Hydroxyapatite Platelets in Physiological Environment

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Statement of Purpose: A carbonated form of hydroxyapatite (HA) $[Ca_{10}(PO_4)_6(OH)_2]$ is one of the most abundant materials in mammal bone. It crystallizes within the spaces between tropocollagen protein chains in an aqueous solution and strengthens the bone tissue. An emerging application of synthetic HA is bone repair and replacement. Although HA is bioactive, it is a brittle material and by itself does not meet the requirements of a suitable bone replacement. Instead, Ti and its alloys have been primary implant materials for several decades combining high mechanical strength and biocompatibility. However, new approaches are sought to initiate a faster biological response, improve adhesion between the bone and the implant, provide a scaffold for bone growth and support the bone healing process by guiding bone tissue over the implant's surface. To meet these demands coating techniques were developed to cover metallic implants with thin layers of HA. Therefore, to improve the implants' physiological properties the interaction between the HA coating and biological environment is of particular interest. Bulk electronic and chemical properties of HA were studied theoretically recently [1,2]. The absorption of H_2O molecules and amino acids of the tropocollagen chains at HA surfaces remains an area of active research [3].

We analyze the electronic properties, surface energetics and reactivity of HA for different orientations and terminations. Considering HA slabs with highly reactive surfaces we build atomistic models of HA covered with up to one monolayer of water. We also analyze the influence of mixing Si in HA on the crystal's thermodynamic stability and electronic properties.

Methods: We use density functional theory as implemented in the VASP code. Projector augmented wave pseudopotentials and the generalized gradient approximation are used to solve the Kohn-Sham equations [4]. The studied surface models are relaxed using the conjugate gradient method for energy and force minimization. To analyze the surface reactivity of our HA surface models we apply the frontier orbital approach.

Results: We calculate a theoretical surface phase diagram of HA. In our study we consider Ca atoms, OH and PO_4 molecules to be the building blocks of the crystal. Therefore, by varying the experimental conditions from for example, being OH poor to OH rich (and similar for Ca and PO_4) we can identify which surface terminations are thermodynamically stable under a particular environment as shown in Fig 1. We consider the crystallographic orientations (001), (010) and (100) with different terminations. The surface energy in Fig. 1 is color coded. The black lines are phase boundaries at which several surface terminations are simultaneously stable. The two stable surfaces over the widest chemical range are oriented in the (010) and (100) direction each terminated with three Ca ions and three PO_4 molecules per unit surface (6 and 11 in the diagram). Their

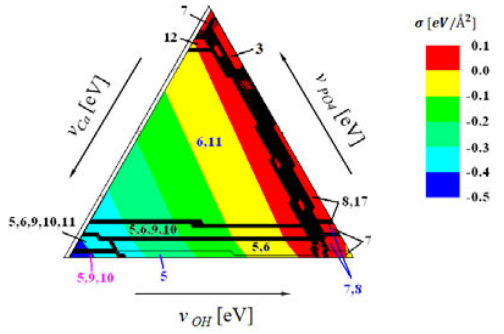

Fig. 1: Ternary phase diagram for stable surface models

highest occupied and lowest unoccupied electronic states at the surface atomic sites are separated by large energy gaps suggesting low surface reactivity. Using the electronic structure analysis, we identify surface model 12 depicted in Fig. 2 as highly reactive.

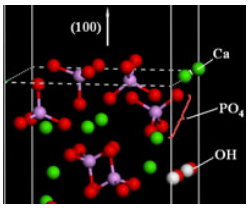

Fig. 2: (100) surface model of high reactivity.

Oriented in (100) direction the surface consists of three PO_4 and two Ca ions per unit surface. We study the interaction between H_2O molecules and this surface for coverage up to one monolayer of water. Water stretches the bond angles of surface phosphates up to 10° and shows significant morphological influence on phosphates located as deep as 10Å in the bulk.

In a separate bulk study we find that Si preferably mixes substitutionally on the P-site of HA. The SiO_4 ions are more negatively charged than PO_4 (-4*e* vs. -3*e*) suggesting a possible enhancement in the interaction strength between H_2O molecules and SiO_4 terminated surfaces.

Conclusions: We find two dominant surfaces which are most stable over the widest chemical range. However, we expect them to show little surface reactivity. A theoretical analysis suggested a reactive HA surface subsequently used in our H_2O adsorption studies. Water deposition not only changes the electronic properties of the surface but also shows significant influence on the crystal's morphology reaching deep into the bulk region.

References:

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