

Supporting information

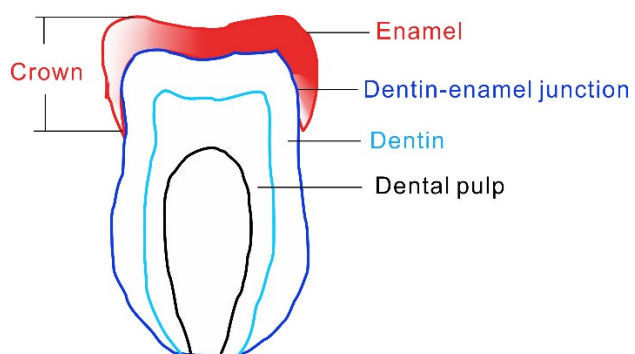


Fig. S1 The detailed sketch of human tooth.

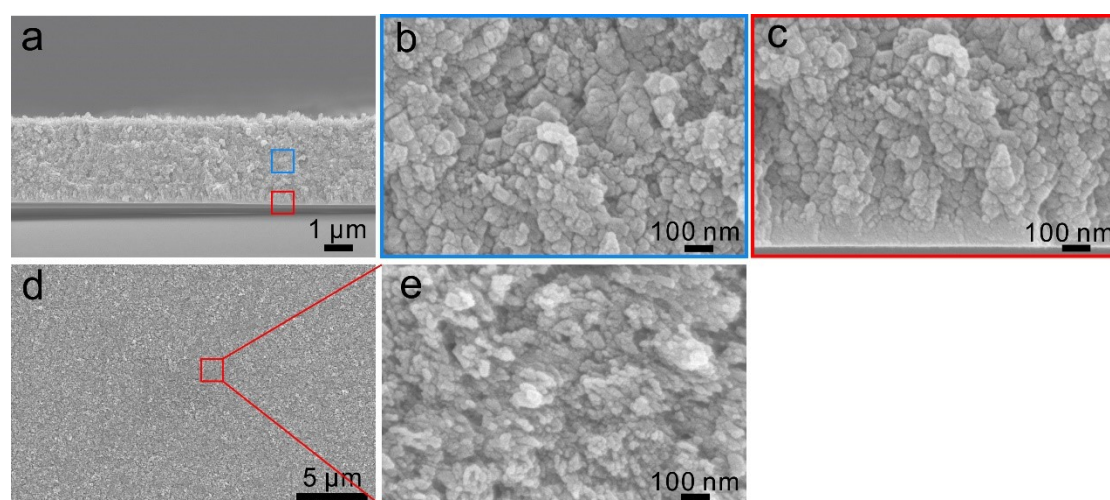


Fig. S2. a-c) Cross-sectional SEM images of CaCO₃ layers and the magnified cross-sectional FESEM images show the morphological features. d-e) Plane SEM images of CaCO₃ layers.

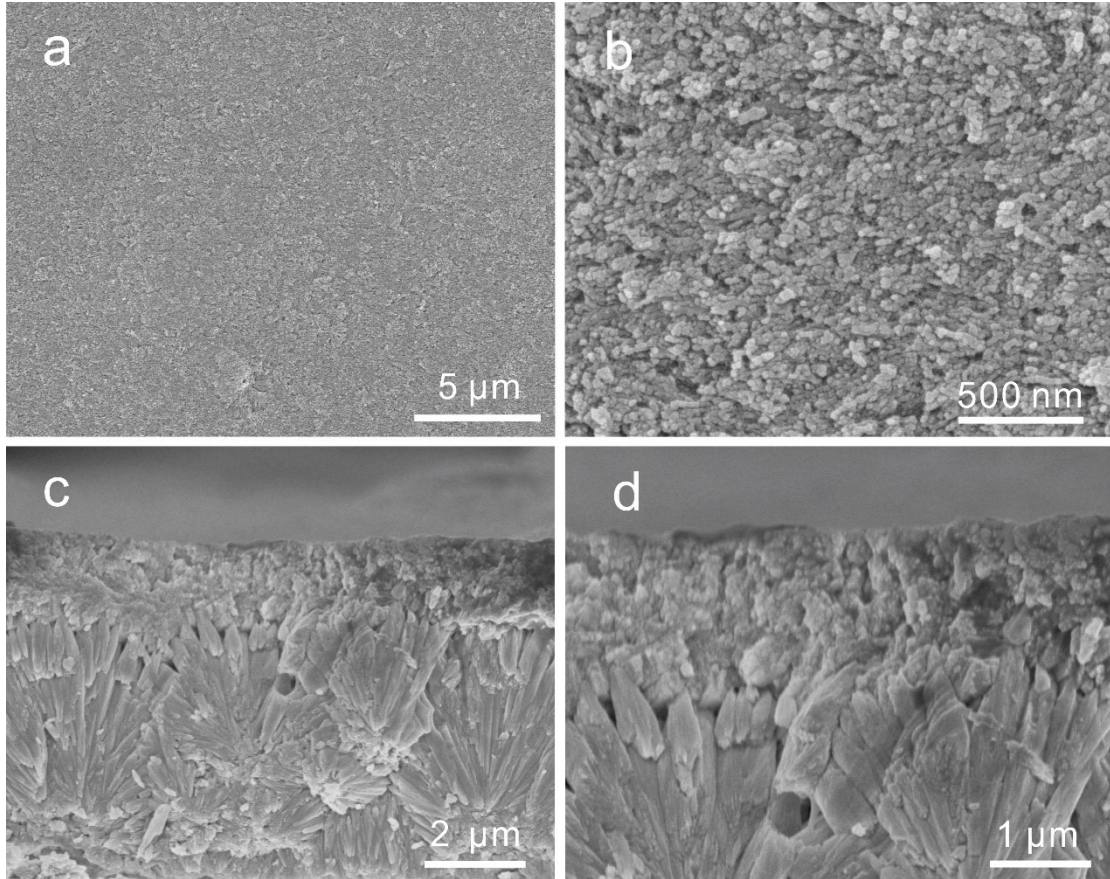


Fig. S3. The microstructure of CaCO₃/FAP heterogeneous structured composites. a-b) The plane SEM images of CaCO₃/FAP heterogeneous structured composites. c-d) The cross-section SEM images of CaCO₃/FAP heterogeneous structured composites.

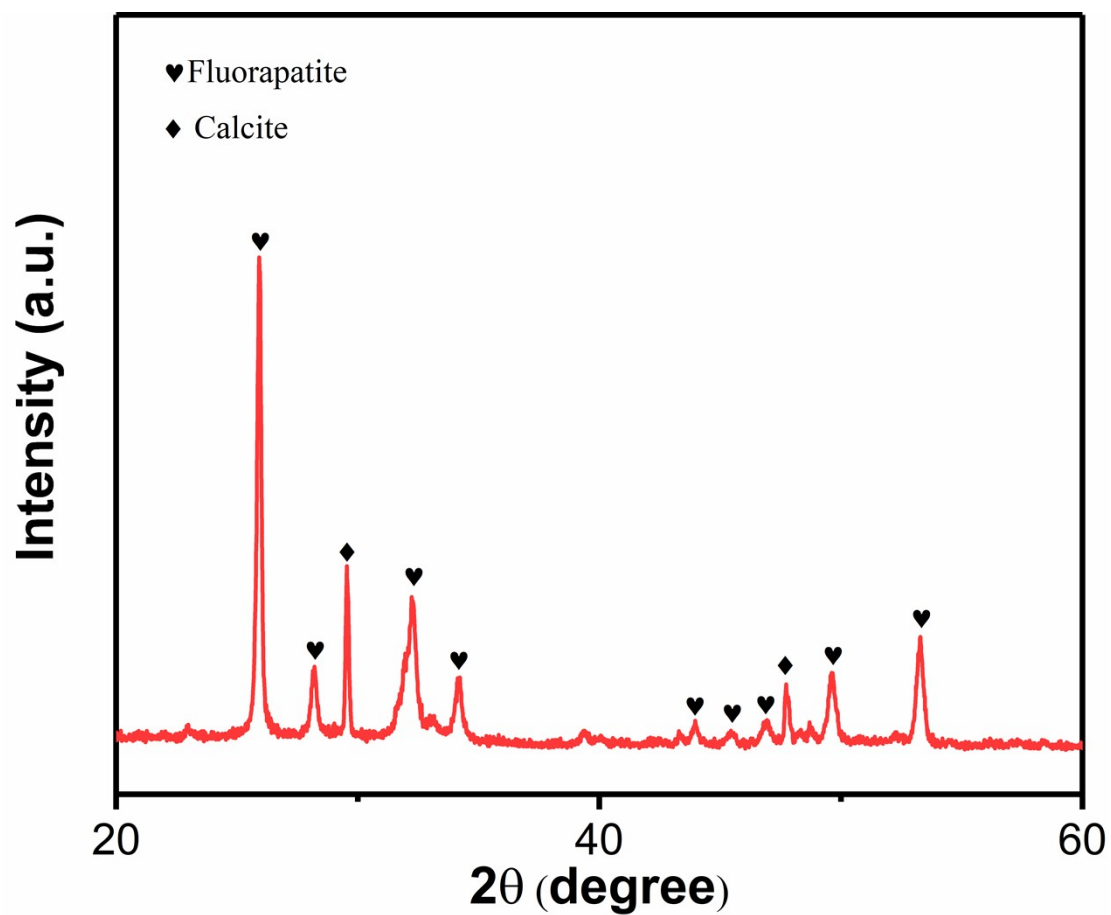


Fig. S4. XRD patterns of FAP/CaCO₃ heterogeneous structured composites.

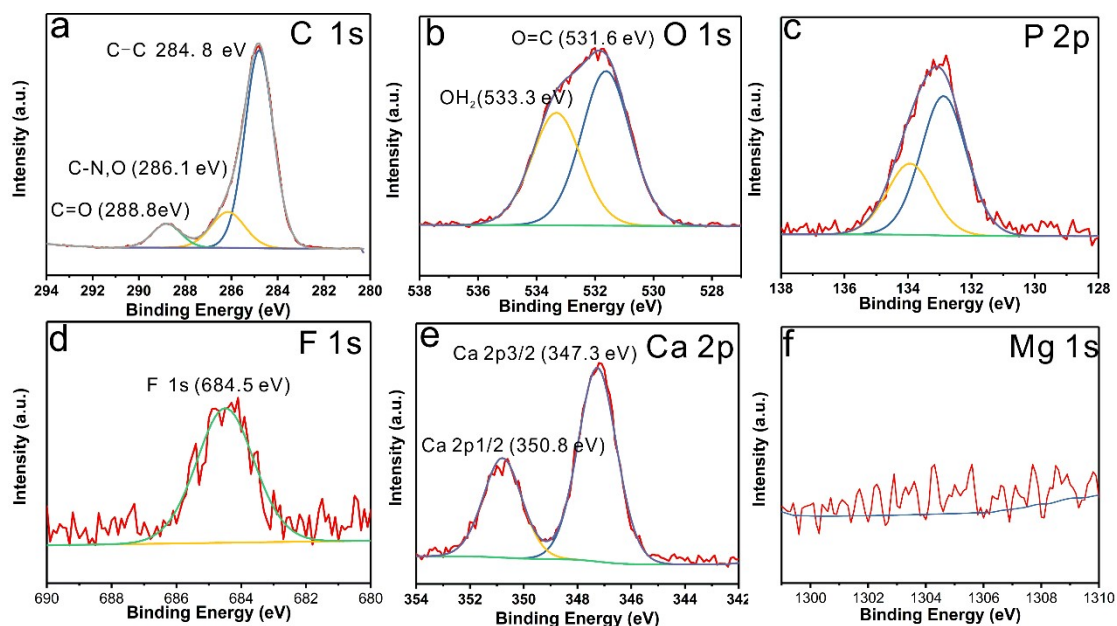


Fig. S5. High-resolution XPS profiles of the FAP/CaCO₃ heterogeneous structured composites: a) C 1s, b) O 1s c) P 2p, d) F 1s, e) Ca 2p and f) Mg 1s.

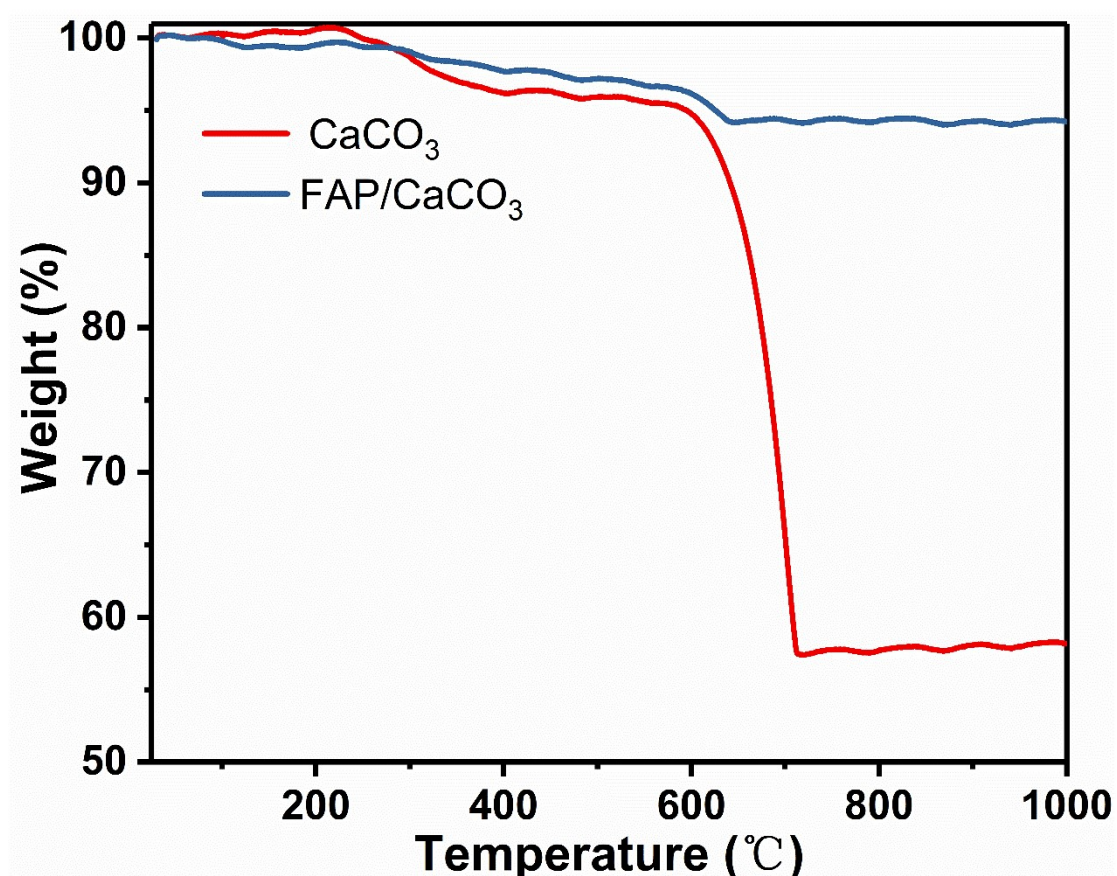


Fig. S6. TGA data for the synthetic FAP/CaCO₃ heterogeneous structured composites and the CaCO₃ layer.

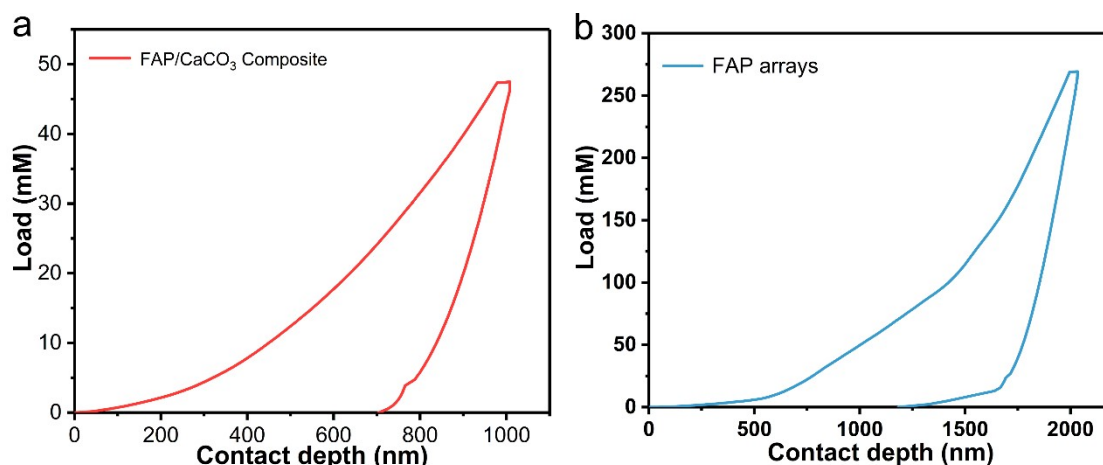


Fig. S7. Load–displacement curves for the FAP/CaCO₃ heterogeneous structured composites and FAP arrays.

Table S1. Compared with the preparation methods of calcium phosphate and calcium carbonate array materials reported in literature.

Literature	Synthesis method	Mechanical properties
Preparation of Calcite and Aragonite Complex Layer Materials Inspired from Biomineralization. <i>Crystal Growth & Design</i> , 2009 ^[1] .	large-area aragonite film is deposited onto a calcite film in the presence of magnesium ion to biomimetically construct an aragonite-calcite complex structure	--
Bioinspired enamel-like oriented minerals on general surfaces: towards improved mechanical properties. <i>J. Mater. Chem. B</i> , 2019 ^[2] .	developed a biomimetic, anodic alumina oxide (AAO)-assisted, double-layered gel system to fabricate well-oriented HAP crystals on a variety of substrates	elastic modulus of 52 GPa and hardness of 0.73 GPa
Artificial enamel induced by phase transformation of amorphous nanoparticles. <i>Scientific Reports</i> , 2017 ^[3] .	synthesized an enamel architecture comprising oriented HAP nanorods via geometrical selection induced by reactive amorphous nanoparticles and the corresponding phase transformations.	elastic modulus of 63.4 GPa and hardness of 2.87 GPa

Solution-Air Interface Synthesis and Growth Mechanism of Tooth Enamel-like Hydroxyapatite/Chondroitin Sulfate Films. <i>Crystal Growth & Design</i> , 2012 ^[4] .	Fabricate a largescale translucent hydroxyapatite (HAP) and chondroitin sulfate (ChS) composite films by a unique solution-air interface method.	--
Bioprocess-Inspired Room-Temperature Synthesis of Enamel-like Fluorapatite/Polymer Nanocomposites Controlled by Magnesium Ions. <i>ACS Appl. Mater. Interfaces</i> , 2021 ^[5] .	adopt a bioprocess-inspired room-temperature mineralization technique to synthesize a multilayered array of enamel-like columnar FAP/polymer nanocomposites	hardness of 2.42 GPa and Young's modulus of 81.5 GPa

Reference.

- [1] LIU R, XU X, CAI Y, et al. Preparation of calcite and aragonite complex layer materials inspired from biomineralization [J]. *Crystal Growth and Design*, 2009, 9(7): 3095-9.
- [2] CHEN Z, MIAO Z, ZHANG P, et al. Bioinspired enamel-like oriented minerals on general surfaces: towards improved mechanical properties [J]. *Journal of Materials Chemistry B*, 2019, 7(34): 5237-44.
- [3] ONUMA K, IJIMA M. Artificial enamel induced by phase transformation of amorphous nanoparticles [J]. *Scientific reports*, 2017, 7(1): 1-10.
- [4] XU Y, MA G, WANG X, et al. Solution-air interface synthesis and growth mechanism of tooth enamel-like hydroxyapatite/chondroitin sulfate films [J]. *Crystal growth & design*, 2012, 12(7): 3362-8.
- [5] LI Y, PING H, WEI J, et al. Bioprocess-Inspired Room-Temperature Synthesis of Enamel-like Fluorapatite/Polymer Nanocomposites Controlled by Magnesium Ions [J]. *ACS Applied Materials & Interfaces*, 2021, 13(21): 25260-9.