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Supporting Information

The effect of chemically preintercalated alkali ion on structure of layered titanates and their electrochemistry in aqueous energy storage systems

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The supplementary information describes in detail the parameters that had to be determined for the efficient and repeatable synthesis of the single-phase alkali metal ion preintercalated layered titanates. Images are also provided at each stage to elucidate for the reader the different color changes, precipitate formations etc. corresponding to the different stages of the reaction process.

Step-by-step description of the synthesis process

One of the most important aspects of the synthesis process of the layered lithium, sodium and potassium titanates (LTO, NTO and KTO) is the *understanding of the important parameters* involved. The principal reaction process involves the dissolution of the titanium powder in a basic solution assisted by hydrogen peroxide addition to form an intermediate peroxo-titanate gel, which rearranges itself to form layered titanates held together by pillaring alkali ions from the added base.

Starting synthesis condition:

The *starting/reference point* for all synthesis parameters were those that were used for the NTO sample (Figure S1) from the literature[1]. 0.2 g of metallic Ti powder were added slowly to a 10 M NaOH solution under stirring at 95 °C (Figure S1(a)), followed by the dropwise addition of 2 ml of 30 % H_2O_2 solution resulting in complete dissolution of Ti powder and formation of a white precipitate (Figure S1(b)). The reaction was allowed to proceed for 8 hours (Figure S1(c)), followed by ageing at room temperature for a week and hydrothermal treatment.

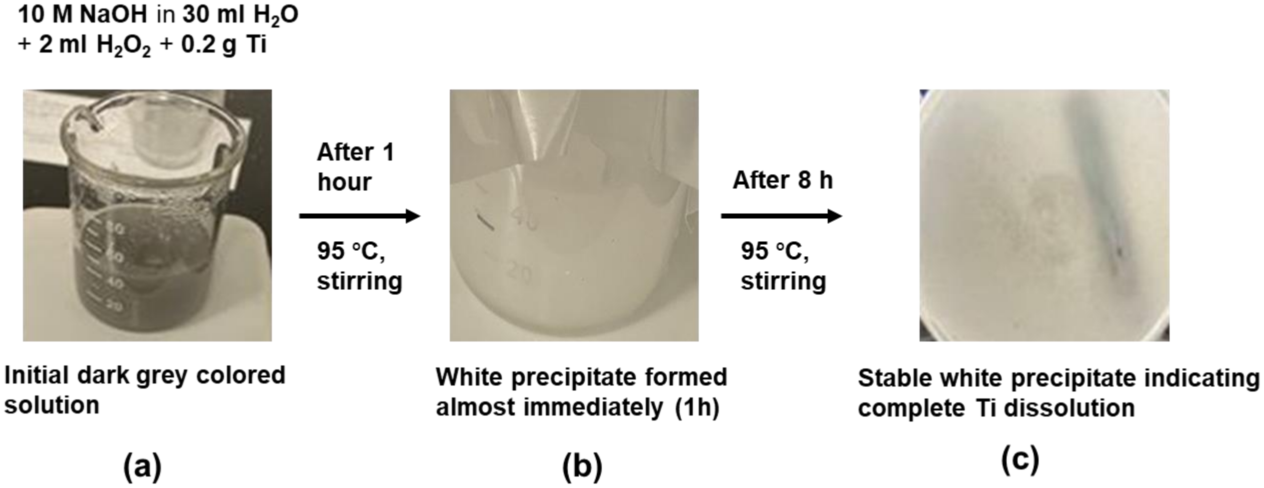


Figure S1. Dissolution of metallic Ti in the presence of 2 ml of 30 % H_2O_2 and 10 M NaOH. (a) 0.2 g Ti powder is added to a 30 ml of 10 M NaOH solution containing 2 ml of 30 % H_2O_2 to form an initial dark greyish suspension; **(b)** a white precipitate forms quickly (approx. 1 h), under stirring and a temperature of 95 °C, which remains during the course of the reaction; **(c)** the white precipitate remains after 8 hours of reaction (stirring) time at 95 °C, indicating the complete dissolution of all metallic Ti.

I. Parameter 1 – Volume of 30 wt. % H_2O_2 added

The *volume of hydrogen peroxide* added is the synthesis parameter that was first determined for complete dissolution of Ti powder. Unlike the NTO sample, the addition of 2 ml of 30 wt. % H_2O_2 does not result in the complete dissolution of all metallic Ti in the LiOH and the KOH containing solutions. The inability of Ti to dissolve with 2 ml of 30 wt. % H_2O_2 is demonstrated in **Figure S2(a-c)** and marked with a red cross.

In case of the KOH containing solution, it is observed that an addition of *extra 3 ml* of 30 wt. % H_2O_2 under stirring at 95 °C results in the formation of a transparent solution after about 4 hours as shown in **Figure S2(e)**. This observation indicates the complete dissolution of metallic Ti and the formation of the intermediate peroxo-titanate complex. When this solution is left to age, very fine white needle-like particles start precipitating around the 4th day, indicating the formation of Ti-O layers as we observe in **Figure S2(f),** marked with a green check sign.

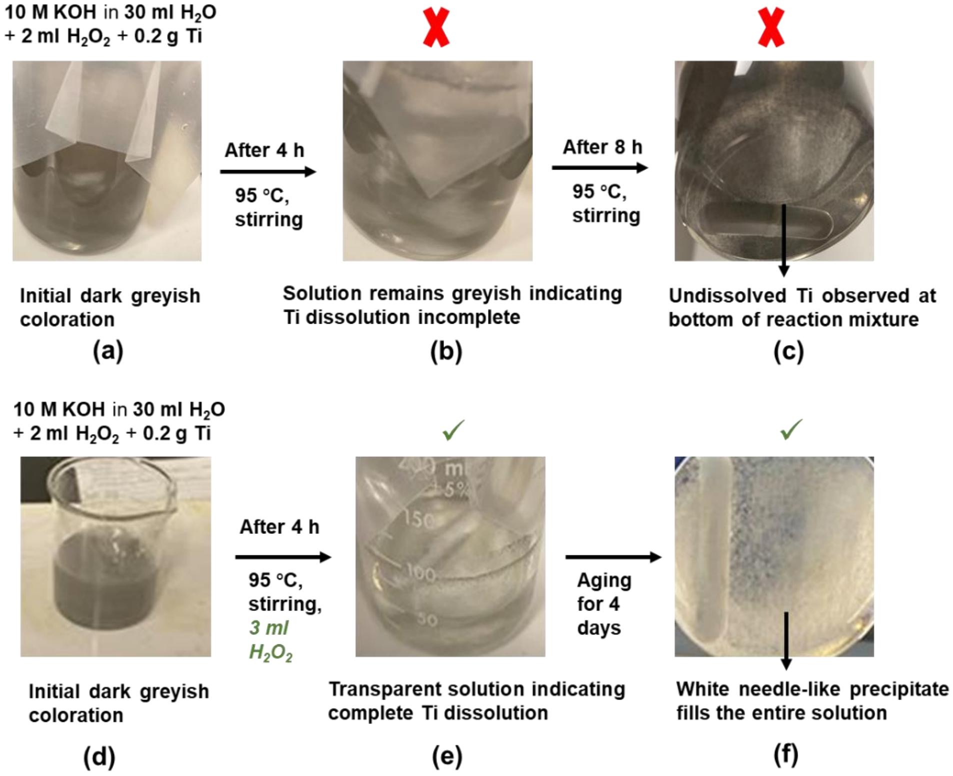


Figure S2. Dissolution of metallic Ti in 10 M KOH by hydrogen peroxide addition. (a) Dark greyish solution formed due to addition of 0.2 g Ti powder is added to a 30 ml of 10 M KOH solution containing 2 ml of 30 % H_2O_2, **(b)** after 4 hours of stirring at 95 °C, the solution color still remains relatively grey, **(c)** dark grey particles at the bottom of the beaker indicate undissolved Ti after 8 hours of stirring at 95 °C, **(d)** Starting dark grey solution containing 0.2 g Ti in 30 ml of 10 M KOH and 2 ml of 30 wt. % H_2O_2, **(e)** formation of a transparent solution after 4 h at 95 °C and the addition of an extra 3 ml of 30 wt. % H_2O_2, demonstrating complete dissolution of all metallic Ti and the formation of a peroxo-titanate complex, **(f)** formation of a fine needle-like precipitate from around the 4th day of aging corresponding to the layered titanate phase.

II. Parameter 2 – Aging time

Aging is the next important parameter considered for the synthesis of single-phase alkali ion preintercalated layered titanates, as aging plays a crucial role in formation of the initial lamellar ordering and the development of Ti-O layers and their assembly. The XRD pattern shown in **Figure S3** (black line) indicates that when filtered immediately after the sol-gel reaction was completed, the NTO samples is largely amorphous material. The two small peaks between 35 and 40° 2θ correspond to the partial formation of the anatase phase. An aging period of 4 days introduces the stacking of the Ti-O layers and a week of aging improves it further, with the gradual evolution of the (001) peak as seen in **Figure S3** for the NTO and KTO phases. Interestingly, aging also leads to disappearance of the anatase phase.

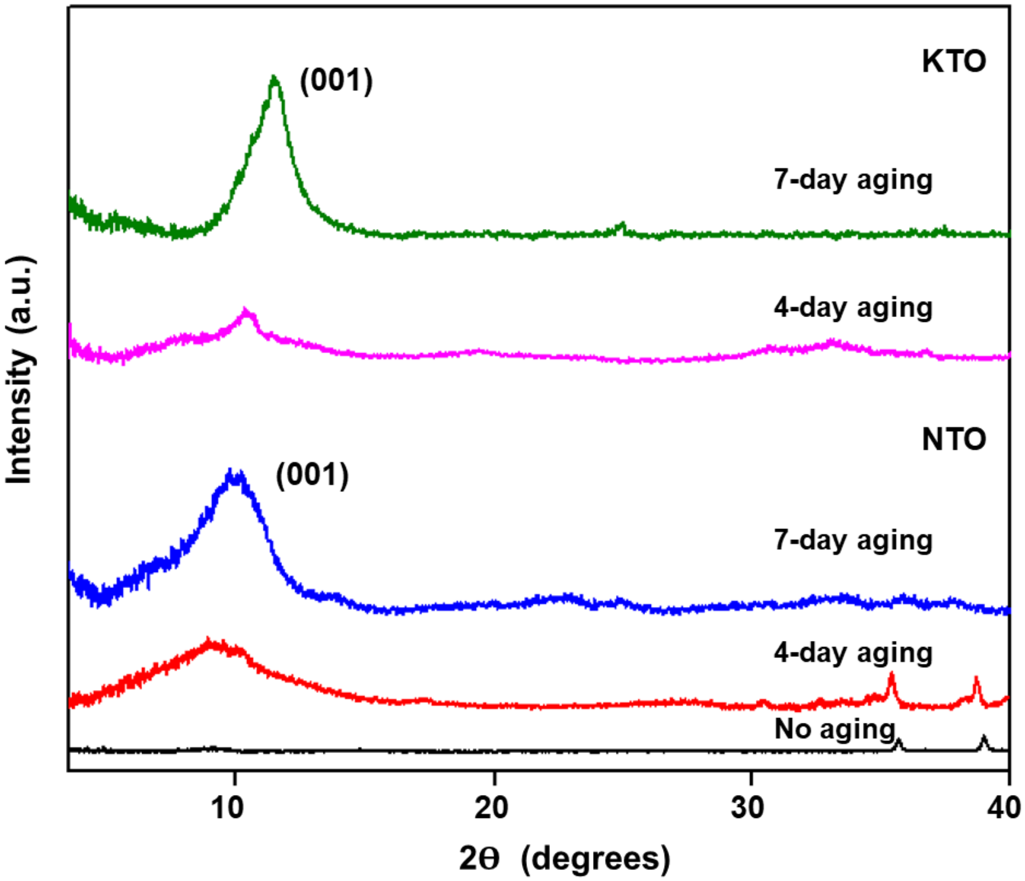


Figure S3. The role of aging in the development of lamellar ordering. XRD patterns of the NTO and KTO samples demonstrating the gradual evolution of the lamellar ordering, as the (001) peak grows in intensity with longer aging time.

III. Parameter 3 – Molarity of the initial base solution

The *molarity of the base added initially* is the third important factor. As mentioned above, for the formation of the NTO and KTO samples, 10 M base is necessary to form the layered structure. However, based on the phase diagram[2], only 1 M LiOH is necessary for complete dissolution of Ti to form the LTO phase. Higher molarities of LiOH results in formation of anatase-TiO_2. Additionally, in case of Li-containing system, significantly larger amount of 30 wt. % H_2O_2 (15 ml) is needed to completely dissolve metallic titanium. Differently from Na- and K-containing systems, the color of the Ti suspension changes gradually over the course of 5-6 hours from the dark grey to white, indicating formation of Ti-O layers (**Figure S4**).

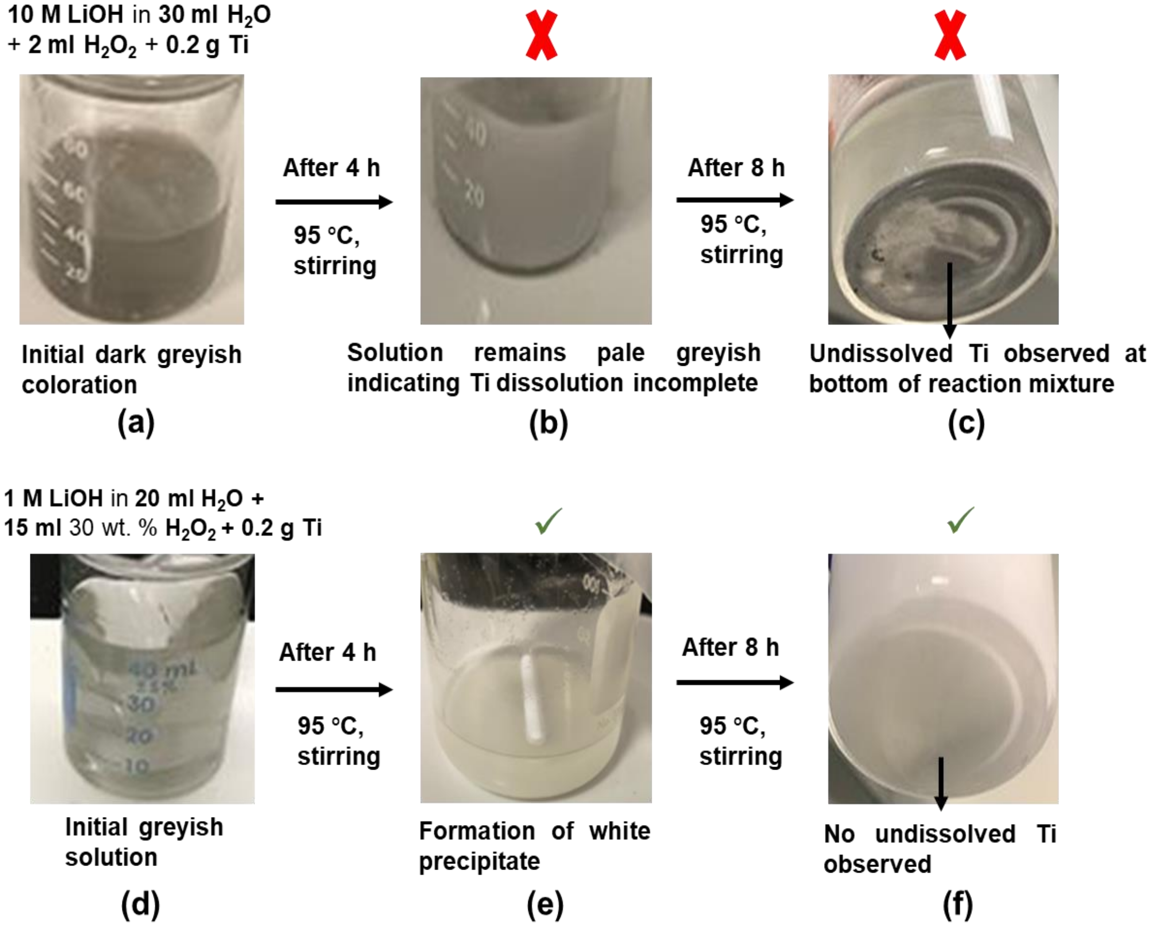


Figure S4. Dissolution of metallic Ti in presence of 15 ml 30 wt. % H_2O_2 and 1 M LiOH. (a) Dark grey suspension formed due to addition of 0.2 g Ti powder into a 30 ml of 10 M LiOH solution containing 2 ml of 30 wt. % H_2O_2, **(b)** after 4 hours of stirring at 95 °C, the solution color changes to a pale grey, **(c)** dark grey particles at the bottom of the beaker indicate undissolved Ti after 8 hours of stirring at 95 °C. **(d)** Starting transparent grey solution containing 0.2 g Ti in 20 ml of 1 M LiOH and 15 ml of 30 wt. % H_2O_2, **(e)** formation of a white precipitate after 4 h at 95 °C demonstrating complete dissolution of all metallic Ti, **(f)** complete dissolution of all Ti powder further demonstrated at the bottom of the beaker, the white precipitate indicating the primitive layered phase.

IV. Parameter 4 – Hydrothermal treatment (HT) conditions

The *hydrothermal treatment conditions* are an important synthesis factor that must be developed to obtain single-phase layered titanates. For the NTO and KTO samples, hydrothermal synthesis of the aged precipitate in 3M corresponding base (NaOH and KOH, respectively) is performed at a temperature of *220 °C* for *24 hours*. However, it is observed that synthesis of the LTO sample using the same starting molarity of base as the NTO/KTO sample, *i.e.* 10 M LiOH and same hydrothermal treatment temperature and time, i.e. 220 °C for 24 h leads to the formation of anatase TiO_2 phase (**Figure S5**). Consequently, hydrothermal treatment conditions were to be developed individually to preserve layered Li-Ti-O framework.

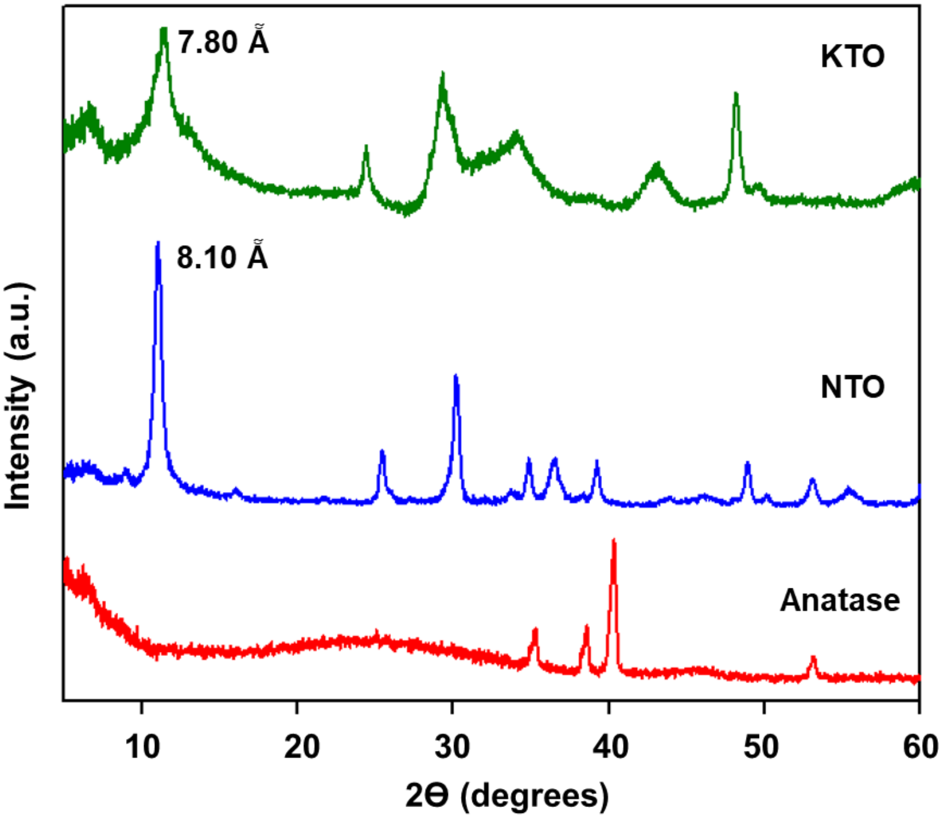


Figure S5. XRD patterns of the layered titanates after hydrothermal treatment at 220 °C for 24 h. Characteristic XRD patterns exhibit the layered structure of the NTO and KTO samples. However, anatase is obtained (red line) instead of the layered LTO sample.

Therefore, based on the literature[2] for the synthesis of layered LTO phase, the aged precipitate was immersed in 1M LiOH and hydrothermal treatment temperature was decreased to *140 °C*, leading to the formation of the single-phase Li-preintercalated layered titanium oxide (**Figure 2a**, red line, in the main manuscript).

The reduced molarity coupled with lower hydrothermal treatment temperature needed to synthesize the single-phase layered LTO phase was a motivation for adopting the same synthesis conditions to synthesize the NTO and KTO phases. This was performed in two ways:

(a) Only the starting molarity of the base used is changed, keeping the hydrothermal treatment conditions the same as before, i.e. 220 °C for 24 hours.

In this technique, 1 M NaOH/KOH was used as the starting concentration. The hydrothermal treatment of the aged precipitate was performed in 1 M NaOH/KOH for 220 °C for 24 h. However, the XRD patterns of the product obtained after hydrothermal treatment (**Figure S6(a)**) indicate that the crystallinity is weak as compared to when the sample synthesized in 10 M NaOH/KOH. Therefore, a low molarity starting basic solution does not necessarily produce highly ordered materials in the case of NTO/KTO, as observed for LTO.

(b) The concentration of base (NaOH and KOH) was kept at 10 M; however, a lower hydrothermal treatment temperature of 150 °C was used.

The XRD patterns of the products reveal reduced lamellar ordering and decreased crystallinity (**Figure S6(b)**), therefore we concluded that lower hydrothermal treatment temperature does not provide satisfactory crystallinity of the sodium and potassium based layered titanates.

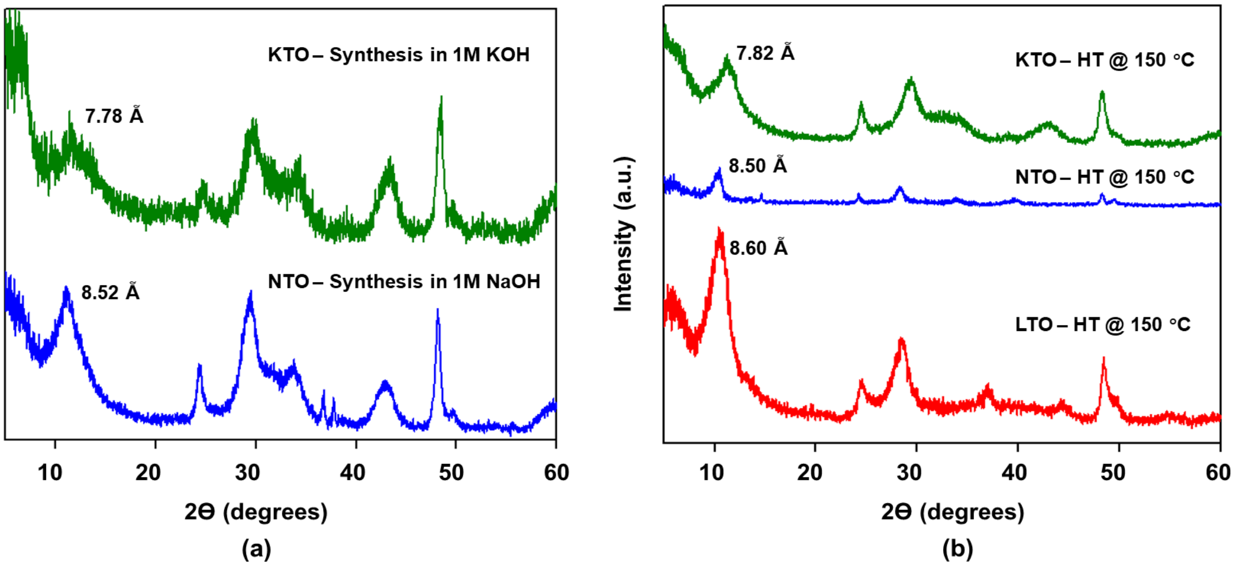
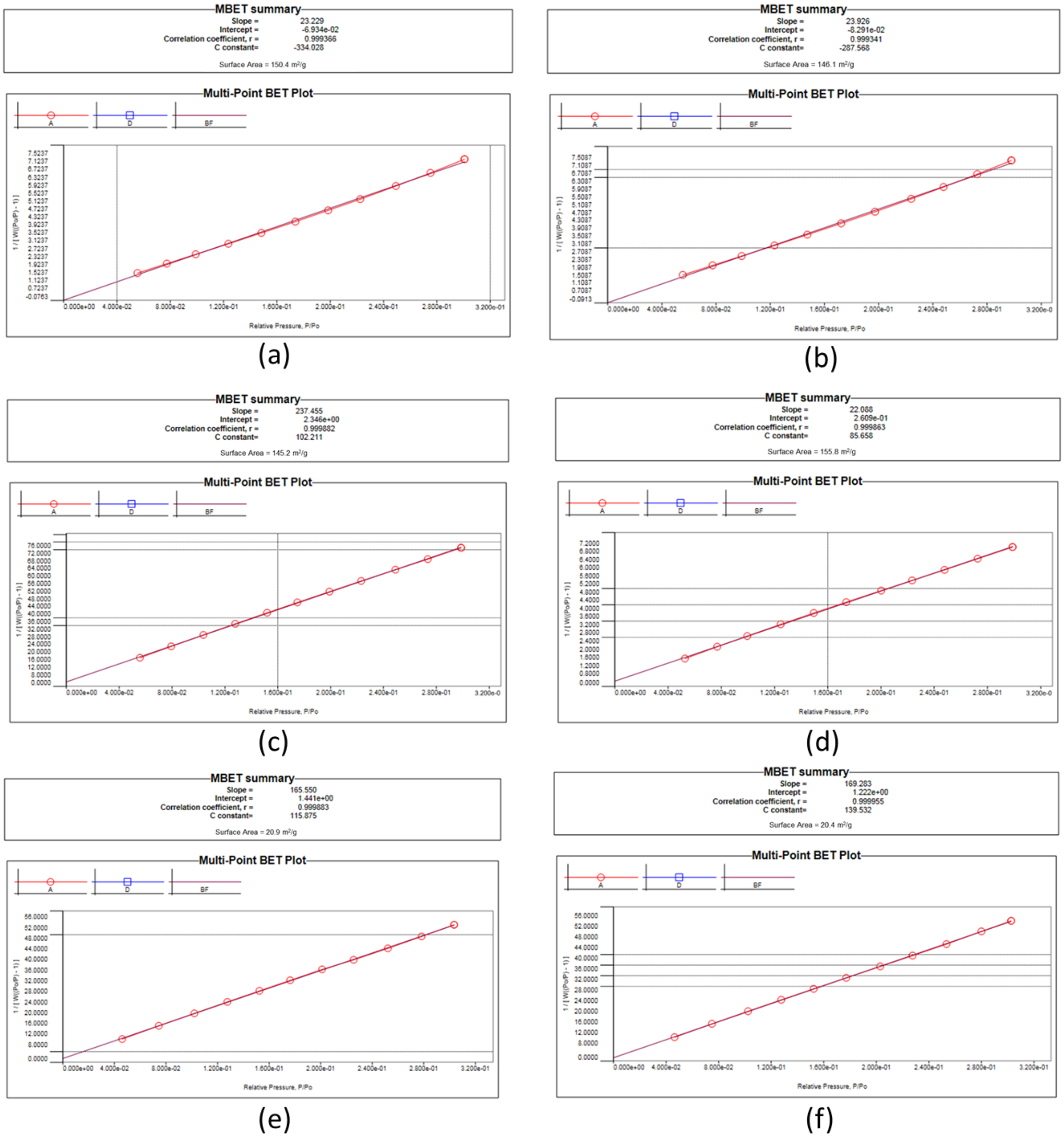


Figure S6. Adaptation of the synthesis conditions found for the LTO sample to the preparation of the NTO and KTO phases. (a) XRD patterns indicating the weak lamellar ordering and low crystallinity for NTO and KTO samples synthesized with a starting 1M concentration of the corresponding base, **(b)** low crystallinity observed in the XRD patterns of the NTO and KTO samples synthesized at HT conditions of 150 °C, as opposed to the highly crystalline LTO sample.

Graphic representations of the BET data are provided below (**Figure S7**).



```
MBET summary
                 Slope =        23.229
             Intercept =          -6.934e-02
Correlation coefficient, r =      0.999366
            C constant=       -334.028

         Surface Area = 150.4 m²/g
```

(a)

```
MBET summary
                 Slope =        23.926
             Intercept =          -8.291e-02
Correlation coefficient, r =      0.999341
            C constant=       -287.568

         Surface Area = 146.1 m²/g
```

(b)

```
MBET summary
                 Slope =        237.455
             Intercept =          2.346e+00
Correlation coefficient, r =      0.999882
            C constant=        102.211

         Surface Area = 145.2 m²/g
```

(c)

```
MBET summary
                 Slope =        22.088
             Intercept =          2.609e-01
Correlation coefficient, r =      0.999863
            C constant=        85.658

         Surface Area = 155.8 m²/g
```

(d)

```
MBET summary
                 Slope =        165.550
             Intercept =          1.441e+00
Correlation coefficient, r =      0.999883
            C constant=        115.875

         Surface Area = 20.9 m²/g
```

(e)

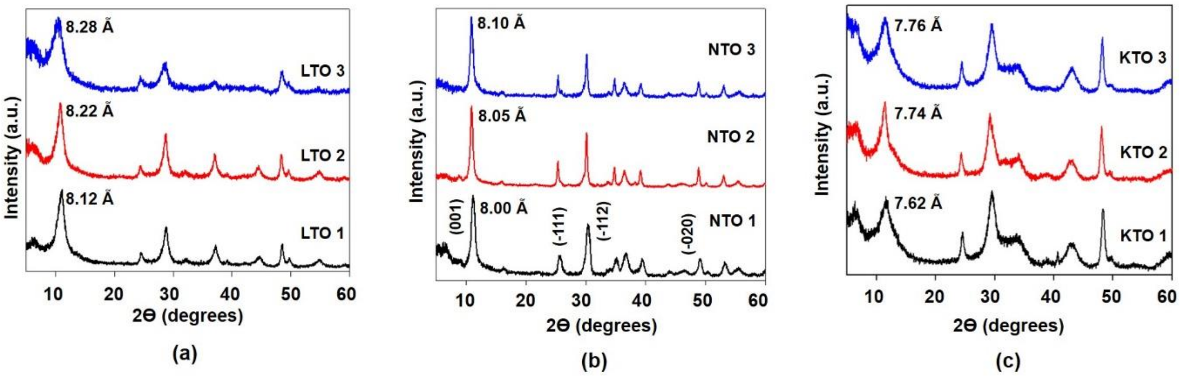
```
MBET summary
                 Slope =        169.283
             Intercept =          1.222e+00
Correlation coefficient, r =      0.999955
            C constant=        139.532

         Surface Area = 20.4 m²/g
```

(f)

Figure S7. Graphical representations of the BET data for the (a,b) KTO, (c,d) LTO, and (e,f) NTO samples degassed at (a,c,d) 200ºC and (b,d,f) 250ºC.

Figure S8 shows three representative XRD patterns of each layered titanate synthesized using conditions leading to the single-phase formation with appropriate crystallinity: LTO, NTO and KTO. The XRD patterns were obtained using powders synthesized in different batches and interlayer spacings were determined from a position of the peak at 11-12^o 2θ. **Figure S8** demonstrates a range of interlayer spacings, which could be attributed to the variability of the sol-gel process and slight variation in chemical composition of the interlayer region, for example, interlayer water content.



(a) (b) (c)

Figure S8. XRD patterns of layered titanates. Characteristic XRD patterns of the Li, Na and K based layered titanates with the prominent peaks indexed, and demonstrating the typical layered structure. Also, the variation in interlayer spacing can be seen, which can be attributed to varying amounts of interlayer water.

Table S1. Correlation between the size of chemically preintercalated ion, M$^+$ (M = Li$^+$, Na$^+$, K$^+$) and experimentally determined interlayer spacing and degree of hydration in LTO, NTO and KTO layered titanates.

Chemically preintercalated alkali ion (M$^+$)	**Ionic radius (Å)**	**Hydrated ion radius (Å)**	**Exemplary interlayer spacing (Å) from Figure 2 in the main article**	**Degree of hydration (the number of H_2O molecules per unit formula)**
Li$^+$	0.76	3.82	8.25	0.34
Na$^+$	1.02	3.58	7.94	1.40
K$^+$	1.38	3.31	7.75	1.96

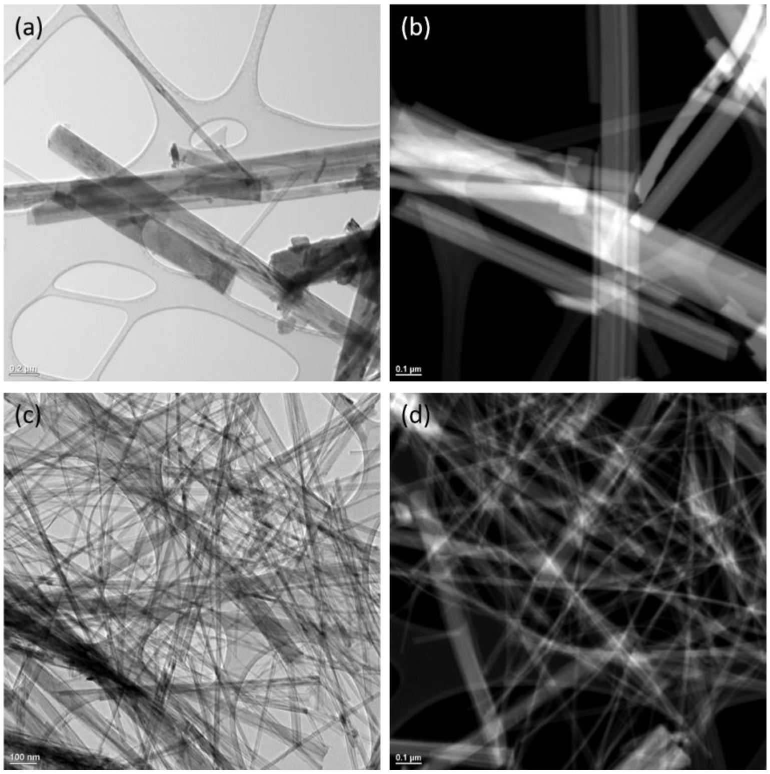


Figure S9. (a) Bright-field TEM and (b) annular dark field scanning TEM (ADF-STEM) imaging of NTO nanobelts. (c) Bright-field TEM and (d) ADF-STEM imaging of KTO nanowires.

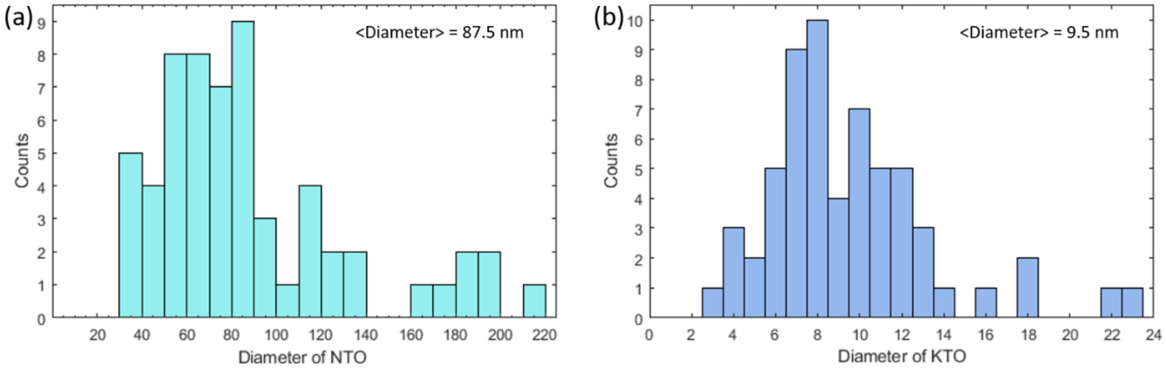


Figure S10. Statistic diameter distributions of (a) NTO nanobelts and (b) KTO nanowires, taken from 60 nanosheets or nanowires, respectively.

Table S2. Atomic positions and thermal parameters of Li_2TiO_3 obtained through Rietveld refinement.

Atom	*x*	*y*	*z*	U_{iso} (Å^2)	Occ.	Site
Li	0.213(2)	½	½	0.001(fixed)	1	4h
Ti	0	0	0	0.030(2)	1	2a
O1	0.9279(5)	0	½	0.001	1	4h
O2	½	0	0	0.001	1	2b
H_2-O1	0.3110(6)	0.082(5)	0.906(6)	0.002(fixed)	0.231(5)	16r
H_2-O2	0.6267(7)	0	½	0.001(fixed)	1	4h

Table S3. Atomic positions and thermal parameters of $NaTi_3O_6OH$ obtained through Rietveld refinement.

Atom	*x*	*y*	*z*	U_{iso} (Å^2)	Occ.	Site
Na	0.755(3)	0	0.886(6)	0.08(2)	1	4i
Ti1	0.75438(1)	0	0.403(2)	0.035(3)	1	4i
Ti2	0.5785(8)	½	0.5320(4)	0.035(3)	1	4i
Ti3	0.576(2)	0	0.295(3)	0.035(3)	1	4i
O1	0.604(6)	0	0.349(9)	0.005(6)	1	4i
O2	0.723(4)	0	0.338(7)	0.005(6)	1	4i
O3	0.693(2)	½	0.672(4)	0.005(6)	1	4i
O4	0.599(3)	½	0.368(4)	0.005(6)	1	4i
O5	0.564(2)	½	0.695(5)	0.005(6)	1	4i
O6	0.533(2)	0	0.419(3)	0.005(6)	1	4i
OH	0.444(2)	0	0.088(5)	0.01(fixed)	1	4i
H_2-O1	0.373(3)	0	0.156(6)	0.01(fixed)	1	4i
H_2-O2	0.888(2)	0	0.914(5)	0.01(fixed)	1	4i

Table S4. Atomic positions and thermal parameters of $K_2Ti_8O_{17}$ obtained through Rietveld refinement.

Atom	*x*	*y*	*z*	U_{iso} (Å^2)	Occ.	Site
K1	0.471(3)	0	0.183(3)	0.01(fixed)	0.31(3)	4i
K2	0.470(5)	0	0.419(4)	0.01(fixed)	0.70(3)	4i
Ti1	0.105(2)	0	0.070(2)	0.01(fixed)	1	4i
Ti2	0.165(2)	0	0.347(3)	0.01(fixed)	1	4i
Ti3	0.180(2)	0	0.581(3)	0.01(fixed)	1	4i
Ti4	0.243(2)	0	0.816(3)	0.01(fixed)	1	4i
O1	0	0	0	0.01(fixed)	1	2a
O2	0.070(3)	0	0.223(7)	0.01(fixed)	1	4i
O3	0.109(7)	0	0.47(1)	0.01(fixed)	1	4i
O4	0.164(7)	0	0.70(1)	0.01(fixed)	1	4i
O5	0.18(1)	0	0.944(7)	0.01(fixed)	1	4i
O6	0.256(6)	0	0.13(1)	0.01(fixed)	1	4i
O7	0.263(6)	0	0.44(1)	0.01(fixed)	1	4i
O8	0.339(7)	0	0.679(7)	0.01(fixed)	1	4i
O9	0.398(6)	0	0.95(1)	0.01(fixed)	1	4i

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1. Mao, Y.; Kanungo, M.; Hemraj-Benny, T.; Wong, S. S., Synthesis and Growth Mechanism of Titanate and Titania One-Dimensional Nanostructures Self-Assembled into Hollow Micrometer-Scale Spherical Aggregates. *Journal of Physical Chemistry B* **2006,** *110*, 702-710.

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