

## **Electronic Supplementary Information (ESI) for**

# **Controllable synthesis of in-situ grown titanate hierarchical microspheres and subsequent chemical modifications for superhydrophobic and oil-water separation properties**

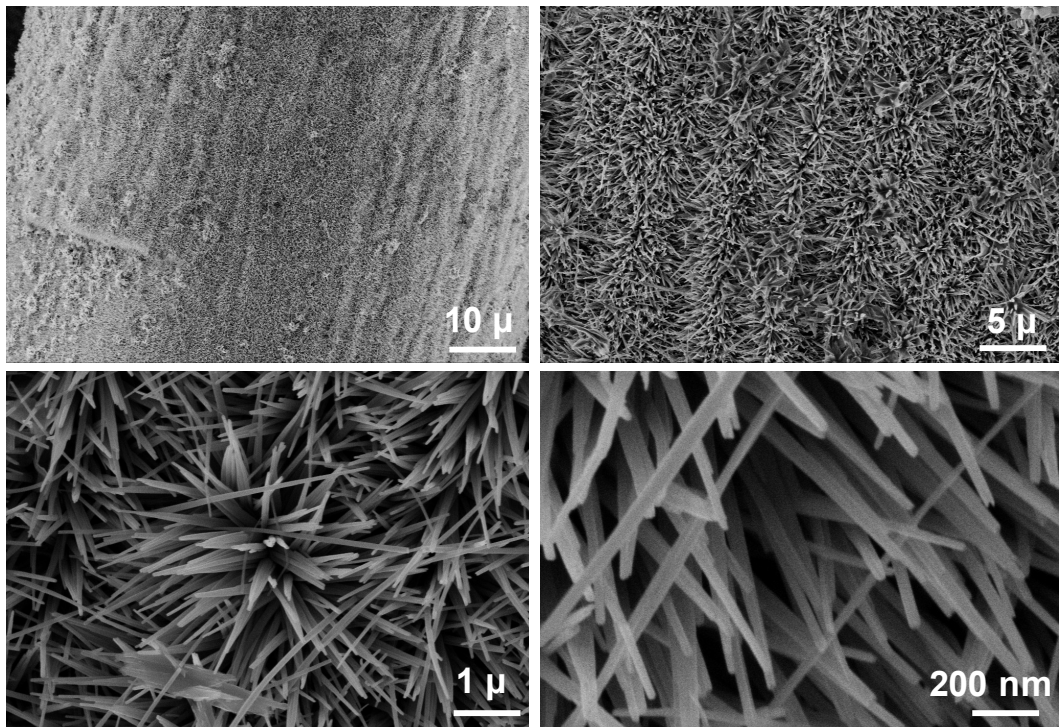
Yong Li,<sup>1,†</sup> Jiyang Xie,<sup>1,†</sup> Changjin Guo,<sup>1</sup> Jian Wang,<sup>2,\*</sup> Huan Liu<sup>1</sup> and Wanbiao Hu<sup>1,2</sup>

<sup>1</sup> key Laboratory of LCR Materials and Devices of Yunnan Province, School of Materials Science and Engineering, Yunnan University, Kunming 650091, P. R. China.

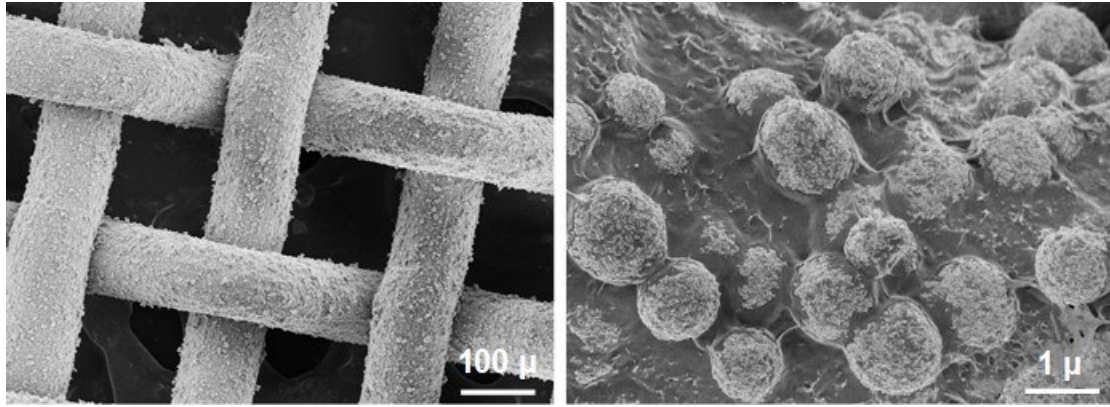
<sup>2</sup> School of Physics and Astronomy, Yunnan University, Kunming 650091, P. R. China

E-mail: wang.jian@ynu.edu.cn

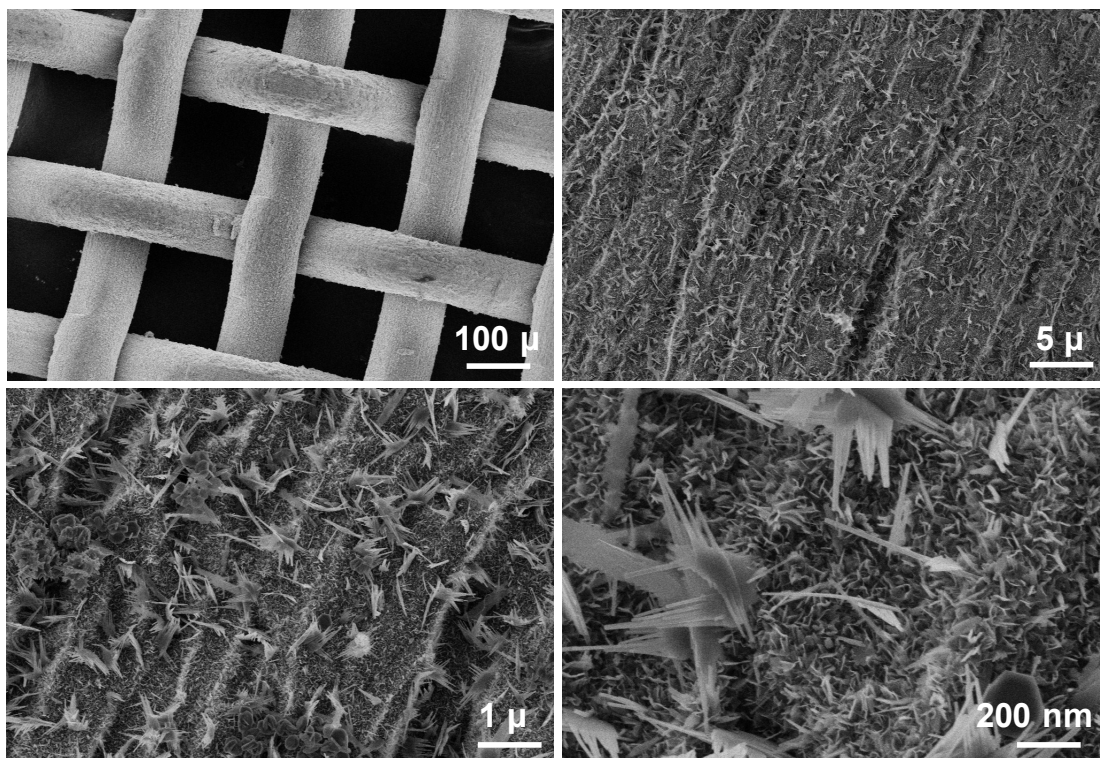
<sup>†</sup> These authors equally contribute to this work.



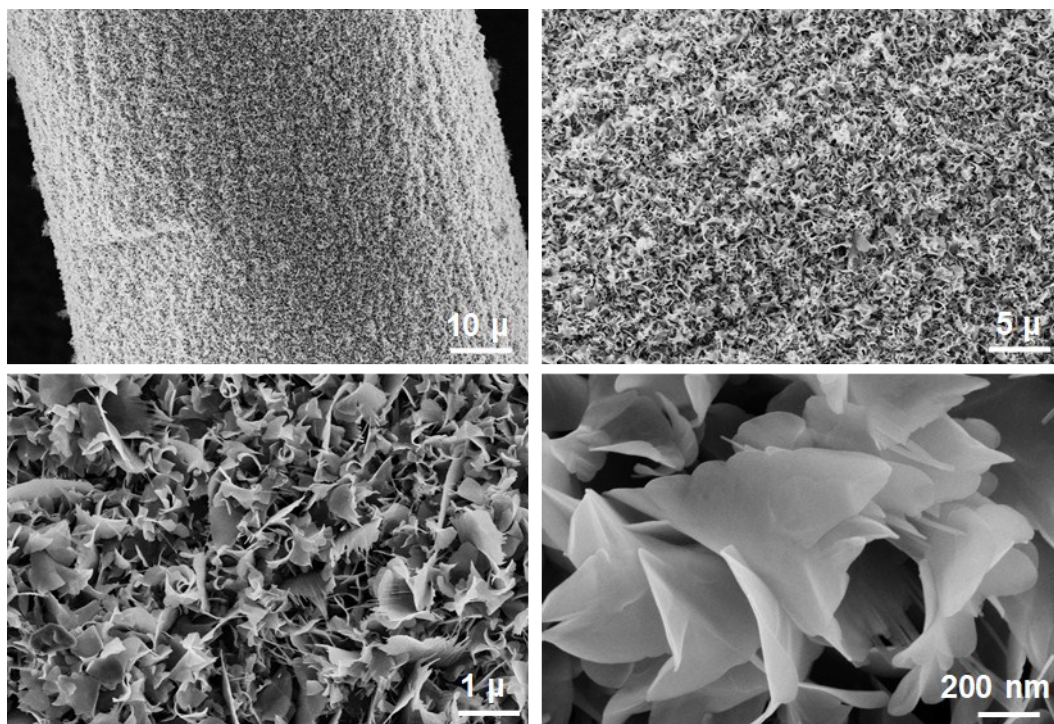
**Figure S1.** Titanate nanostructures synthesized by the hydrothermal reaction at a NaOH concentration of  $C_{\text{NaOH}} = 1 \text{ M}$  and temperature of  $T_{\text{hydro}} = 180 \text{ }^\circ\text{C}$  with using the Ti mesh that was not treated by an initial etching process, i.e. the conditions:  $C_{\text{NaOH}} = 1 \text{ M}$ ;  $T_{\text{hydro}} = 180 \text{ }^\circ\text{C}$ ; without initial etching. The resulting morphologies are nearly the nanowires that uniformly grow on the Ti mesh. This, on the one hand, is consistent with the results that the nanowires consisting of the microspheres were also obtained at same  $C_{\text{NaOH}}$  and  $T_{\text{hydro}}$ , and on the other hand, indicates that the initial etching process i.e. surface acidification reaction in a mixture of HCl and NaCl at  $120 \text{ }^\circ\text{C}$  is necessary to form final microspheres. Therefore, all the other synthesis experiments carried out were all based on the initial etching treatments.



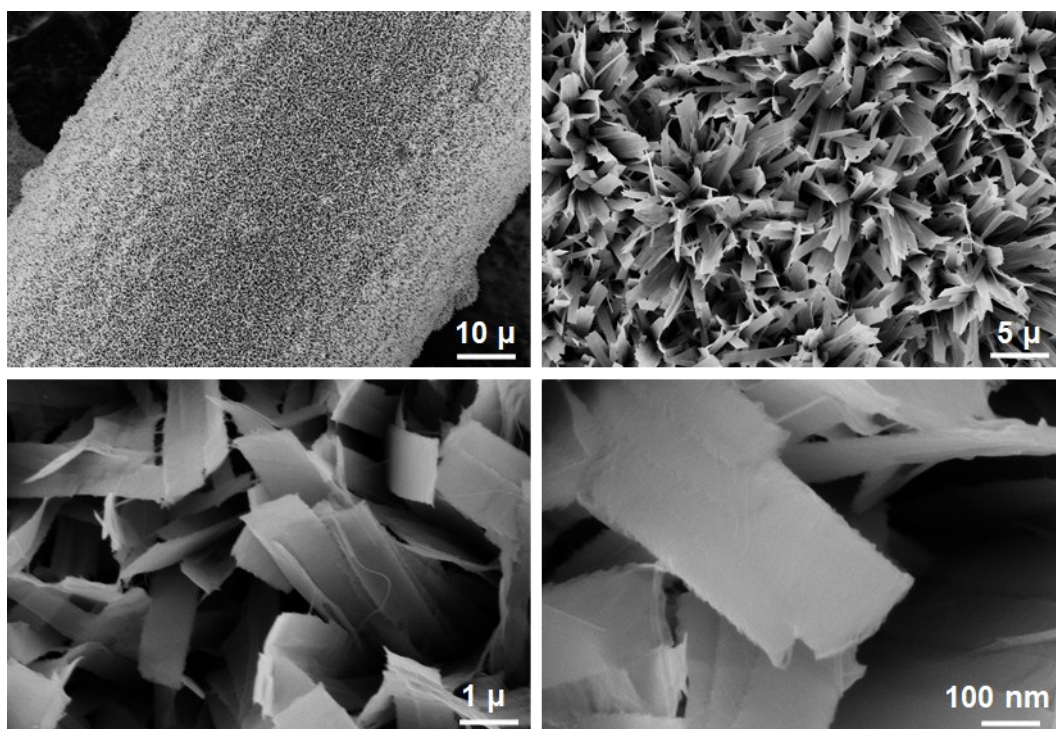
**Figure S2.** Titanate nanostructures synthesized by the hydrothermal reaction under the conditions:  $C_{\text{NaOH}} = 1 \text{ M}$ ;  $T_{\text{hydro}} = 180 \text{ }^\circ\text{C}$ ;  $t_{\text{hydro}} = 0.5 \text{ h}$ ; with initial etching. It can be seen that with shorter hydrothermal reaction duration, only very small spheres can form, which however would grow into larger spheres when prolonging the reaction durations, e.g., 6h in Figure 1d and Figure 2d-h.



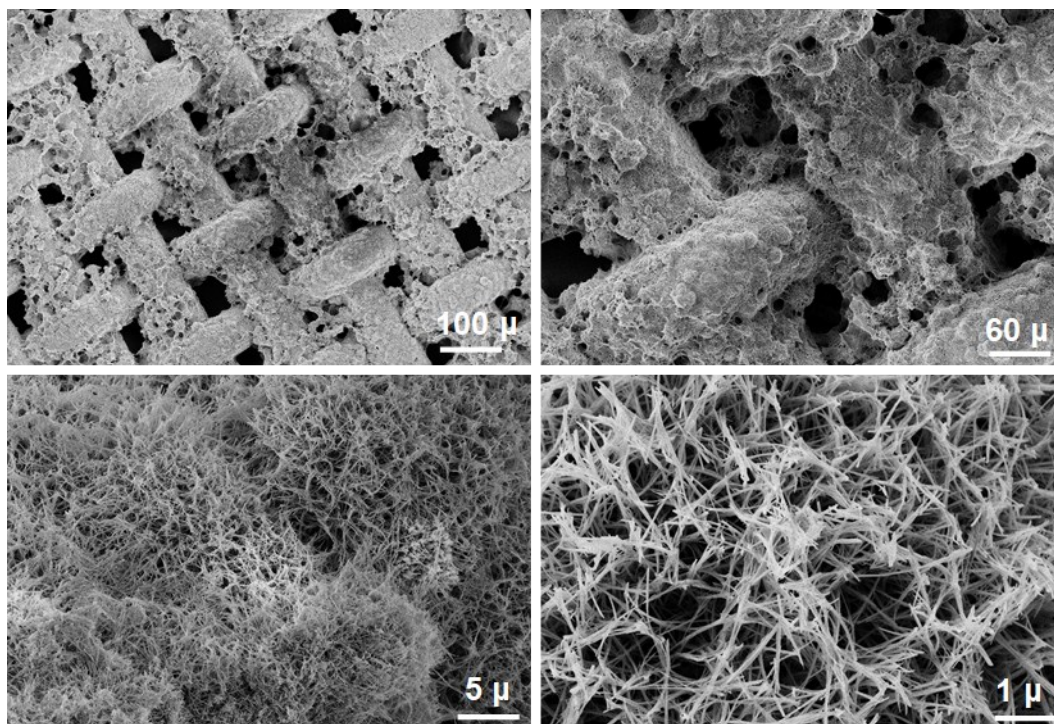
**Figure S3.** Titanate nanostructures synthesized by the hydrothermal reaction under the conditions:  $C_{\text{NaOH}} = 0.02 \text{ M}$ ;  $T_{\text{hydro}} = 180 \text{ }^\circ\text{C}$ ; with initial etching. Because the  $C_{\text{NaOH}}$  is quite low, the titanate nucleation should be quite slow. That is, the nucleation at different regions on/near the Ti mesh has enough time to happen, making the titanate nucleation forms everywhere. When prolonging the hydrothermal reaction duration, titanate nanoneedles or some nanosheets that uniformly distribute on the Ti mesh can form. These nanoneedles or nanosheets under the relatively low  $C_{\text{NaOH}}$  are hard to grow too large because the NaOH needs participates into the hydrothermal reaction as Na source.



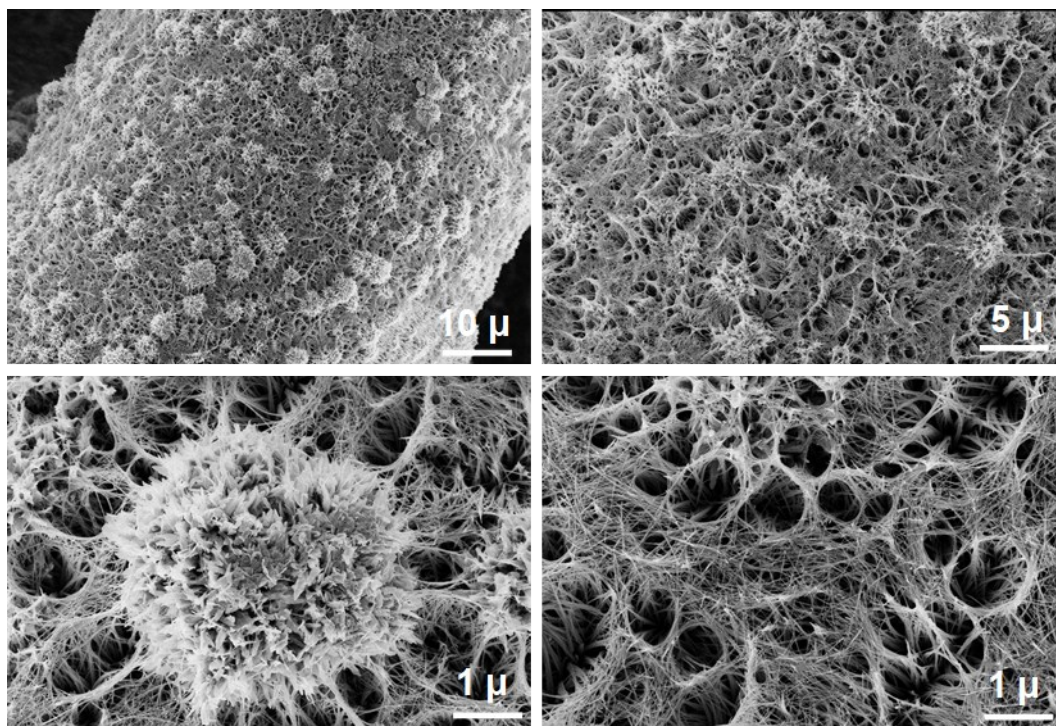
**Figure S4.** Titanate nanostructures synthesized by the hydrothermal reaction under the conditions:  $C_{\text{NaOH}} = 0.1 \text{ M}$ ;  $T_{\text{hydro}} = 180 \text{ }^\circ\text{C}$ ; with initial etching. When increasing the  $C_{\text{NaOH}}$ , the original nanoneedles or some nanosheets (see Figure S2) develop into nanosheets, which all uniformly grow on the Ti mesh similarly. This should be due to the relatively low  $C_{\text{NaOH}}$  still makes the titanate nucleation happens everywhere, similar to the case with  $C_{\text{NaOH}} = 0.02 \text{ M}$  (Figure S2).



**Figure S5.** Titanate nanostructures synthesized by the hydrothermal reaction under the conditions:  $C_{\text{NaOH}} = 0.5 \text{ M}$ ;  $T_{\text{hydro}} = 180 \text{ }^\circ\text{C}$ ; with initial etching. Continuing to increasing the  $C_{\text{NaOH}}$ , the nanobelts can be obtained. These nanobelts still uniformly grown on the Ti mesh. The formation reason or mechanism should be similar to that obtained in Figures S2 and S3. Therefore, the formation of the titanate microspheres that consist of the sodium titanate nanowires requires a certain concentration of NaOH solution (i.e.  $C_{\text{NaOH}} = 1\text{-}2 \text{ M}$  in this work that was seen in Figures 1 and 2 in the main text.) for hydrothermal reaction.

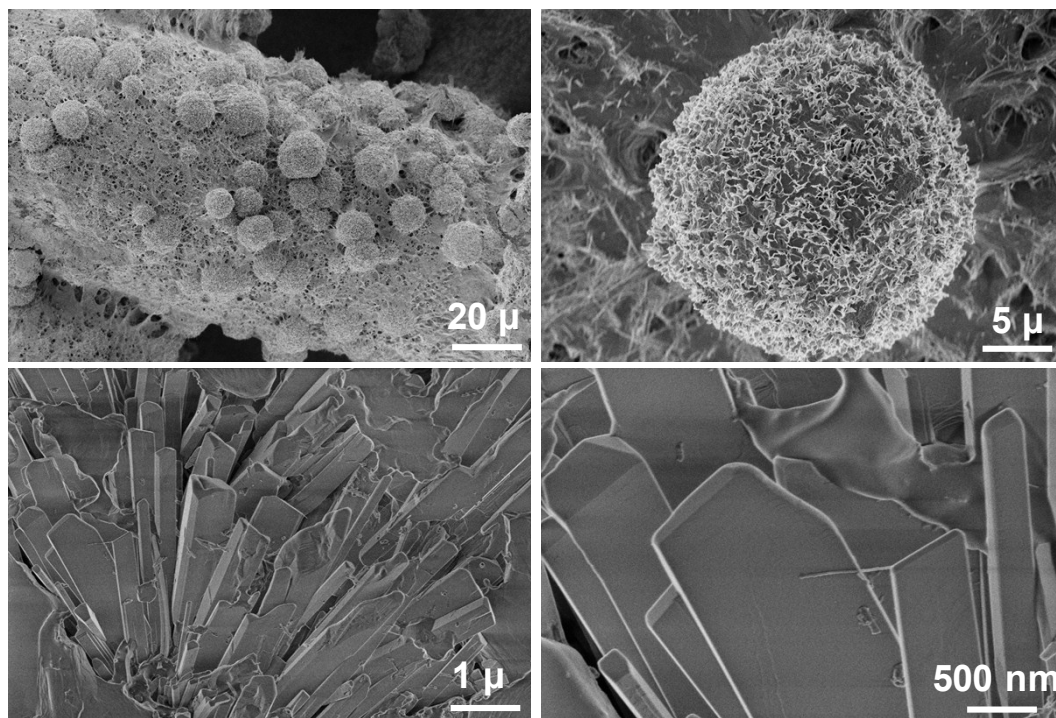


**Figure S6.** Titanate nanostructures synthesized by the hydrothermal reaction under the conditions:  $C_{\text{NaOH}} = 5 \text{ M}$ ;  $T_{\text{hydro}} = 180 \text{ }^\circ\text{C}$ ; with initial etching. When the  $C_{\text{NaOH}}$  is too high (far beyond the  $C_{\text{NaOH}}$  condition for hierarchical microsphere synthesis), both the microspheres and nanowires were simultaneously obtained, which cover on the Ti mesh in a form of disordered distributions. This might be due to the quite high  $C_{\text{NaOH}}$  would quickly dissolve the Ti metal with forming  $\text{Ti}^{4+}$ -based complexes. These  $\text{Ti}^{4+}$ -based complexes in the solution near the Ti mesh surface could react with NaOH to generate sodium titanate nanowires (it is worth noting that there have extensive experimental works reported that  $\text{Ti}^{4+}$ -based species could react with NaOH to give sodium titanate nanowires under the relatively high  $C_{\text{NaOH}}$ , e.g. 5-12 M). Therefore, the reaction occurring near the Ti mesh surface should not be ascribed to the sort of in-situ nucleation and growth any more, which would lead to the normal nanowires formation instead of microspheres.

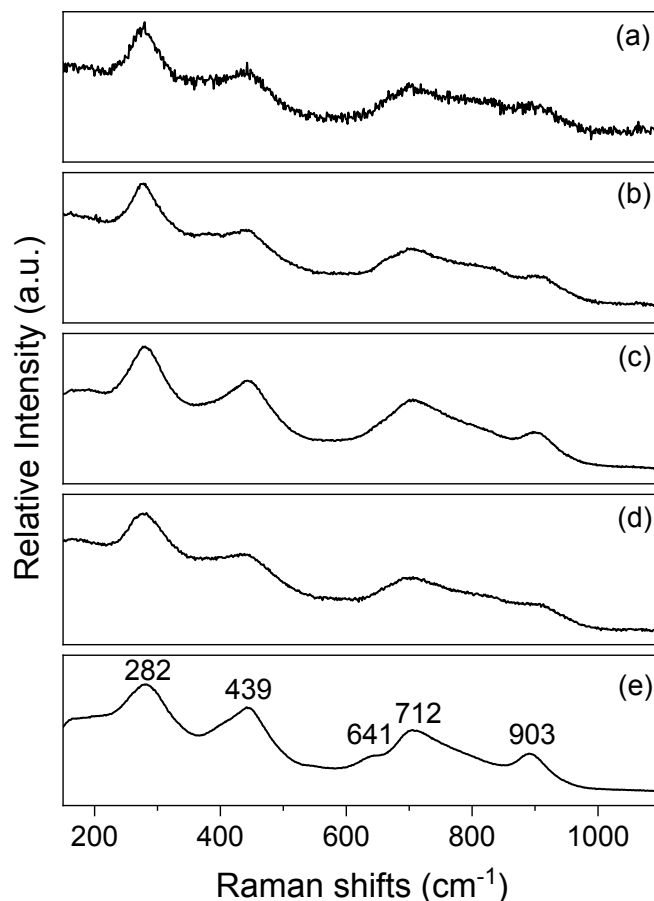


**Figure S7.** Titanate nanostructures synthesized by the hydrothermal reaction under the conditions:  $C_{\text{NaOH}} = 1 \text{ M}$ ;  $T_{\text{hydro}} = 150 \text{ }^{\circ}\text{C}$ ; with initial etching. It can be seen that both the microspheres and nanowires were obtained at a relatively low reaction temperature. The diameters for the microspheres and nanowires are obviously smaller than those synthesized at higher temperatures (e.g.  $180 \text{ }^{\circ}\text{C}$  in Figure 2 in main text). Under the low temperatures, the titanate nucleation and growth are expected to be relatively slow. Such a slow nucleation, similar to the case at relatively low  $C_{\text{NaOH}}$  (Figures S2-4), could lead to the titanate nanostructure formation everywhere. Therefore, in addition to the microspheres, the nanowires could also simultaneously grow on the Ti mesh.



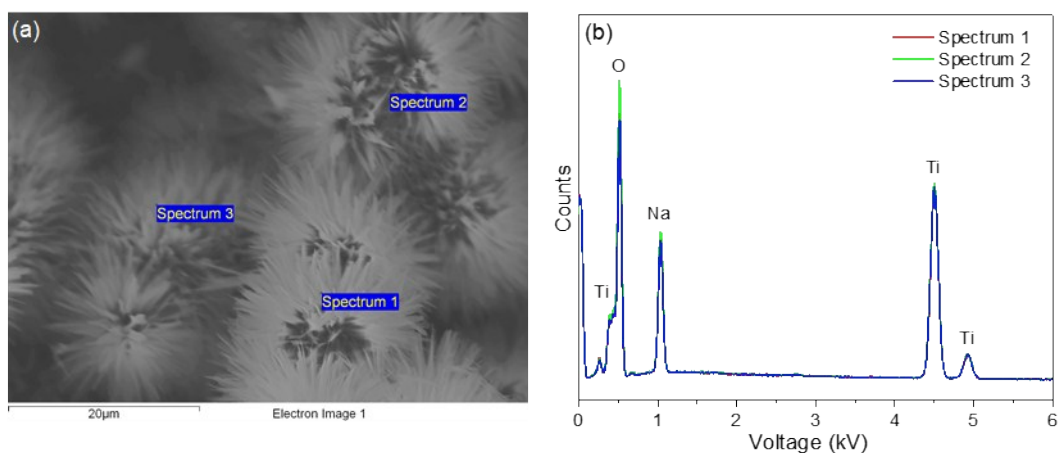


**Figure S8.** Titanate nanostructures synthesized by the hydrothermal reaction under the conditions:  $C_{\text{NaOH}} = 1 \text{ M}$ ;  $T_{\text{hydro}} = 200 \text{ }^\circ\text{C}$ ; with initial etching. Under too high hydrothermal temperature, both the microspheres and nanowires were obtained. The original nanowires (i.e. synthesized at relatively low temperatures e.g.  $180 \text{ }^\circ\text{C}$ ) cannot be maintained any more. Instead, they would quickly grow into large bulks. This combines with the low temperature case (Figure S6) to indicate that the temperature of the hydrothermal reaction is also a crucial factor to synthesize titanate hierarchical microspheres. Appropriate control over the temperature is quite important and necessary.

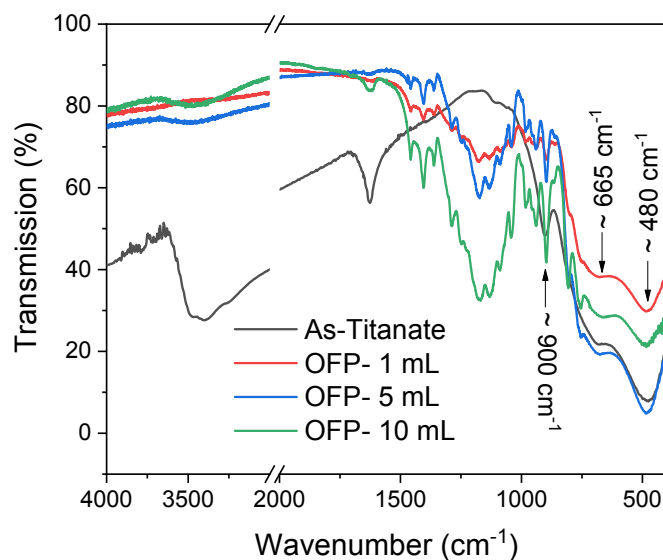


**Figure S9.** Raman spectra of the titanate nanostructures synthesized by the hydrothermal reaction under the different conditions: (a)  $C_{\text{NaOH}} = 0.1 \text{ M}$ ,  $T_{\text{hydro}} = 180 \text{ }^\circ\text{C}$ ; (b)  $C_{\text{NaOH}} = 0.5 \text{ M}$ ,  $T_{\text{hydro}} = 180 \text{ }^\circ\text{C}$ ; (c)  $C_{\text{NaOH}} = 5 \text{ M}$ ,  $T_{\text{hydro}} = 180 \text{ }^\circ\text{C}$ ; (d)  $C_{\text{NaOH}} = 1 \text{ M}$ ;  $T_{\text{hydro}} = 150 \text{ }^\circ\text{C}$ ; (e)  $C_{\text{NaOH}} = 1 \text{ M}$ ;  $T_{\text{hydro}} = 200 \text{ }^\circ\text{C}$ . These Raman spectra correspond to the samples presented in Figures S3-S7. All the spectra show the nearly same Raman peaks at around 282, 439, 641, 712 and 903  $\text{cm}^{-1}$ , respectively. These peaks can be well indexed to an orthorhombic structure of the layered lepidocrocite titanate, which has a general composition formula of  $A_{2-x}\text{Ti}_{2-x/4}\square_{x/4}\text{O}_{4+\Delta}$  ( $\square \sim \text{vacancy}$ ). It is also noted that Raman spectroscopy is a better technique to distinguish the phase structure of the titanate nanostructures synthesized from the alkaline conditions comparing to XRD because the titanate nanostructures have quite weak XRD lines and similar  $2\theta$  positions.

In addition, although possessing different morphologies (Figures S3-S7 and Figure 2 in the main text), the titanate nanostructures prepared at different conditions have the same crystal structure, i.e. all showing layered lepidocrocite titanate phase.



**Figure S10.** SEM image and corresponding EDX spectra of the as-synthesized titanate hierarchical microspheres on Ti mesh. Three EDX spectra collected from different areas demonstrate the quite similar distributions of Ti and Na elements. This gives a Na/Ti atomic ratio of around 0.92. It is noted that the O element content in three EDX spectra show a slight difference. This should be related to the hydrated groups which are quite common in such sorts of the titanate nanostructures. According to the Na/Ti ratio and the general composition of orthorhombic layered lepidocrocite titanate as determined by the XRD and Raman, the composition of the present sodium titanate could be estimated to be  $\text{Na}_{1.8}\text{Ti}_{1.95}\square_{0.05}\text{O}_{4.8}$  ( $\square \sim$ vacancy).



**Figure S11.** FT-IR spectra of the as-synthesized titanate hierarchical microspheres (As-Titanate) as well as the OFP modified microspheres. All the titanate show three main IR peaks at around 900, 665, and 480  $\text{cm}^{-1}$  (these can be easily observed from the as-synthesized titanate (black curve)), which are ascribed to the Na-O-Ti bond vibrations. This further confirms the as-synthesized titanate belongs an orthorhombic layered lepidocrocite phase, consistent with the Raman and XRD results. There have strong IR peaks in the range of 1500-750  $\text{cm}^{-1}$ , all of which can be attributed to the chemical bond vibrations of the modifier 2,2,3,3,4,4,5,5-octafluoro-1-pentanol (OFP). Qualitatively, the relative intensity of the IR peaks gradually increases with the increase in the OFP amounts, indicating the surface modification of the  $\text{CF}_2$  groups depends on the OFP concentrations that could obviously affect the wettability properties.