresponding author’s Email: sunjine0406@163.com

Abstract. In order to improve the corrosion resistance of magnesium alloys, ZnO-HA coating was prepared on the surface of magnesium alloys by using ultraviolet (UV) irradiation and hydrothermal method. The effects of ultraviolet irradiation time on the microstructure, the electrochemical properties and corrosion resistance of ZnO-HA coating were studied. The results indicated that the ZnO-HA coating obtained by 24 h of UV irradiation combined hydrothermal method was dense and uniform, without any cracks, and it was mainly composed of nanoparticle-like HA and flake-like ZnO. Electrochemical properties and corrosion resistance of ZnO-HA coated magnesium alloys were studied in simulated body fluid (SBF). Compared with the bare magnesium alloys, the coated magnesium alloys have good corrosion resistance. In vitro immersion experiments, ZnO-HA coating could provide good protection for the magnesium alloys substrate, indicating that ZnO-HA coating prepared by UV irradiation combined hydrothermal method can be used as a potential modified biomaterial for magnesium alloys.

1. Introduction
As the degradable biomedical materials, magnesium alloys have been praised as the third generation of biomedical materials in the world due to their elastic modulus similar to natural bone, excellent biodegradability, good strength and low toxicity [1]. However, too rapid degradable rate of magnesium alloys in complex physiological environment [2] leads to the premature failure of mechanical properties and the excessive bone healing time, which has become the major bottleneck limiting their clinical application. Therefore, it is very important to improve the corrosion resistance of magnesium alloys to prolong their service life in the human body.

Surface modification with bioactive coating is one of the effective methods to reduce degradation rate and enhance the bioactivity of magnesium alloys. Hydroxyapatite (HA) [3], as a biodegradable modified material, is quite similar to the mineral composition and structure of natural bone and plays an important role in improving the corrosion resistance of magnesium alloys, promoting cell adhesion, proliferation and differentiation, and new bone formation. Zinc oxide (ZnO) is a semiconductor oxide,
which can stimulate a large number of active hydroxide radicals (·OH) on the surface of ZnO by UV irradiation, and improve the hydrophilicity and the biological activity of the material [4]. In addition, ZnO has almost same band gap energy (3.2 eV) as titanium dioxide (TiO$_2$), and its photocatalytic capacity is similar to that of TiO$_2$. In the latest research, Liu et al. [5] stimulated nano TiO$_2$ coating to generate hydroxide radicals (·OH) on its surface by UV irradiation, which improved its hydrophilicity and further enhance the quick formation of the bioactive apatite layer. Moreover, the in vivo results indicated that there were mineralized apatite and bone tissue formed around the implants after implanting the animals for 2 months. Compared with TiO$_2$, ZnO is considered to have higher photocatalytic efficiency due to its higher quantum efficiency [6]. Therefore, more hydroxide radicals (·OH) could be generated on the surface of ZnO by using UV irradiation, and promote the heterogeneous nucleation and growth of HA [7]. As a consequent, it is reasonably believed that ZnO-HA coating on magnesium alloys surface modified by UV irradiation is expected to improve the corrosion resistance of magnesium alloy, promote the formation of new bone, significantly shorten the time of bone integration, and finally obtain the optimal implantation effect.

In order to make the coating possess favorable protection effect for magnesium alloys, in this present work, ZnO-HA coating was successfully prepared on the magnesium alloys surface by the UV irradiation modified technology combined hydrothermal method, and the microstructure, the electrochemical properties, corrosion resistance, and in vitro degradation behavior of ZnO-HA coating on the magnesium alloys were investigated.

2. Materials and experimental methods

2.1 Preparation of ZnO-HA coating on magnesium alloys

0.01782 g Zn(NO$_3$)$_2$·6H$_2$O was mixed with 20 ml 28 % ammonia water to prepare the mixture solution. Measuring 37.5 ml of the mixture solution to the reaction kettle, in which the treated AZ31 magnesium alloys samples were placed. Afterwards, ZnO coating was prepared on magnesium alloys surface by hydrothermal method at 95 °C for 10 h. The resultant samples were divided into three groups and irradiated by UV light for 0 h, 12 h and 24 h, respectively and the intensity of UV irradiation was 5 uW/cm$^2$. After that, they were put into the reaction kettle with 37.5 ml of the mixed solution, in which EDTA$\text{Na}_2\text{Ca}$ was as the calcium source and Na$_2$HPO$_4$ was as the phosphorus source and the concentrations of Ca$^{2+}$ and PO$_4^{3-}$ in the mixed solution were both 0.20 mol/L. ZnO-HA coating was prepared on the magnesium alloys surface by hydrothermal method at 120 °C for 13 h, finally, they were defined as UV0h-ZnO-HA, UV12h-ZnO-HA and UV24h-ZnO-HA sample, respectively.

2.2 Coating characterization and tests

The phase and surface morphologies of the obtained coatings were characterized using X-ray diffraction (XRD, D/Max-2500 Rigaku, Japan) with Cu Kα radiation in the range of 5-70 °(2θ values) and scanning electron microscopy (SEM, S-4800, Hitachi, Japan). To evaluate the electrochemical property of samples, the coated magnesium alloys were examined by potentiodynamic polarization test in SBF solution at 37 °C based on a CHI660C electrochemical workstation with a typical three-electrode cell. In this test, 3 samples were investigated to take the average. Moreover, the prepared ZnO-HA coated magnesium alloy samples were soaked in simulated body fluids (SBF) at 37 °C for different periods for assessing the corrosion behavior in vitro. The pH value of SBF solution was measured and recorded on time every day (24 h), and the SBF solution was changed every 2 days.

3. Results and discussion

3.1 Composition and microstructure of coatings
Figure 1. XRD pattern (a) and SEM morphology (b) of ZnO coated magnesium alloys

Figure 2. SEM morphologies of coated samples with different UV-irradiated time (a, b: 0 h; c, d: 12 h; e, f: 24 h) after the hydrothermal method for 13 h.

Figure 1. showed the XRD pattern and SEM morphology of ZnO coated magnesium alloys samples. Obviously, the diffraction peaks detected were consistent with the diffraction peaks of standard card ZnO (JCPDS. No 03-0752) (figure 1. (a)). As shown in figure 1. (b), ZnO coating was composed of irregular flakes growing on the magnesium alloys substrate in a vertical and random direction, these flakes distributed relatively uniformly and their size ranged from about 200 nm to 2 μm, which formed the micro-nano structural ZnO coating. In addition, some small gaps existed among the irregular plates, constructing a porous network of micro-nano structure, which could effectively improve the hydrophilicity of the coating surface. Zhang et al. [8] has indicated that under UV irradiation, compared with acicular ZnO, micro-nano flake-like ZnO could produce more active hydroxyl groups (·OH) and have stronger hydrophilicity, providing a good foundation for subsequent preparation of HA coating on the magnesium alloy surface.

Figure 2. presented SEM morphologies of coated samples with different UV-irradiated time of 0 h, 12 h and 24 h after the hydrothermal method at 120 °C for 13 h. It could be observed that the surface morphologies of coated samples displayed an enhanced densification with the extension of UV irradiation time. In the absence of UV irradiation, the surface of the coated sample was uneven and irregular. After 12 h of UV irradiation, the coating on the sample was consisted of spherical shape particles, and there were some pores with uneven size around them, ranging from 1 to 5 μm. Continuing to increase UV irradiation time to 24 h, the coating surface of sample was mainly composed of uniform small particles with the size of about 100 nm. Moreover, the coating texture
became more uniform and flat without any obvious pores in comparison with those after UV irradiation of 0 h and 12 h. In addition, the XRD pattern of the UV24h-ZnO-HA sample was shown in figure 3. It could be evidently found that the diffraction peaks in the XRD pattern were consistent with the standard card HA (JCPDS No. 86-0740). Besides, the diffraction peaks of ZnO (JCPDS No. 03-0752) were also detected, indicating that ZnO-HA coating was successfully prepared on the surface of magnesium alloys by the UV irradiation of 24 h combined hydrothermal method, and the diffraction peaks and their intensity revealed that the prepared HA had good crystallinity.

Figure 3. XRD pattern of coated sample with UV irradiation of 24 h after the hydrothermal method for 13 h.

Figure 4. Electrochemical properties of ZnO-HA coated and naked samples in SBF solution (a: Potentiodynamic polarization curves; b: Nyquist plots)

3.2 Corrosion resistance

Table 1. Corrosion properties of ZnO-HA coated and naked samples

| Samples     | $E_{corr}$ (V) | $i_{corr}$ (A/cm$^2$) | $R_t$ (Ω·cm$^2$) |
|-------------|----------------|------------------------|-------------------|
| AZ31        | -1.6658        | 56.400 × 10$^{-7}$     | 0.05 × 10$^4$     |
| UV0h        | -1.5913        | 2.764 × 10$^{-7}$      | 5.00 × 10$^4$     |
| UV12h       | -1.5824        | 1.994 × 10$^{-7}$      | 7.80 × 10$^4$     |
| UV24h       | -1.5736        | 0.973 × 10$^{-7}$      | 11.50 × 10$^4$    |

In order to evaluate the influence of UV-irradiated time on corrosion properties of ZnO-HA coating, the electrochemical measurements of ZnO-HA coated and naked magnesium alloys in SBF were performed and the results were revealed in figure 4 and Table 1. With the prolonging of UV irradiation time, both of the corrosion potential and charge transfer resistances of coated samples gradually increased, and the corrosion current density gradually decreased. Among them, the $E_{corr}$ of UV24h-ZnO-HA samples was the largest (-1.5736 V), and its $i_{corr}$ was the smallest (0.9737 × 10$^{-7}$ A·cm$^{-2}$), which reduced by an order of magnitude compared with those of UV0h-ZnO-HA and UV12h-ZnO-HA samples. Furthermore, its $R_t$ reached 11.50 × 10$^4$Ω·cm$^2$ that was in exceed of those of UV0h-ZnO-HA and UV12h-ZnO-HA samples, even improved the three orders of magnitude with respect to naked magnesium alloys. Generally speaking, the greater the corrosion potential is, the smaller the corrosion current density is, and the greater the charge transfer resistance is, implying that the test sample has favorable anti-corrosion property [9]. Therefore, it could be concluded that UV24h-ZnO-HA sample had good corrosion resistance. According to the analysis from figure 2, the micro-cracks and pores on the surface of UV0h-ZnO-HA and UV12h-ZnO-HA samples were the main reasons leading to the decline of electrochemical performance. Nevertheless, as for UV24h-ZnO-HA sample, ZnO-HA coating with high density, uniformity and integrity could be used as a good physical barrier to prevent the penetration of aggressive ions in SBF into magnesium alloys and improve the corrosion resistance of magnesium alloys [8, 10]. Consequently, UV24h-ZnO-HA sample was selected as the representative samples to further study the degradation behavior in SBF for different time.
3.3 Degradation behavior in vitro

Figure 5. (a) pH variation; (b) corrosion rate of ZnO-HA coated samples with UV irradiation for 24 h after soaking in SBF solution for different times.

The pH variation of naked magnesium alloys and ZnO-HA coated samples immersed in SBF solution for different time were illustrated in figure 5. (a). During the immersion of 14 days, the pH value of naked magnesium alloys in SBF rose linearly, and exceeded 11 on the 14th days. On the contrary, pH value of coated samples fluctuated a little with the increasing of immersion time, and the overall pH value was relatively stable, ranging from 7.5 to 8.5, which was primarily owing to the synergistic effect between HA and Ca$^{2+}$ and OH$^-$ ions, that was, ions exchange and neutralization reaction would occur when Ca$^{2+}$ and OH$^-$ ions were adsorbed by HA, so that OH$^-$ was also consumed when PO$_4^{3-}$ on the protonized surface reacted with Ca$^{2+}$, as a result, new mineralized layer was gradually formed on the surface of coated samples, thereby inhibiting the pH increase in solution environment [11]. Meanwhile, the corrosion rate of coated sample and naked sample soaked in SBF for 1, 4, 7 and 14 days was further analyzed as shown in figure 5. (b). During the whole soaking process, the corrosion rate of naked magnesium alloys was obviously higher than that of coated samples and its corrosion rate was 20.8 mm/y when immersed to 14 days. However, the corrosion rate of the coated samples was more stable, only 0.48 mm/y on the 14th day of immersion, which met the requirement that the corrosion rate of the biodegradable materials in SBF solution should be less than 0.5 mm/y [6]. ZnO-HA coated samples exhibited good corrosion resistance during 14 days of immersion, further illustrating that ZnO-HA coating played an important role in protection for magnesium alloys during the whole process of soaking in SBF, specifically, ZnO-HA bilayer as two solid barrier, effectively blocked the erosion of erosion ions in SBF solution. Besides, the good corrosion resistance might be linked to the formed mineralized products on the coating surface. Relative studies have also demonstrated that the new mineralized products formed on the coating surface due to the presence of HPO$_4^{2-}$, Ca$^{2+}$, and PO$_4^{3-}$ in SBF made up for cracks on the surface of coated samples and hindered the corrosion of magnesium alloys [8]. As a consequence, it could be inferred that the ZnO-HA bilayer on the surface of the coated sample and the rapidly formed mineralized layer during the soaking process effectively protected the magnesium alloys substrate together, improved the corrosion resistance of the magnesium alloys, and slowed down the corrosion rate of ZnO-HA coated samples.

4. Conclusion

In this paper, a compact ZnO-HA coating was prepared on the surface of magnesium alloys by UV irradiation combined hydrothermal method. When the UV irradiation time was 24 h, the coating surface was dense and uniform. Electrochemical measurement results indicated that the coated magnesium alloys with UV irradiation of 24 h had good corrosion resistance, and the corrosion potential was the greatest (1.5736 V), the corrosion current density was the smallest (0.9737 × 10$^{-7}$ A·cm$^{-2}$), the charge transfer resistance was the greatest (11.50 × 10$^{4}$ Ω·cm$^{-2}$). In addition, during 14
days of in vitro immersion test, the pH value of coated samples in SBF solution remained within the range of 7.5–8.5, and the corrosion rate of the coated samples was only 0.480 mm/y, indicating that the ZnO-HA coated samples had a good protective effect on the magnesium alloy substrate, effectively improved the corrosion resistance of magnesium alloys, and slowed down the degradation rate. Therefore, UV radiation combined hydrothermal method could be acted as a potential technology to improve corrosion resistance of biodegradable magnesium alloys.

Acknowledgements
The work was financially supported by the Scientific Research Project of Tianjin Education Commission (Grant No. 2018KJ264)

References
[1] Wang G, Li J and Zhang W 2014 Int. J. Nanomed 9 2387–98
[2] Wang M J, Chao S C and Yen S K 2016 Corros. Sci 104 47–60.
[3] Shen S B, Cai S and Ling R 2017 Chem. Eng. J. 309 278–87
[4] Feng W, Jing G L and Zhang G P 2008 Chemosphere 72 407
[5] Liu X Y, Zhao X B, Li B and Cao C 2008 Acta. Biomater 3 544–52
[6] Chen X, Shen S, Guo L and Mao S 2010 Chem. Rev 11 6503–70
[7] Shen S B, Cai S, Li Y and Ling R 2017 J. Chem. Engi 309 278–87
[8] Zhang Y 2018 J. Mater. Sci. Mater. Electron 29 1576–83
[9] Amaravathy S, Sathyanara S and Sowndarya N 2014 Ceram. Int 40 6617–30
[10] Hornberger H, Virtanen S and Boccaccini A R 2012 Acta. Biomater 8 2442–55
[11] Chen Y, Xu Z and Smith C 2014 Acta. Biomater 10 4561–73