## Facile Synthesis and the Phase Transition Mechanism of

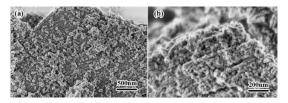
## Fluoridated Hydroxyapatite with Hierarchical Architecture

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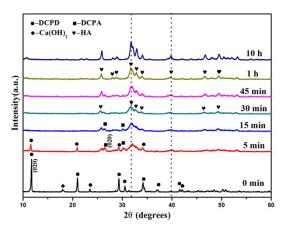
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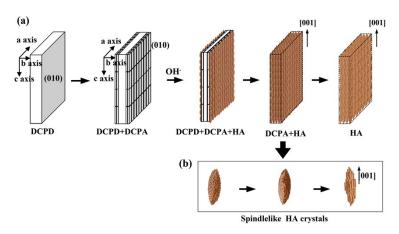
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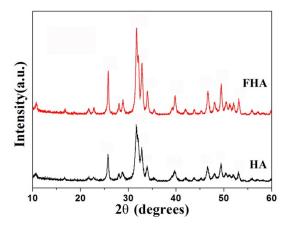
**Fig. S1** SEM images of HA nanocrystals synthesized by hydrothermal process at  $150^{\circ}$ C for 10 h: (a) oriented HA short rod-like nanoparticles around 100 nm in length are assembled into the plate-like particles in a head-to-tail way; (b) the lateral view shows that HA short-rod nanoparticles are well-organized together<sup>1</sup>.



**Fig. S2** XRD spectra of 0-min product at room temperature and products of various hydrothermal reaction time (5, 15, 30, 45, 60 min and 10h) at 150°C when synthesize HA. DCPD is formed at 0 min, DCPA is formed at 5 min and HA is formed at 30 min. The chemical changes have been demonstrated from DCPD to DCPA and further to HA.



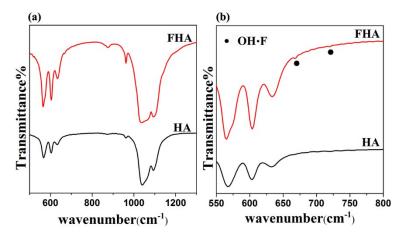
**Fig. S3** The crystal growth schematic illustration of (a) hydrothermal process from DCPD to HA; and (b) HA nanocrystal aggregates on the plate surface. <sup>1</sup>



**Fig. S4** XRD spectra of 10-h products of HA in Fig. S2 and the FHA in Fig. 1. The peak intensity of FHA is much greater than HA because of the successful introduction of F<sup>-</sup> in FHA, demonstrating the successful formation of HA and FHA.

Samples	Lattice constants		S. (Å)
	a-axis(Å)	c-axis(Å)	Size(Å)
НА	9.418	6.884	276
FHA	9.406	6.885	264

**Table. S1** The lattice constants, sizes of 10-h products of HA in Fig.S2 and FHA in Fig.1. The reduction of the a-axis and size of cell unit for the product of FHA demonstrate the successful formation of FHA.



**Fig. S5** FTIR spectra of 10-h products of HA and FHA. The peaks of FHA are much stronger than HA as the formation of FHA. Moreover the peaks at 668 and 718 cm<sup>-1</sup> are assigned to the OH  $\cdot$  F hydrogen bonds in FHA.

## References

1 Wang, M.; Gao, J.; Shi, C.; Zhu, Y.; Zeng, Y.; Wang, D. Cryst. Growth Des. 2014, 14, 6459-6466.