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Dental enamel-like hydroxyapatite transformed directly from monetite

Zhaoyong Zou[a,b], Kaili Lin[a], Xiaoguo Liu[a,b], Lei Chen[a], and Jiang Chang[a*]

a State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, People's Republic of China

b Graduate School of the Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, People's Republic of China.

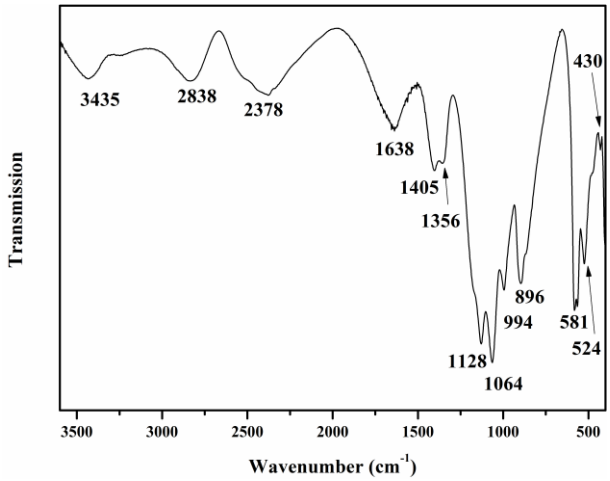

Fig. S1. FTIR spectrum of the as-synthesized products after simultaneous irradiation of microwave and ultrasound for 30 min. The peaks at 430, 524, 581, 896, 994, 1064, and 1128 cm^{-1} were attributed to the characteristic bands of PO_4^{3-}. The bands at 1128, 1064 and 994 cm^{-1} were assigned to the P-O stretching modes, and the P-O(H) stretching mode appeared at 896 cm^{-1}. The O-P-O(H) bending modes at 581, 524 and 430 cm^{-1} and weak peaks at 1405 and 1356 cm^{-1} were assigned to P-O-H scissoring vibration modes. The broad O-H stretching bands induced by hydrogen bonds were observed clearly at 2838 and 2378 cm^{-1} indicating a relatively strong hydrogen bonds in the CaHPO4 structure. The broad peaks at 3435 and 1638 cm^{-1} were assigned to the O-H stretching and H-O-H bending of residual free water, respectively. The FTIR result confirmed the functional groups of the as-synthesized $CaHPO_4$ single crystals.

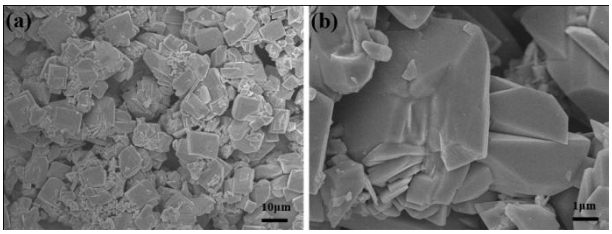

Fig. S2. SEM images of the as-synthesized products under microwave irradiation alone (a-b) for 30 min.

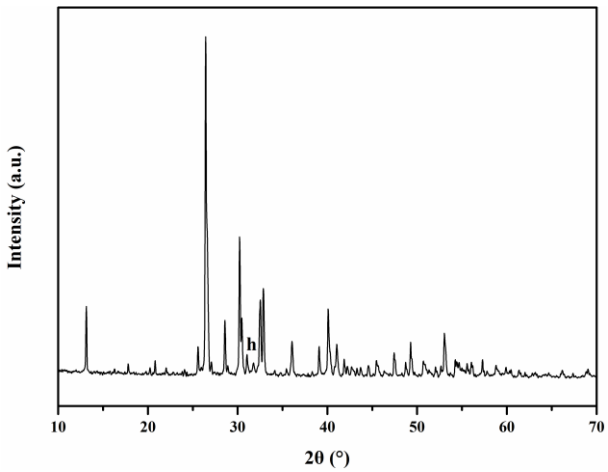

Fig. S3. XRD pattern of the as-synthesized products after simultaneous irradiation of microwave and ultrasound for 60 min (h stands for HA). The XRD pattern suggested that a minor phase of HA appeared.

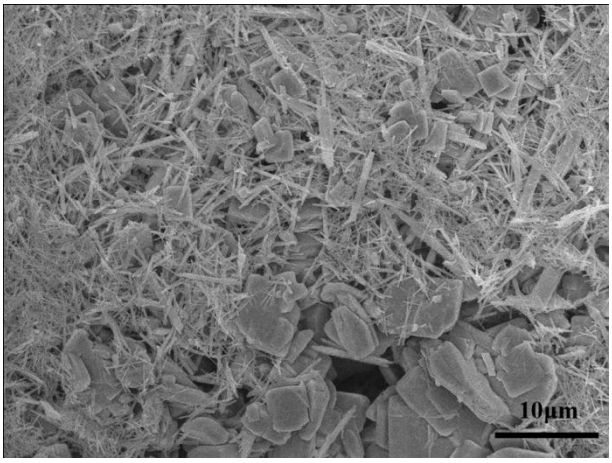

Fig. S4. SEM image of the as-synthesized products after simultaneous irradiation of microwave and ultrasound for 60 min. The fiber-like products confirmed the transformation from $CaHPO_4$ to HA, which was in consistence with the XRD result in Fig. S3.

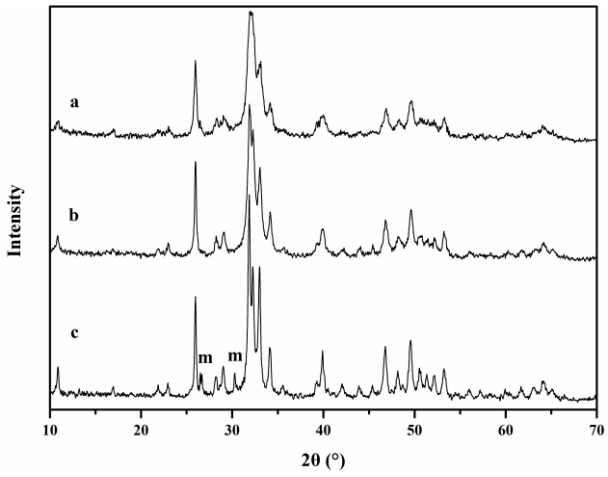

Fig. S5. XRD patterns of the as- synthesized products after transformation in (a) 1 M, (b) 0.1 M and (c) 0.01 M NaOH solution for 5 min (m stands for $CaHPO_4$), respectively. The XRD patterns of the samples transformed in 1M (a) and 0.1 M (b) NaOH aqueous solution showed a single phase of well crystallized HA (ICDD 09-0432), while a minor residual phase of $CaHPO_4$ was

remained in 0.01 M NaOH aqueous solution (c). The difference in the relative intensity of the peaks around 32° indicated that the crystallinity increased with the decrease of alkali concentration.

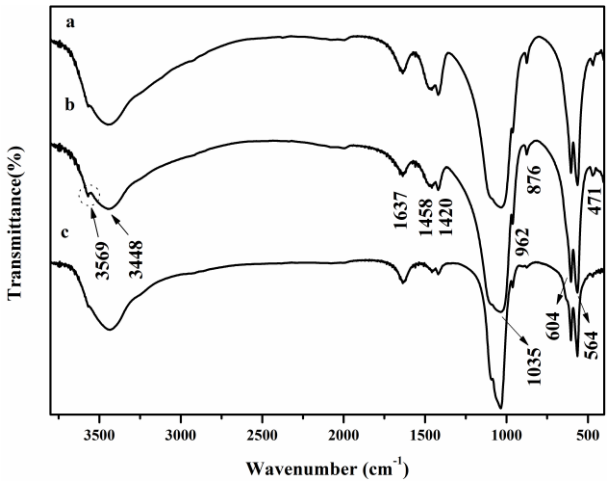

Fig. S6. FTIR spectra of HA obtained in (a) 1 M, (b) 0.1 M and (c) 0.01 M NaOH solution for 5 min. The peaks at 471, 564, 604, 962 and 1035 cm^{-1} were attributed to the characteristic bands of PO_4^{3-}. The characteristic bands for the vibrations of OH^{-1} ions appeared at 3569 cm^{-1}. The peaks at 3448 and 1637^{-1} were assigned to the absorbed water. The peaks at 873, 1420 and 1458 cm-1 corresponded to the vibrations of CO_3^{2-} groups absorbed from atmosphere during the transformation process. The carbonate substitution in HA also existed in dental enamel crystals.

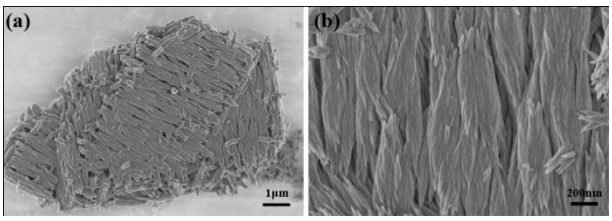

Fig. S7. SEM images of HA obtained after transformation in 1M NaOH solution under simultaneous irradiation of microwave and ultrasound for 5 min. The SEM images showed highly oriented HA with hierarchical structure, which suggested that irradiation of high intensity ultrasound had little impact on the ordered assembly of HA bundles.