New nonspherical hollow $\alpha$-Fe$_2$O$_3$ structures synthesized by stepwise effect of fluoride and phosphate anions

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**Fig. S1** XRD of the Tube-in-Dodecahedral $\alpha$-Fe$_2$O$_3$ crystals at different times.

**Fig. S2** (a) The inner tube with a triangle ektexine. If the etching at the top facets is not selective, the morphology should be retained as (b).
**Fig. S3** SAED patterns when the incident electron beam is from [120] direction.

**Fig. S4** Transition states that possess the characters of both X-shaped α-FeOOH and α-Fe₂O₃ particles when the concentration of H₂PO₄⁻ anions is (a), (b) 0.16 mM and (c), (d) 0.08 mM.
Fig. S5 (a) The size and (c) morphology of X-shaped FeOOH are comparable with (b) the size and (d) morphology of the hole in α-Fe₂O₃ particles, which is because that α-Fe₂O₃ grows until enwrapping the FeOOH substrate.

Fig. S6 (a) and (b) are samples in different magnification when the reaction time is prolonged to 192h. Obviously, all the side faces still exist while parts of the inner tube disappeared.
Fig. S7 XPS spectrum of TDFe at (a) 3 h and (b) 48h. The tables in the pictures support that the adsorptions of $F^-$/H$_2$PO$_4^-$ anions on FeOOH are higher than that on α-Fe$_2$O$_3$.

Fig. S8 SAED patterns when the incident electron beam is from [1-10] direction.
Fig. S9 When NaH$_2$PO$_4$ is 0.08 mM, the Hollow Octadecahedral α-Fe$_2$O$_3$ particles at (a) 3 h, (b) 9 h, (c) 24 h and (d) 48 h.

Fig. S10 PH at different times when the concentrations of H$_2$PO$_4^-$ anions are 0.08 mM, 0.16 mM and 0.24 mM
**Fig. S11** SEM images of the products that were obtained by adding 0.24 mM NaH₂PO₄ for 1h. [FeCl₃]=23 mM and [NaF]=23 mM. T=220 °C.

**S12** The pH value variation statistical histograms during the degradation