

# In-Situ Synthesis of Mesoporous Single-Grain Layer Anatase TiO<sub>2</sub> Nanosheets without Additives via a Mild and Simple Process for Long-term Li Ion Battery

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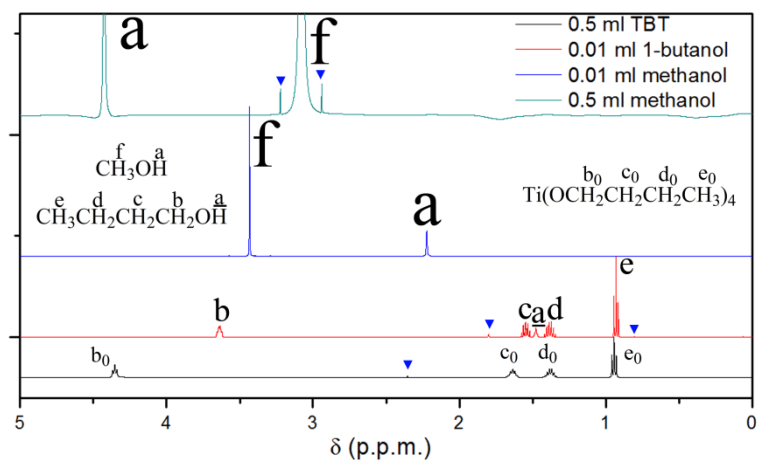
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## Section 1:

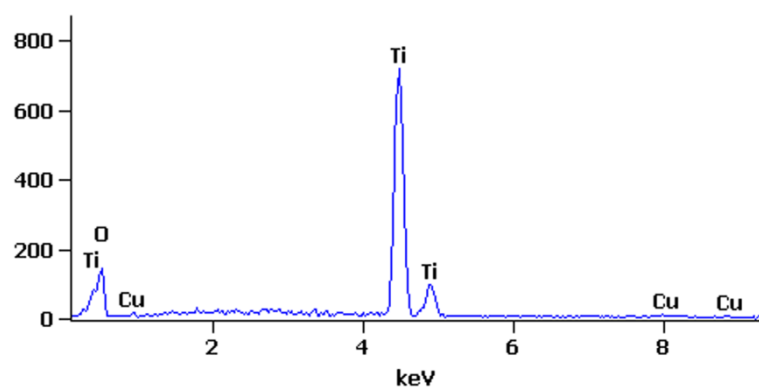
**Table S1.** Sizes of as-prepared TiO<sub>2</sub> with M/T= ~ 319, 160, 80 and 40. TiO<sub>2</sub> obtained after as-prepared TiO<sub>2</sub> with M/T= ~ 40 calcined at 500 °C for 2 h in air. Note: We randomly select over 20 samples to obtain the length parameters and over 50 samples to obtain the diameter parameters. It is noted that some wires in Fig. 1c are aggregated, but we estimate their size using single wires.

Samples	M/T	Diameter (nm)	Average diameter (nm)	Length (μm)	Average length (μm)	Thickness (nm)
TiO <sub>2</sub> in Figure 1a	~ 319	80-350	170	1.5- 7.8	3.8	
TiO <sub>2</sub> in Figure 1b	~ 160	110-410	210	1.5-5.1	3.0	
TiO <sub>2</sub> in Figure 1c	~ 80	120-460	240	1.3- 4.5	2.5	
TiO <sub>2</sub> in Figure 1d	~ 40	210-570	310	0.6- 3.1	1.9	40- 60
TiO <sub>2</sub> in	~ 40	100- 460	160	0.4-1.4	0.93	15- 30

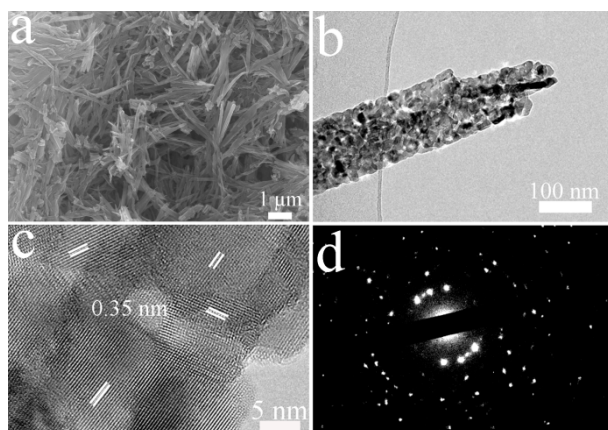
Figure 3a						
TBM in	~ 40	62-646	240	0.5-2.8	1.4	~ 50
Figure 5a						
TBM in	~ 319	30-390	150	1.6-5.4	3.8	
Figure S5						
TiO <sub>2</sub> in	~ 40	91-657	240	0.6-3.7	1.7	20-60
Figure 5f						



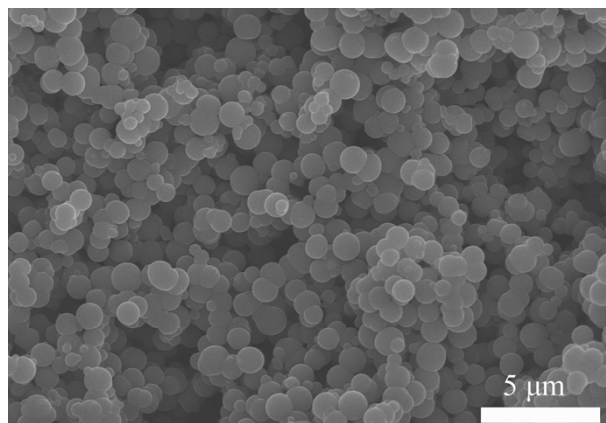
**Figure S1.** <sup>1</sup>HMR (500 MHz, 0.55 ml CDCl<sub>3</sub>) observation of TBT, 1-butanol and methanol.



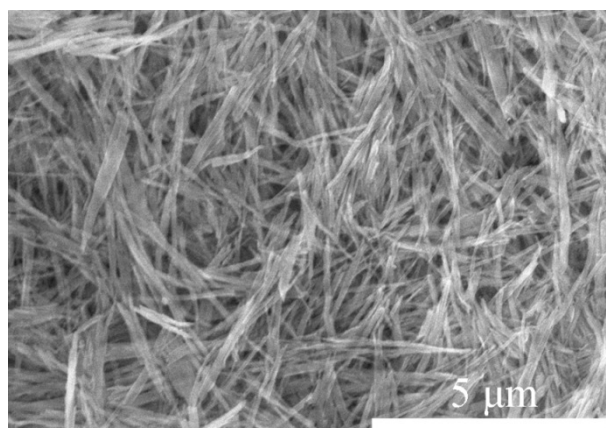
**Figure S2.** EDX of TiO<sub>2</sub> xerogel. The peak of Cu is from Cu substrate.



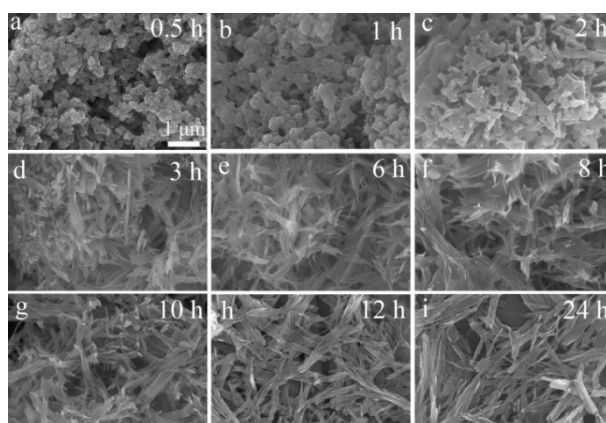
**Figure S3.** (a) FESEM image of sample with  $M/T \sim 160$  calcined at  $500\text{ }^\circ\text{C}$  for 2 h in air. TEM (b) and high-resolution TEM (c) images, and SEAD (d) pattern of a nanowire.



**Figure S4.** SEM image of sample obtained using ethanol instead of methanol. Reaction solution composed of 2 ml TBT and 18 ml ethanol.

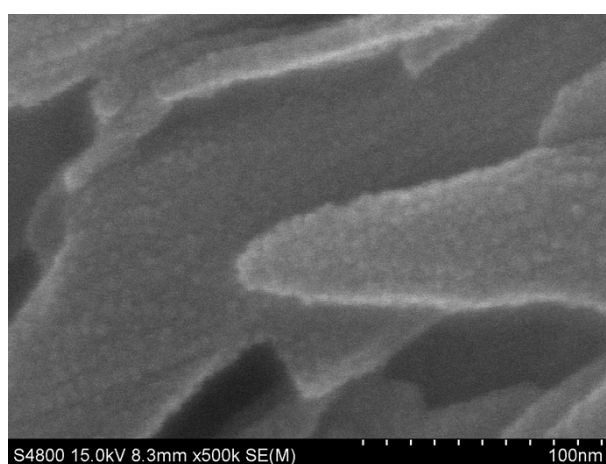


**Figure S5.** FESEM image of TBM wires.

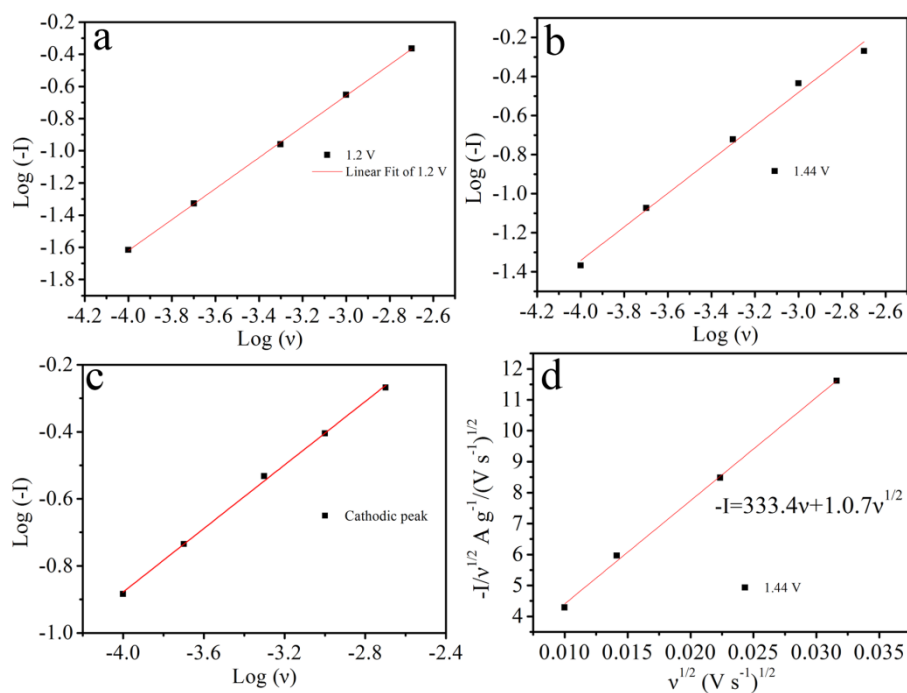


**Figure S6.** FESEM images of  $\text{TiO}_2$  obtained via hydrolysis of TBM fabricated with 0.5-24 h reaction time ( $M/T \sim 160$ ). With shorter reaction time, such as 0.5 and 1 h, there is small amount of TBM produced and TBT rapidly hydrolyzes with water when exposed to air, only leading to emergence of irregular spherical particles being similar

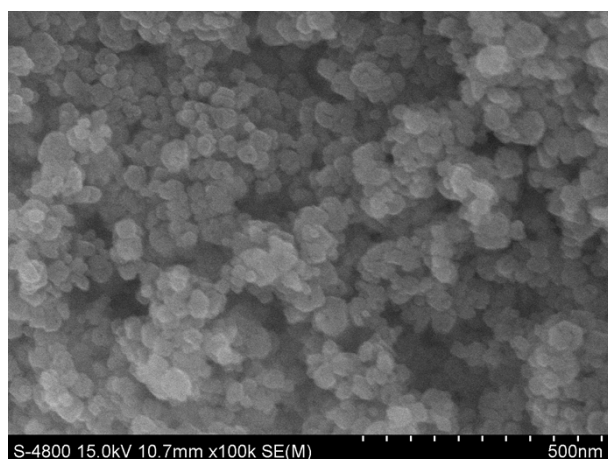
with those prepared using ethanol (Figure S4).  $\text{TiO}_2$  wires appear when reaction time is prolonged to 2 h. Furthermore, spherical particles gradually disappear and wires tend to grow longer and more uniform with increasing reaction time (Figure S6d-S6h). When the reaction time is increased to 12 h, the transesterification reactions basically finish and maintain a dynamic equilibrium state due to its reversibility. In accordance with our direct observation of white precipitate, it is suggested that no more TBM is produced (Figure S12b). As a result, the  $\text{TiO}_2$  maintains an unchanged morphology (Figure S6h and S6i) with a reaction time longer than 12 h. It is evident that  $\text{TiO}_2$  irregular particles are produced from rapid hydrolysis of TBT when there is little or no amount of TBM with a short reaction time, and the morphology of  $\text{TiO}_2$  varies with formation of TBM until the formation of TBM finishes with a dynamic equilibrium state.



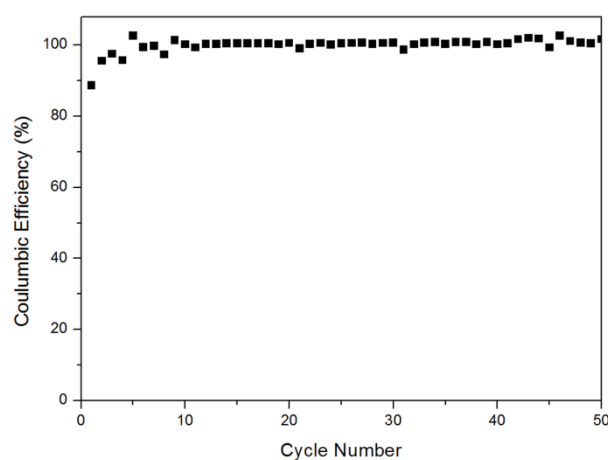
**Figure S7.** HR-FESEM image of  $\text{TiO}_2$  sheets extracted from Figure 3f.



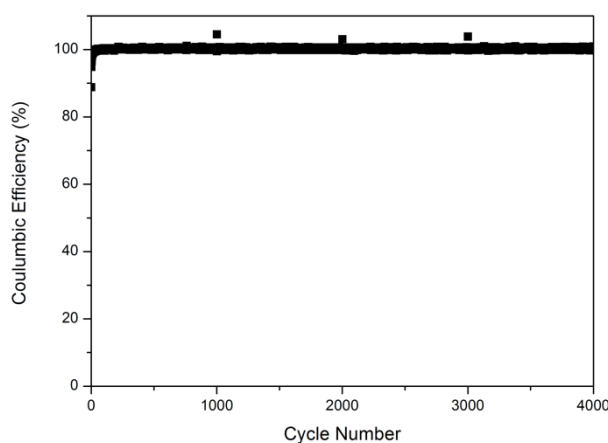
**Figure S8.** (a-c)  $\log v$  vs  $\log I$  curves at 1.2 V, 1.44 V location and cathodic peak for obtaining a and b values. (d) The plot of  $v^{1/2}$  vs  $I(V)/v^{1/2}$ .



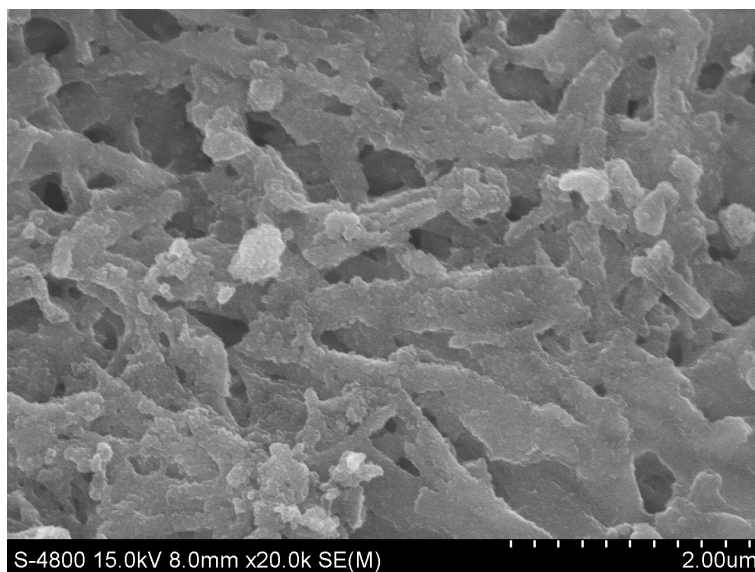
**Figure S9.** SEM image of commercial anatase TiO<sub>2</sub> particles after calcined at 500 °C for 2 h. The spherical particles are ~ 25 nm in size but are serious agglomerated.



**Figure S10.** Coulombic efficiency curves of TiO<sub>2</sub> nanosheets at 1 C over 50 cycles



**Figure S11.** Coulombic efficiency curves of TiO<sub>2</sub> nanosheets at 5 C over 4000 cycles.



**Figure S12.** SEM image of anatase  $\text{TiO}_2$  nanosheets after discharge-charge at 5 C over 4000 cycles. The spherical particles are acetylene black used as conductive additive.

## Section 2:

**Exploration of component of TBM and role of methanol.** Methanol was firstly added into a vial at room temperature ( $\sim 25\text{ }^\circ\text{C}$ ). Then, TBT was poured into methanol immediately and mixed well. The solution was sealed by a cap and kept static for certain time at room temperature. Detailed amounts of methanol and TBT were listed in Table S2. All the operations were conducted in a glove box full of high-purity argon ( $> 99.99\%$ ) with concentration of water below 1 ppm to avoid possible effect of water in air on TBT. For comparison, TBT was replaced by TTIP or methanol was replaced by other alcohols (ethanol, n-propanol, isopropanol and n-butanol) with other conditions unchanged.

When TBT is added into methanol ( $M/T > 6$ ) at room temperature in a glove box filled with high-purity argon to avoid possible effect of the water in air on TBT, white solid tetramethyl titanate ( $\text{Ti}(\text{OCH}_3)_4$ )<sup>1</sup> immediately appears and the time for appearance of white colloid is closely related to  $M/T$  (Figure S13a and S13b, Table S2). If TBT is replaced by other titanium alkoxides (e.g. titanium isopropoxide), the similar phenomenon emerges. However, no white colloid but homogeneous solutions are observed when TBT is added into other monohydric alcohols, such as ethanol, n-propanol, isopropanol and n-butanol (Figure S13c). Thus, methanol can play a role as ‘precipitant’ for titanium alkoxide and reacts with titanium alkoxide to produce white precipitation  $\text{Ti}(\text{OCH}_3)_4$ ,<sup>1</sup> whereas other alcohols (e.g. ethanol) are just solvents for TBT.

Supernatant was collected from upper layer of reaction solution ( $M/T = 79.79$ ) and a mixture of methanol and 1-butanol (molar ratio of methanol and 1-butanol denoted as  $M/B = 79.79$ ) was prepared to smoothly confirm the component of the

supernatant. As revealed by NMR spectrum (Figure S14a), the supernatant can be determined to be composed of methanol and 1-butanol. In addition, more 1-butanol is produced (Figure S14b) from reaction solution by increasing the addition of TBT, clearly suggesting that  $\text{Ti}(\text{OCH}_3)_4$  is fabricated using alcoholysis<sup>1</sup> via transesterification reaction of methanol and TBT (reaction 1 in Scheme 1). Methanol is also confirmed to be contained in the supernatant by FTIR spectra (Figure S15), while 1-butanol is not observed due to its low concentration. In addition, it is noted that chemical shifts of the supernatant are not completely the same as those of the mixture, whereas it is reasonable. This is because the supernatant is obtained from upper layer of reaction solution ( $M/T = 79.79$ ) which involves reversible transesterification reactions (see below). This leads to a different concentration and component for upper layer of reaction solution ( $M/T = 79.79$ ) compared to those for mixture of methanol and 1-butanol ( $M/B = 79.79$ ). Moreover, chemical shifts vary with different concentration and different component (Figure S14a-S14c). This is especially true for  $H_a$ . Its signal shifts to low field with increasing concentration (Figure S14a and S14b), which is caused by intramolecular hydrogen bonding of methanol and 1-butanol, and intermolecular hydrogen bonding between methanol and 1-butanol, whereas other chemical shifts move to high field.

For the white precipitation, its component is complicated and the <sup>1</sup>HMR spectrum is unrecognized (Figure S14d). However, we discovered that white gel-like colloid disappears when heated, whereas it appears again after the temperature drops to room temperature (Figure S16a). We speculated that the transesterification reactions could be a reversible reaction and prepared as solid-like white gel (Figure S16b) by mixing 12 ml methanol and 10 ml TBT ( $M/T = 10.64$ ) under vigorous stirring for 24 h at room temperature. The white gel turns into a clear solution with methanol evaporated after heated for 12 h at 50 °C under a vacuum condition of -0.08 MPa. However, white gel reappears after fresh 12 ml methanol is added into the clear solution at room temperature, strongly reflecting that the transesterification reactions (reaction 1) are reversible when heated.

When the reaction solutions are prepared with  $M/T$  less than 6, no white precipitation is obtained at the bottom of a glass vial (Figure S12a and table S2). For example, after 15 ml TBT is poured into 7 ml ( $M/T = 4.14$ ), the solution is still clear and transparent even after being left to react for more than one year. However, NMR spectrum indicates that new substance emerges (Figure S17). It is suggested that there is insufficient TBT to produce  $\text{Ti}(\text{OCH}_3)_4$ , but some new methyl derivatives<sup>1</sup> such as  $\text{Ti}(\text{OC}_4\text{H}_9)_{4-n}(\text{OCH}_3)_n$  ( $n = 1, 2$  and  $3$ ) are fabricated. Thus, it is indicated that the transesterification reactions could be multi-step reactions (Scheme S1).

Based on the above information, the transesterification reactions probably composed of multi-step reactions as presented by reaction 2-5 (Scheme S1) could be expressed as reaction 1 (Scheme 1). The transesterification reactions are reversible when heated. Thus, the product obtained by the transesterification reactions of methanol and TBT could be a composite of  $\text{Ti}(\text{OC}_4\text{H}_9)_{4-n}(\text{OCH}_3)_n$  ( $n = 1, 2, 3$  and  $4$ ) and we express this complex product as  $\text{Ti}(\text{OC}_4\text{H}_9)_{4-n}(\text{OCH}_3)_n$  ( $1 \leq n \leq 4$ ) (TBM).

Furthermore, intermolecular interactions, such as hydrogen bonding interactions, universal exist in our system, leading to complicated  $^1\text{HMR}$  spectra (Figure S14 and S17) of the products.

**Table S2.** Different M/T and TP of reaction solutions

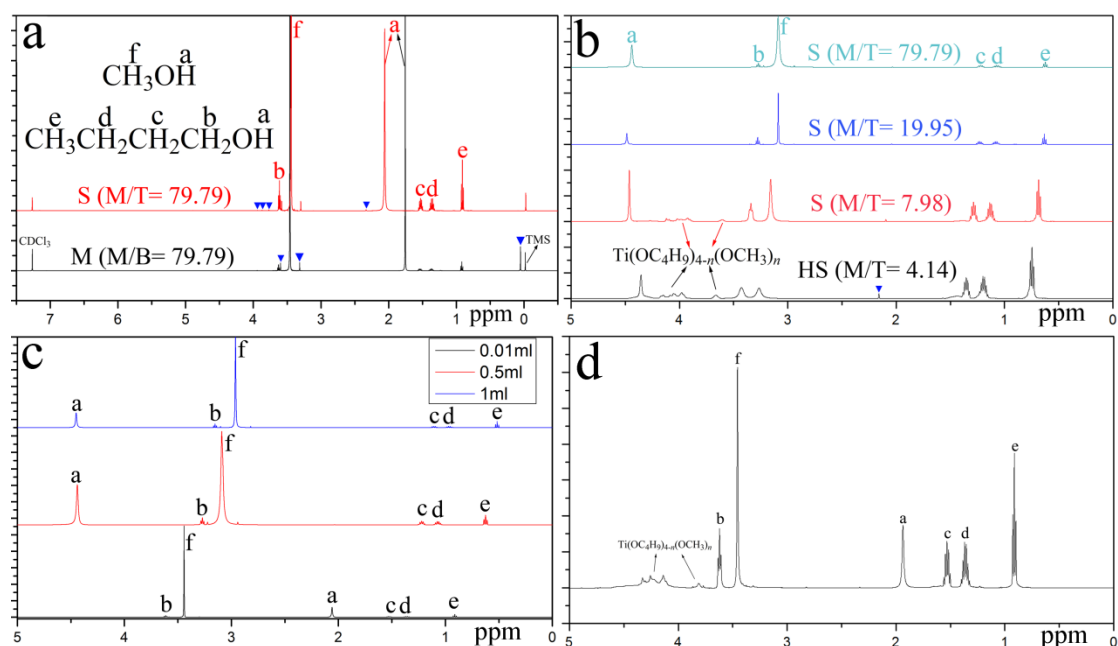
Methanol (ml)	TBT (ml)	M/T	TP
18	0.5	319.14	Few seconds
18	1	159.56	Few seconds
15	1	132.98	Few seconds
18	2	79.79	Few seconds
18	4	39.89	Few seconds
18	8	19.95	Few seconds
13.5	10	11.97	Few minutes
12	10	10.64	Few minutes
9	8	9.97	~2 hours
9	10	7.98	~12 hours
9	13	6.14	~72 hours
8	14	5.07	NP
9	16	4.99	NP
7	15	4.14	NP
6	16	3.32	NP
1	9	0.985	NP

Note: TP denoted as time for appearance of white colloid. NP denoted as no precipitation

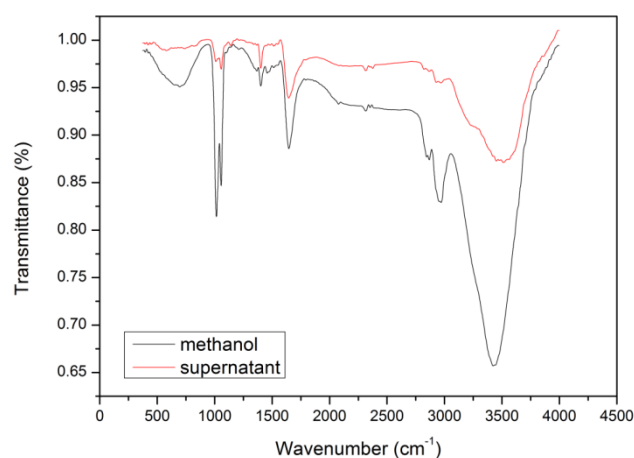


**Figure S13.** (a) Picture of solutions with M/T of 4.14, 4.99, 5.07, 6.14, 7.98, 9.97, 19.95, 39.89 and 79.79 (from left to right). (b) Pictures of reaction solution composed of 1 ml TBT and 18ml methanol (M/T= ~ 160) kept static at room temperature for 10 min, 30 min, 1 h, 12 h and 24 h (from left to right). (c) Pictures of reaction solutions composed of 1 ml TBT and 18ml alcohols (ethanol, n-propanol, isopropanol and n-butanol, from left to right) were kept static at room temperature for 24 h.

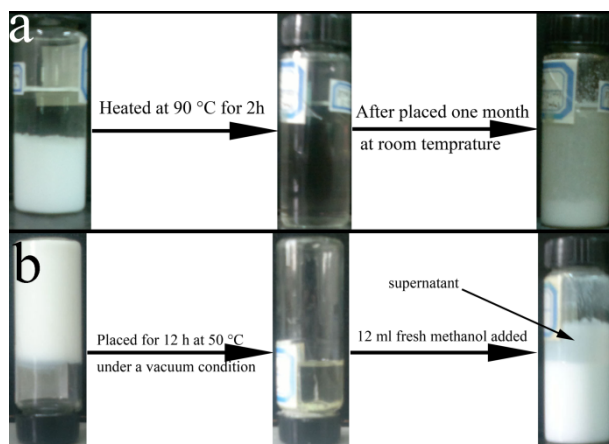




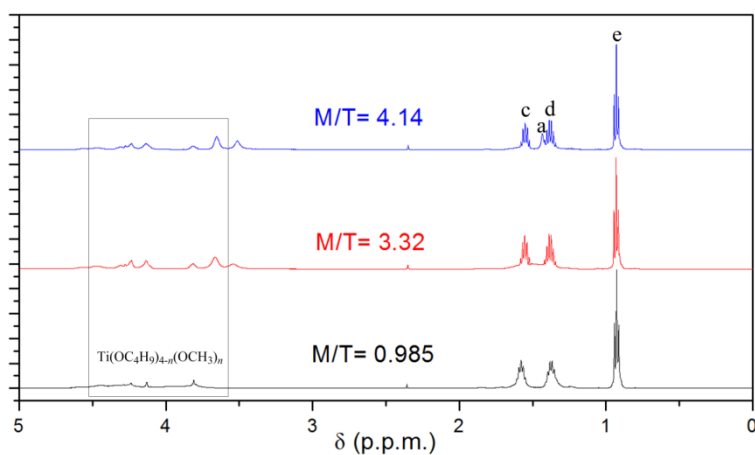
**Figure S14.** (a) <sup>1</sup>HMR (500 MHz) observation of supernatant (S) and mixture (M) of methanol and 1-butanol. 0.01 ml sample dissolved in 0.55 ml CDCl<sub>3</sub> for the measurement. (b) <sup>1</sup>HMR (500 MHz) observation of supernatant (S), homogenous solution (HB) of methanol and TBT, and mixture (M) of methanol and 1-butanol. 0.5 ml sample dissolved in 0.55 ml CDCl<sub>3</sub> for the measurement. Triangle denoted as impurities from methanol, 1-butanol, and TBT (see Figure S1). (c) <sup>1</sup>HMR (500 MHz, 0.01, 0.5 and 1 ml sample dissolved in 0.55 ml CDCl<sub>3</sub>) observation of supernatant (M/T= 79.79) (d) <sup>1</sup>HMR (500 MHz, 0.55 ml CDCl<sub>3</sub>) observation of white precipitate. Note: some amount of supernatant is contained.



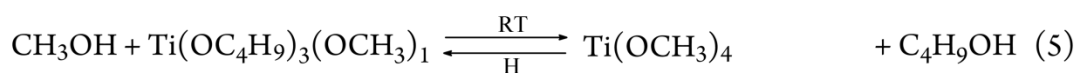
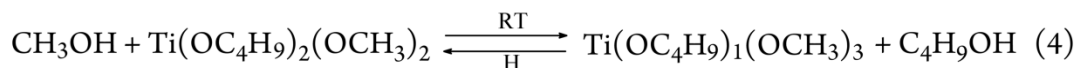
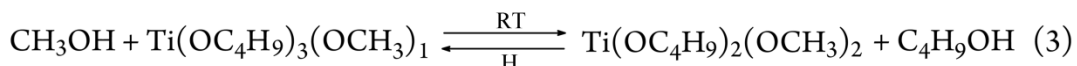
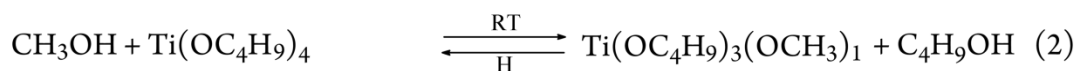
**Figure S15.** FTIR spectra of supernatant (M/T = 79.79) and methanol.



**Figure 16.** (a) Pictures of reaction solution (M/T= 9.70) varying with temperature. (b) Pictures of changes of reaction solution (M/T= 10.64). Note: supernatant which appeared in the third picture could be the residual methanol in sample shown in the second picture.



**Figure S17.**  $^1\text{HMR}$  (500 MHz) observation for homogenous solution of methanol and TBT. 0.01 ml sample dissolved in 0.55 ml  $\text{CDCl}_3$  for the measurement.



**Scheme S1.** Multi-step reactions between TBT and methanol at room temperature. RT: room

temperature, H: heat.

## REFERENCES

- (1) Bischoff, F.; Adkins, H. The alkyl titanates. *J. Am. Chem. Soc.* **1924**, *46*, 256-259.