Modification of Ti6Al4V Substrates with Well-defined Zwitterionic Polysulfobetaine Brushes for Improved Surface Mineralization

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Osteoconductive mineral coatings are beneficial for improving the osteointegration of metallic orthopedic/dental implants, but achieving adequate structural integration between the surface minerals and underlying metallic substrates has been a significant challenge. Here, we report covalent grafting of zwitterionic poly(sulfobetaine methacrylate) (pSBMA) brushes on the Ti6Al4V substrates to promote the surface-mineralization of hydroxyapatite with enhanced surface mineral coverage and mineral-substrate interfacial adhesion. We first optimized the atom transfer radical polymerization (ATRP) conditions for synthesizing pSBMA polymers in solution. Well-controlled pSBMA polymers (relative molecular weight up to 26,000, PDI = 1.17) with high conversions were obtained when the ATRP was carried out in trifluoroethanol/ionic liquid system at 60 °C. Applying identical polymerization conditions, surface-initiated atom transfer radical polymerization (SI-ATRP) was carried out to graft zwitterionic pSBMA brushes (PDI < 1.20) from the Ti6Al4V substrates, generating a stable superhydrophilic and low-fouling surface coating that inhibited non-specific protein absorptions without compromising the bulk mechanic property of the Ti6Al4V substrates. The zwitterionic pSBMA surface brushes, capable of attracting both cationic and anionic precursor ions during calcium phosphate apatite mineralization, increased the surface mineral coverage from 32% to 71%, and significantly reinforced the attachment of the apatite crystals on the Ti6Al4V substrate. This facile approach to surface modification of metallic substrates can be exploited to generate multifunctional polymer coatings and improve the performance of metallic implants in skeletal tissue engineering and orthopedic and dental care.