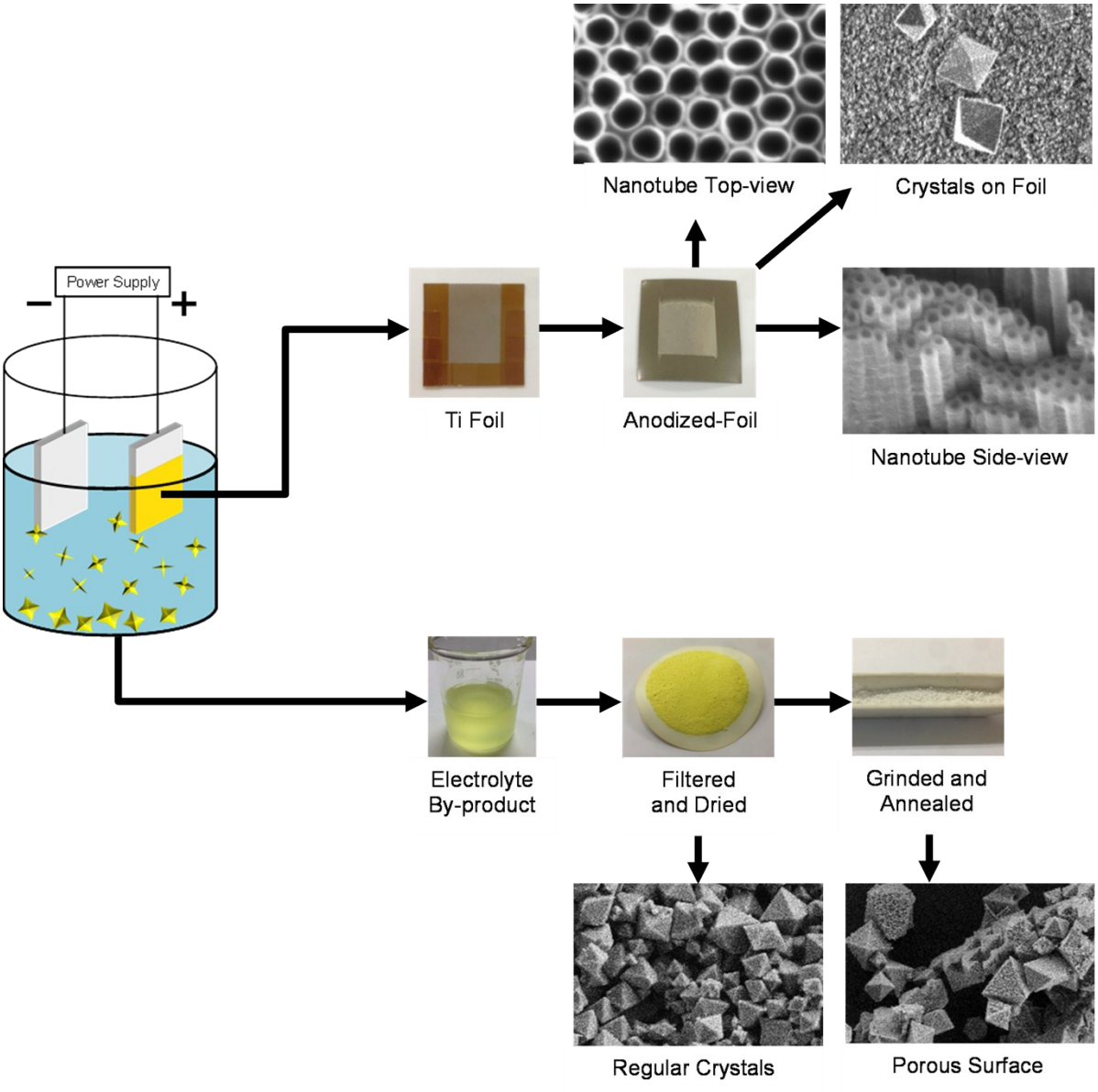
Electronic Supplementary Information 1

Schematic Representation of Experimental Finding



ESI Figure 1| Anodization produces Titania Nanotube (TNT) on foil surface and generate unwanted electrolyte (by-product). Nanotube and octahedral crystals are found on foil surface. The yellowish electrolyte is filtered and dried. After annealing, the yellowish precipitate turns into whitish compounds.

Electronic Supplementary Information 2

Part I: Proposed Reaction on Nucleation Event

Anodization triggers solvation of Ti foil and releases Ti^{4+} species into the electrolyte. Based on the XRD analysis, the changes in electrolyte leading to nucleation event is attributed to the general Reaction 4, where z can be represented by integers (z = 0, 1, 2, and 3) and further expressed as Reaction S1, S2, S3 and S4.

$(TiF_6)^{2-} + H_2O_2 + z(NH_4)^+ \rightarrow (NH_4)_z(TiOF_{z+2}) + (4-z)F^- + H_2O$ Reaction 4

z=0,

$(TiF_6)^{2-} + H_2O_2 \rightarrow TiOF_2 + 4F^- + H_2O$ Reaction S1

z=1,

$(TiF_6)^{2-} + H_2O_2 + (NH_4)^+ \rightarrow (NH_4)(TiOF_3) + 3F^- + H_2O$ Reaction S2

z=2,

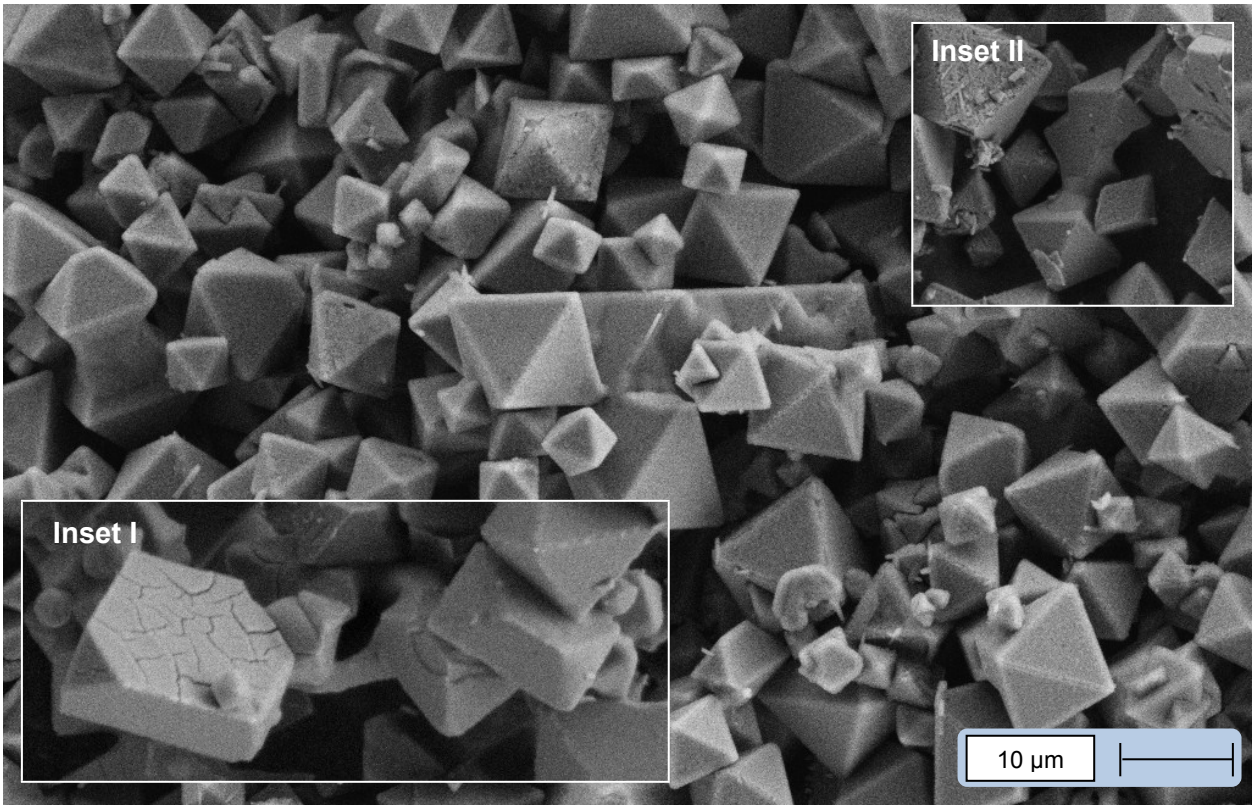
$(TiF_6)^{2-} + H_2O_2 + 2(NH_4)^+ \rightarrow (NH_4)_2(TiOF_4) + 2F^- + H_2O$ Reaction S3

z=3,

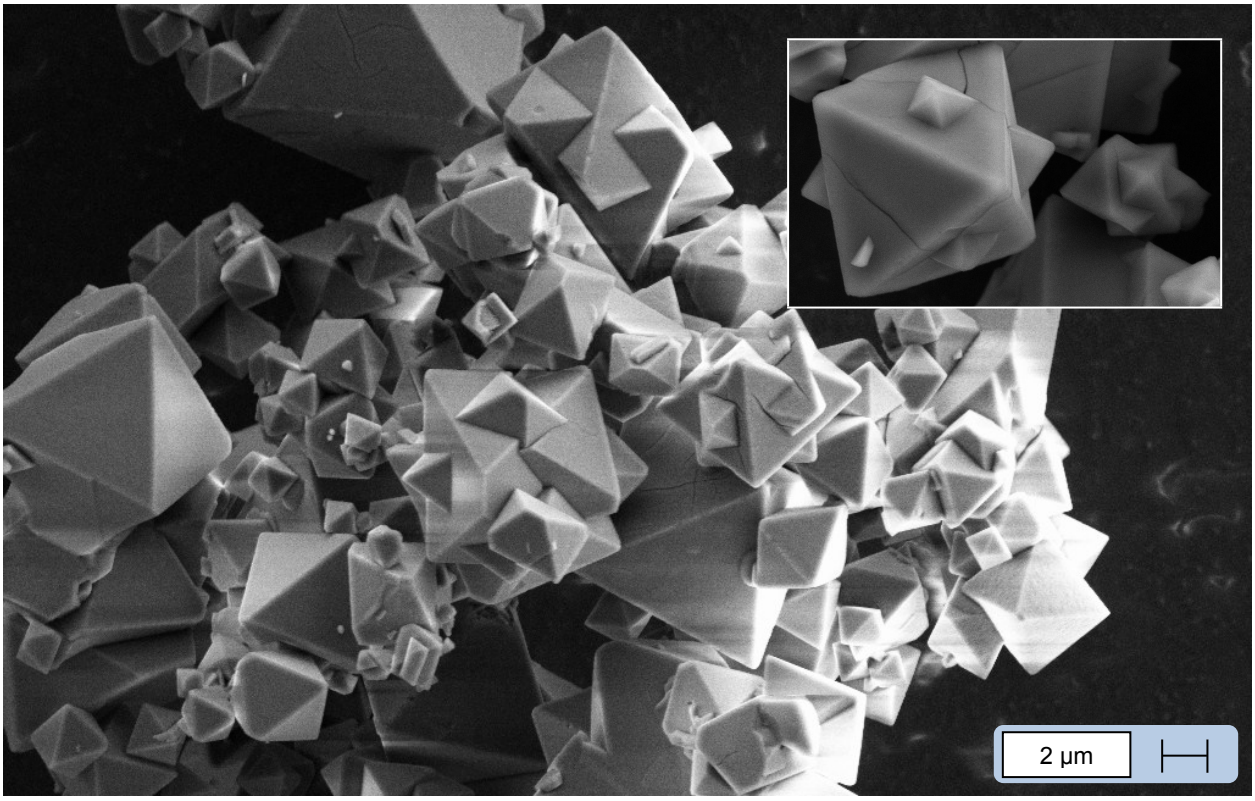
$(TiF_6)^{2-} + H_2O_2 + 3(NH_4)^+ \rightarrow (NH_4)_3(TiOF_5) + F^- + H_2O$ Reaction S4

Based on the XRD diffractograms, the obtained yellowish precipitates are Tri-ammonium oxopentaflurotitanate, $(NH_4)_3(TiOF_5)$ following Reaction S4. This is due to the presence of excessive ammonium fluoride, NH_4F during the nucleation event and prolonged duration for fluorination.

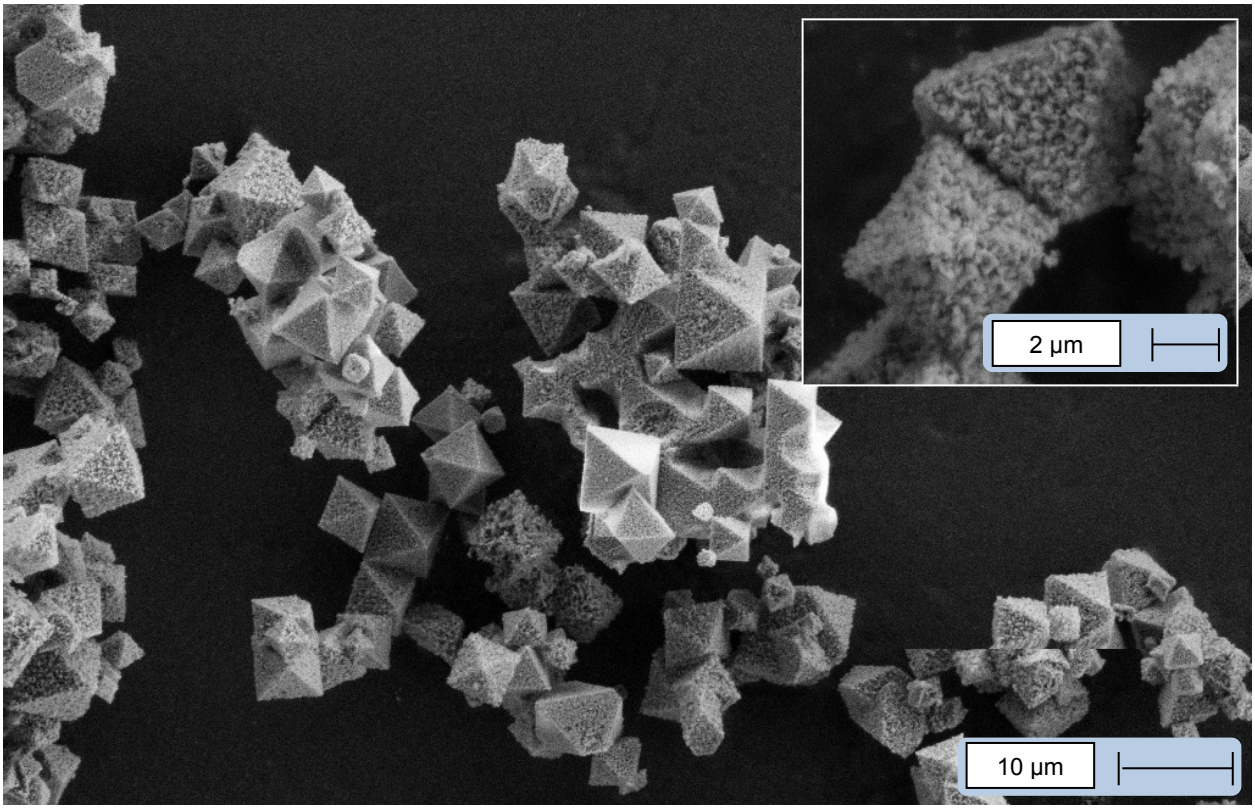
Electronic Supplementary Information 3



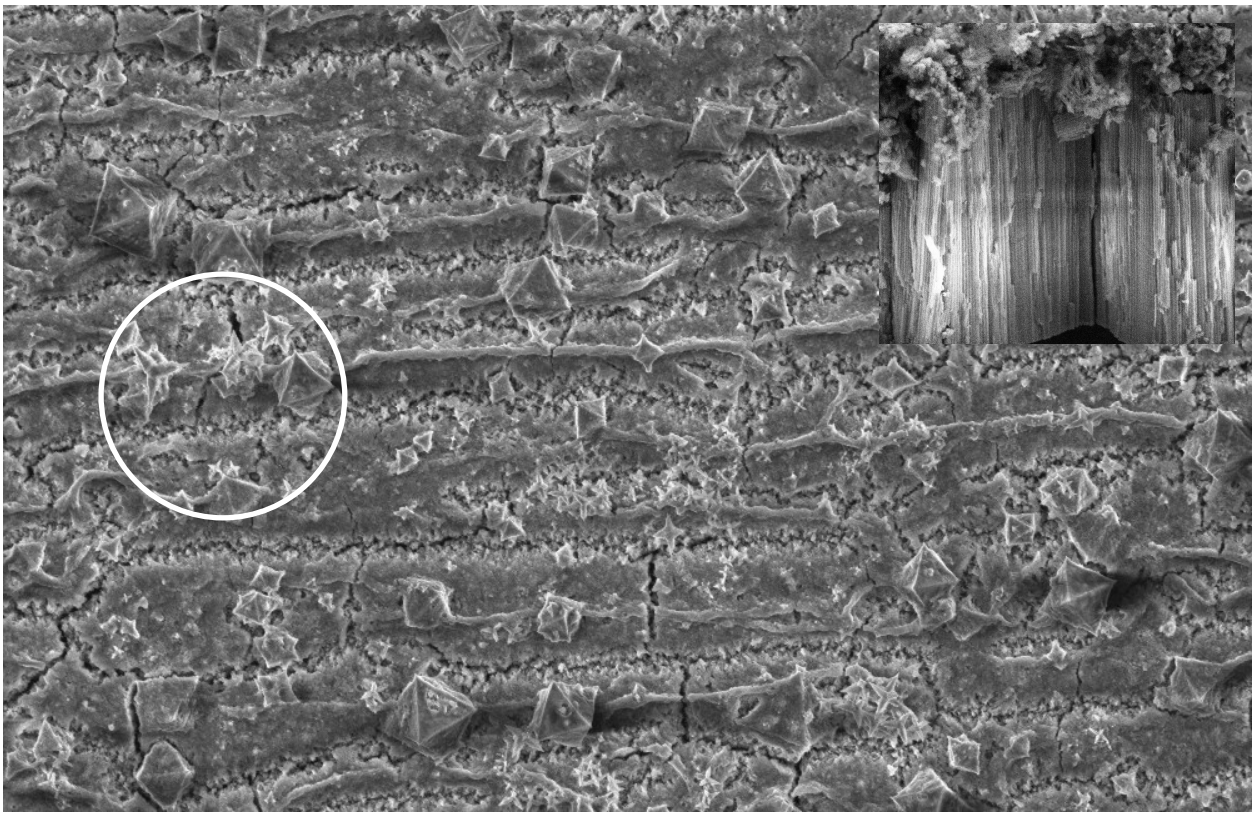
ESI Figure 2| FESEM overview on the pre-annealed precipitate. **Inset I**, (Left) Truncated structure (Right) Elongated structure. **Inset II,** Stacking of octahedron crystals at (001) and (111) planes.



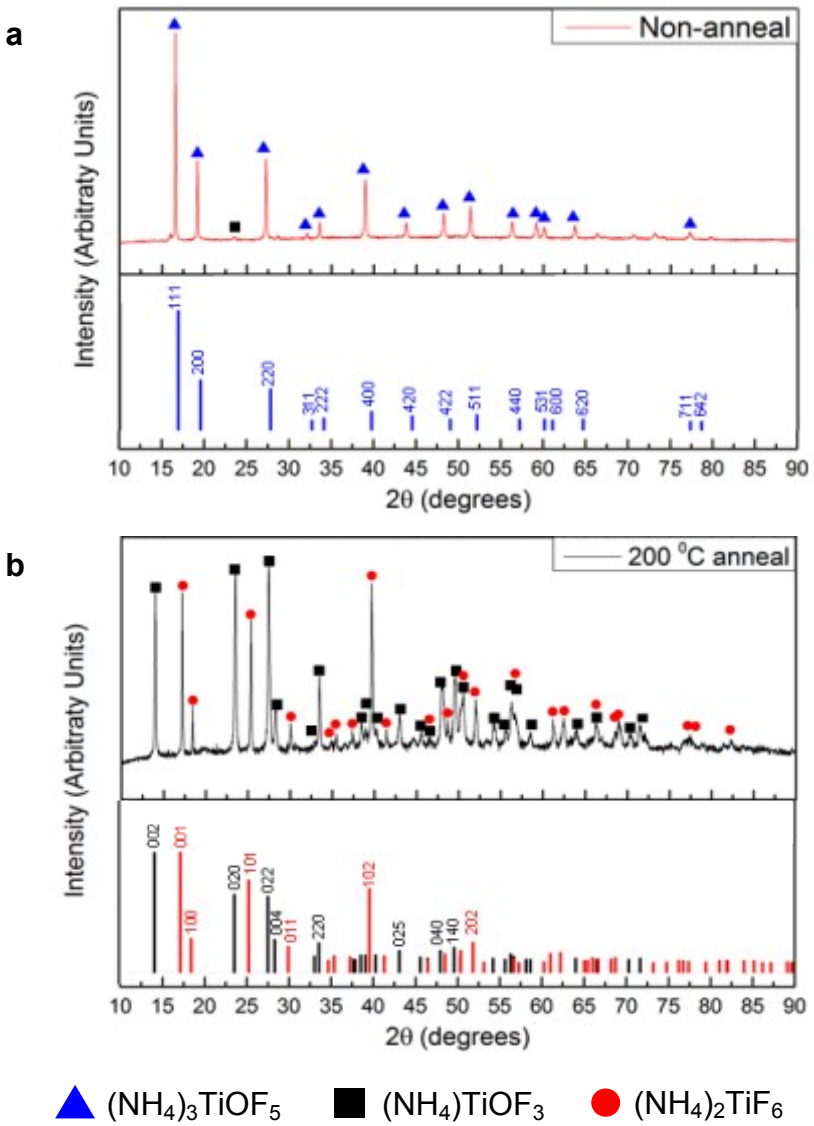
ESI Figure 3| FESEM pre-annealed pseudomorph crystals.



ESI Figure 4| FESEM overview on the post-annealed precipitate. **Inset,** Magnified view on post-annealed octahedral crystal. The crystal retains its octahedron shape with roughen surface due to decomposition of $(NH_4)_3TiOF_5$ compounds.



ESI Figure 5| FESEM on the as anodized Ti foil. Octahedron crystals can be found sitting on the Ti foil surface after anodization for 60 minutes. Some crystals are fully grown as in while some nuclei are at their infantry, showing 6 vertices extending from nuclei center (Circled region). These crystals are situated on the anionic precipitation layer above the nanotube. **Inset,** Side view of the anodized Ti foils revealing nanotubes underneath the anionic precipitation layer after 90 minutes of anodization.



ESI Figure 6| XRD diffractograms with *hkl* information. a, Pre-anneal yellowish powder fits well with $(NH_4)_3TiOF_5$. b, Post-anneal white powder show the presence of $(NH_4)TiOF_3$ and $(NH_4)_2TiF_6$.

Electronic Supplementary Information 4

Table 1| XPS Atomic Concentration and Mass Concentration

Pre-Annealed	Atomic Concentration (%)	Mass Concentration (%)
F1s	34.02	37.75
O1s	13.57	12.00
Ti2p	8.11	21.46
N1s	12.29	8.52
C1s	32.01	21.26

Post-Annealed	Atomic Concentration (%)	Mass Concentration (%)
F1s	37.55	38.01
O1s	12.79	10.91
Ti2p	9.43	24.06
N1s	12.05	8.99
C1s	28.18	18.04

$2(NH_4)_3TiOF_5 \rightarrow (NH_4)TiOF_3 + (NH_4)_2TiF_6 + (HF + H_2O + 3NH_3)$ Reaction 5

The annealing process follows reaction 5 as shown above where the yellowish precipitate is de-fluorinated and de-hydrated to mildly release HF and H_2O in gaseous form. A more rigorous de-fluorination could not be achieved at low annealing temperature (200 ºC for 2 hours). As a result, the pre-annealed $(NH_4)_3TiOF_5$ at the octahedron surface are partially converted into $(NH_4)TiOF_3$ while others are converted into $(NH_4)_2TiF_6$ via fluorination due to the rich fluoride content in the core of the octahedron. The reduction of C1s is expected as carbon merely exists as organic compound on the surface of the octahedron.