Effect of van der Waals Interactions on the Adhesion Strength at the Interface of the Hydroxyapatite–Titanium Biocomposite: A First-Principles Study

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Supplementary Information

S1. Computational Model

We used the classical ReaxFF force field for generating a series of reasonable amorphous structures, and for the subsequent rough scanning (single point calculations on a grid at 0K) of the interface interaction between a-HAP and the a-TiO_2 surfaces. In practice, this means that we generated several hundreds of interface structures, which were energetically analyzed. For the actual DFT calculations, we used those ReaxFF-created interfacial models as input that were the most stable.

Then, we explored the interfacial bonding mechanism of a-HAP surface onto a-TiO_2. The obtained results revealed that the a-HAP / a-TiO_2 interface with two possible stacking positions (1_a-TiO_2 and 2_a-TiO_2) has a more preferable interaction and it is thermodynamically more

stable than the other interfaces (Please see Table 3 of Ref. 1 a-HAP / a-TiO_2(3) (1_ a-TiO_2(3) and 4_ a-TiO_2(3)).

Therefore, we used this interface model at two stacking positions as the initial structure for constructing the interfaces between the Si substituted a-HAP and a-TiO_2.

We created 12 geometry structures for the interface for one stacking position through the substitution of one P atom by one Si atom in each of the six PO_4 groups in a-HAP (a-Si-HAP) with the creation of OH-vacancies as charge compensation (Figure S1).

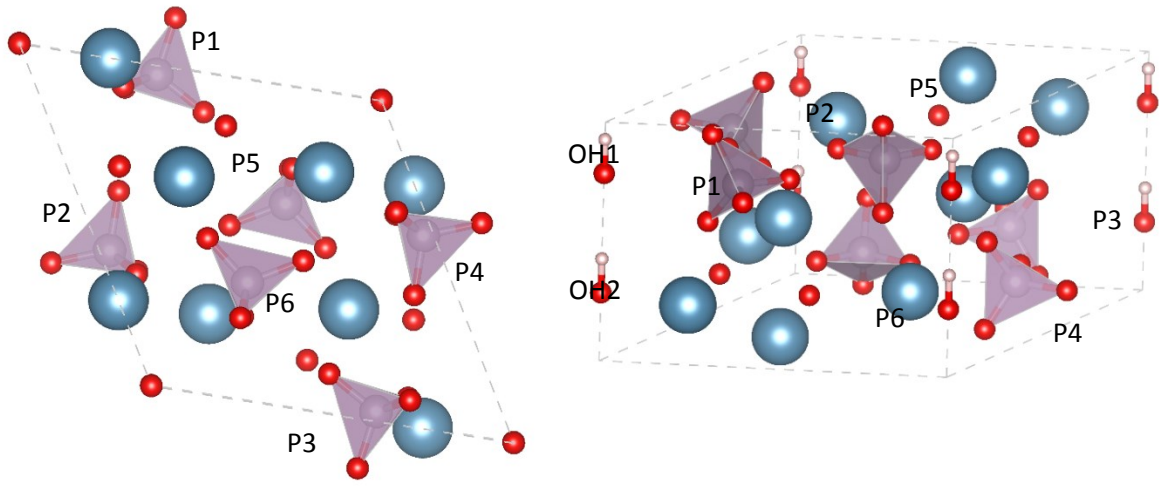

Figure S1. Schematic representation of the phase-pure HAP unit cell (Ca - blue, O - red, H - white, P - purple). The six phosphate atoms labelled P1-P6, and the two hydroxyl groups are OH1 and OH2.

The geometry of these partition boundaries was optimized in the VASP software package, after which the work of adhesion was calculated. The calculated W_{ad} of 24 geometries for a-Si-HAP / a-TiO_2 interface are listed in Table A1. The higher absolute value of the obtained W_{ad} is, the more stable the interfacial bonds. For the further calculation of the van der Waals forces, we have chosen the interface (the a-Si-HAP (P5, OH1) / 1_a-TiO_2 and the a-Si-

HAP (P5, OH2) / 2_a-TiO_2 interface at the initial stage), which gave us the best interaction at the interface (i.e., with higher W_{ad} value (Table S1)).

Table S1. Calculated Work of Adhesion for a-Si-HAP / a-TiO_2 interface as function of the substitution position.

system	W_{ad} (J/m^2)		system	W_{ad} (J/m^2)
1_a-TiO_2			2_a-TiO_2	
OH1			OH1	
P1	−2.466		P1	−2.322
P2	−2.272		P2	−2.268
P3	−2.118		P3	−2.147
P4	−2.278		P4	−2.337
P5	−2.785		P5	−2.395
P6	−2.305		P6	−2.149
OH2			OH2	
P1	−2.619		P1	−2.413
P2	−2.376		P2	−2.238
P3	−2.390		P3	−2.399
P4	−2.417		P4	−2.207
P5	−2.638		P5	−2.608
P6	−2.356		P6	−2.476

A detailed description of the construction of the considered interfaces and the amorphization procedure can be found in our previous work.[1,2]

References

(1) Grubova, I. Y.; Surmeneva, M. A.; Huygh, S.; Surmenev, R. A.; Neyts, E. C. Density Functional Theory Study of Interface Interactions in Hydroxyapatite/Rutile Composites for Biomedical Applications. *J. Phys. Chem. C* **2017**, *121*, 15687–15695.

(2) Grubova, I. Y.; Surmeneva, M. A.; Huygh, S.; Surmenev, R. A.; Neyts, E. C. Effects of Silicon Doping on Strengthening Adhesion at the Interface of the Hydroxyapatite–Titanium Biocomposite: A First-Principles Study. *Comp. Mater. Sci*. **2019**, *159*, 228–234.