

## Supplementary Information

# **Ultra-Tough and Highly Ordered Macroscopic Fibers Assembly from 2D Functional Metal Oxides Nanosheets Liquid Crystals and Strong Ionic Interlayer Bridging**

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## Experimental

**Materials:** Cesium carbonate ( $\text{Cs}_2\text{CO}_3$ ) and tungsten trioxide ( $\text{WO}_3$ ) were purchased from Aladdin Bio-Chem Technology Co., Ltd. Tetrabutylammonium hydroxide (TBAOH) was purchased from Macklin Biochemical Co., Ltd. All other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. All chemicals were used as received.

**Synthesis of the layered tungstate crystals:** The layered tungstate crystals with the composition of  $\text{Cs}_{6+x}\text{W}_{11}\text{O}_{36}$  were prepared by the protocol described previously with minor modifications (14,34,35).  $\text{Cs}_2\text{CO}_3$  and  $\text{WO}_3$  were mixed at a molar ratio of 4:11 and heated at 1173 K for 5 h.

**Protonation of the tungstate crystals:** The layered tungstate crystals with particle size less than 75  $\mu\text{m}$  were treated by 38% aqueous HCl solution at room temperature (RT) for 2 days, and the solution was replaced with a fresh one every day. The suspension should be filtered and then washed with deionized water to remove the excess HCl. The resulting protonated products ( $\text{H}_2\text{Cs}_4\text{W}_{11}\text{O}_{36}$ ) were moved to a culture dish and dried in air for 2 to 3 days.

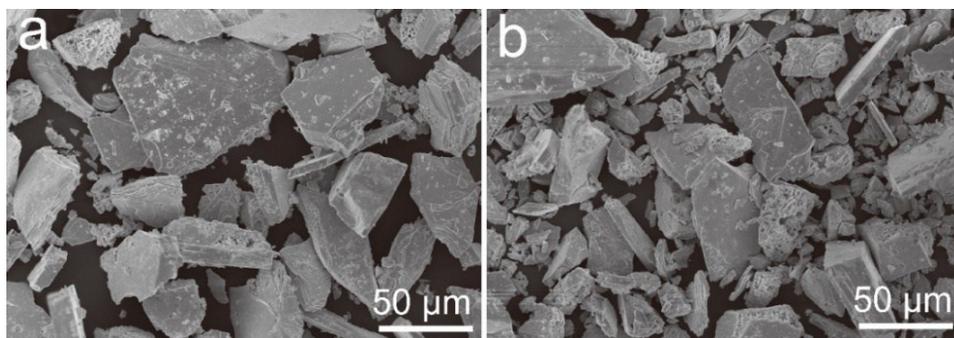
**Delamination of 2D tungstate LCs colloid:** The protonated products were stirred with TBAOH for 0.5 h at RT. After that, the suspension should be filtered and then washed with deionized water until  $\text{pH}=7$ . Finally, the resultant crystals should be dispersed in deionized water and shaken intermittently for about 8 h at RT. The 2D tungstate LCs colloid will be achieved when the solution appears a milky appearance of anisotropic shiny textures. The volume fraction ( $\varphi$ ) of the LCs colloid was calculated by  $\varphi=\omega_m/\rho_{\text{tungstate nanosheets}}$ , where  $\rho_{\text{tungstate nanosheets}}$  was the density of tungstate nanosheets which could be estimated as  $6.14 \text{ g}\cdot\text{cm}^{-3}$ , and the  $\omega_m$  was the mass fraction.

**Preparation of the tungstate fibers:** The 2D tungstate LCs colloid as the spinning dope should be preloaded into a syringe pump and slowly injected into a rotating coagulation bath. The 5 wt% Na<sub>2</sub>SO<sub>4</sub>, 5 wt% KCl, 5 wt% CaCl<sub>2</sub>, 5 wt% NiSO<sub>4</sub>, 5 wt% MgSO<sub>4</sub>, and 5 wt% Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution, and the 5 wt% PVA and 0.8 wt% chitosan in acetic acid solution (4 wt% acetic acid) were chosen as the coagulation bath, respectively. During the spinning, the injection rate should be finely adjusted to match the rotating speed for achieving a continuous gel fiber. Finally, the gel fiber should be soaked in the coagulation bath for a quarter of time before the water washing process, and then dried on a shelf under axial tension at RT.

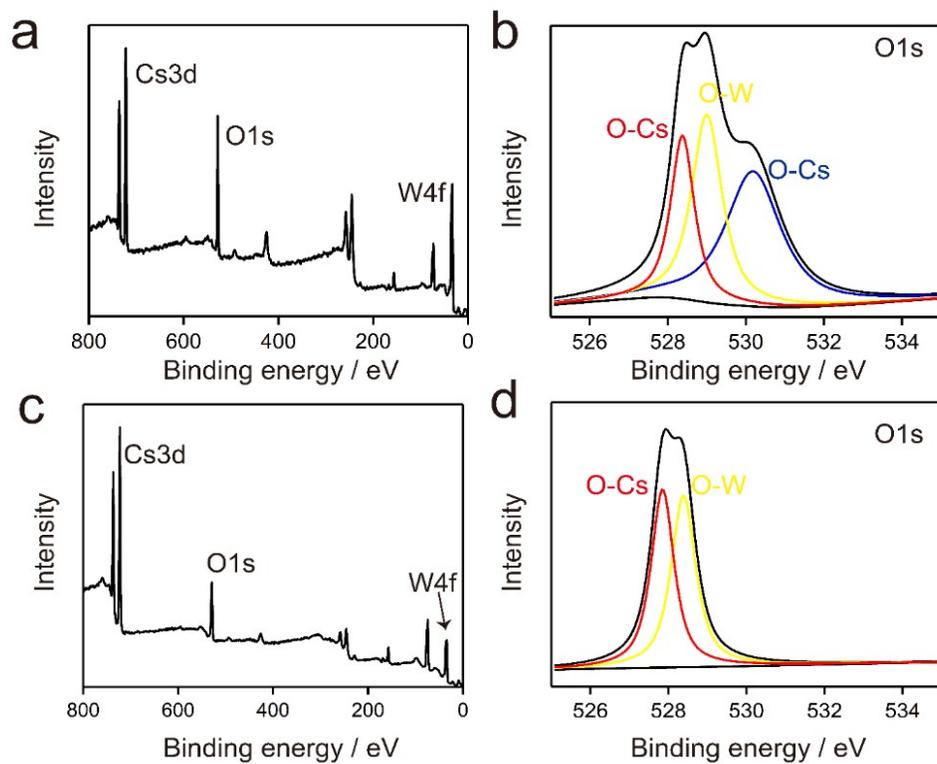
**Calculation method:** The charge density difference was calculated by the plane wave code Vienna ab initio simulation package. The Perdew-Burke-Ernzerh of generalized gradient approximation was used to the exchange-correlation potential. Geometry optimizations of all structures were terminated when the total energy difference between successive steps reduced to 10<sup>-6</sup> eV. The plane-wave cutoff energy was set at 550 eV. The charge density difference was defined as  $\Delta\rho = \rho_{AB} - \rho_A - \rho_B$ . Where A represents the tungstate nanosheet, and B represents the protonated chitosan. All of the charge data were processed by the 3D visualization system for electronic and structural analysis package.

**Characterizations:** The wide-angle XRD data were collected with the PANalytical Empyrean diffractometer using monochromatic Cu K $\alpha$ 1 radiation ( $\lambda = 0.1541$  nm) at 40 kV. SEM images were taken on FEI Helios NanoLab 600i. The ICP analysis was carried out on PerkinElmer Optima 8300. XPS was collected on Thermo Fisher ESCALAB 250Xi using Al K $\alpha$  X-rays as the source of excitation. POM observations were performed by Leica DM4P polarization microscopy. AFM images of tungstate nanosheets were taken in Peak Force tapping mode by using the Bruker Dimension. TEM images and SAED were taken on a JEOL JEM-2100 Electron

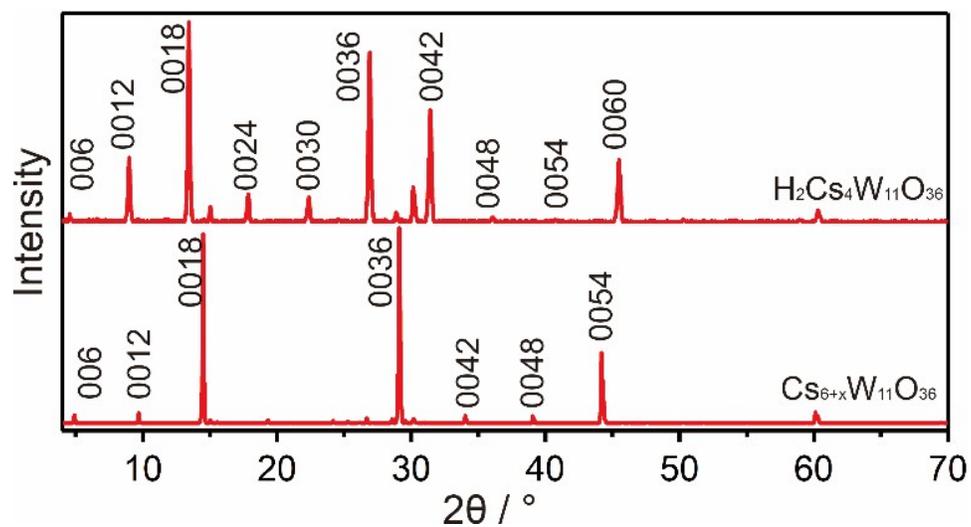
Microscope. The ultrathin sections of fiber were obtained on ultramicrotome Leica EM UC7. FTIR has collected on Thermo Electron Nicolet Avatar 330 spectrophotometer. TG analysis was carried out on Netzsch STA449F3 from RT to 800 °C with the 10 °C min<sup>-1</sup> heating rate under air flow. Mechanical properties were carried out on SANS testing machine CMT-C102.



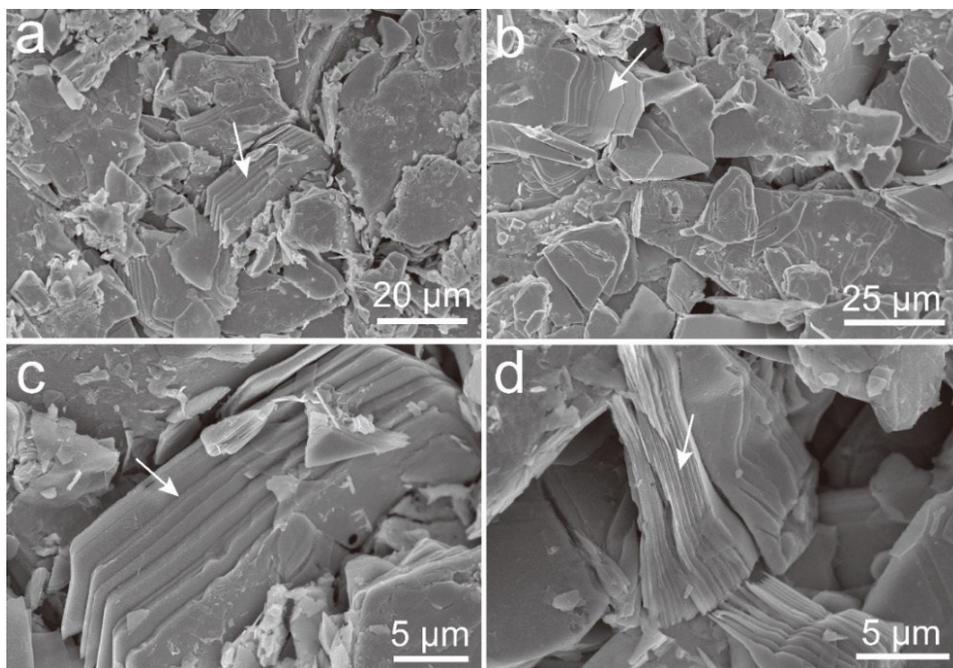
**Fig. S1** (a, b) SEM images for the layered tungstate crystals.



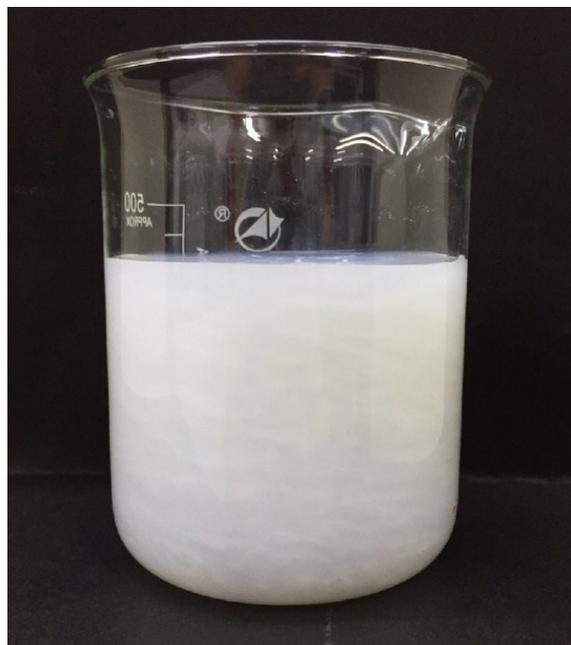
**Fig. S2** (a, b) The survey spectrum and O1s spectrum of layered tungstate crystals. (c, d) The survey spectrum and O1s spectrum of protonated tungstate crystals.



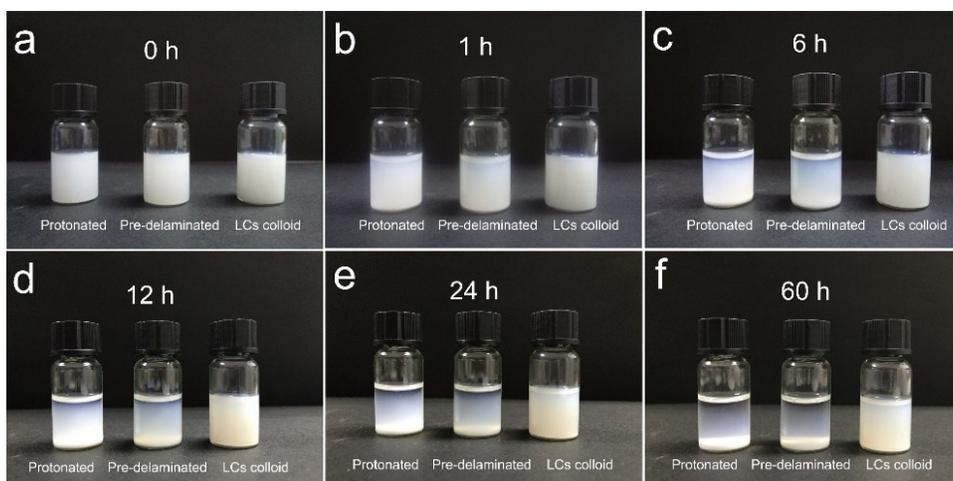
**Fig. S3** XRD patterns for the layered tungstate crystals ( $\text{Cs}_{6+x}\text{W}_{11}\text{O}_{36}$ ) and their protonated products ( $\text{H}_2\text{Cs}_4\text{W}_{11}\text{O}_{36}$ ).



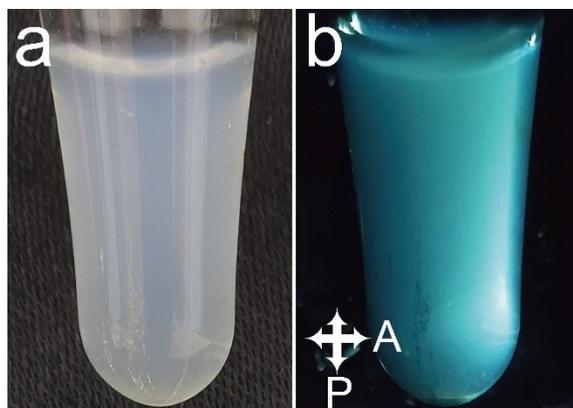
**Fig. S4** (a, b) SEM images of the protonated tungstate crystals at low magnifications. (c, d) SEM images of the protonated tungstate crystals at high magnifications.



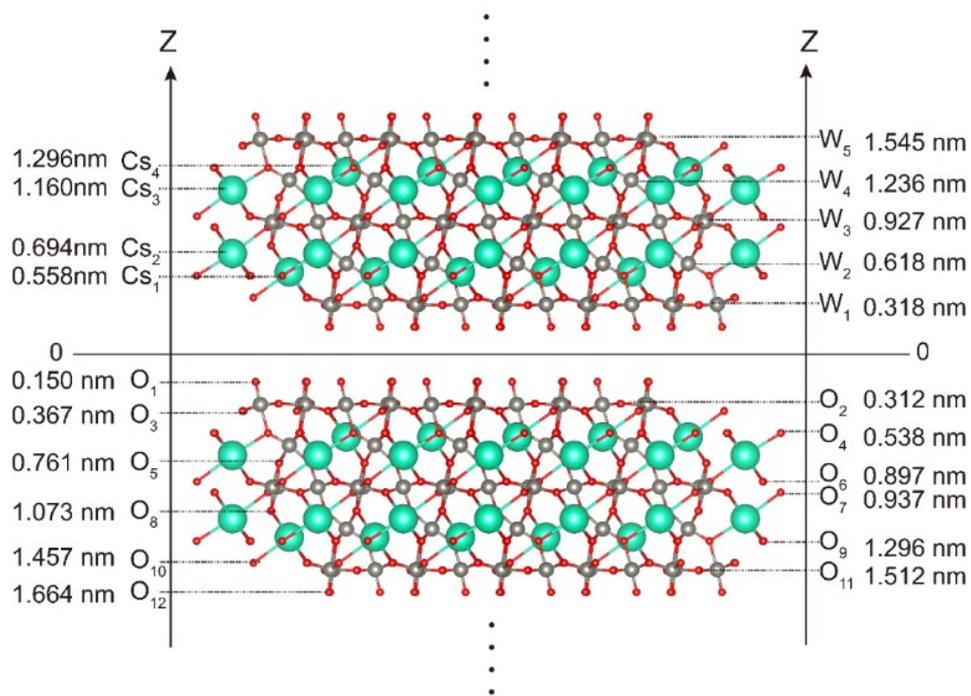
**Fig. S5** Photograph of the 2D tungstate LCs colloid displaying the typical textures of LCs phase.



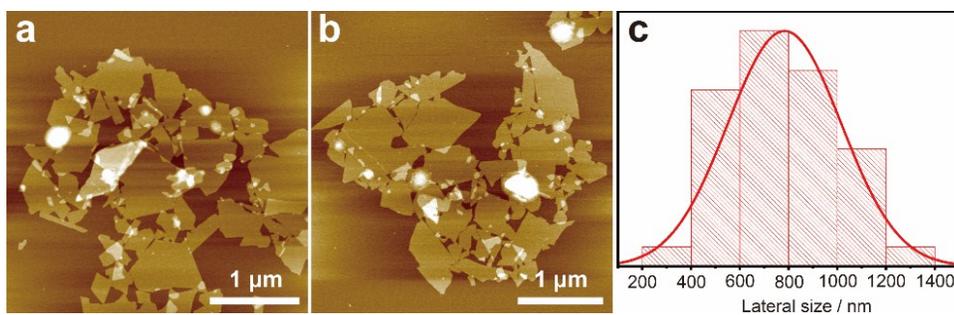
**Fig. S6** (a–f) Photographs of sedimentation experiment for the protonated tungstate crystals, pre-delaminated tungstate crystals and 2D tungstate LCs colloid with the settling time of 0, 1, 6, 12, 24, and 60 h, respectively.



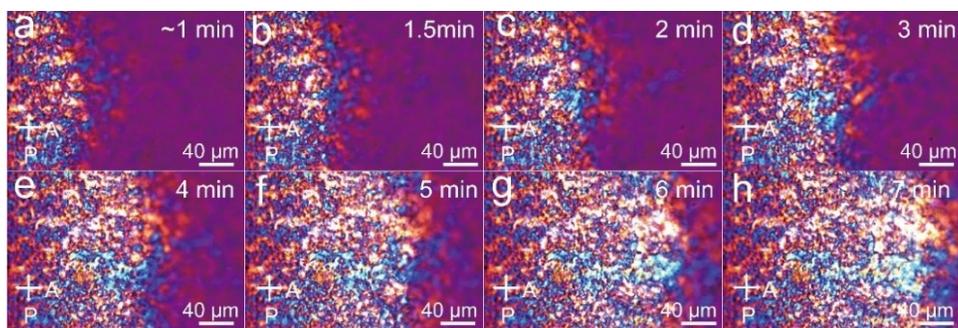
**Fig. S7** (a) Photographs of the prepared tungstate colloid. (b) Macroscopic photographs between crossed polarizers of the tungstate colloid after being placed at room temperature for one week. P and A represent the directions of polarizer and analyzer, respectively



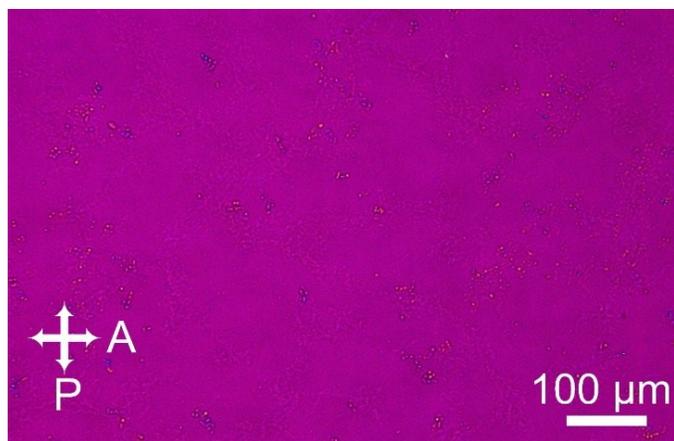
**Fig. S8** The side view of tungstate nanosheet and the corresponding positional parameters of atoms in the Z-axis direction.



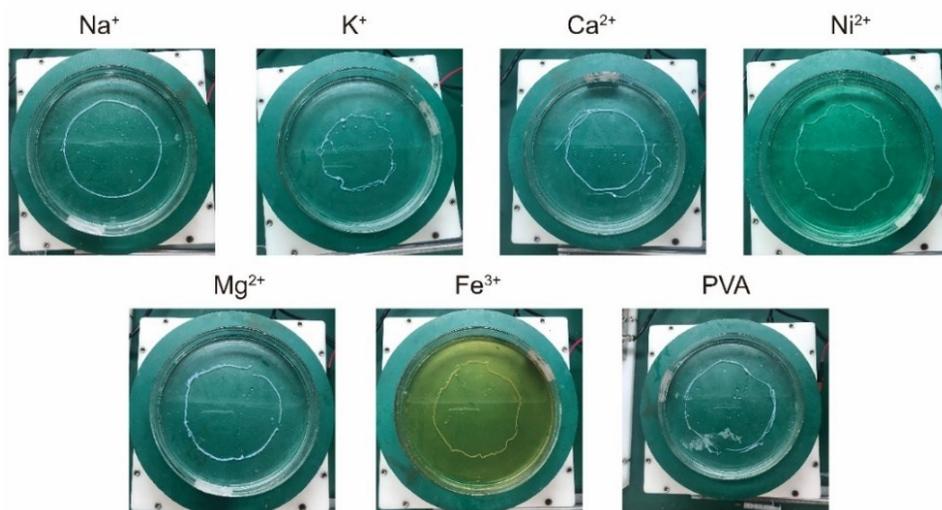
**Fig. S9** (a, b) Typical AFM images of the tungstate nanosheets. (c) The lateral size distribution of the nanosheets (39 nanosheets that are included in Fig. 1c and Fig. S8 a,b, are taken and counted into the lateral size analysis).



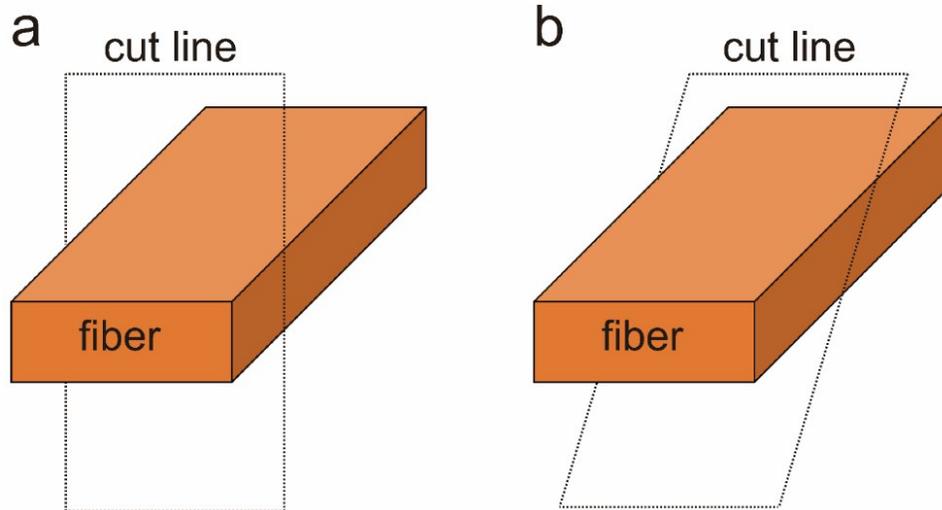
**Fig. S10** (a–h) High-resolution time sequence POM images of 2D tungstate LCs colloid with self-assembly time of 1, 1.5, 2, 3, 4, 5, 6 and 7 min, respectively. P and A represent the directions of polarizer and analyzer, respectively.



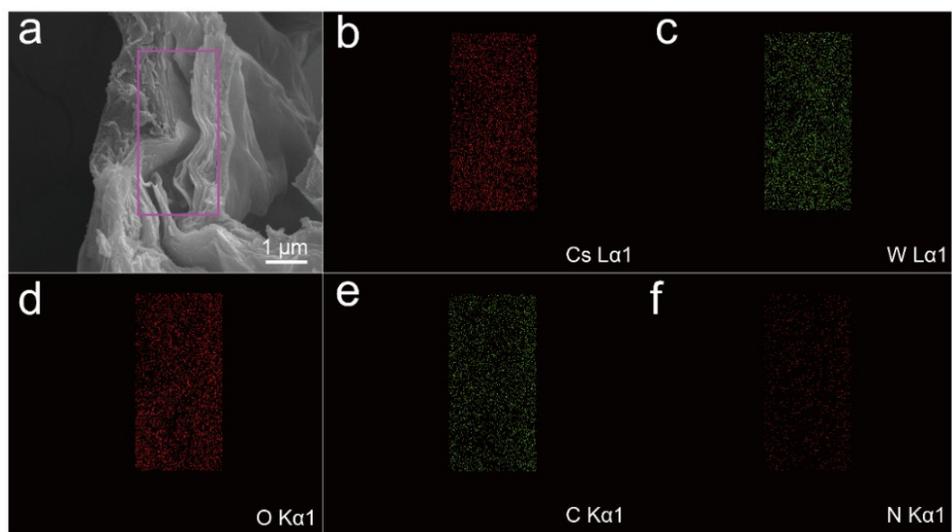
**Fig. S11** POM image of the tungstate nanosheets dispersion prepared by the general method.



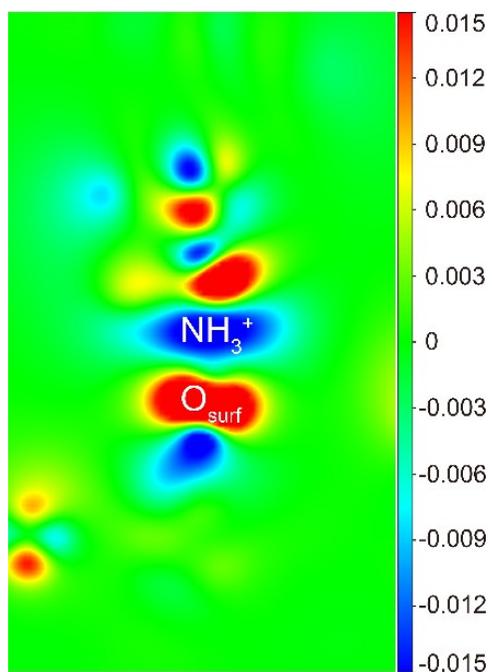
**Fig. S12** Photographs of the tungstate fibers produced by ionic bonding agents



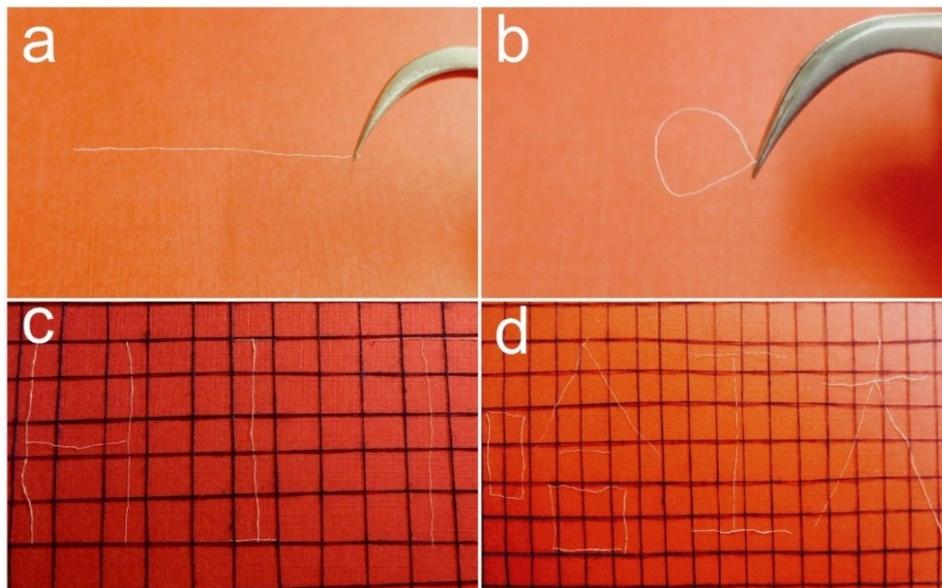
**Fig. S13** (a, b) Schemes of HRTEM ultramicrocut along the fiber cross-section and fiber axial direction, respectively.



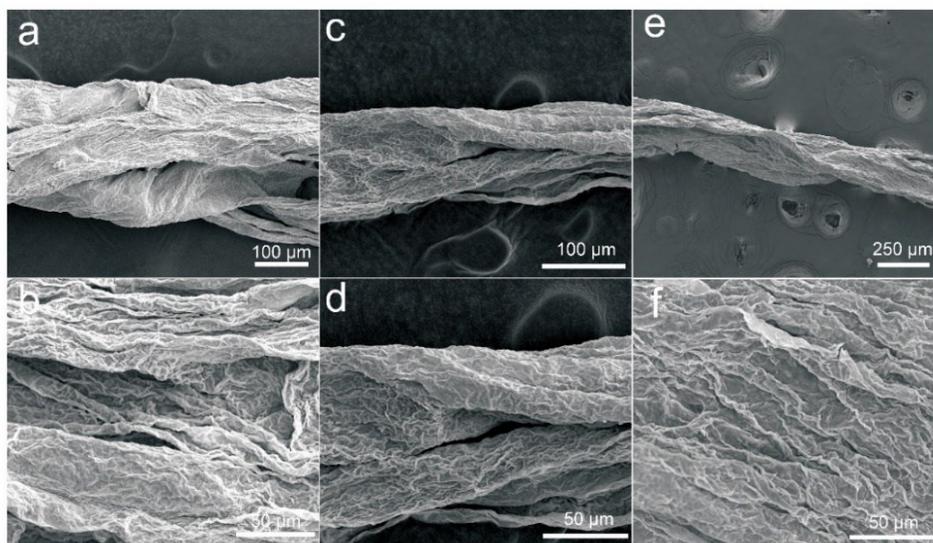
**Fig. S14** (a) SEM image of the fiber cross-section and (b–f) its corresponding EDS element mapping images of Cesium (Cs), Tungsten (W), Oxygen (O), Carbon (C), and Nitrogen (N), respectively.



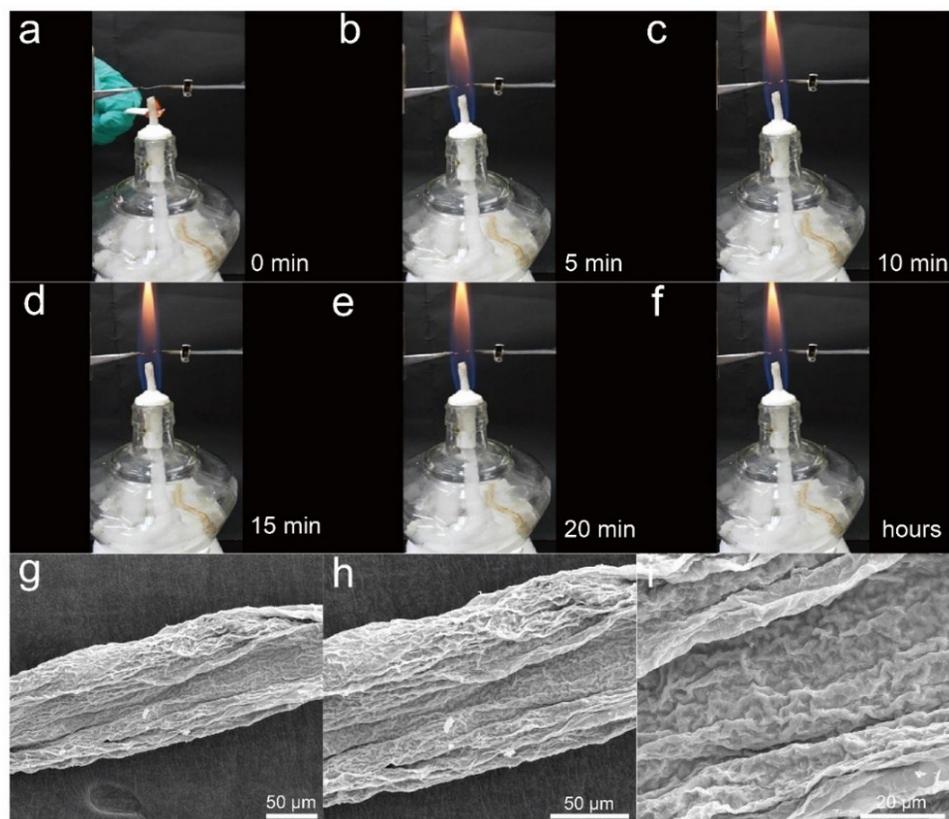
**Fig. S15** The charge density difference 2D slice for the model of  $-\text{NH}_3^+$  group on single tungstate nanosheet, through the co-plane of amino nitrogen and surface oxygen. The color bar represents the charge accumulation and depletion.



**Fig. S16** (a, b) Photographs of tungstate fibers under bending test. (c, d) Photographs of the fibers that have been weaved into a cotton network (black lines) in an English abbreviation (“HIT”, Harbin Institute of Technology) and a Chinese character (‘哈工大’, Hagongda), respectively.



**Fig. S17** SEM images of the tungstate fibers after the treatments of (a, b) sulfuric acid solution ( $1\text{ mol L}^{-1}$ , soaking for 3 days), (c, d) sodium hydroxide solution ( $1\text{ mol L}^{-1}$ , soaking for 3 days), and (e, f) ultrasonic ( $100\text{ W}$ ,  $40\text{ kHz}$ , for 1 hour) in water, respectively.



**Fig. S18** (a–f) Time-series photographs of the tungstate fiber during the burning test and (g–h) its corresponding SEM images after the test.