Electrodeposition of organic-inorganic films for biomedical applications

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Electrochemical methods have been developed for the deposition of biopolymer films containing hydroxyapatite, and other bioceramics, such as titania, silica and bioglass. Different electrochemical methods have been utilized for the deposition of natural biopolymers, such as chitosan, alginate and hyaluronate. Chitosan was protonated and dissolved in acidic solutions and then deposited cathodically. In this approach the charge neutralization of cationic chitosan in the high pH region at the electrode surface resulted in the precipitation of insoluble chitosan. Electrodeposition of alginic acid was performed from sodium alginate solutions. In this method the pH decrease at the anode surface resulted in the charge neutralization of alginate macromolecules and the fabrication of alginic acid films on anodic substrates. A similar approach has been utilized for the deposition of hyaluronic acid from the sodium hyaluronate solutions. It was demonstrated that cathodic and anodic deposition methods can be used for the deposition of other biopolymers.

Nanoparticles of hydroxyapatite were prepared by a chemical precipitation method. Precipitation was performed at 70 °C by the slow addition of a 0.6 M ammonium phosphate solution into a 1.0 M calcium nitrate solution. The pH of the solutions was adjusted to 11 by NH_4OH. Stirring was performed during 8 h at 70 °C and then 24 h at room temperature. The precipitate was washed with water and finally with ethanol. The average length of the needle-shape HA crystals, prepared by this method, was about 150 nm and the average aspect ratio was 8. The composite films containing HA nanoparticles in chitosan, alginic acid and hyaluronic acid matrix were prepared on stainless steel, Ti and NiTi alloy substrates. The results of thermogravimetric analysis showed that hydroxyapatite content in the polymer matrix was varied in the range of 35-80 wt% by variation of hydroxyapatite or polymer concentration in the solutions. The deposition yield was studied at different deposition conditions. It was shown that film thickness can be varied in the range of 0.1-200 microns by variation of the deposition time in the range of 1-10 min and deposition voltage in the range of 10-60 V. The composite films were prepared as monolayers or multilayers containing hydroxyapatite-polymer layers, separated by the layers of pure polymer.

The co-deposition of inorganic materials with biopolymers resulted in the fabrication of novel composite materials containing bioactive glass and other bioactive materials, such as silica and titania in a polymer matrix. Electrochemical techniques have been also applied for the fabrication of materials of graded composition (FGM) containing biopolymers, hydroxyapaite and other bioceramics and bioglass. Electrochemical impedance spectroscopy and potentiodynamic polarization studies showed that the composite coatings provided corrosion protection of the metallic substrates in simulated body fluid solutions. The use of biopolymers enabled the room temperature processing of the coatings, eliminating the problems related to the sintering of hydroxyapatite and other bioceramics. Moreover, the method enabled the incorporation of drugs and proteins in the composite material. Electrochemical strategies have been developed for the deposition of composite films containing heparin and albumin in a biopolymer matrix. The room temperature processing offers a possibility of co-deposition of other functional materials and fabrication of advanced nanocomposite coatings for biomedical applications.

New deposition methods were developed for cathodic deposition of chiral biopolymers, such as poly-l-lysine and polyl-ornithine. As an extension of these investigations, the composite films, containing HA nanoparticles and other functional biomaterials in the matrix of chiral biopolymers were obtained and investigated. Further development of new deposition methods resulted in the development of electrophoretic strategies and deposition mechanisms for the deposition of linear polyethylenimine, polypyrrole, polyetheretherketone, polyacrylic acid.

Fundamental mechanisms were developed for the co-deposition of enzymes and proteins with various biopolymers. We discovered a possibility of electrophoretic co-deposition of halloysite nanotubes with cationic and anionic biopolymers, such as chitosan, poly-l-lysine and polyl-ornithine, alginic acid, hyaluronic acid, polyacrylic acid. The halloysite nanotubes can be loaded with drugs and antimicrobial agents for the controlled release.

The new composite materials are prtomising for applications in biomedical implants and biosensors. We investigated functional properties of new materials, fundamental deposition mechanisms and kinetics of deposition.