## Supporting Information

# *p-n* tungsten oxide homojunction for Vis-NIR light-enhanced electrocatalytic hydrogen evolution

Bin Chang, Zizheng Ai, Dong Shi, Yueyao Zhong, Kang Zhang, Yongliang Shao, Lei

Zhang, Jianxing Shen, Yongzhong Wu\* and Xiaopeng Hao\*

Email: xphao@sdu.edu.cn; wuyz@sdu.edu.cn

This file includes:

- S1. Materials
- S2. Synthesis of Ti<sub>3</sub>C<sub>2</sub>
- **S3.** Characterization Methods
- S4. Photo/electrochemical Tests
- **S5.** Supplementary Figures S1-S29
- **S6. Supplementary Table S1-S8**

#### S1. Materials

Titanium, aluminum and graphite were purchased from Aladdin. Hydrofluoric acid (HF), ammonium tungstate hydrate, hydrochloric acid (HCl) and sodium hypophosphite (NaH<sub>2</sub>PO<sub>2</sub>) were purchased from Sinopharm Chemical Reagent Co. Ltd. All chemicals were of analytical reagent grade and used without further purification. Solutions were freshly prepared with deionized water.

#### S2. Synthesis of Ti<sub>3</sub>C<sub>2</sub>

Ti, Al and graphite powders were mixed with a molar proportion of 3:1.5:2. Then, the mixture was ball-milled for 2 h and pressed into discs. Under the flowing of Ar gas, the discs were heated at 1473 K for 2 h in a tube furnace. The discs were taken out at room temperature and ground into powders.  $Ti_3C_2$  was obtained through immersing  $Ti_3AlC_2$  in 40% HF at room temperature for 48 h. In this process the Al species were selectively removed by HF etching and OH<sup>-</sup>, O<sup>-</sup> or F<sup>-</sup> replaced Al as the terminal groups. The as-prepared sample was filtered, washed with deionized water several times and dried at 353 K for 24 h in a vacuum drying chamber.

#### **S3.** Characterization Methods

Powder X-ray diffraction (XRD) patterns of the materials were obtained on a diffractometer (Bruker D8) using a Cu K $\alpha$  radiation source ( $\lambda$  =0.15418 nm) with a 2 $\theta$  scan from 10° to 90° with a step size of 0.04. 0 X-ray photoelectron spectrometer with a monochromatic Al K $\alpha$  source (hv <sup>1</sup>/<sub>4</sub> 1486.6 eV) and a charge neutralizer. All the binding energies were calibrated to the C 1s peak at 284.6 eV of the surface

adventitious carbon. Scanning electron microscopy (SEM) images were collected using a Hitachi S-4800 microscope equipped with an energy-dispersive X-ray analyser (EDS, Horiba EMAX Energy EX- 350). High-resolution TEM (HRTEM) images were obtained using a Philips Tecnai 20U-Twin microscope at an acceleration voltage of 200 kV. The solution of samples was achieved after 20 min ultrasonic pretreatment. The TEM samples were prepared by dropping the primed solution onto a copper grid with polyvinyl formal support film and dried in air. AFM 3100 Digital Instruments Dimension was used to investigate surface morphology. Raman spectra were obtained using the LabRam HR system from Horiba Jobin Yvon at room temperature with a 532 nm solid laser as the exciting source. UV-*Vis* diffuse reflectance spectroscopy spectra (UV-*Vis* DRS) was conducted using a Shimadzu UV2550 recording spectrophotometer equipped with an integrating sphere with wavelength of 200 nm to 900 nm.  $BaSO_4$  was used as a reference.

#### S4. Photo/electrochemical Tests

The photoelectrochemical (PEC) test system and electrocatalytic properties of the products for HER were evaluated with a three-electrode system using an electrochemical workstation (CHI 760E). Ag/AgCl (KCl saturated,  $E^{0}_{Ag/AgCl} = 0.2046$  V, at 25 °C) and Pt were used as reference and counter electrodes, respectively. The as-prepared composites were employed as working electrode. The preparation process of the electrode is shown as follows: Firstly, 5 mg sample was dispersed into a mixed solution containing 20 µL 5 wt% Nafion, 800 µL alcohol and 200 µL deionized water. The mixture was under ultrasonic dispersion for 60 min. Then, 100 µL of the

homogeneous fresh ink catalyst was directly deposited onto a fluoride-doped thin oxide (FTO) conductive glass plate and then dried at 80 °C in a vacuum oven. The loading amount was estimated to be 0.5 mg cm<sup>-2</sup> for all samples. A 300 W xenon lamp (PLS-SXE300C, Beijing Perfect Light Company) was used as the light source, providing visible light throughout the photoelectrochemical test. The light intensity was measured with a spectroradiometer (International Light Technologies Model ILT950). The incident-photon-to-current-conversion efficiency (IPCE) was obtained by measuring the photocurrent density under monochromatic light irradiation with a 500 W Xe lamp coupled with a grating monochromator, and then calculating the IPCE using following eqn, where  $I_{ph}$  is the photocurrent density,  $\lambda$  is the incident light wavelength, and  $P_{mono}$  is the calibrated and monochromated illumination power intensity. The illumination intensities of the monochromatic light were measured with a PM 100A Optical Power Meter (ThorLabs).

$$IPCE = \frac{1239.8(V \times nm) \times |I_{ph}(mA/cm^2)|}{\lambda(nm) \times P_{mono}(mW/cm^2)} \times 100\%$$

Polarization curves of hydrogen generation were obtained using linear sweep voltammetry (LSV) with scan rate of 2 mV·s<sup>-1</sup> at 25 °C in the aqueous solutions (1.0 M KOH) with constant  $N_2$  (g) continually purging for 30 min prior to the measurements. Electrochemical impedance spectroscopy (EIS) was carried out in potentiostatic mode from 10<sup>5</sup> to 0.01 Hz. All the polarization curves are the steady-state ones after several cycles. All polarization curves were IR corrected. The long-term stability test was carried out using chronoamperometry measurements.

## S5. Supplementary Figures S1-S18



Figure S1. Low and high magnification SEM images of  $Ti_3C_2$  nanosheets (a),  $Ti_3C_2@HWO_4$  precursor (b) and M@P-WO<sub>3</sub> (c).



Figure S2. The original EDS spectrum of the M@P-WO<sub>3</sub>.



Figure S3. Elemental mapping of  $M@P-WO_3$  in both low (a) and high (b) magnification SEM images.



**Figure S4.** XPS survey spectrum of P-WO<sub>3</sub> (a). High-resolution XPS spectra of P 2p region (b), W 4f region (c) and O 1s region (d) corresponding to P-WO<sub>3</sub>.

The survey XPS spectrum of P-WO<sub>3</sub> reveals the composition of P, W and O (Figures S4a). The P 2p spectrum in Figure S4b reveals the presence of P-W-O bonding without any other additional peaks. Similar to M@P-WO<sub>3</sub>, two additional peaks at ~34.06 and 36.26 eV corresponding to  $3d_{5/2}$  and  $3d_{3/2}$  of W<sup>5+</sup> appear in the W 4f spectrum (Figure S4c). In addition to the main O 1s peak for O-W bond, other additional peaks represent physisorbed/chemisorbed water (~532.04 eV), oxygen vacancy (~531.28 eV) and O-P bond (~532.81 eV) respectively (Figure S4d). These observations effectively confirm that phosphorus doping induced the generation of oxygen vacancies.



**Figure S5.** (a) Comparison of the Tafel slope of M@P-WO<sub>3</sub> under the irradiated light



with single wavelength. (b) Influence of the wavelength on Nyquist plots.

**Figure S6.** XRD patterns (a) and Raman spectra (b) of control samples with different doping amount of phosphorus.



Figure S7. EPR spectra of bare  $Ti_3C_2$  and P-WO<sub>3</sub> (a) and P-WO<sub>3</sub> with different

doping amount of phosphorus (b).

As shown in Figure S7a, there is no signal for bare  $Ti_3C_2$ . Using the same synthesis method of M@P-WO<sub>3</sub>-a/b/c/d, control samples named P-WO<sub>3</sub>-a/b/c/d were prepared without  $Ti_3C_2$ . The intensity of EPR signal increases along with the doping amount (Figure S7b).



**Figure S8.** High-resolution XPS spectra of P 2p region (a) and W 4f region (b) of  $M@P-WO_3$  with different doping amount of phosphorus  $M@P-WO_3-a/b/c/d$ .



**Figure S9.** High-resolution XPS spectra of Ti 2p region (a) and C 1s region (b) of M@P-WO<sub>3</sub> with different doping amount of phosphorus M@P-WO<sub>3</sub>-a/b/c/d.

The P 2p spectra reveal the presence of P-W-O bonds. The peak intensity P-C bonds beside P-W-O bonds increases along with phosphorus doping amounts (Figure S8a). Two additional peaks at ~34.1 and ~36.2 eV corresponding to 3d<sub>5/2</sub> and 3d<sub>3/2</sub> of W<sup>5+</sup> appear in the W 4f spectrum of M@P-WO<sub>3</sub>-b/c/d (Figure S8b). And there are only two W<sup>6+</sup> peaks in the spectra of M@P-WO<sub>3</sub>-a, implying that oxygen vacancies are mainly produced by phosphorus doping. In addition to M@P-WO<sub>3</sub>-a, all the other control samples possess the peaks of Ti-P bond in Ti 2p spectra and C-P bond in C 1s spectra (Figure S9). And the variation tendency of the peak intensity of Ti-P bond and

C-P bond is consistent with that of oxygen vacancy.



Figure S10. UV-vis diffuse reflectance spectra (g) of M@P-WO<sub>3</sub> with different

doping amount of phosphorus.



**Figure S11.** Nyquist plots of M@P-WO<sub>3</sub> with different amount of oxygen vacancy in alkaline condition.



**Figure S12.** The polarization curves using different reference electrodes at M@P-WO<sub>3</sub>-a (a), M@P-WO<sub>3</sub>-b (b), M@P-WO<sub>3</sub>-c (c) and M@P-WO<sub>3</sub>-d (d), respectively.

There is no significant difference about the HER ability between Ag/AgCl electrode electrode system and Hg/HgO electrode system, which avoids the negative influence of Ag/AgCl electrode in alkaline solution (Figure S12).



**Figure S13.** Comparison of the polarization curves of control samples with different doping amount of phosphorus before and after light irradiation. The Tafel slope curves (a), comparison of Tafel slope (b), overpotential for driving 10 mA·cm<sup>-2</sup> (c) and current density at -0.1 V (d).

For the sample M@P-WO<sub>3</sub>-c, the photon-excited charge carriers acutely reduce the Tafel slope to 41 mV/dec, 40.2 % of that in darkness, decrease the overpotential to 43.6 mV (driving 10 mA cm<sup>-2</sup>), and increase the current density to 21.4 mA cm<sup>-2</sup> ( $\eta$  = 100 mV), 4.1 times higher than the value in darkness. Comparing to the control samples, M@P-WO<sub>3</sub>-c actes the largest reduction amplitude of overpotential and largest growing rate of current density after light irradiation.



**Figure S14.** Electrochemical cyclic voltammetry curves at different potential scanning rates for M@P-WO<sub>3</sub>-a/b/c/d.



Figure S15. The fitting plots showing Cdl for M@P-WO<sub>3</sub>-a/b/c/d.

From CV cycles in the range of nonfaradaic processes, and a linear relationship

between scan rates and current densities is obtained. The current density differences at the intermediate value of the voltage window is calculated by the formula  $(\Delta j=j_a-j_c)$ ,  $j_a$ and  $j_c$  are the positive and negative current density, respectively.



Figure S16. BET surface area of precursor WO<sub>3</sub> and M@P-WO<sub>3</sub>-a/b/c/d.



Figure S17. Photocurrent responses of samples in 1.0 M KOH solution under light ON-OFF cycling.

The photocurrent decreases in an order:  $M@P-WO_3-c > M@P-WO_3-d > M@P-WO_3-b > M@P-WO_3-a$ , indicating the highest charge separation efficiency of M@P-WO\_3-c, which favors the photo-enhanced electrocatalysis.



**Figure S18.** Nyquist plots of M@P-WO<sub>3</sub> with different amount of MXene  $(Ti_3C_2)$  (a) and MXene  $(Ti_3C_2)$  (b) in alkaline condition.



Figure S19. Comparison of the polarization curves of M@P-WO<sub>3</sub> with different doping amount of  $Ti_3C_2$  before and after light irradiation.



**Figure S20.** Comparison of the polarization curves of control samples with different doping amount of  $Ti_3C_2$  before and after light irradiation. The Tafel slope curves (a), comparison of Tafel slope (b), overpotential for driving 10 mA·cm<sup>-2</sup> (c) and current density at -0.1 V (d).

The photon-excited charge carriers acutely reduce the Tafel slope to 78 mV/dec (P-WO<sub>3</sub>, 63.9 % of that in darkness), 60 mV/dec (M@P-WO<sub>3</sub>-1, 54.5 % of that in darkness), 53 mV/dec (M@P-WO<sub>3</sub>-2, 49.5 % of that in darkness), 41 mV/dec (M@P-WO<sub>3</sub>-3, 40.1 % of that in darkness) and 47 mV/dec (M@P-WO<sub>3</sub>-4, 47.5 % of that in darkness), respectively. To drive 10 mA cm<sup>-2</sup>, the overpotential ranges from 161.6 mV to 294.6 mV after light irradiation. M@P-WO<sub>3</sub>-3 exhibits the lowest overpotential. A similar phenomenon has emerged in rank of current density. M@P-WO<sub>3</sub>-3 acts the highest current density at 100 mV ( $\eta$ ).



Figure S21. XRD patterns of M@P-WO<sub>3</sub> before and after stability test.



**Figure S22.** High-resolution XPS spectra of P 2p region (a), Ti 2p region (b), C 1s region (c) and W 4f region (d) of M@P-WO<sub>3</sub> after stability test.



Figure S23. The convergence curves of WO<sub>3</sub> bulk (a) and surfaces (b) calculations.



Figure S24. Slab models for WO<sub>3</sub>, P-WO<sub>3</sub> (with oxygen vacancies) and MXene@ P-





Figure S15. DFT calculated density of states (DOS) of single elements for WO<sub>3</sub>.



**Figure S25.** DFT calculated density of states (DOS) of single elements for P-WO<sub>3</sub> (with oxygen vacancies).



Figure S26. DFT calculated density of states (DOS) of single elements for MXene@ P-WO<sub>3</sub>.



Figure S27. Mott-Schottky plots of M@P-WO<sub>3</sub>-a/b/c/d at an AC frequency of 100 Hz in darkness.

![](_page_20_Figure_2.jpeg)

Figure S28.  $(\alpha hv)^{1/2}$  versus hv curves (a) and valence-band XPS spectra (b) of M@P-WO<sub>3</sub> with different amount of oxygen vacancy.

![](_page_21_Figure_0.jpeg)

Figure S29. The electronic band structure diagram of  $M@P-WO_3$  with different amount of oxygen vacancy.

### S6. Supplementary Table S1-S8.

Element	Weight%	Atomic%
СК	16.39	45.90
O K	18.59	40.16
РК	1.33	1.43
Ti K	1.59	1.24
W M	62.10	11.27
Totals	100.00	

Table S1. EDS elements analysis of M@P-WO<sub>3</sub>.

Table S2. EDS elements analysis of control samples.

Element Atomic%	СК	Ti K	РК	O K	W M	O/W
M@P-WO <sub>3</sub> -a	44.50	1.37	-	43.86	10.27	4.27
M@P-WO <sub>3</sub> -b	51.78	1.14	0.58	36.91	9.59	3.85
M@P-WO <sub>3</sub> (M@P-WO <sub>3</sub> -c/3)	45.90	1.24	1.43	40.16	11.27	3.56
M@P-WO <sub>3</sub> -d	47.64	1.09	3.83	36.21	11.23	3.22
M@P-WO <sub>3</sub> -1	61.32	0.36	1.05	28.85	8.41	3.43
M@P-WO <sub>3</sub> -2	49.39	0.77	1.47	38.92	9.45	4.12
M@P-WO <sub>3</sub> -4	54.49	2.88	1.12	32.79	8.72	3.76

All the samples exhibit the O/W proportions greater than 3, owing to the existence of physico/chemical adsorbed water.

Sample	Peak	Position	Area	FWHM	L/G Mix(%)
Р	1	130.1	13344.72	2.00	30
	1	34.06	3173.70	1.30	30
W	2	35.30	17616.18	1.30	30
••	3	36.26	2787.38	1.30	30
	4	37.45	13054.92	1.30	30
0	1	530.35	45782.81	1.40	30
	2	531.28	13322.91	1.40	30
	3	532.04	10446.61	1.40	30
	4	532.81	8435.91	1.40	30

Table S3. The corresponding XPS parameters of XPS spectra for P-WO<sub>3</sub>.

Sample	Peak	Position	Area	FWHM	L/G Mix(%)
M@P-WO <sub>2</sub> -a	1	455.35	232.48	2.00	30
	2	458.85	1176.16	2.00	30
	3	464.60	550.73	2.00	30
	1	455.36	794.46	1.60	30
	2	458.86	1646.86	1.60	30
M( <i>a</i> ) <b>P-WO</b> <sub>3</sub> -D	3	461.32	290.98	1.60	30
	4	464.63	tionAreaFWHM $.35$ $232.48$ $2.00$ $.85$ $1176.16$ $2.00$ $.60$ $550.73$ $2.00$ $.36$ $794.46$ $1.60$ $.36$ $794.46$ $1.60$ $.32$ $290.98$ $1.60$ $.63$ $433.91$ $1.60$ $.63$ $433.91$ $1.60$ $.38$ $1523.47$ $2.10$ $.35$ $730.62$ $2.10$ $.35$ $730.62$ $2.10$ $.39$ $1172.17$ $2.50$ $.38$ $1256.90$ $2.50$ $.35$ $790.69$ $2.50$ $.466$ $410.38$ $2.50$	30	
	1	455.38	1523.47	2.10	30
	-WO <sub>3</sub> -b 2 3 4 1 2 -WO <sub>3</sub> -c 3 4	458.88	1436.92	2.10	30
M( <i>u</i> ) <b>P-WO</b> 3-C	3	461.35	730.62	2.10	30
	4	455.35232.482.00458.851176.162.00464.60550.732.00455.36794.461.60458.861646.861.60461.32290.981.60464.63433.911.60455.381523.472.10458.881436.922.10461.35730.622.10464.65580.912.10455.391172.172.50458.881256.902.50461.35790.692.50464.66410.382.50	30		
	1	455.39	1172.17	2.50	30
	2	458.88	1256.90	2.50	30
$\mathbf{W}(\boldsymbol{w})^{\mathbf{r}} - \mathbf{W} \mathbf{U}_{3} - \mathbf{d}$	3	461.35	790.69	2.50	30
	4	464.66	.35 $232.48$ $2.00$ .851176.16 $2.00$ .60 $550.73$ $2.00$ .36 $794.46$ $1.60$ .36 $794.46$ $1.60$ .36 $1646.86$ $1.60$ .32 $290.98$ $1.60$ .63 $433.91$ $1.60$ .38 $1523.47$ $2.10$ .38 $1436.92$ $2.10$ .35 $730.62$ $2.10$ .65 $580.91$ $2.10$ .39 $1172.17$ $2.50$ .88 $1256.90$ $2.50$ .35 $790.69$ $2.50$ .66 $410.38$ $2.50$	30	

Table S4. The corresponding XPS parameters of Ti spectra for  $M@P-WO_3-a/b/c/d$ .

Sample	Peak	Position	Area	FWHM	L/G Mix(%)
	1	284.70	6622.87	1.40	30
M@P-WO <sub>3</sub> -a	2	286.25	1550.60	1.40	30
	3	288.17	670.09	1.40	30
	1	282.40	219.63	1.50	30
M@D.WO. k	2	284.65	5972.52	1.50	30
M@ <b>P-WO</b> 3-D	3	286.25	1745.67	1.50	30
	4	288.20	450.18	1.50	30
	1	282.40	334.79	1.50	30
	2	284.64	4125.91	1.50	30
M( <i>u</i> ) <b>P-WO</b> <sub>3</sub> -C	3	286.36	942.81	1.50	30
	4	288.25	371.46	1.50	30
	1	282.40	1546.91	2.00	30
<b>W</b> ( <i>W</i> ) <b>F</b> - <b>WU</b> <sub>3</sub> - <b>d</b>	2	284.65	12482.96	2.00	30
	3	286.37	1517.38	2.00	30
	4	288.40	1546.91	2.00	30

Table S5. The corresponding XPS parameters of C spectra for  $M@P-WO_3-a/b/c/d$ .

Sample	Peak	Position	Area	FWHM	L/G Mix(%)
M@P-WO <sub>3</sub> -a	-	-	-	-	-
M@P-WO3-b	1	130.1	660.40	1.80	30
	2	131.1	122.34	1.80	30
M@P-WOc	1	130.1	2271.11	1.80	30
	2	131.1	454.72	1.80	30
M@P-WO <sub>2</sub> -d	1	130.1	3555.09	1.80	30
	2	131.1	659.03	1.80	30

Table S6. The corresponding XPS parameters of P spectra for  $M@P-WO_3-a/b/c/d$ .

Sample	Peak	Position	Area	FWHM	L/G Mix(%)
WO <sub>3</sub>	1	35.22	24135.41	1.28	30
precursor	2	37.40	17664.65	1.28	30
M@P-WO <sub>2</sub> -a	1	35.25	23479.33	1.25	30
	PeakPositionAreaF135.2224135.41237.4017664.65135.2523479.33237.5017695.00134.073055.66235.2839369.37336.202442.83437.4529803.98134.096776.56235.3033501.76336.228497.03437.4725768.90134.103311.57235.3133832.87	1.25	30		
	1	34.07	3055.66	1.15	30
	2	1 34.07 3035.00 1.13   2 35.28 39369.37 1.15   3 36.20 2442.83 1.15	1.15	30	
M( <i>a</i> ) <b>P-W</b> O <sub>3</sub> -D	3	36.20	2442.83	1.15	30
	4	3 36.20 2442.83 1.15   4 37.45 29803.98 1.15   1 34.09 6776.56 1.35	30		
	1	34.09	6776.56	1.35	30
	2	35.30	33501.76	1.35	30
<b>WI(<i>W</i>)F</b> - <b>WO</b> <sub>3</sub> - <b>C</b>	3	36.22	8497.03	1.35	30
	4	37.47	25768.90	1.35	30
	1	34.10	3311.57	1.15	30
M@DWO J	2	35.31	33832.87	1.15	30
1v1( <i>W</i> ) <b>F</b> - vv O3-U	3	36.23	4704.86	1.15	30
	4	37.49	25586.87	1.15	30

Table S7. The corresponding XPS parameters of W spectra for WO<sub>3</sub> precursor and  $M@P-WO_3-a/b/c/d$ .

Sample	Peak	Position	Area	FWHM	L/G Mix(%)
WO <sub>3</sub>	1	530.30	43994.43	1.80	30
precursor	3	532.38	11847.85	1.80	30
	1	530.34	38922.75	1.60	30
	2	PositionAreaFWHMI530.3043994.431.80532.3811847.851.80530.3438922.751.60531.282054.641.60532.199674.721.60533.302492.471.60531.245364.831.60532.086569.841.60532.772783.821.60533.402258.711.60531.2512120.891.30532.047482.931.30532.783174.981.30533.382605.791.30530.3820907.711.40531.2612004.861.40532.057382.401.40532.744899.311.40533.521651.221.40	30		
M( <i>a</i> ) <b>P-WO</b> 3-a	3	532.19	9674.72	1.60	30
	4	533.30	2492.47	FWHM   1.80   1.80   1.60   1.60   1.60   1.60   1.60   1.60   1.60   1.60   1.60   1.60   1.60   1.60   1.60   1.30   1.30   1.30   1.30   1.30   1.40   1.40   1.40   1.40   1.40   1.40	30
	1	530.34	33828.03	1.60	30
	2	531.24	5364.83	1.60	30
M@P-WO <sub>3</sub> -b	3	532.08	6569.84	1.60	30
	4	532.77	2783.82	1.60	30
	5	533.40	2258.71	1.60 1.60 1.60 1.30	30
	1	530.35	46945.69	1.30	30
	2	530.3043994.431.80532.3811847.851.80530.3438922.751.60531.282054.641.60532.199674.721.60533.302492.471.60531.245364.831.60532.086569.841.60532.772783.821.60531.2512120.891.30531.2512120.891.30532.783174.981.30532.783174.981.30531.2612004.861.40532.057382.401.40532.744899.311.40533.521651.221.40	30		
M@P-WO <sub>3</sub> -c	3	532.04	7482.93	1.30	30
	4	532.78	3174.98	1.30	30
	5	533.38	2605.79	1.30	30
	1	530.38	20907.71	1.40	30
	2	531.26	12004.86	1.40	30
M@P-WO <sub>3</sub> -d	3	532.05	7382.40	1.40	30
	4	532.74	4899.31	1.40	30
	5	533.52	38922.75 2054.64 9674.72 2492.47 33828.03 5364.83 6569.84 2783.82 2258.71 46945.69 12120.89 7482.93 3174.98 2605.79 20907.71 12004.86 7382.40 4899.31 1651.22	1.40	30

**Table S8.** The corresponding XPS parameters of O spectra for  $WO_3$  precursor andM@P-WO\_3-a/b/c/d.