

**Electronic Supplementary Information**

**Superior Ternary Hybrid Photocatalysts of TiO<sub>2</sub>/WO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> Thoroughly  
Mesoporous Nanofibers for Visible-Light-Driven Hydrogen Evolution**

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## **Experimental Procedure**

### **1) Raw materials**

The raw materials, such as urea, polyvinylpyrrolidone (PVP,  $M_w \approx 1300000$ ), butyl titanate (TBOT), diisopropyl azodiformate (DIPA), paraffin oil, absolute ethyl alcohol, acetic acid, tungsten hexachloride ( $WCl_6$ ), methanol and deionized water, were all purchased from Aladdin. All the reagents were used as received without further purification.

### **2) Preparation of $TiO_2$ and $TiO_2/WO_3$ mesoporous nanofibers**

$TiO_2/WO_3$  mesoporous nanofibers were synthesized through the foaming-assisted electrospinning approach, as schematically illustrated in Scheme 1. Typically, 4.0 g of tetrabutyl titanate (TBOT) was dissolved into a mixture, which was composed of 7 ml of ethanol and 3 ml of acetic acid. Then, 0.7 g of polyvinylpyrrolidone (PVP) and 0.2 g of tungsten hexachloride ( $WCl_6$ ) were slowly added into the solution, followed by vigorous stirring at room temperature (RT) overnight. Afterwards, 1.0 g of the diisopropyl azodiformate (DIPA), which was used as the foaming agents to generate mesoporous structure, was introduced into the above solution and continues to be magnetically stirred for 2 h. Subsequently, the electrospinning was carried out under an applied voltage of 20 kV, in which the needle tip-to-plate collector distance was typically fixed at 20 cm. The as-spun polymer products were referred to PVP/TBOT/ $WCl_6$ /DIPA precursor fibers, which were dried in a constant temperature oven at 60 °C. The resultant samples were located in a quartz crucible and placed at the center of a conventional tube furnace, and then heated up to the desired temperature of 550 °C with a heating rate of 1 °C  $min^{-1}$  for 2 h in air, followed by furnace cool to ambient temperature. For comparison, the  $TiO_2$  mesoporous nanofibers were synthesized through the same process.

### **3) Synthesis of g- $C_3N_4$ flake**

The g-C<sub>3</sub>N<sub>4</sub> materials were prepared by heating melamine (urea) in a muffle furnace at 500 °C for 4 h, followed by furnace cool to RT. Then, 0.2 g of g-C<sub>3</sub>N<sub>4</sub> was added into 15 ml of methanol, and subjected to ultrasonic treatment for 100 min to completely disperse and exfoliate the g-C<sub>3</sub>N<sub>4</sub> particles into nanoflakes.

#### **4) Fabrication of TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> and TiO<sub>2</sub>/WO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> hybrid photocatalysts**

In a typical experiment, 0.5 g of TiO<sub>2</sub> and TiO<sub>2</sub>/WO<sub>3</sub> mesoporous nanofibers was added into the above g-C<sub>3</sub>N<sub>4</sub> nanoflake methanol suspensions, and stirred in a fume hood until the methanol was volatilized completely, followed by being dried in a constant temperature oven at 70 °C. After that, the powders were collected and calcined at 300 °C for 2 h in an air atmosphere, to make a solid connection of the TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> and TiO<sub>2</sub>/WO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>.

#### **5) Structural Characterization**

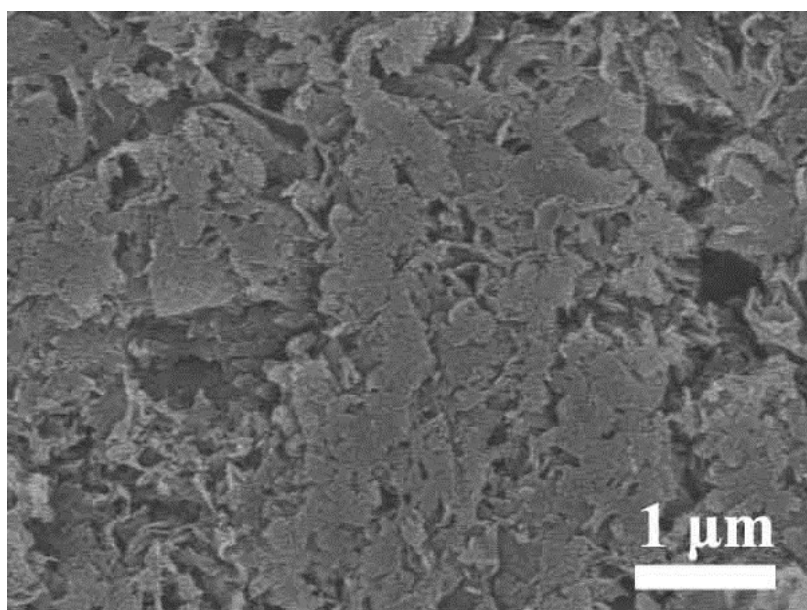
The obtained products were firstly characterized with X-ray powder diffraction (XRD, D8 Advance, Bruker, Germany) with Cu K $\alpha$  radiation ( $\lambda=1.5406$  Å), field emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan), and high-resolution transmission electron microscopy (HRTEM, JEM-2010F, JEOL, Japan) equipped with energy dispersive X-ray spectroscopy (EDX, Quantax-STEM, Bruker, Germany). The porous properties of the as-prepared mesoporous nanofibers were characterized using N<sub>2</sub> adsorption at -195.8 °C on a specific surface area and porosity analyzer (Micromeritics, ASAP 2020M, USA). The sample was further studied by using X-ray photoelectron spectroscopy (Shimadzu, AXIS ULTRA DLD, Japan). The diffuse reflectance absorption spectra of the products were recorded on a UV-visible spectrophotometer (UV-3900, Hitachi, Japan) equipped with an integrated sphere attachment.

#### **6) Photocatalytic Activity Measurements**

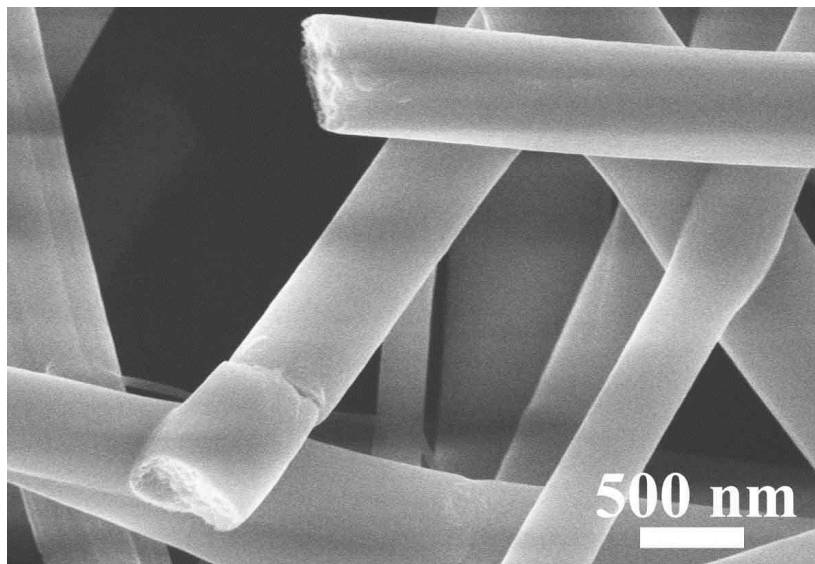
The visible-light photocatalytic reaction is performed in an inner-irradiation quartz annular reactor, a vacuum pump, a gas collection, a recirculation pump and a water-cooled condenser. The as-synthesized samples (0.05 g) were suspended in deionized water and methanol mixed solutions (40mL, 3:1) by an ultrasonic oscillator, respectively. Then the mixture was transferred into the reactor and deaerated by a vacuum pump. A 300W Xenon lamp (CEL, HUL300), with a cutoff filter to remove the light of wavelengths below 400 nm, was used as the visible light source, with the cooling water circulated through a cylindrical Pyrex jacket located around the light source to maintain the reaction temperature. The reactor was sealed with ambient air during irradiation, and the hydrogen evolution was monitored by an online gas chromatography (GC, 7900) equipped with a Porapak-Q column, high-purity nitrogen carrier and a thermal conductivity detector (TCD).

## **7) Photoelectrochemical measurement**

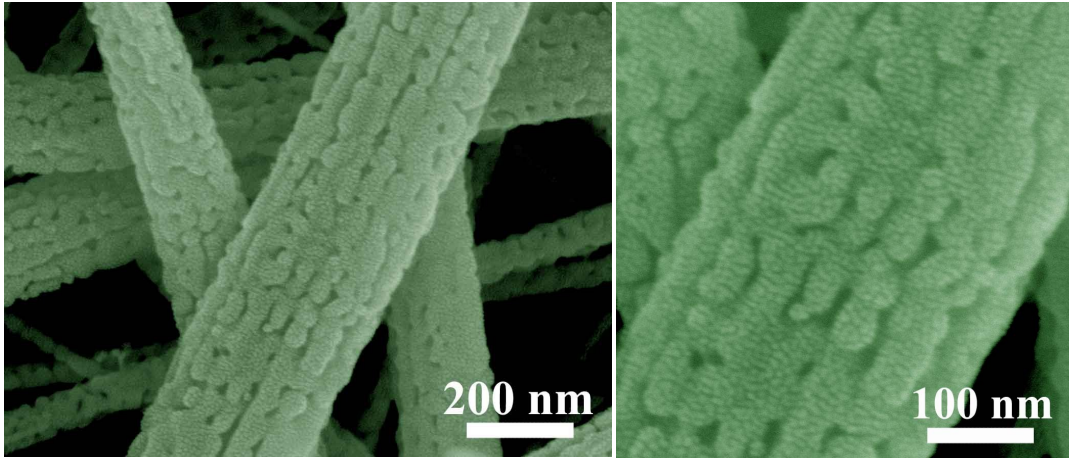
A working electrode was prepared as follows: 0.1 g sample was ground with 0.8 g ethanol to make a slurry. The slurry was then coated onto an indium-tin oxide glass (FTO glass) by a drop method, and then dried and calcined at 300 °C for 1 h to obtain working electrodes with a similar film thickness. Photocurrents were measured on an electrochemical analyzer (CHI 760e Instruments) in a standard three-electrode system by using the prepared film as the working electrode, a Pt flake as the counter electrode, and Ag/AgCl as the reference electrode. A 500 W Xe-lamp (CEL-S500, Beijing) with a 400 nm cutoff filter served as a light source, and 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution was used as the electrolyte.



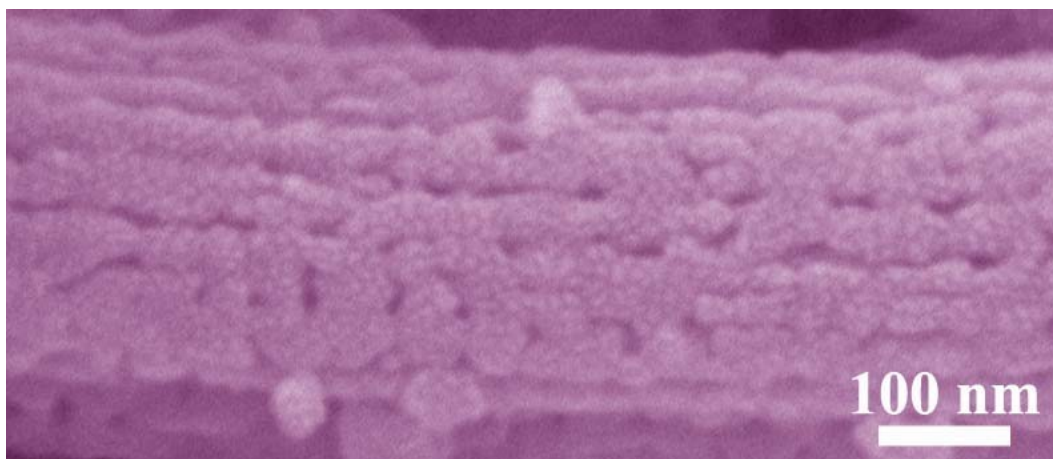
**Fig. S1.** A typical SEM image of the the as-prepared g-C<sub>3</sub>N<sub>4</sub> bulk.



**Fig. S2.** Typical SEM image of the as-spun polymer precursor of  $\text{TiO}_2/\text{WO}_3$  sample.

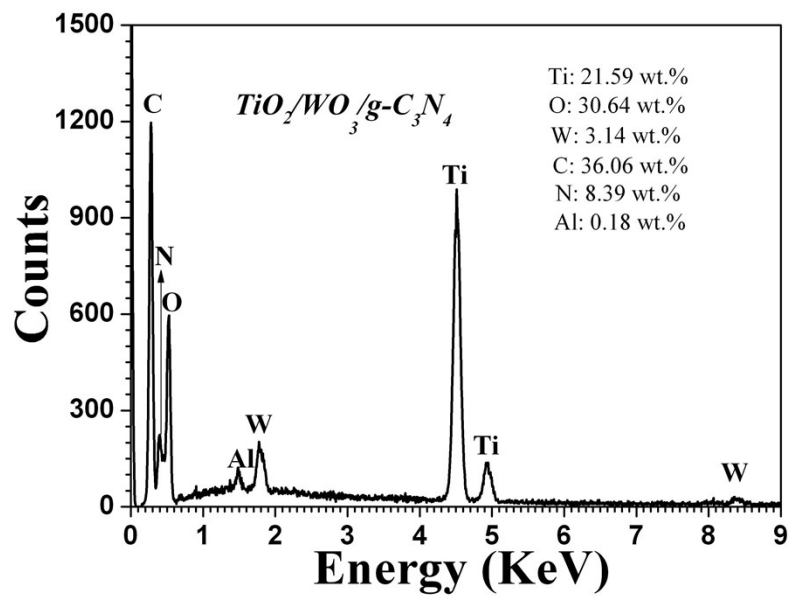


**Fig. S3.** Representative SEM images of the calcined TiO<sub>2</sub>/WO<sub>3</sub> mesoporous fibers.

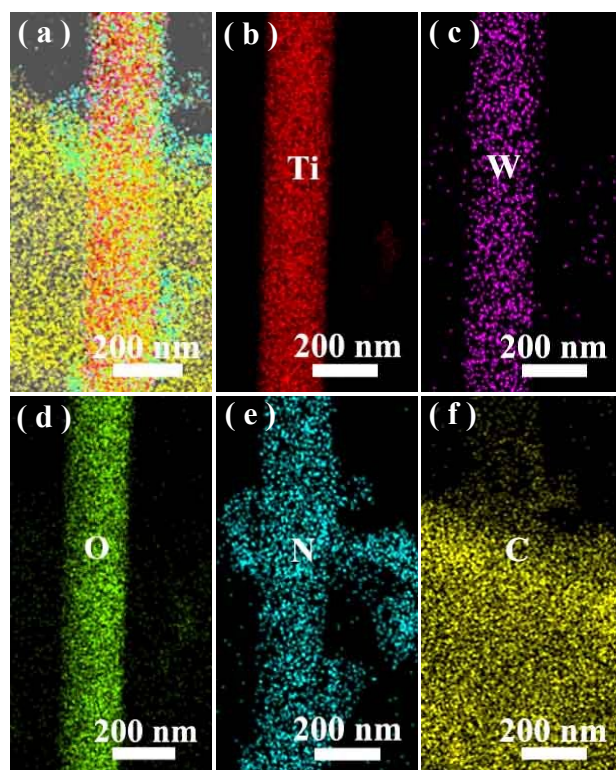


**Fig. S4.** A representative SEM image of the  $\text{TiO}_2/\text{WO}_3/g\text{-C}_3\text{N}_4$  thoroughly mesoporous nanofibers under a higher magnification.

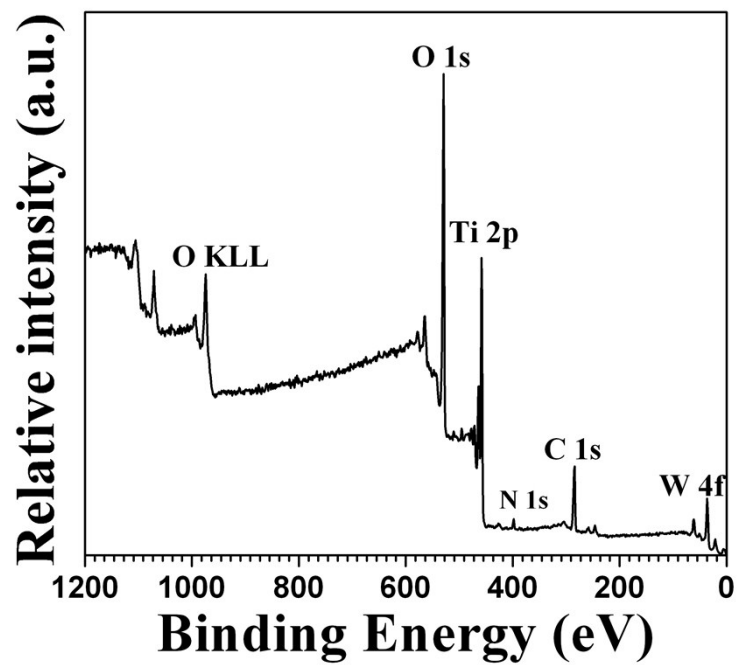




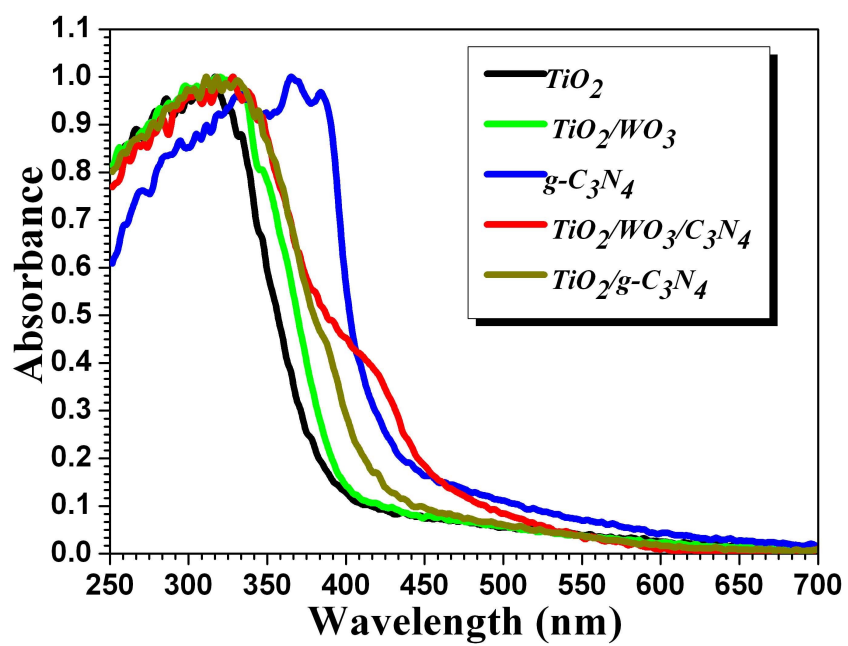
**Fig. S5.** A respective EDX pattern recorded from the as-prepared  $TiO_2/WO_3/g-C_3N_4$  products under SEM.



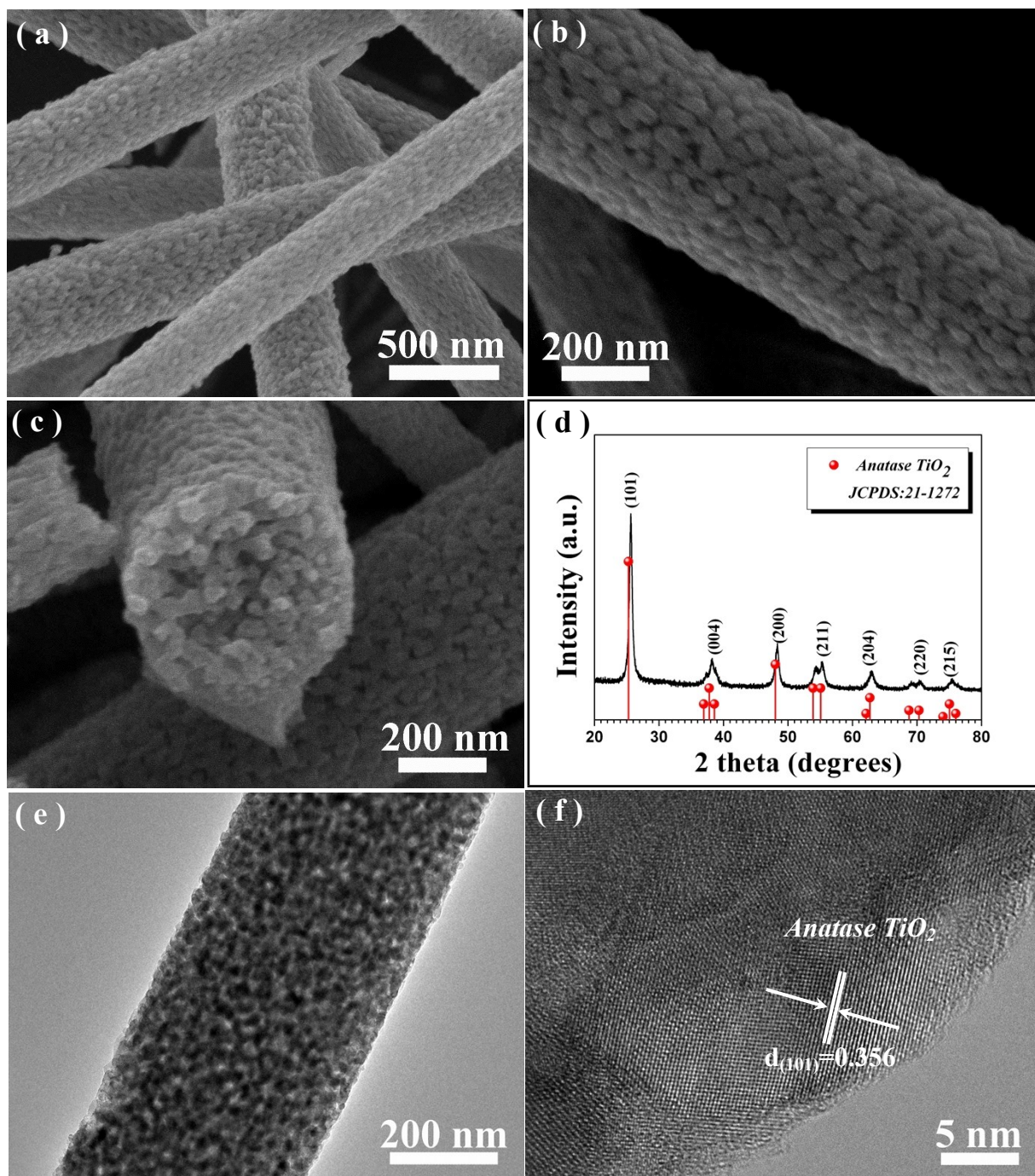
**Fig. S6.** The elemental mappings within the  $\text{TiO}_2/\text{WO}_3/g\text{-C}_3\text{N}_4$  ternary hybrid nanofibers.



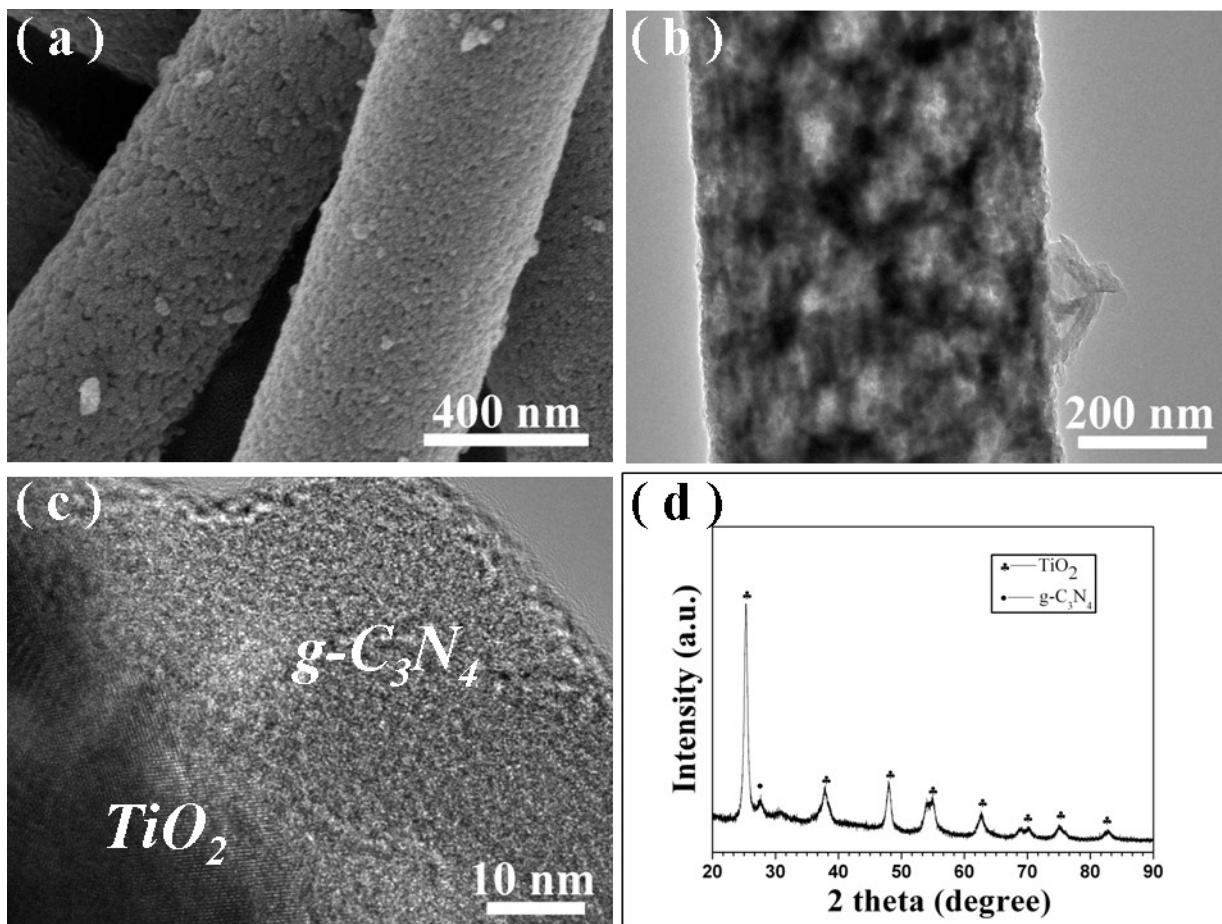
**Fig. S7.** A typical X-ray photoelectron spectra (XPS) of  $\text{TiO}_2/\text{WO}_3/g\text{-C}_3\text{N}_4$  ternary hybrid nanofibers.



**Fig. S8.** UV-vis diffuses reflection spectra of  $TiO_2$ ,  $g-C_3N_4$ ,  $TiO_2/WO_3$ ,  $TiO_2/g-C_3N_4$  and  $TiO_2/WO_3/g-C_3N_4$  samples.

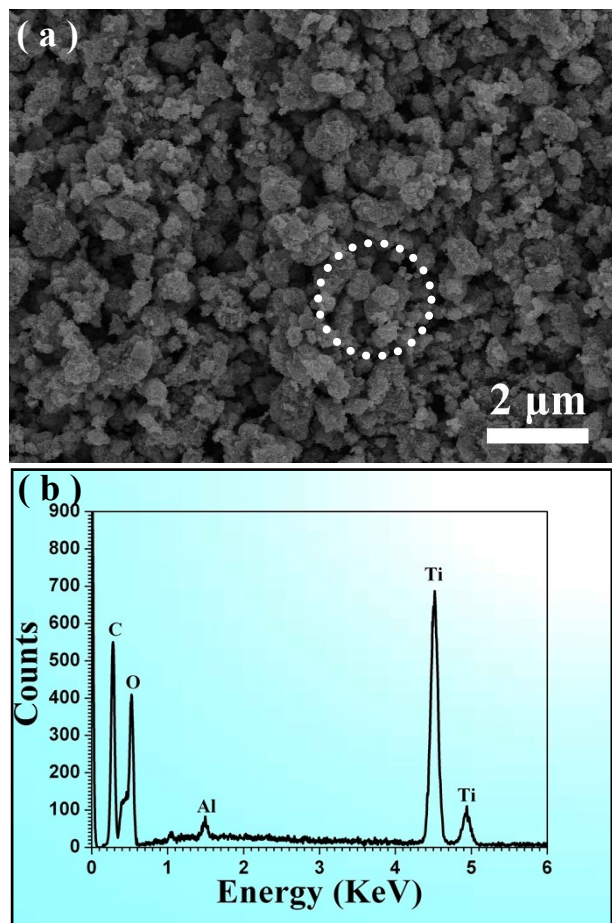


**Fig. S9.** The detailed characterizations of the pure TiO<sub>2</sub> thoroughly mesoporous nanofibers: SEM images (a-c), XRD patterns (d), TEM (e) and HRTEM image (f).



**Fig. S10.** The detailed characterizations of the  $\text{TiO}_2/\text{g-C}_3\text{N}_4$  thoroughly mesoporous nanofibers:

SEM images (a), TEM (b), HRTEM image (c) and XRD patterns (d).



**Fig. S11** (a) A representative SEM image of P25. (b) The corresponding EDS pattern recorded from the marked area in (a).

**Tab. S1.** Comparison of the related works for photocatalytic H<sub>2</sub> production

<b>Material</b>	<b>Morphology</b>	<b>Irradiation conditions</b>	<b>Reaction solution</b>	<b>Activity (μmol g<sup>-1</sup>h<sup>-1</sup>)</b>	<b>Reference</b>
g-C <sub>3</sub> N <sub>4</sub>	3D porous framework	λ>420 nm	Water+triet hanolamine +H <sub>2</sub> PtCl <sub>6</sub>	140	1
TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	particles	λ>420 nm	Water+Me OH+H <sub>2</sub> PtCl <sub>6</sub>	22.4	2
g-C <sub>3</sub> N <sub>4</sub>	plate-like	λ>420 nm	Water+ triethanolam ine	60.5	3
g-C <sub>3</sub> N <sub>4</sub>	layered agglomerate sheet	λ>400 nm	Water+ triethanolam ine+H <sub>2</sub> PtCl <sub>6</sub>	33.75	4
WO <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub>	particles	>420 nm	Water + triethanolam ine	110	5
g-C <sub>3</sub> N <sub>4</sub> /TiO <sub>2</sub>	particles	whole spectrum	Water+Me OH	55.97	6
TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	sheet	>400 nm	Water+ triethanolam ine +H <sub>2</sub> PtCl <sub>6</sub>	352.7	7
g-C <sub>3</sub> N <sub>4</sub>	particles	>420 nm	Water+ triethanolam ine +H <sub>2</sub> PtCl <sub>6</sub>	1.3	8
g-C <sub>3</sub> N <sub>4</sub> /W O <sub>3</sub>	Mesoporous particles	λ>420 nm	Water+triet hanolamine +H <sub>2</sub> PtCl <sub>6</sub>	326	9
TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	particles	>400 nm	Water+ triethanolam ine +H <sub>2</sub> PtCl <sub>6</sub>	98	10
<b>TiO<sub>2</sub>/ WO<sub>3</sub>/g- C<sub>3</sub>N<sub>4</sub></b>	<b>Mesoporous nanofibers</b>	<b>&gt;400 nm</b>	<b>Water+Me OH</b>	<b>286.6</b>	<b>Our work</b>



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