Hydroxyapatite/poly(ether imide) micro-patterned protective coating on magnesium for biomedical applications

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Statement of Purpose: Magnesium (Mg) has a great potential as a biodegradable implant material due to its favorable combination of mechanical properties, biodegradability and biocompatibility [1]. However, notwithstanding these beneficial characteristics, rapid corrosion of Mg in physiological environments has limited its clinical use. In order to mitigate fast degradation of Mg, protective coating layers have been proposed using various polymers, bioceramics or their composites, but both mechanical stability and bioactivity of those coating layers on Mg have not been achieved at the same time [2]. Thus, in this study, we have introduced micro-patterned hydroxyapatite (HA) and poly(ether imide) (PEI) coating on Mg to improve both coating stability and bioactivity, where PEI tolerates the deformation of the Mg substrate and HA improves bioactivity of the coating layer.

Methods: Pure Mg plates were polished up to 4000 grit with SiC papers. Prior to the coating process, the designed microdot array-structure was developed on the Mg by photolithography. Next, the samples were treated in Ca/P solution to form HA as described in [3]. Then, PEI was spin-coated on Mg with HA micro-pillars using 12.5 wt% PEI solution. Computer simulation and corrosion test of coated Mg were performed so as to analyze the patterning effect on coating stability after deformation ($\varepsilon = 0.04$). Bioactivity of coating layers on Mg was evaluated via *in vitro* cell tests using MC3T3-E1 cells. Cells were cultured on coated Mg surfaces for 1 h, and were observed by SEM.

Results and Discussion: HA micro-pillars with a diameter of ~9 μm and a height of ~1 μm were uniformly fabricated with the interspacing distance of ~ 9 μm on the Mg surface and were well embedded in the PEI matrix as shown in **Fig. 1**. This hybrid coating layer was found to be sufficiently flexible under significant deformation of the underneath Mg substrate. **Fig. 2A** exhibits three different coating layers made of pure HA, pure PEI and patterned HA/PEI under tension at $\varepsilon = 0.04$. The relatively brittle HA appeared to have cracks while PEI and hybrid coatings tolerated the deformation. The corresponding simulation result that predicted the strain distribution on the hybrid coating at $\varepsilon = 0.04$ clearly shows that strain concentrates within PEI in between HA micro-pillars. Even though the elevated strain of PEI significantly exceeded the applied strain, 4%, flexibility of PEI allows large deformation without any prominent cracks. After deformation, all coated Mg samples were immersed in simulated body fluid (SBF) to observe the coating stability of each sample. Even after elongated, the coating layers containing PEI protected the underneath Mg from rapid degradation (**Fig. 2C**). Cells on the patterned hybrid surface were found to be well spread on the HA micro-pillars, utilizing those pillars as a center of attachment on the surface (**Fig. 3**).

Conclusions: The micro-patterned HA/PEI was successfully fabricated on Mg via sequential processes including photolithography patterning, selective HA formation and PEI spin coating. The HA/PEI patterned coating allows deformation of underneath Mg substrates without any surface cracks, maintaining the coating stability in the physiological environments. Additionally, the HA micro-pillars of the hybrid coating likely promote cell affinity as a center of cell attachment.

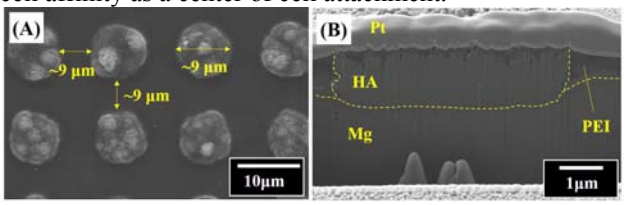

Figure 1. (A) Surface and (B) cross-section morphologies of micro-patterned HA/PEI coating layer on Mg surface.

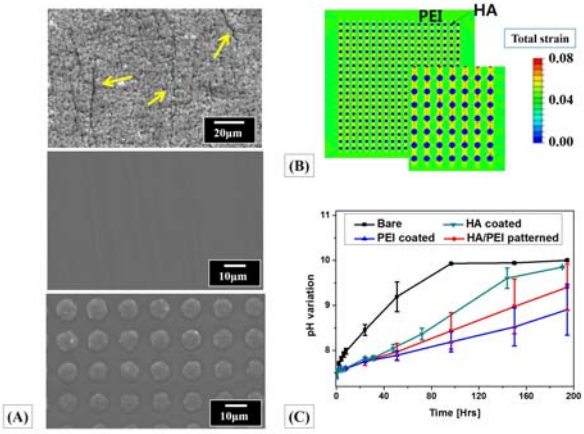

Figure 2. (A) Surface morphology of HA coated, PEI coated, and HA/PEI micro-patterned Mg after deformation ($\varepsilon = 0.04$), (B) simulated true strain distribution of HA/PEI patterned layer on Mg at $\varepsilon = 0.04$ and (C) pH variation of Mg soaked in SBF after deformation.

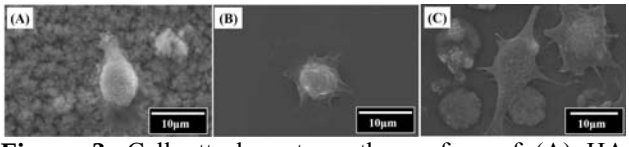

Figure 3. Cell attachment on the surface of (A) HA coated, (B) PEI coated, and (C) HA/PEI micro-patterned Mg after cultured for 1hr.

References:

1. Staiger MP, Biomaterials. 2006;27:1728-34
2. Lu P, J Biomed Mater Res B Appl Biomater, 2011;96:101–9.
3. Kim, S.M., J Biomed Mater Res A, 2014;102A:429-441