

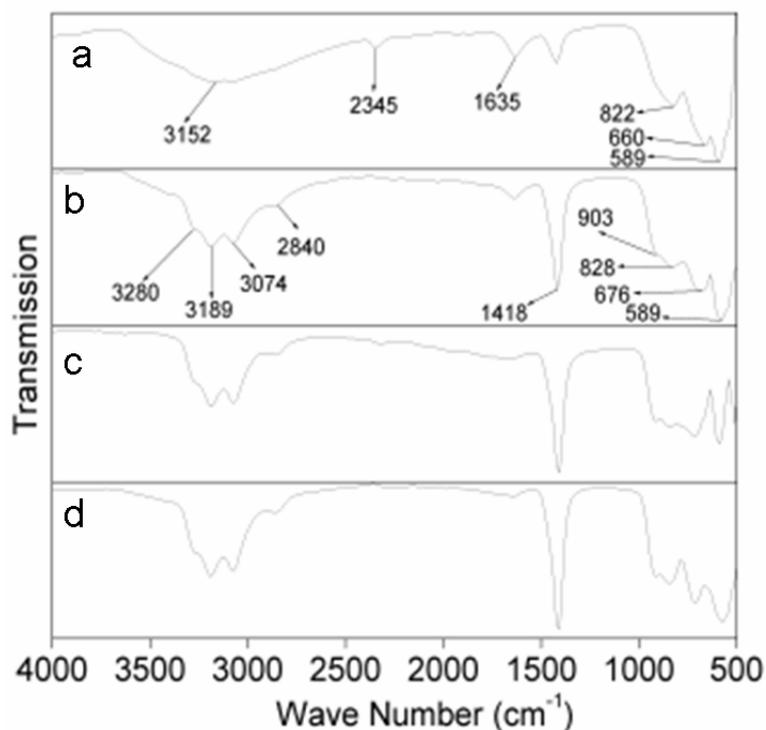
Electronic Supporting Information

Table A: X-ray diffraction data for as-prepared NH_4TiOF_3 using Brij 58

*Previously reported			Present study			
<i>d-spacing</i>	<i>2θ</i>	<i>l/o</i>	<i>hkl</i>	<i>d-spacing</i>	<i>2θ</i>	<i>l/o</i>
6.30	14.1	100	002	6.30	14.1	100
3.78	23.5	62	020	3.78	23.5	55.5
3.24	27.5	60	002	3.24	27.5	62.7
3.15	28.3	21	004	3.15	28.3	21.8
2.71	33.0	6	114	2.71	33.0	4.3
2.67	33.6	18	220	2.67	33.6	18.8
2.39	37.7	3	105	2.42	37.1	2.2
2.37	37.9	3	310			
2.34	38.5	7	311	2.33	38.5	7.2
2.30	39.1	7	124	2.30	39.1	6.4
2.24	40.3	7	132	2.24	40.3	4.7
2.10	43.1	11	025	2.10	43.0	11.0
1.99	45.6	5	232	1.99	45.6	4.4
1.95	46.5	4	116	1.95	46.5	1.9
1.90	48.0	11	040	1.89	48.0	12.2
1.84	49.7	14	140	1.84	49.7	19.6
1.81	50.4	6	042	1.81	50.4	7.7
1.69	54.2	4	240	1.68	54.3	4.7
1.65	55.7	3	226	1.65	55.7	4.2
1.63	56.3	8	242	1.63	56.3	8.1
1.62	56.7	6	044	1.62	56.7	5.4
1.59	58.2	3	144			
1.57	58.7	3	316	1.57	58.7	3.7
1.45	64.1	4	208	1.45	66.1	4.0
1.41	66.5	3	250	1.41	66.5	2.9
1.34	70.4	3	038	1.36	69.2	3.4

*Data compiled from ref. 21.

Fig A. Fourier-Transform (FT) IR spectroscopy



FT-IR spectra shown above provides further evidence for formation of NH_4TiOF_3 from baths containing non-ionic polyoxyethylene surfactants (Brij 56, 58 and 70), $(\text{NH}_4)_2\text{TiF}_6$ and H_3BO_3 . *a.* TiO_2 (anatase) formed in absence of organic surfactants *b.* As-prepared sample using B56 *c.* B58 and *d.* B70. Peak assignments are taken from ref 21. No IR vibrational modes attributed to surfactants were obtained in FT-IR spectra from samples. The peak at 589 cm^{-1} is attributed to the $\nu(\text{Ti-F})$ modes associated with layered octahedral in NH_4TiOF_3 . The band at 903 cm^{-1} is indicative of terminal oxygen ($\nu(\text{Ti=O})$ mode). Modes for NH_4^+ are represented at 1418 cm^{-1} (ν_4), 3074 cm^{-1} , ν_1 (or $\nu_2 + \nu_4$) and 3189 cm^{-1} (ν_3) respectively. The band at 2840 cm^{-1} is an overtone ($2\nu_4$) of the bending vibration of NH_4^+ . Due to their hydroscopic nature, samples are expected to exhibit features associated with absorbed water (deformation bands at 1635 and 3280 cm^{-1}). The general broad IR absorption seen in *a.* in the $3600\text{--}2800\text{ cm}^{-1}$ range, with a maximum at 3152 cm^{-1} , arises from the superposition of the $\nu(\text{O-H})$ mode of molecular water coordinated to Ti^{4+} cations.

Fig. B XRD patterns of samples prepared in presence of 23.1 wt% Brij 58 at 35 °C for 20 hours and thereafter topotactically converted to anatase, *via* sintering at 450 °C for 2 hours or H₃BO₃ washing.

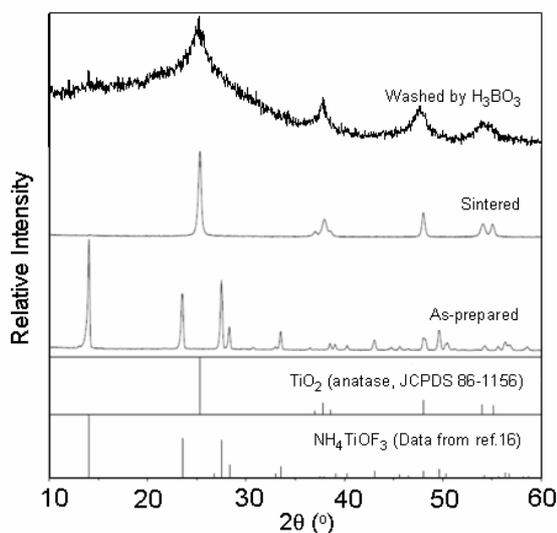
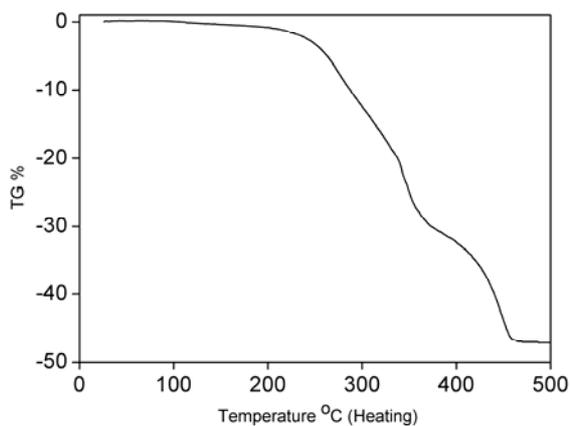


Fig C. Thermogravimetric analysis (TGA)



TGA of as-prepared material (using Brij 58) indicates there is about 47 % mass loss through heating to 450 °C (*cf.* predicated value of 40 % for the conversion of 95.5% anhydrous NH₄TiOF₃ to TiO₂). As described in main text, we ascribe the difference to chemisorbed water/minority impurities within pores of the as-synthesized mesocrystals. Above 450 °C no mass loss was detected. Analysis of the TGA trace and associated mass changes *cf.* as-prepared material (47%) suggests existing of the following possible intermediate materials:

1. NH₄TiOF₃ (25 – 245.7 °C, ~1.4% mass loss associated with physisorbed water)
2. HTiOF₃ (245.7 – 309.8 °C, ~12.3% mass loss consistent with loss of NH₃).

3. TiOF_2 (309.8 – 361.2 °C, ~14.6% mass loss suggests loss of HF at this stage)
4. TiOF_2 (361.2 – 424.0 °C, ~5.5% mass loss. This feature appears to be associated with loss of volatile boron-containing species as elemental analysis of initial material shows B ~1 wt%; no B is detected beyond this stage 4. Obvious candidates include H_3BO_3 and/or NH_4BF_4 , however FT-IR measurements have been unable to detect such species.
5. Formation of TiO_2 (424.0 – 457.6 °C, ~12.6% mass loss to yield final product TiO_2).