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Short communication

# Structure, corrosion behavior, and antibacterial properties of nano-silica/graphene oxide coating on biodegradable magnesium alloy for biomedical applications

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ABSTRACT

In the present study, a novel nano-silica ($SiO_2$)/graphene oxide (GO) coating was deposited on Mg alloy via physical vapor deposition (PVD) combined with dip coating. The structural characterization clearly revealed that the nano-$SiO_2$ underlayer had a compact columnar microstructure with a thickness of 1 μm, while the GO overlayer presented a sheet-like morphology with a thickness of around 30 μm. The in-vitro degradation rate revealed that the presence of GO as an overlayer on the nano-$SiO_2$ layer significantly decreased the corrosion rate of the Mg alloy. The antibacterial results demonstrated that the both nano-$SiO_2$/GO and nano-$SiO_2$ coatings exhibited a strong antibacterial activity against the *Streptococcus mutans*. However, the nano-$SiO_2$/GO coating exhibited better antibacterial activity compared to the nano-$SiO_2$ coated and uncoated samples. These results exhibit that nano-$SiO_2$/GO coating has effective antibacterial activity and high corrosion resistance in vitro, thus, it can be considered as a promising material for implant applications.



Currently, the study of biocompatibility and biodegradability of implant materials received great attention in the biomedical applications. Mg and its alloys as biodegradable implant materials were applied for biomedical application in the field of cardiovascular, musculoskeletal and tissue [1,2]. This is attributed to their good biocompatibility, low density, and close elastic modulus to human bone and non-toxicity [1,3]. However, the application of magnesium is restricted by its poor corrosion resistance, which worsens the mechanical properties of the implant resulting in the inability of tissue to heal [4–6]. To address this issue, two main approaches were applied, which include alloying of Mg with Zn and Ca to improve its in-vitro corrosion resistance [7–9]. On the other hand, surface modifications were performed in order to further enhance the corrosion resistance of Mg alloy [3,6,7]. Therefore, this study used PVD for coating of nano-$SiO_2$ as underlayer and dip coating for graphene oxide (GO) deposition as an overlayer. In this view, silicon is an essential ion in osteogenic cells with good biocompatibility and corrosion resistance as well as it is beneficial to bone and cartilage, providing inertness to biological tissues [3]. In this regard, Kuo et al. [6] showed that SiO*x* coating on AZ31 alloy significantly decreased corrosion current density and improved corrosion resistance. However, the presence of a great amount of porosities in plasma coating also can absorb more aggressive medium leading to more penetration of corrosive species to the substrate [10]. Therefore, GO has been deposited as a top layer to seal the micro-pores of PVD coating to enhance the corrosion resistance and antimicrobial activity of the substrate. Graphene oxide (GO) has been reported as an interesting additive for coatings due to its unique structural properties, surface functionalization, exceptional mechanical behavior, interesting biological response, and

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anticorrosion properties [7,11–13]. In this view, Gao et al. [14] illustrated that HA/GO coating could significantly decrease the corrosion resistance of Mg alloys. A similar study [7] showed that GO/HA/phosphate coating presented lower in-vitro degradation rate compared to the HapNP/phosphate coating and uncoated ultra-high purity Mg substrates. Yet another study [15] revealed that graphene coating effectively inhibited the magnesium alloy from corrosion. However, a study on the corrosion behavior and antibacterial properties of bi-layer nano-$SiO_2$/GO coating on magnesium alloys could not be found in the literature. Hence, in the present study, the PVD coupled with dip coating methods was performed for the first time to prepare nano-$SiO_2$ coating as an underlayer and GO coating as an overlayer on magnesium alloy in order to assess its potential for orthopedic applications.

In this study, samples of Mg-1wt% Ca-6wt% Zn alloy with dimensions of 15 mm × 10 mm × 10 mm were used as substrates. For the nano-$SiO_2$ coating, a hybrid ion beam deposition system, consisting of a linear ion source and magnetron sputtering source with a $SiO_2$ target, was selected. An ion source with Ar gas was used to clean the surface of the Mg alloys for 40 min. This pre-treatment was performed when the base pressure of the chamber was below $2.55 \times 10^{-3}$ Pa. PVD was performed at room temperature with argon as the sputtering gas. The process used a sputtering pressure of 0.24 Pa, an RF sputtering current of 200 W, the deposition time of 90 min, and a bias voltage of −150 V. Graphene oxide was synthesized by a modified Hummer's method [16] via chemical oxidation without further purification. The solution of GO (1 mg/ml) and deionized water was sonicated for 1 h at 100 W to form a stable dispersion. The $SiO_2$ coated sample was dipped into the dispersed GO solution for 30 min under sonication and then dried at 100 °C for 1 h. This step has been repeated 3 times in order to increase the loading of GO on the surface of the alloy. X-ray diffractometry (Siemens-D500) was used for phase identification using Cu-Kα radiation generated at 40 kV and 35 mA. The microstructural observation was performed using scanning electron microscopy (SEM; JEOL JSM-6380LA) and transmission electron microscopy (TEM; HT7700 Hitachi). A three-electrode cell was used for potentiodynamic polarization tests (PARSTAT 2263) and electrochemical impedance spectroscopy (EIS) in SBF solution according to [2]. The immersion test was carried out according to ASTM G1-03 in the SBF at 37 °C and the pH value of the uncoated and coated samples were monitored with a pH meter. The antibacterial activity of the uncoated, $SiO_2$ coated, and $SiO_2$/GO coated of Mg alloy against *Streptococcus mutans* PTCC 1683 (Gram-positive bacteria) were investigated according to the disc diffusion antibiotic sensitivity testing. These bacteria were provided from Persian Type Culture Collection, Iran. The glassware was sterilized for 15 min in an autoclave at 121 °C prior to the experiment. Bacteria stock solution was prepared by mixing 5–10 colonies with a sterile loop in Muller Hinton broth (Merck) and incubated or 24 h at a temperature of 37 °C and then compared with turbidity of suspension to 0.5 McFarland standard. For disc diffusion antibiotic sensitivity testing, a Muller-Hinton agar media (Merck) was swabbed with the respective organisms, and each sample was placed on the agar plate and incubated at 37 °C for 24 h in an incubator. In this study, penicillin discs for bacteria (10 μg/disc) were used as positive control. The experiment was repeated three times and only one best image was photographed using a digital camera. The mean zone of inhibition (mm) around the film was measured using an ImageJ software version 1.47.

The SEM micrographs show the presence of eutectic structure at the grain boundaries of the uncoated Mg–Ca–Zn alloy (Fig. 1 a,d).

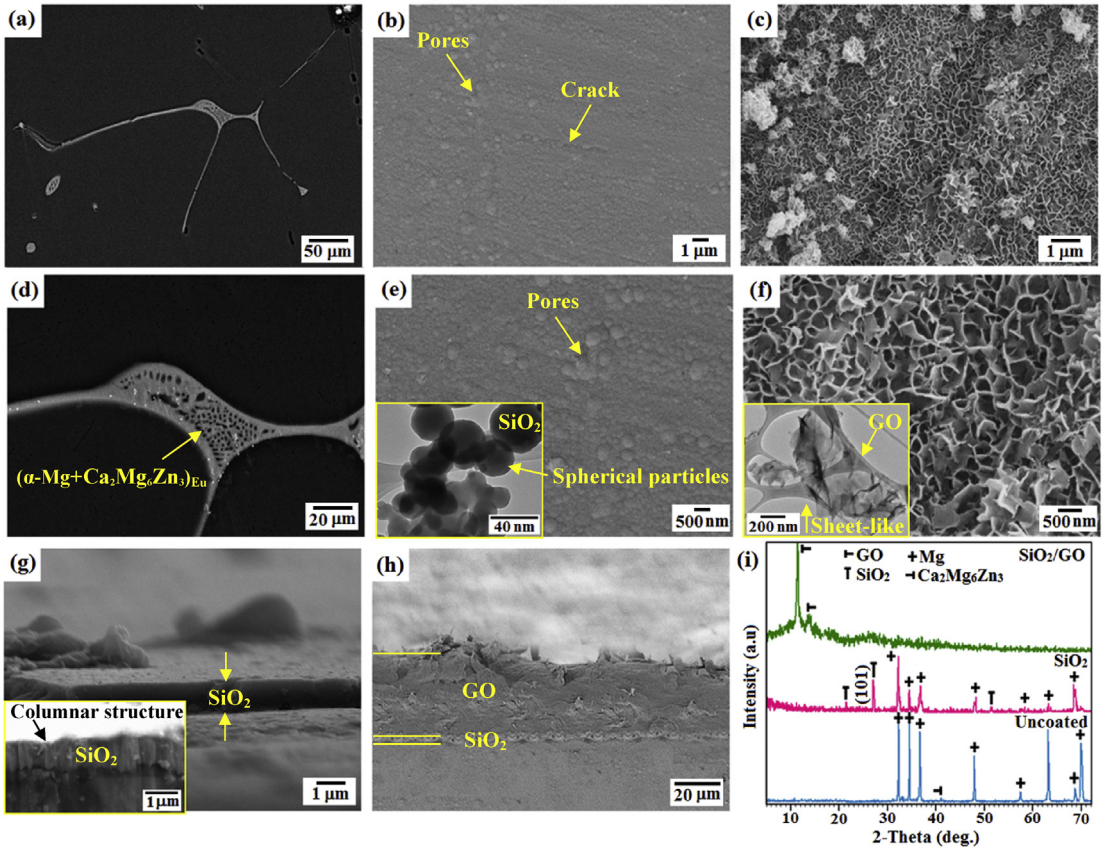


**Fig. 1.** Surface morphology of (a,d) uncoated Mg alloy, (b,e) single-layer $SiO_2$ coated and (c,f) bi-layer $SiO_2$/GO coated and cross sectional SEM micrographs of (g) single-layer $SiO_2$ coated and (h) bi-layer $SiO_2$/GO coated and (g) X-ray diffraction patterns of uncoated and coated Mg alloy samples.