Direct Atomic-Resolution Imaging of Fluorine in Shark Teeth and Its Strengthening Function

ChunLin Chen[1], ZhongChang Wang[1], Mitsuhiro Saito[1], Tetsuya Tohei[2], Yoshiro Takano[3], and Yuichi Ikuhara[1, 2, 4]

[1]World Premier International Research Center, Advanced Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
[2]Institute of Engineering Innovation, The University of Tokyo, 2-11-16 Yayoi, Bunkyo-ku, Tokyo 113-8656, Japan
[3]Section of Biostructural Science, Graduate School of Tokyo Medical and Dental University, 1-5-45 Yushima, Bunkyo-ku Tokyo, 113-8510, Japan
[4]Nanostructures Research Laboratory, Japan Fine Ceramics Center, 2-4-1 Mutsuno, Astuta, Nagoya 456-8587, Japan

Structural characterization of biominerals is of considerable significance in many research fields of biological science because biominerals are responsible for not only many physiological processes (e.g. bone growth and teeth development) but also pathological processes (e.g. formation of kidney and salivary stones) [1, 2]. Structural characterization of biominerals reveals key information for understanding the processes, offering a basis for elucidating mechanisms of biomineralization.

Several different experimental methods can be used to characterize biominerals, but most of them are difficult to provide localized, atomic-resolution knowledge of their structures. X-ray spectroscopy yields an ensemble average of a whole sample and hence falls short of providing localized information. Scanning tunnelling microscopy can offer atomic-scale features of materials, but is restricted by the poor conductivity of biomineral samples. Transmission electron microscopy (TEM) shall in principle be more suitable to fulfil atomic-resolution structural characterizations. However, atomic-resolution TEM characterization of biominerals remains challenging due to the electron beam damage. For decades, TEM characterization of biominerals offers, at best, structural information at nanoscale [3, 4]. In this study, we use low-dose imaging techniques within aberration-corrected electron microscopy to minimize damages caused by irradiation of electron beam, and demonstrate a successful direct resolution of every individual atomic column in the shark tooth enameloid.

Since the discovery that fluorine takes on an excellent caries-reducing effect is a landmark in the history of dentistry [5, 6], the direct atomic-resolution imaging of all atomic columns in teeth particularly the F atoms should represent a critical step forward in our understanding of teeth strengthening function. In order to understand the caries-reducing effect of fluorine from the viewpoint of materials science, we further carry out density-functional-theory (DFT) calculations. We find surprisingly that the bonding between fluorine atoms and their neighboring calcium atoms can be of a mixed covalent-ionic nature, which is relevant for understanding the origin underlying the fluorine-strengthening effect in teeth.

References

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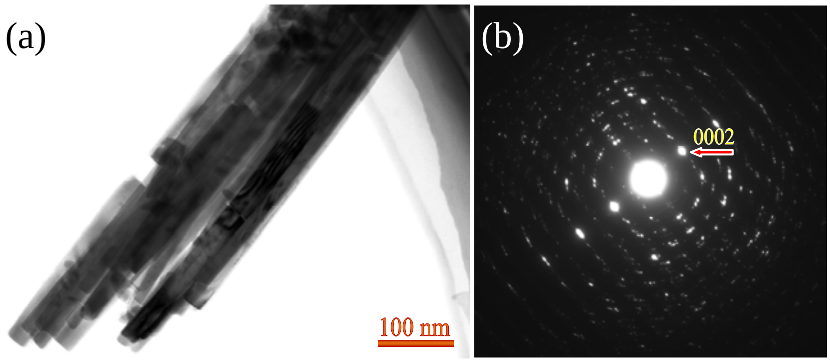

FIG. 1. Microstructure of shark teeth enameloid. (a) Bright-field TEM image and (b) corresponding SAED pattern taken along $[2\bar{1}\bar{1}0]$ direction

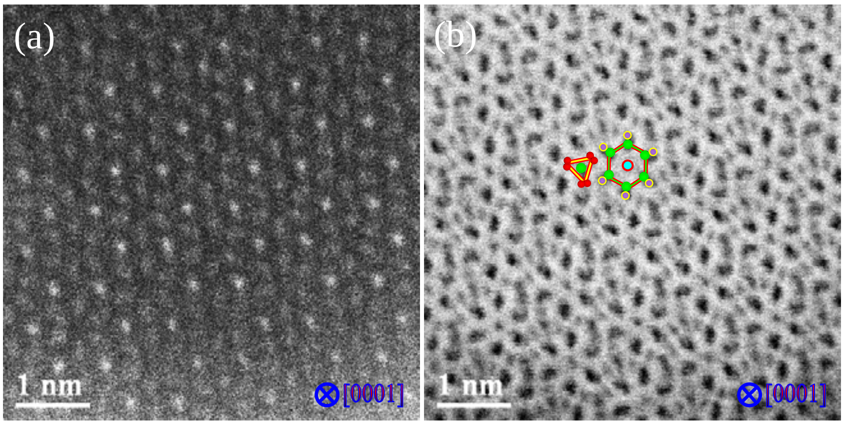

FIG. 2. HAADF and ABF STEM images of shark teeth enameloid viewed along [0001] direction. The F atoms sit at the center of hexagons formed by the Ca atoms.