

## Electrochemically Preparation of HA/Collagen Composite Coatings and Its Formation Mechanism

Yanli Xu, Hui Wang, Changjian Lin

State Key Laboratory for Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

Hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , HA) is the main mineral component of human hard tissues. It has great bioactivity and biocompatibility, and after implanting, it can form a kind of osteal bond with the organic tissues within a short time. Collagen existing in the extracellular matrix is an essential component of the connective tissue and it has excellent biocompatibility, complete biodegradability, low immunity and low antigenicity. And it can protect and support human tissue, enhance the tensile strength of bond and its viscosity and shows special biomechanics. Natural bone consists of a kind of inorganic/organic composite assembled by ordered nano-HA and collagen protein, in which the HA crystal diameter is about 20 nm and the length is about 60 nm. The c-axis of the crystal grows along the collagen 3D helical axis and it has special nano-micro two level of structure. At present, some research groups have done a mass of research about HA/collagen composites by using coprecipitation methods, biomimic methods, and et al. But these composites cannot completely meet the needs of the heavy load part in the body. In this work, we mimic the basic composition and structure of bone and combine the advantages of the coating and the Ti substrate to achieve an excellent bioactive and mechanical bone substitute material.

In this work, an electrochemical co-deposition technique in low concentration system has been developed to prepare HA/collagen and HA/chitosan composite coatings on Ti substrate. Meanwhile, we also tried to change reaction conditions to find formation mechanism of the nano-micro porous structure, which is explained by a proposed concept of "Bubble Template".

The electrolyte contained  $10^{-4}$  mol/L  $\text{CaCl}_2$ ,  $\text{NaH}_2\text{PO}_4$  and 0.1 mol/L NaCl with Ca/P ratio 1.67, in which collagen concentration was 0.1~0.3mg/mL and pH value was adjusted to 6.0~6.3 by 0.1 mol/L NaOH. The SEM, AFM, XRD, FTIR and XPS spectroscopic measurements were performed to characterize the morphologies, chemical composition and crystalline structures of the composite coating. It is found that the composite coating exhibits a homogeneous and porous morphology with nano-micro structure. Compared with the pure HA coating, the peak intensity of the (002) crystal face of the composite coating in the XRD measurements is greatly weakened, due to the block effect of collage during the nucleation and growth of HA crystallizing process. The FTIR spectroscopy exhibits the typical peaks of the collagen: the amide I band and the amide II band, and their peaks derived a little from the same peaks of the pure collagen, indicating that there is a kind of chemical bond between collagen and HA. The XPS results indicate that the C and N atom content increases greatly. The in vitro cell culture and MTT tests reveal that, compared with pure HA and pure Ti, the HA/collagen composite coating exhibits best biological properties. And the bonding strength of the hybrid coating is improved markedly.

The effects of substrate materials, additives, reaction temperature and deposition time on nano-micro porous structure were also studied. From silicon slice with gold

film, Ge wafer to pure Ti plate, the smoothness decrease in sequence and the addition of additives made viscosity of the electrolyte increased. The experiments indicate that the smoothness of the substrate, viscosity of the electrolyte, reaction temperature and deposition time are important factors in nano-micro porous structure. A concept of "Bubble Template" is proposed to explain the formation mechanism of nano-micro porous structured HA/collagen coating on Ti substrate.

The composite coating of HA/chitosan has also been prepared by electrochemical co-deposition method. The preliminary characterization has been carried out by SEM and AFM images, and it is shown that the composite coating of HA/chitosan has ordered uniform porous tow-level structure. The EDS spectrum and the sharp peaks of the XRD patterns indicate that the main components is high crystal HA. The bonding strengths between the HA/chitosan coating and the titanium substrate has been improved in a certain extent.