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### SURFACE FUNCTIONALIZATION OF METAL MEDICAL DEVICES BY PLASMA POLYMERIZATION

Marco Morra\*, Clara Cassinelli, Linda Cahalan (1), Patrick Cahalan (1)

Nobil Bio Ricerche, Str. S. Rocco 36, 14018 Villafranca d'Asti, Italy,

e-mail: [mmorra@tin.it](mailto:mmorra@tin.it)

(1) Percardia, Merrimack, Heron Cove Office Park, 10 Al Paul Lane, Suite 202,

Merrimack, NH 03054, USA

Despite progress of polymeric and biodegradable implant materials, metal medical devices still play an important role for many applications. Titanium dental implants and stainless steel coronary stents are possibly among the most relevant and intriguing examples. The control of the interfacial interaction at the device/host-tissue interface is a key issue of today biomedical devices science and technology<sup>1</sup>. Metal implants surfaces are in general covered by an oxide overlayer, which is not particularly suitable to direct interfacial interactions involving biomolecules. Surface modification of metal medical devices by covalent linking of suitable biomolecules is an interesting opportunity, yet metal surfaces do not bear chemical functionalities that can be straightforwardly used for coupling reactions. As of today, and despite some shortcoming, silane chemistry is still the preferred way to surface functionalization aimed at further “biochemical” modification of metal surfaces<sup>2</sup>. Surface functionalization by plasma deposition offers a very interesting alternative to silane chemistry, and it is finding more and more applications in the surface modification of metal medical devices. In this communication we present our results on two approaches to the surface functionalization and immobilization of biomolecules by Rf or microwave plasma deposition on titanium dental implants and stainless steel coronary stent surfaces. These approaches are largely taken from analogous work performed on polymeric substrates. Yet, when it come to metal devices, the substrate-plasma deposited film adhesion in aqueous media plays a specially important role. Both the coupling reaction and

the actual implant site involve aqueous environment, and the interfacial-energy-driven delamination of the deposited films, or other post-deposition hydrolytic reactions, can alter film properties and impair performances.

The first approach we discuss involves the possibly simplest plasma deposition process, that is the deposition of a hydrocarbon layer from propene or other hydrocarbon precursors on metal surfaces. The organic film deposited on the metal surface makes the latter “polymer-like” and allows the application to metal devices of typical reactions of polymer surfaces modification, such as Ce(IV) ion induced grafting<sup>3</sup>. In particular, grafting of an acrylic acid (AA) hydrogel layer to the plasma-deposited hydrocarbon film yields a carboxyl group-rich surface that can be subjected to further coupling reactions. Extensive characterization by XPS, ATR-IR, atomic force microscopy and AFM force-separation curves is used to check the plasma film-substrate adhesion, its dependence on the deposition conditions and the occurrence of side-reactions induced by the aqueous environment. The second approach involves the formation of carboxyl groups or amino functionalities on stainless steel surfaces of stents by pulsed plasma deposition from acrylic acid or allylamine. While both of these processes are rather standard treatments, the nature and geometry of the substrate, together with the aqueous working environment, create special challenges. In particular, there is a strong dependence of the stability in water of the surface functionalized layer on the power and time of the on/off cycles. The coupling of heparin and other glucosaminoglycans to the stent surface requires a high density of amino groups, which can be achieved by a low on/off ratio. Yet, these same conditions, which work very well on standard flat samples, are not optimal when it comes to the lateral homogeneity on surfaces with complex geometry, such as that of coronary stents. In this case, it is shown that the increase of the on/off ratio can improve lateral homogeneity, while keeping the surface density of functional groups high enough to achieve effective coupling.

## References

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