

### S1. Verification of theoretically obtained isoelectric points

Our results of  $pH_{PZC}$  in the implicit solvation model were verified by comparing to an isoelectric point estimation obtained from another solvation model. The combination of the effective screening medium and the reference interaction site methods (ESM-RISM) implemented in QUANTUM ESPRESSO<sup>1</sup> was used because this framework can incorporate an open boundary condition in the direction normal to a surface plane. Another solvation model (Laue-RISM) was used for a HAp surface immersing in an aqueous solution<sup>2</sup>. The surface structures obtained from VASPsol were used for the simulation cells, and their solution layers were expanded to over 30 Å for the Laue-RISM calculation. The solvent system was set to an aqueous solution with 1 mol/L NaCl and a temperature of 300 K. Consequently,  $\varphi_{PZC}$  values with respect to that of the MgO {100} surface were calculated to be 0.9 V, 0.8 V, and 0.1 V for the N-pole {0001}, P-pole {0001}, and Ca-rich {10 $\bar{1}$ 0} surfaces, respectively. This result indicates that the {0001} and Ca-rich {10 $\bar{1}$ 0} surfaces have  $pH_{PZC}$  values around 5-6 and 11-12, respectively, by assuming that the MgO {100} surface shows a  $pH_{PZC}$  value of 12.3. In this respect, the estimated isoelectric points can confirm the anisotropy of the surface charge states on the {0001} and the Ca-rich {10 $\bar{1}$ 0} surfaces around neutral pH.

## S2. Ionic concentrations in the aqueous solution saturated with respect to HAp.

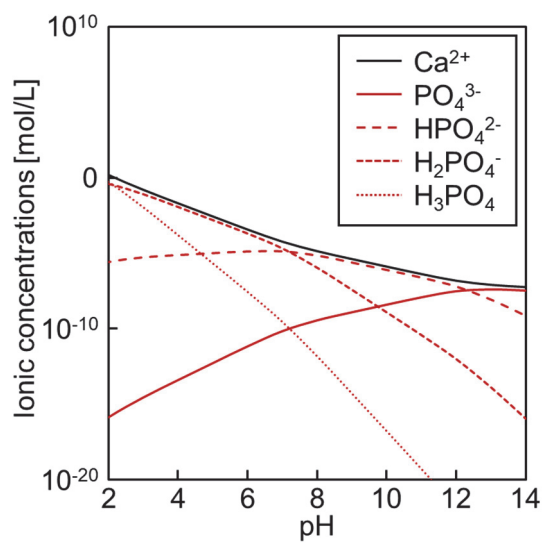


Fig. S1 Ionic concentrations in the HAp-saturated aqueous solution as a function of pH.

### **S3. Most stable surface terminations for binary compounds**

To determine  $\varphi_{\text{PZC}}$  values of the binary compounds, their most stable surfaces were examined. It was found that the surface structures with the lowest  $\Delta E_s$  value are  $\{100\}$  for MgO (0.66 J/m<sup>2</sup>),  $\{10\bar{1}4\}$  for calcite (0.04 J/m<sup>2</sup>) and  $\{\bar{1}011\}$  for  $\alpha$ -SiO<sub>2</sub> (1.17 J/m<sup>2</sup>) in the implicit solvation. These trends agree with previous experimental and theoretical studies<sup>3-45</sup>. For  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, both the  $\{0001\}$  and  $\{\bar{1}012\}$  surfaces are energetically favorable (1.12 J/m<sup>2</sup>). However,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is usually obtained in a normal air over 1000 K, and the  $\{\bar{1}012\}$  surface has by 0.09 J/m<sup>2</sup> a lower surface energy under vacuum than the  $\{0001\}$  surface. this trend also agrees with a previous experiment<sup>6</sup>. Assuming that the  $\{\bar{1}012\}$  surface is maintained in the aqueous solution, the  $\{\bar{1}012\}$  surface was used to calculate  $\varphi_{\text{PZC}}$ .

#### S4. Surface structure of the stoichiometric $\{10\bar{1}0\}$ surface relaxed under vacuum

As pointed in Sec. 3.1, our results showed that the stoichiometric  $\{10\bar{1}0\}$  surface has lower  $\Delta E_s$  ( $0.57 \text{ J/m}^2$ ) than the stoichiometric  $\{11\bar{2}0\}$  surface ( $1.02 \text{ J/m}^2$ ) under vacuum, which disagrees with a previous theoretical study<sup>7</sup>. Since the  $\Delta E_s$  value for the stoichiometric  $\{11\bar{2}0\}$  surface is similar to the previous result ( $1.25 \text{ J/m}^2$ ), our stoichiometric  $\{10\bar{1}0\}$  surface is likely to decrease its surface energy. Accordingly, surface atomic arrangement was investigated for the stoichiometric  $\{10\bar{1}0\}$  surface.

It was found that our stoichiometric  $\{10\bar{1}0\}$  surface are largely relaxed under vacuum, as is shown in Fig. S2. For the unrelaxed surface (Fig. S1(a)), the atomic structure has two O of  $\text{PO}_4$  with no O-Ca bonds (labelled A and B). On the surface relaxed under vacuum,  $\text{Ca}^{2+}$ (C) is displaced by  $2.4 \text{ \AA}$  with a large rotation of  $\text{PO}_4$ (D). The displaced ions form new O(A)-Ca(B) ( $2.26 \text{ \AA}$ ) and O(B)-Ca(C) ( $2.17 \text{ \AA}$ ) bonds, suggesting that the number of Ca-O bonds are increased at the stoichiometric  $\{10\bar{1}0\}$  surface. The surface relaxation thus leads to decreasing its surface energy, and as a result, the stoichiometric  $\{10\bar{1}0\}$  surface can more stable than the stoichiometric  $\{11\bar{2}0\}$  surface.

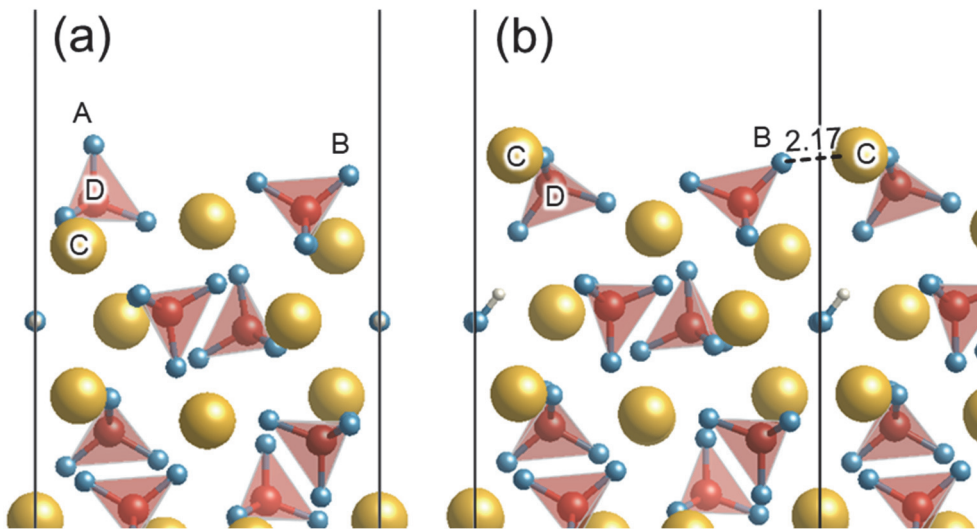


Fig. S2 The surface structure for stoichiometric  $\{10\bar{1}0\}$  (a) unrelaxed and (b) relaxed under vacuum.

## References

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