Electronic Supplementary Information (ESI)

Guided growth and alignment of millimetre-long titanate nanofibers in solution

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Fig. S1. Typical XRD pattern of the titanate network indicates that sodium trititanate $(Na_2Ti_3O_7)$ as a primary crystalline phase in the networks (JCPDs file, No. 31-1329). Sample for XRD measurement is the network grown under the guidance of parallel grooves. The remarkably strong diffraction from (001) plane is indicative of the preferred orientation in the sample.



Fig. S2. a) Photograph of the network grown under the guidance of parallel grooves, where the texture is visible to naked eyes. b) Optical microscopy image of the network indicates the nanofibers are readily visualized. c-e) SEM images taken at the corresponding sites marked in S2b. It can be seen that the nanofibers are well-aligned and isolated at the middle portions of the bundles (Fig. S2e). At the sites close to the end portions of the bundles (Fig. S2d), the nanofibers begin to twist. At the end portions of the bundles (Fig. S2c), the nanofibers are twisted severely. With such an intelligent way, single nanofibers are bound together and are able to organize into macroscopic systems. f) A series of TEM images taken on an individual nanofiber confirm that the nanofibers are uniform and ultralong. On the right side, the nanofiber is sheltered by the copper grid, as indicated by the red arrow.



Fig. S3. a) Photography of the network grown under the guidance of concentric grooves, where the texture is also visible to naked eyes. b) A panoramic SEM image of the network. c-e) SEM images of the network at magnification from low to high. It can be seen that the network is macroscopically ordered, but the nanofibers are curved at microscale because they are affected by the curvature effect of the concentric grooves.



Fig. S4. Proposed mechanism for interpreting the guided growth and alignment of the titanate nanofibers, where R is the inside diameter of the reactor and w is the gap width of the groove. The red dots indicate the nucleus atttched on the grooves. Sites A and B indicate the top surface and side surface of the grooves, respectively.

According to the interface theories (D. P. Woodruff, *The Solid-Liquid Interface*, Cambridge University Press, 1973.), there exist liquid-solid interfacial tensions around the grooves and the nucleus, with the direction pointing to the solution. Therefore, the nucleus are subject to the tension F_1 and F_2 , respectively. The strengths of the tensions are determined by the following equations:

$$F_1 = \gamma/R \qquad (1)$$
$$F_2 = 2\gamma/w \qquad (2)$$

Where γ is the surface energy. The tension F_1 will guide the nanofibers to grow and stretch into the solution. The tension F_2 will guide the nanofibers to grow and align along the wall of the reactor.



Fig. S5. TG and DSC measurement of the protonated network, which reveals that the phase transition from titanate to TiO_2 is accompanied by a mass loss as large as 19.01%.



Fig. S6. A panoramic SEM image of the network after protonation and thermal annealing



Fig. S7 XRD pattern of the network after calcination at 700 °C for 5 hours. It can be seen that the peaks from TiO_2 -B disappeare and the sample is comprised of pure anatase TiO_2 .