

## Effect of the surface structure of hydroxyapatite nanoparticles on the orientation of adsorbed proteins

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The development of biomaterials with well-defined relationship between surface features and behavior towards biomolecules is among the main targets of modern biological surface science [1]. In this respect, we considered Hydroxyapatites (HA) nanoparticles, which are of actual interest as bone fillers for applications in orthopedics and dentistry [2], and bovine serum albumin (BSA), one of the most exploited proteins for this kind of investigation [3]

In previous works we established that the most abundant surfaces exposed by lab-made HA nanoparticles (NP) are of the {010} type. The actual terminations depend on the interruption of the sequence of ...-A-B-A-A-B-A-A-B-A-... layers constituting the bulk of HA, where the A and B layers have the  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{Ca}_4(\text{PO}_4)_2(\text{OH})_2$  chemical compositions, respectively. Thus, for such facets the exposed layers can result in ...-A-B-A, ...-A-A-B, or ...-B-A-A termination, giving rise to the stoichiometric HA(010) and the nonstoichiometric HA(010)\_Ca-rich and HA(010)\_P-rich surfaces, respectively [4]. Thus, in this study, the main structural property investigated was the ratio of Ca<sub>rich</sub> and P<sub>rich</sub> surfaces exposed and its effect on the adsorption of BSA.

By adopting a recently established method [4], the (010)-Ca<sub>rich</sub>: (010)-P<sub>rich</sub> ratio for two types of nano-HA (hereafter HA1 and HA2) was determined by probing the surface of nanoparticles by IR spectroscopy of adsorbed CO. The results indicated that such ratio was 2:1 and 1: 2.2 for HA1 and HA2, respectively. BSA was then adsorbed following the same protocol on the two nano HA samples, attaining in both cases the complete coverage of surfaces accessible to protein molecules. Noticeably, an opposite change in the value of the  $\zeta$ -potential as a consequence of BSA adsorption was observed for HA1 and HA2. Such a difference can be quite unambiguously related to a difference in the domain(s) of adsorbed proteins exposed to the aqueous medium, which, in turns, is(are) that(those) not involved in the contact with the HA surfaces. Thus, such difference in the orientation of adsorbed proteins appeared related to the only difference in surface feature between the two HA samples, i.e. the (010)-Ca<sub>rich</sub>: (010)-P<sub>rich</sub> ratio. In agreement with this statement, the behavior of BSA on HA2 nanoparticles, mainly exposing (010)-P<sub>rich</sub> surfaces, which exhibit a tricalcium phosphate (TCP) structure, resulted similar to the findings obtained when adsorbing BSA on a HA sample actually containing a significant amount of TCP nanoparticles.

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