

## A Quick Biomimetic Method for Hydroxyapatite Coating with Gradient Structure

Fei Peng,<sup>1</sup> Montgomery T. Shaw,<sup>1,2</sup> James R. Olson,<sup>3</sup> Mei Wei<sup>1,\*</sup>

<sup>1</sup>Department of Chemical, Materials, and Biomolecular Engineering

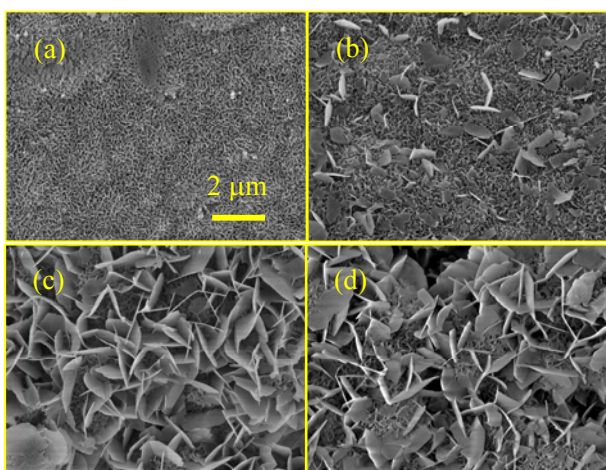
<sup>2</sup>Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269, USA

<sup>3</sup>Teleflex Medical, 1295 Main Street, P. O. Box 219, Coventry, Connecticut 06238, USA

**Statement of Purpose:** Human bone is an organic-inorganic hybrid and the inorganic component is mainly hydroxyapatite (HA), which comprises 65-70 wt% of the bone.<sup>1</sup> To mimic the components of nature bone, biomimetic coating method has been used to prepare HA-mineralized biopolymer composites for bone tissue engineering.<sup>1</sup> Unfortunately, the traditional biomimetic method requires a long time, days to weeks, to form the coating.<sup>1</sup> In this work, a modified biomimetic method was used to generate HA coating on poly(L-lactic acid) (PLLA) substrate within 1-6 h at a mild condition. Thus generated HA coating demonstrates a gradient structure with a dense coating adjacent to the substrate and a porous coating on the surface.

**Methods:** PLLA fibres (diameter=52  $\mu\text{m}$ ) were immersed in a modified simulated body fluid (m-SBF) at 60 °C for 1 to 6 h to attain HA coatings.<sup>2</sup> The  $\text{Ca}^{2+}$  concentration change in the m-SBF solution was measured using atomic absorption spectroscopy. The composition and morphology of the coating were characterized using XRD and FESEM, respectively.

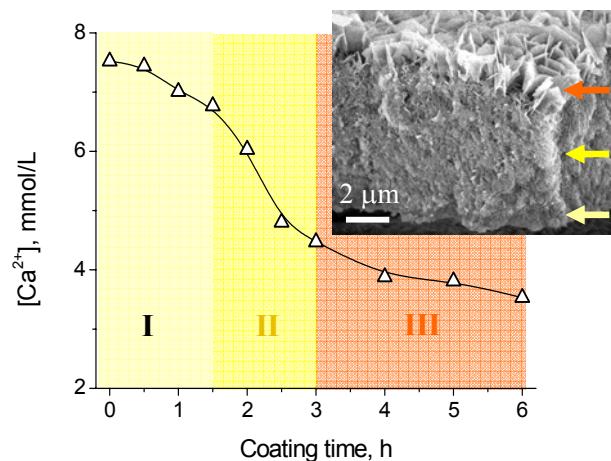
**Results:** Homogenous apatite coating with different topographies was formed on PLLA fibers at various coating forming times. The coating formed at 1 h was dense (Figure 1-(a)), while that formed at 2 h was porous with some large platy-shaped HA crystals scattered on the top (Figure 1-(b)). The surface of the coating formed at 3 and 4 h demonstrates a more porous structure composed of larger HA crystals than those formed at earlier time points (Figure 1-(c) and (d)). The XRD results indicate that pure HA coating was attained at all time points.<sup>2</sup>



**Figure 1.** Topographies of biomimetic HA coating formed after a coating time of (a) 1 h, (b) 2 h, (c) 3 h and (d) 4 h.

As the HA coating is formed, the concentration of  $\text{Ca}^{2+}$  in the m-SBF decreased from 7.5 to 3.8 mmol/L at different rates (Figure 2). The coating process can be

divided into three stages. Stage I: 0-1.5 h, HA coating grew slowly at a high  $\text{Ca}^{2+}$  concentration. A thin but dense HA layer was formed (indicated by the light yellow block and arrow). Stage II: 1.5-3 h,  $\text{Ca}^{2+}$  concentration decreased at a faster rate due to the rapid growth of the HA coating. The coating formed at Stage II was much more porous and thicker than that formed at Stage I (yellow block and arrow). Stage III: 3-6 h, HA coating grew very slowly and the  $\text{Ca}^{2+}$  concentration leveled off around 3.8 mmol/L. The coating layer formed at this stage was also thin but very porous due to large HA crystals formed at a low  $\text{Ca}^{2+}$  concentration (orange block and arrow).



**Figure 2.** The profile of  $\text{Ca}^{2+}$  concentration in m-SBF during a 6-h coating process. The inserted FESEM image shows the cross-section of the coating obtained after 6 h.

**Conclusions:** Pure HA coating with a gradient structure was formed on PLLA substrate after a 1-6 h immersion in an m-SBF at 60 °C. The coating process could be divided into three stages. At Stage I, a thin, dense coating layer was formed at a low rate but high  $\text{Ca}^{2+}$  concentration. At Stage II, a much thicker coating was formed within a short time period but demonstrated a more porous morphology. At Stage III, the coating remained to be porous due to the growth of the HA crystals into large crystals at a low  $\text{Ca}^{2+}$  concentration. This coating method can also be applied to other substrates, such as titanium plates.<sup>3</sup>

### References:

1. Tanahashi, M; Yao, T; Kokubo, T; Minoda, M; Miyamoto, T; Nakamura, T; Yamamuro, T. *J Am Ceram Soc* 1994;77(11):2805-2808.
2. Peng, F; Olson, JR; Shaw, MT; Wei, M. *J Biomed Mater Res B*. 2009;88B:220-229.
3. Qu, HB; Wei, M. *J Biomed Mater Res B*. 2008;87B:204-212.