



Full Length Article

First-principles study on the hydroxyl migration from inner to surface in hydroxyapatite

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ABSTRACT

Understanding to the surface structure of hydroxyapatite (HAp) is crucial for the design of HAp-based biomaterials. While most bioactive HAp materials have disordered structures, the ordered surface structures relaxed from HAp crystal are commonly used for studying their interaction with biomolecules. Using a combined approach of molecular dynamics simulated annealing simulations and density functional theory calculations, we proposed a disordered surface structure model for HAp. In this model hydroxyls beneath the surface move outward and cover the exposed calcium ions. The destabilization caused by hydroxyl vacancy is compensated by the stabilization of hydroxyl coverage. The Ca-exposed surface with strong electrophilicity changes into the hydroxyl- and phosphate-covered surface with moderate activity. The new surface model would be useful for regulating the surface activity of HAp-based biomaterials.

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1. Introduction

Hydroxyapatite (HAp), the predominant inorganic component of mammalian teeth and bones [1,2], is often used as bioactive materials for tissue repair and remodeling because of its good capabilities in biocompatibility and osteoinductivity [3,4]. Numerous studies [5–11] have indicated that the interfaces between biomolecules and HAp inorganic materials are important in many fields including biomaterials science and biomineralization. The growth or inhibition of teeth and bones is relevant to the biomolecule–HAp interaction at their interfaces [12–15]. Knowledge about the HAp surface structural properties and dynamic basis is therefore fundamental to understand the interaction mechanism between HAp and physiological environment [16–20].

The importance of the surface structures of HAp has long been addressed [21–23]. Many studies have focused on the surface activities of HAp, such as its anisotropic growth kinetics [24,25], adsorption toward biomolecules [12,26–28] and modifications with doped ions [29,30]. In addition to numerous experimental studies [21–23,31], density functional theory (DFT) calculations and molecular dynamics (MD) simulations at force-field level have been widely used to investigate the surface structure and activity of HAp [32–37], which are complicated due to their multiple orientations and various terminations. While the phosphate- and

calcium-terminated HAp surfaces were concerned in most studies, some experimental and computational studies revealed the existence and importance of HAp surface with hydroxyl termination [38–42].

Sato et al. [38] observed with high-resolution electron microscopy (HRTEM) that both hydroxyl columns beside calcium sites and PO₄ tetrahedra are exposed on the (1 0 0) surface. Using nuclear magnetic resonance (NMR) and Fourier Transform Infrared Spectroscopy (FTIR), Osman et al. [39] and Boujday et al. [40] found that the surface hydroxyls have different distribution from those in bulk. Diallo-Garcia et al. [41] verified that hydroxyls on the HAp surface are the most likely basic active sites involved in many catalytic reactions with FTIR. Developing a NMR spectroscopy method, Isobe et al. [42] found OH groups present in the disordered HAp surface layer and consumingly interact with Ca²⁺ sites.

Computationally, Slepko et al. [43] found that the OH-rich condition is the most significant surface reconstruction stabilizing the surface using DFT calculations with PW91 functional. Corno et al. [44] and Rimola et al. [45] predicted at B3LYP level that the HAp (0 0 1) surface is terminated with hydroxyl ions and studied its absorption toward serine. Astala et al. [6] and Almora-Barrios et al. [46] studied the hydroxyl-terminated (0 0 1) and (0 1 0) facets of HAp, revealing that the disordering of hydroxy groups on (0 1 0) is more notable than those on (0 0 1). Ma et al. [16] and Zeglinski et al. [47] studied the HAp surface stability with DFT calculations and found the hydroxyl-terminated (0 1 0) surface is the most stable, and the (0 0 1) and (0 1 0) surfaces with

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hydroxyl termination is immune to water molecules. Meanwhile, Leeuw et al. [48] and Lee et al. [49] investigated at a force-fields level the HAp (0 0 1) and (0 1 0) surface structures, revealing that the topmost surface hydroxyls distort and form hydrogen bonds (HB) with phosphates, while their oxygen atoms interact with the surface calcium ions. Bhowmik et al. [50] used the OH-terminated (1 0 0) and (0 0 1) surface as a model to study the adsorption of polyacrylic acid (PAAc) using MD simulations with consistent valence force fields (CVFF), exploring the interaction between the surface hydroxyls with PAAc.

Hydroxyl has two sources. Bone generates and grows in alkaline physiological environment that may provide hydroxyls to cover the calcium-exposed surface. In addition, the hydroxyls in HAp may migrate from inner to surface [39]. The latter case is of particular importance because the hydroxyls come from HAp itself in the preparation process and therefore affect the performances of HAp-based biomaterials. In the previous studies [51,52], we investigated the HAp surface structures by using simulated annealing MD approaches and found the hydroxyls inside move to surface and cover the surface calcium ions, forming a disordered surface layer which lowers the surface energy and stabilizes the surface structure. Our predictions unraveled one of the origins of experimentally identified disordered HAp surface layer. Other factors, such as formation of hydroxyl vacancy, substitution by other ions, interaction with environment, etc., may also disorder the surface structure [43,53–58].

Although experiments [21,23,42,59–63] have identified that the HAp surface structure with bioactivity is highly disordered, the simplified surface models sliced directly from crystal were still used in many studies [6,32,44,64]. It is necessary to build a reasonable HAp surface model that matches with the experimental findings. While the direct detection for hydroxyl migration from inner to surface is infeasible currently, and our previous predictions [51,52] were based on the force-field level, we studied further in this work the hydroxyl migration on the HAp surface at the first-principles level. Since hydroxyl migration from inner to surface lasts long time in simulation, it is too demanding to complete the simulation for such a big system at first-principles level. Moreover, since the structures after simulated annealing at high temperature are disordered, the commonly used approach of cutting a small piece from the bulky structure produces a non-stoichiometric model. To overcome these difficulties, in this work we used a computational strategy in which the HAp surface was firstly simulated at force-field level and then its surface layer with stoichiometry was selected for DFT calculations. By this way, we verified at first-principles level that the hydroxyl migration from inner to surface is energetically favorable for HAp. In addition, the DFT calculations enabled us to assess the surface reactivity HAp that is difficult at force-field level. Hydroxyl groups have distinct reactivity from calcium and phosphate ions, which certainly have great influence on the performance of HAp-based biomaterials. Our calculations addressed further the importance of proper surface model of HAp.

2. Computational method

The slab surface models of HAp with (1 0 0) and (0 0 1) Ca-exposed facets were constructed by slicing the crystal structure with $2 \times 2 \times 2$ supercells. A 50 Å thick vacuum layer was applied to avoid the interaction between the adjacent slabs, as depicted in Figs. S1 and S2. A simulated annealing MD approach [65,66] was used to obtain the surface structures of HAp at the force-field level. During this step, the atoms in the bottom layers ($2 \times 2 \times 1$) were constrained, while those in upper layers were allowed to relax. The simulations were performed with an NVT ensemble

implemented in the LAMMPS program [67]. In our MD simulations, the surface structures were firstly relaxed for 100 ps at 300 K. Then, the temperature rapidly rose up to the target of 2400 K, which is well above the melting point (1923 K [68]) of HAp. After equilibration for 200 ps at 2400 K, the system was cooled with a stepped cooling pattern at a speed of 100 K/20 ps until it reached 300 K and then equilibrated for 100 ps. The details of simulated annealing MD process can be found in Refs. [51,52]. Finally, the annealed surface structures were sent to the next step for DFT study.

To balance between accuracy and cost in the DFT calculations, the annealed surface models were modified by removing the constrained atoms in the bottom layers ($2 \times 2 \times 1$), as displayed in Figs. S3 and S4. These models are labeled as Model A hereafter. In addition to the annealed structures, some other surface models were constructed for comparison. These additional models were constructed by slicing the HAp crystal and sent to DFT calculations without annealing. The Ca-exposed surface structure is labeled as Mode B. In Model C, the hydroxyls were artificially moved from inner to surface and covered the exposed Ca ions, as depicted in Figs. S3 and S4. A 15 Å thick vacuum layer perpendicular to the slab was applied in these surface models. Furthermore, the atoms in the bottom layer of the supercell were fixed, while all the atoms in the upper layer (88 atoms in total) were allowed to relax.

In the MD simulations, the PCFF force fields [69] was applied, which has the form of

$$U_{\text{total}} = U_{\text{inter}} + U_{\text{intra}} \quad (1)$$

where

$$U_{\text{inter}} = \sum_{ij} \frac{q_i q_j}{4\pi\epsilon_0 \gamma_{ij}} + \sum_{ij} \epsilon_{ij} \left[2 \left(\frac{\sigma_{ij}}{\gamma_{ij}} \right)^9 - 3 \left(\frac{\sigma_{ij}}{\gamma_{ij}} \right)^6 \right] \quad (2)$$

and

$$U_{\text{intra}} = \sum_{\text{bonds}} K_{\gamma,ij} (r_{ij} - r_{0,ij})^2 + \sum_{\text{angles}} K_{\theta,ijk} (\theta_{ijk} - \theta_{0,ijk})^2 \quad (3)$$

U_{inter} consists of 9–6 Lennard-Jones potential and Coulomb potential. In these equations, ϵ_0 and σ_{ij} are the vacuum dielectric constant and the nonbond diameter representing the van der Waals size of each atom type, respectively. r_{ij} is the distance between the i th and j th atoms with charges q_i and q_j , and ϵ_{ij} concerns with the polarization of each atom type in the first order approximation. The intra-atomic equation contains a quadratic potential for bond and angle stretching. $K_{r,ij}$ and $K_{\theta,ijk}$ are harmonic bond stretching and angle bending coefficient, respectively, $r_{0,ij}$ and $\theta_{0,ijk}$ are equilibrium bond length and angle, respectively. The parameters of atoms in HAp used in our computations are listed in Tables S1 and S2.

In the DFT calculations, the exchange-correlation energy of electrons was treated with generalized gradients approximation (GGA) of Perdew-Wang 1991 (PW91) functional and the projection augmented wave (PAW) type of pseudopotential [70], as implemented in the Vienna ab-initio simulation package (VASP) [71]. The cut-off energy was set to 500 eV in all the calculations. A Monkhorst–Pack k-point mesh of $2 \times 2 \times 1$ was applied for Brillouin zone sampling. Atom positions were optimized with the conjugate-gradient (CG) [72] method and the force convergence was set to 0.01 eV/Å. The DFT-D method of Grimme [73] was used to correct long-range dispersion interactions. Because of highly charged ions in the slab mode, a dipolar correction [74] along the normal direction of the slabs was used to avoid the polarization interaction between the slab and its periodic images.

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