

# Interface-modulated nanojunction and microfluidic platform for photoelectrocatalytic chemicals upgrading

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**Abstract:** Photoelectrocatalytic oxidation provides a technically applicable way for solar-chemical synthesis, but its efficiency and selectivity are moderate. Herein, a microfluidic photoelectrochemical architecture with 3-D microflow channels is constructed by interfacial engineering of defective WO<sub>3</sub>/TiO<sub>2</sub> heterostructures on porous carbon fibers. Kelvin probe force microscopy and photoluminescence imaging visually evidence the charge accumulation sites on the nanojunction. This efficient charge separation contributes to 3-fold enhancement in the yield of glyceraldehyde and 1,3-dihydroxyacetone during glycerol upgrading, together with nearly doubled production of high value-added KA oil and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> oxidant through cyclohexane and HSO<sub>4</sub><sup>-</sup> oxidization, respectively. More importantly, the microfluidic platform with enhanced mass transfer exhibits a typical reaction selectivity of 85%, which is much higher than the conventional planar protocol. Integrating this microfluidic photoanode with an oxygen reduction cathode leads to a self-sustained photocatalytic fuel cell with remarkably high open-circuit voltage (0.9 V) and short-circuit current (1.2 mA cm<sup>-2</sup>).

**Keywords:** chemicals upgrading; photoelectrocatalysis; microflow channels; charge separation; photocatalytic fuel cells

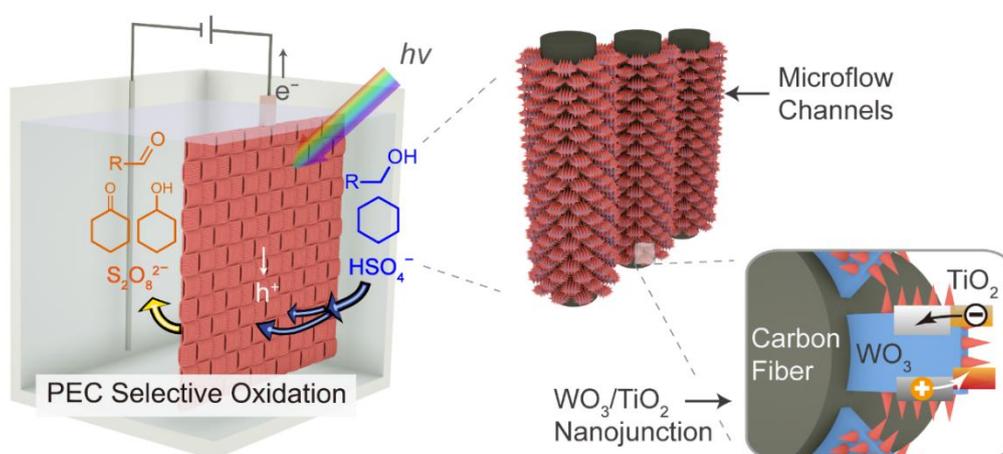
## 1. Introduction

1 Oxidative production of value-added chemicals is a fundamental transformation  
2 process in the fine chemical, pharmaceutical, biological, and agrochemical realms [1-  
3 3]. For example, the oxidation of glycerol to glyceraldehyde (GLAD) and/or 1,3-  
4 dihydroxyacetone (DHA) could essentially increase the commercial value by thousands  
5 of times [4,5]. The oxidation of other biomass-derived alcohols (benzylic alcohols and  
6 5-hydroxymethylfurfural) [6,7], the activation of C-H bonds [8], as well as the  
7 production of various oxidizing reagents ( $S_2O_8^{2-}$ ,  $ClO^-$ , and  $H_2O_2$ ) [9] are also of  
8 significant importance for the chemical industry. However, the commonly employed  
9 thermo- and electrochemical routes not only rely greatly on adsorbed oxidants and  
10 noble metal catalysts (e.g., Pt, Pd, and Au), but also require massive energy  
11 consumption, thus seriously hindering their potential applications [3,10-12]. The  
12 alternative green oxidation process to produce valuable building-block chemicals  
13 remains one of the most important challenges of modern chemistry.

14 In recent years, selective organic transformation using earth-abundant  
15 semiconductors as catalysts and solar energy as the driving force has spurred  
16 tremendous research activities toward green synthesis [13-16]. Unfortunately, low  
17 quantum yields of particulate photocatalysts (<5% in most cases) and difficulties in the  
18 recovery of nanosized catalysts make the suspension systems less economically viable  
19 [17,18]. In this regard, immobilized photoelectrodes with electric-field-enhanced  
20 charge separation should be more promising for generating value-added products with  
21 low energy input. In the photoelectrochemical (PEC) processes, photon utilization and  
22 charge separation are two of the most important factors affecting the overall energy  
23 conversion efficiency. Recently, various strategies have been reported to enhance  
24 photon absorption and electron-hole separation efficiency, such as constructing  
25 multijunction structure [19-21], tuning crystal facets [22-24], as well as defect  
26 engineering [25-27]. Although promising PEC performances have been achieved, the  
27 charge transfer mechanisms remain unclear and are still under debate in many cases  
28 [28,29]. On the other hand, the mass transfer of reactants and their subsequent  
29 adsorption on the electrode surface are also essential factors determining the reaction  
30 rate and efficiency [30,31]. However, most current prevailing approaches for PEC  
31 oxidative upgrading focus on planar photoelectrodes, which suffer from low efficiency  
32 caused by limited reactants diffusion around the semiconductor-liquid interface [32-  
33 35]. Moreover, sluggish mass transfer unavoidably results in the overoxidation of  
34 valuable chemicals into undesired byproducts [36-38]. Microfluidic nanostructures can

1 provide new opportunities to circumvent the above drawbacks, due to the intensified  
2 mass transfer and improved reaction kinetics in the 3-D channels for precise product  
3 control [39-43]. Nevertheless, the combination of photoelectrodes with microfluidic  
4 architectures for PEC oxidative upgrading is less explored by far.

5 Herein, we set out to construct 3-D microfluidic PEC architecture with significantly  
6 enhanced charge and mass transfer for the oxidative upgrading of various chemicals. In  
7 such a miniaturized system, branched  $\text{WO}_3$  nanostructures decorated by  $\text{TiO}_2$  overlayer  
8 were used as photoactive materials, with carbon fibers as flexible, robust, and low-cost  
9 support for electron collection (Scheme 1) [44]. Kelvin probe force microscopy (KPFM)  
10 and photoluminescence imaging (PL) techniques were originally employed to visualize  
11 the spatial distribution and interfacial transfer of charge carriers in  $\text{WO}_3/\text{TiO}_2$   
12 heterostructures. Our results revealed that microfluidic nanojunction with oxygen  
13 vacancy defects exhibited exceptional PEC activity and selectivity for chemical  
14 upgrading reactions, such as the oxidation of glycerol and cyclohexane. We further  
15 presented the inspiring principle of self-sustainable photocatalytic fuel cell by  
16 integrating the microfluidic photoanode with an oxygen reduction cathode.



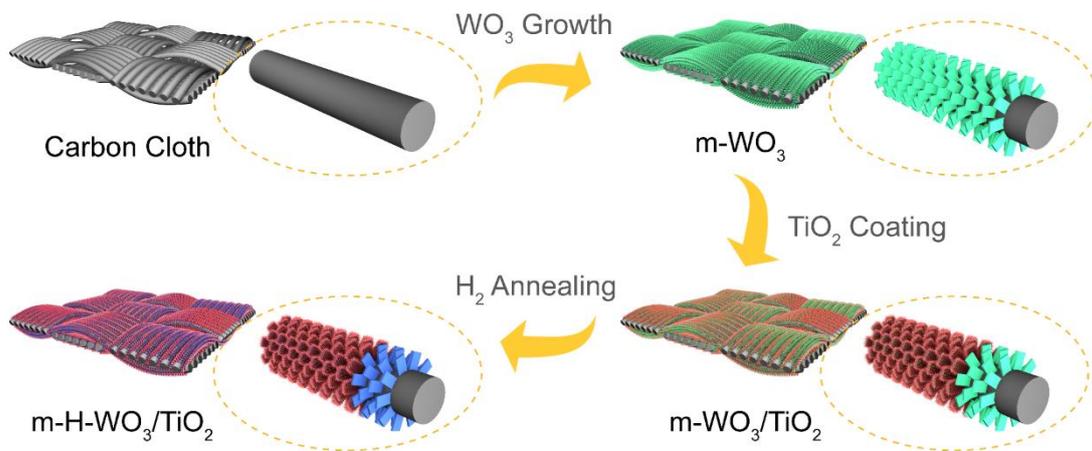
17 **Scheme 1.** Schematic diagram of the 3-D microfluidic PEC architecture with  
18  $\text{WO}_3/\text{TiO}_2$  nanojunction for oxidative upgrading of alcohols, hydrocarbon, and  
19 inorganic chemicals to their corresponding value-added products.  
20

## 21 **2. Experimental section**

### 22 *2.1 Preparation of $m\text{-H-WO}_3$*

23 The electrode was fabricated by a seed-assisted hydrothermal method, as illustrated in  
24 Scheme 2 [45]. Briefly, a seed solution was prepared by adding 400 mg  $\text{WCl}_6$  and 2  
25 mL 30%  $\text{H}_2\text{O}_2$  into 20 mL ethanol. Carbon cloth with a size of 1.5 cm  $\times$  3 cm was

1 dipped into the seed solution for 1 min and then dried at 40 °C for 30 min in an oven.  
2 After repeating this dip-coating process three times, the carbon cloth was annealed in  
3 air at 400 °C for 2 h. Then, 330 mg  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  was dissolved in 90 mL deionized  
4 water, followed by adding 6 mL of 6 M HCl and 1.8 g oxalic acid dihydrate. After  
5 stirring for 30 min, 20 mL of the mixture was transferred into a 50 mL Teflon-lined  
6 stainless autoclave. The seeded carbon cloth was held by a self-made PTFE holder and  
7 placed vertically in the autoclave (Fig. S1). The autoclave was then sealed and heated  
8 at 180 °C for 8 h. This hydrothermal treatment was repeated one more time with a  
9 refreshed precursor solution to obtain a dense layer of  $\text{WO}_3$ . After the reaction, the  
10 carbon cloth was taken out and rinsed with deionized water. Finally, the sample was  
11 annealed in air at 500 °C for 2 h with a heating rate of 2 °C  $\text{min}^{-1}$  and referred to as m-  
12  $\text{WO}_3$ . To obtain defective m- $\text{WO}_3$  film (denoted as m-H- $\text{WO}_3$ ), the electrode was  
13 placed in a tube furnace with 50  $\text{mL min}^{-1}$  gas flow (10%  $\text{H}_2$  and 90% Ar) and annealed  
14 at 350 °C for 2 h with a ramping rate of 2 °C  $\text{min}^{-1}$ . The fabrication of pI-H- $\text{WO}_3$  is  
15 similar to m-H- $\text{WO}_3$  except that the substrate is FTO conductive glass.



16  
17 **Scheme 2.** Schematic diagram of the preparation process for m-H- $\text{WO}_3/\text{TiO}_2$   
18 photoanode.

## 19 2.2 Preparation of m-H- $\text{WO}_3/\text{TiO}_2$

20 A facile wet chemical method was employed to prepare m-H- $\text{WO}_3/\text{TiO}_2$  [29]. In brief,  
21 m- $\text{WO}_3$  film was placed in an aqueous mixed solution of 30 mM ammonium  
22 hexafluorotitanate and 150 mM boric acid in a water bath at 30 °C for 24 h. Then, the  
23 film was washed with deionized water and dried at room temperature. After that, the  
24 electrode was annealed in air at 350 °C for 2 h with a ramping rate of 2 °C  $\text{min}^{-1}$  to

1 obtain the m-WO<sub>3</sub>/TiO<sub>2</sub> heterostructure. The defective m-H-WO<sub>3</sub>/TiO<sub>2</sub> film was  
2 obtained by replacing the air with 50 mL min<sup>-1</sup> gas flow (10% H<sub>2</sub> and 90% Ar).

### 3 *2.3 Preparation of H-WO<sub>3</sub>/TiO<sub>2</sub> heterojunction for KPFM measurements*

4 Graphite was used as the conductive support for the loading of defective WO<sub>3</sub>/TiO<sub>2</sub>  
5 heterostructure to represent the interfacial contact of WO<sub>3</sub> and carbon cloth. Firstly, a  
6 piece of graphite plate (1 cm × 3 cm) was polished by abrasive paper and ordinary  
7 printing paper to obtain a shiny surface. Then the graphite plate was placed in a Teflon-  
8 lined stainless autoclave containing 2 mM Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O, 70 mM HCl, and 7 mM  
9 ammonium oxalate with the smooth side facing down. The autoclave was then sealed  
10 and heated at 120 °C for 3 h. After the hydrothermal reaction, the sample was annealed  
11 in air at 500 °C for 2 h. TiO<sub>2</sub> nanoplate with exposed (001) facet was prepared using a  
12 well-established method [46]. In brief, 25 mL aqueous solution containing 2.67 mM  
13 TiF<sub>4</sub> and 70 mM HF were added to a Teflon-lined autoclave, followed by heating up to  
14 180 °C for 12 h. The obtained TiO<sub>2</sub> nanocrystals were washed several times and  
15 dispersed in deionized water. Then, a certain amount of TiO<sub>2</sub> dispersion was drop-  
16 casted onto the graphite plate with WO<sub>3</sub>. The defective H-WO<sub>3</sub>/TiO<sub>2</sub> was finally  
17 obtained after annealing the sample at 350 °C for 2 h with 50 mL min<sup>-1</sup> gas flow (10%  
18 H<sub>2</sub> and 90% Ar). For comparison, a similar WO<sub>3</sub>/TiO<sub>2</sub> heterostructure without defect  
19 was annealed in air to investigate the impact of oxygen vacancies on the interfacial  
20 charge transfer. The similar method was used to prepare WO<sub>3</sub>/TiO<sub>2</sub> samples on glass  
21 for PL measurements.

### 22 *2.4 Characterization*

23 The morphology of samples was characterized by a scanning electron microscope  
24 (SEM, JSM-7001F). Transmission electron microscopy (TEM) and the corresponding  
25 energy-dispersive X-ray spectroscopy (EDS) were taken on a transmission electron  
26 microscope (JEM-2100F) with an acceleration voltage of 200 kV. Electron spin  
27 resonance (ESR) analysis was carried out using a Bruker E500 spectrometer. X-ray  
28 diffraction (XRD) patterns were recorded on a PANalytical X-ray diffractometer with  
29 Cu K $\alpha$  radiation. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a  
30 Thermo ESCALAB250Xi spectrometer with a monochromated Al-K $\alpha$  X-ray source.  
31 The photoluminescence (PL) images of WO<sub>3</sub>/TiO<sub>2</sub> heterojunction were recorded on

1 Leica TCS SP8 nanoscope with an excitation wavelength of 405 nm and emission  
2 wavelengths of 450–500 nm.

### 3 *2.5 KPFM measurement*

4 The surface potential images were taken with a Bruker Dimension Icon system under  
5 ambient atmosphere in an amplitude-modulated (AM)-KPFM mode [47]. The lift mode  
6 was adopted with a lift height of 100 nm and the AC voltage was set to 0.5 V. The Pt/Ir-  
7 coated Si tip (PIT-V2) was used with a spring constant of 1.5-6 N m<sup>-1</sup> and resonant  
8 frequency of 50-100 kHz. The light from a 500 W Hg lamp (CEL-M500, light intensity  
9 ~150 mW cm<sup>-2</sup>) was irradiated on the sample with a ~5° grazing angle. The surface  
10 photovoltage (SPV) is the difference in the surface potential (or contact potential  
11 difference, CPD) before and after illumination, defined as  $SPV = CPD_{light} - CPD_{dark}$ .

### 12 *2.6 Computational fluid dynamics (CFD) study*

13 The flow fields in the micro-channels were simulated using COMSOL Multiphysics  
14 5.2. The 3-D geometry “CFD” module was used to solve the flow velocity distribution  
15 in the electrodes. For the microfluidic WO<sub>3</sub> electrode, two parallel carbon fibers in the  
16 diameter of 8 μm were separated by a distance of 4 μm. WO<sub>3</sub> nanoplates with the  
17 dimension of 2 μm × 1 μm × 200 nm were vertically aligned on the surface of both  
18 carbon fibers and FTO, with loading densities of about 1 plate per μm<sup>2</sup>. The water flow  
19 direction in the microfluidic system was set to be perpendicular to the plane of carbon  
20 fibers, with an inlet velocity of 1 mm s<sup>-1</sup>. For the planar system, water flow direction  
21 was parallel to the electrode plane and the inlet velocity was also set to be 1 mm s<sup>-1</sup>.

### 22 *2.7 Photoelectrochemical measurement*

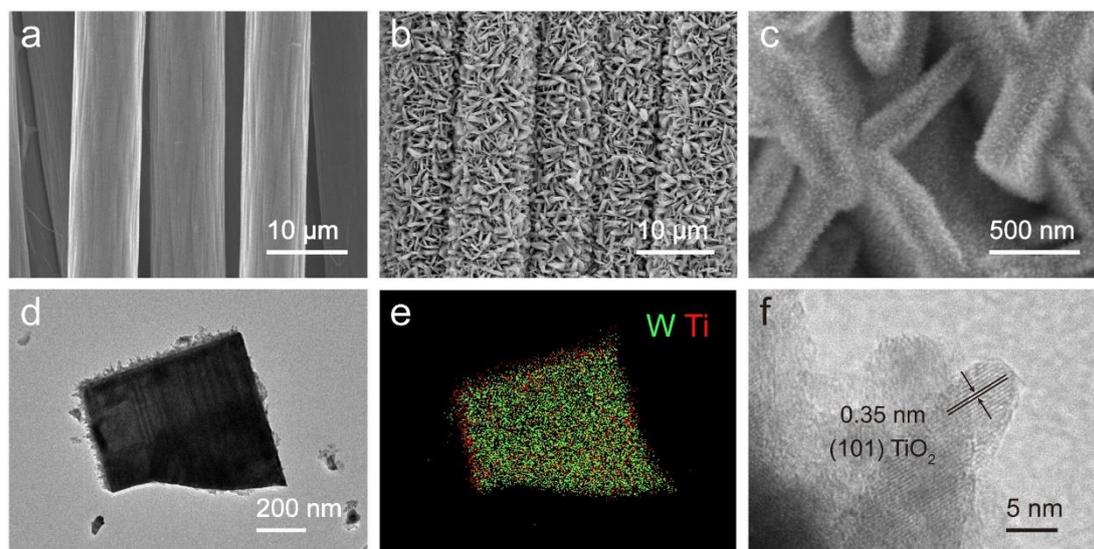
23 All the photoelectrochemical measurements were carried out on a Gamry Interface  
24 1000 electrochemical workstation. For the typical three-electrode configuration, the  
25 saturated Ag/AgCl electrode and Pt-wire electrode were used as the reference and  
26 counter electrode, respectively. For the chemical transformation experiments, a two-  
27 compartment cell was used, where the same anolyte and catholyte were separated by  
28 Nafion 211 membrane. A 500 W Xe lamp (CEL-S500) coupled with an AM 1.5 G filter  
29 was used to simulate solar irradiation and the light intensity was calibrated to 100 mW  
30 cm<sup>-2</sup>. Photocurrent-voltage (J–V) curves were measured at a scan rate of 5 mV s<sup>-1</sup>.  
31 Before data collection, the J–V scans were repeated for at least three times to reach a  
32 steady state. In all the PEC experiments, oxygen was bubbled into the electrolyte with

1 a flow rate of  $20 \text{ mL min}^{-1}$  to ensure efficient oxygen reduction reaction (ORR) and  
2 mass transfer.

### 3 **3. Results and discussion**

#### 4 *3.1. Structural characterization*

5 SEM image suggests that the carbon cloth substrate is comprised of an interwoven  
6 network of carbon fibers (diameter  $\approx 8 \mu\text{m}$ ) with massive microflow channels (Fig. 1a).  
7 After hydrothermal growth, the staggered carbon fibers were covered with a thick layer  
8 of vertically aligned  $\text{WO}_3$  nanoplates (Fig. S2). The typical thickness and height of  
9 these nanoplates are 200 nm and  $2 \mu\text{m}$ , respectively. The formation of hierarchical  
10  $\text{WO}_3/\text{TiO}_2$  nanojunctions with a high surface roughness on carbon fibers is clearly  
11 revealed by Fig. 1b and 1c. According to the TEM observation, the length of  $\text{TiO}_2$   
12 nanoprickles is about 50 nm (Fig. 1d and S3). EDS elemental mapping image of m-H-  
13  $\text{WO}_3/\text{TiO}_2$  evidences the dense and uniform wrapping of  $\text{WO}_3$  nanoplates by  $\text{TiO}_2$   
14 branches (Fig. 1e). The uniform coverage of  $\text{TiO}_2$  on m-H- $\text{WO}_3$  can be also revealed  
15 by the appearance of Ti 2p peaks and substantial diminishment of W 4f signal in the  
16 XPS spectra of m-H- $\text{WO}_3/\text{TiO}_2$  (Fig. S4). Furthermore, high-resolution TEM (HRTEM,  
17 Fig. 1f) image of  $\text{TiO}_2$  nanoprickle presents a lattice spacing of 0.35 nm, which well  
18 matches up with the (101) plane of anatase  $\text{TiO}_2$  [48]. Benefiting from the microfluidic  
19 architecture and ample nanojunctions, m-H- $\text{WO}_3/\text{TiO}_2$  could possess higher contact  
20 efficiency with the solution in comparison to its planar counterpart (Fig. S5).

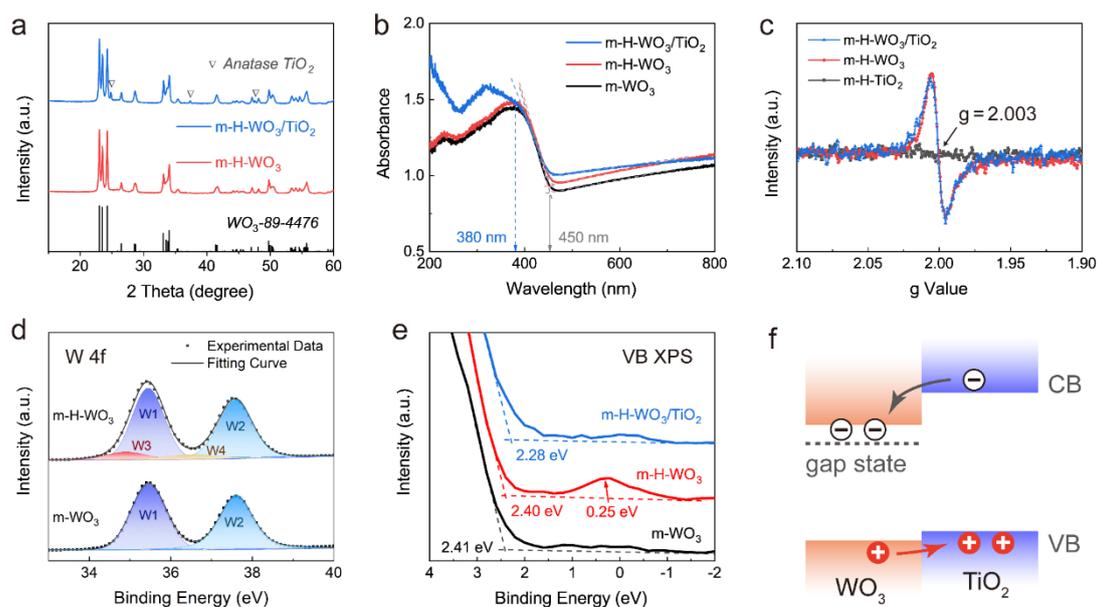


21 **Fig. 1.** SEM images of (a) carbon cloth and (b,c) m-H- $\text{WO}_3/\text{TiO}_2$  photoanode. (d) TEM  
22 image of  $\text{WO}_3/\text{TiO}_2$  nanoplate and (e) the corresponding EDS elemental mapping  
23 image. (f) HRTEM image of  $\text{TiO}_2$  nanoprickle.  
24

1 The crystal and electronic structure of these microfluidic electrodes were thereafter  
2 comprehensively characterized. As shown in Fig. 2a, m-H-WO<sub>3</sub> displays three strong  
3 XRD peaks in the range of 22°–25°, suggesting the monoclinic phase structure of WO<sub>3</sub>  
4 (JCPDS 89-4476). After the decoration of TiO<sub>2</sub>, the emerging diffraction peaks at 25.3°,  
5 37.8°, and 48.1° can be well indexed to the (101), (004), and (200) planes of anatase  
6 TiO<sub>2</sub> (JCPDS 21-1272). UV-visible absorption spectra of m-WO<sub>3</sub>, m-H-WO<sub>3</sub>, and m-  
7 H-WO<sub>3</sub>/TiO<sub>2</sub> were measured and displayed in Fig. 2b. All these samples exhibit similar  
8 absorption edges of about 450 nm, corresponding to the band gap (2.7 eV) of WO<sub>3</sub>.  
9 Compared to m-WO<sub>3</sub>, m-H-WO<sub>3</sub> shows higher absorption coefficient in the visible  
10 region, which can be attributed to the formation of defect states in WO<sub>3</sub> [39]. For m-H-  
11 WO<sub>3</sub>/TiO<sub>2</sub>, there is an additional absorption edge at around 380 nm, which is in  
12 accordance with the deposition of TiO<sub>2</sub> (band gap of ~3.2 eV). ESR measurements were  
13 then conducted to investigate the electronic structure of m-H-WO<sub>3</sub>/TiO<sub>2</sub>. As displayed  
14 in Fig. 2c, both microfluidic architectures with (m-H-WO<sub>3</sub>/TiO<sub>2</sub>) and without TiO<sub>2</sub> (m-  
15 H-WO<sub>3</sub>) exhibit strong signals at  $g = 2.003$ , which is a typical sign of oxygen vacancies  
16 (Fig. 2c) [25]. As this peak is not observed in the spectrum of m-H-TiO<sub>2</sub>, oxygen defects  
17 should locate in WO<sub>3</sub> rather than TiO<sub>2</sub>. Based on previous reports, this is attributed to  
18 the higher structural stability of anatase TiO<sub>2</sub> against thermal reduction [49].

19 To further confirm the defective structure of WO<sub>3</sub>, high-resolution XPS spectra of W  
20 4f were measured (Fig. 2d). The doublet peaks centered at 35.5 eV (W1) and 37.6 eV  
21 (W2) are assigned to the characteristic 4f<sub>7/2</sub> and 4f<sub>5/2</sub> states of W<sup>6+</sup>, respectively [50].  
22 Compared to m-WO<sub>3</sub>, m-H-WO<sub>3</sub> exhibits two new peaks at 34.8 eV (W3) and 36.6 eV  
23 (W4), which can be attributed to the 4f<sub>7/2</sub> and 4f<sub>5/2</sub> states of W<sup>5+</sup>, respectively. The low  
24 valence of W confirms the introduction of oxygen vacancies and unpaired electrons into  
25 m-H-WO<sub>3</sub>. The impact of oxygen vacancies on the electronic structure of WO<sub>3</sub> was  
26 thereafter examined by valence band (VB) XPS spectra. As shown in Fig. 2e, both m-  
27 WO<sub>3</sub> and m-H-WO<sub>3</sub> display similar band edges at ~2.40 eV, corresponding to the VB  
28 maximum of WO<sub>3</sub>. For m-H-WO<sub>3</sub>, it is evident that an additional electronic state  
29 emerges at 0.25 eV. This mid-gap state can be assigned to the localized electrons in the  
30 d-orbitals of low-valence W species, with enhanced electron migration and increased  
31 carrier density [51]. Compared to bare WO<sub>3</sub>, m-H-WO<sub>3</sub>/TiO<sub>2</sub> shows a smaller VB  
32 maximum value of 2.28 eV. This upward shift of band edge indicates a higher VB  
33 position of TiO<sub>2</sub> than WO<sub>3</sub>, as schematically illustrated in Fig. 2f. Considering the larger  
34 band gap of TiO<sub>2</sub> than WO<sub>3</sub>, the conduction band (CB) of TiO<sub>2</sub> would also locate at a

1 higher position than that of  $\text{WO}_3$ . A type-II heterojunction can therefore form between  
 2  $\text{WO}_3$  and  $\text{TiO}_2$ , which is likely to provide a driving force for the charge separation. The  
 3 photogenerated holes can migrate from  $\text{WO}_3$  to  $\text{TiO}_2$  for surface oxidation reactions,  
 4 while the electrons would transfer in the opposite direction, thus achieving spatial  
 5 separation of photocarriers. Moreover, the gap state located near the CB of  $\text{WO}_3$  can  
 6 act as an electron mediator and further accelerate the charge transfer process [52].

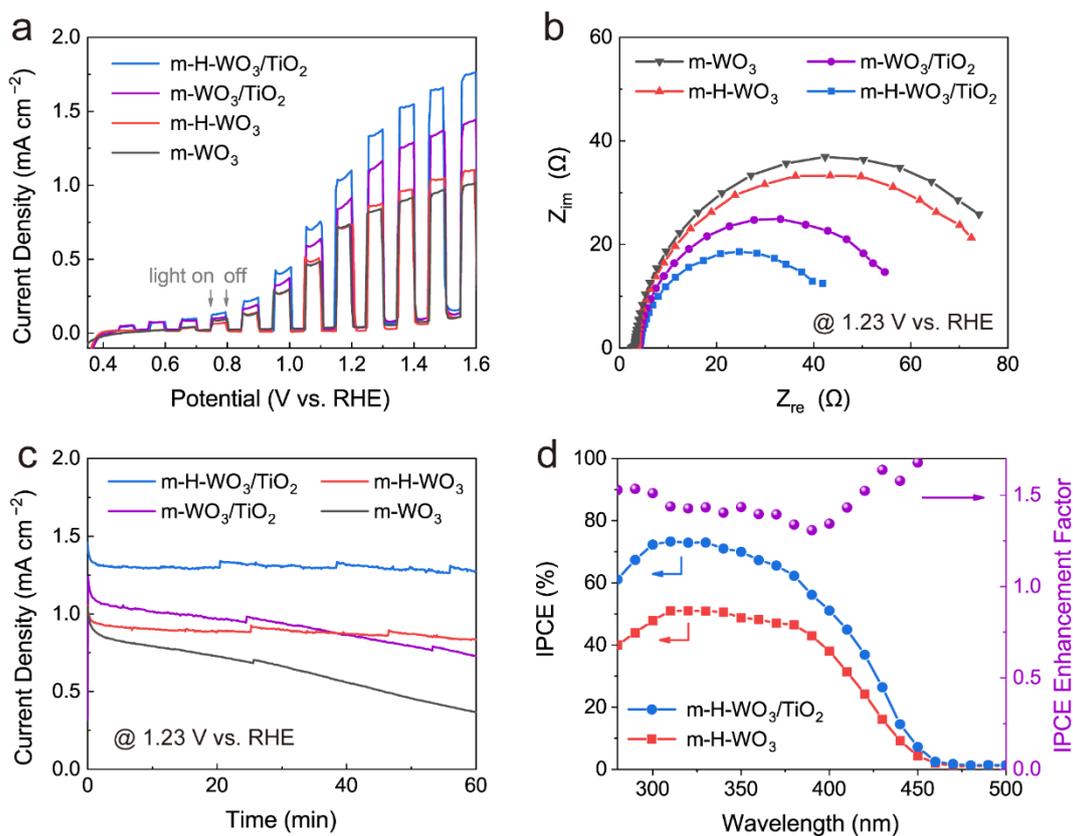


7  
 8 **Fig. 2.** (a) XRD patterns, (b) UV-visible absorption spectra, (c) ESR spectra, (d) W 4f  
 9 XPS spectra, and (e) VB XPS spectra of different microfluidic photoelectrodes. (f)  
 10 Schematic diagram of the band alignment between  $\text{WO}_3$  and  $\text{TiO}_2$ .

### 11 3.2. Charge separation behavior

12 The photoelectrochemical performance of microfluidic electrodes was evaluated using  
 13 a standard three-electrode system under simulated solar irradiation (AM 1.5 G,  $100 \text{ mW}$   
 14  $\text{cm}^{-2}$ ). According to the chopped J–V curves in Fig. 3a, m- $\text{WO}_3$  photoanode achieves a  
 15 photocurrent density of  $0.8 \text{ mA cm}^{-2}$  at 1.23 V vs. RHE, while the value for m-H- $\text{WO}_3$   
 16 is slightly higher. The formation of  $\text{WO}_3/\text{TiO}_2$  heterointerface significantly improves  
 17 the photoresponse of microfluidic photoanodes, together with the negatively shifted  
 18 onset potential of 0.4 V vs. RHE for m- $\text{WO}_3/\text{TiO}_2$ . It is also worth noting that the  
 19 introduction of oxygen defects into  $\text{WO}_3/\text{TiO}_2$  heterostructure gives rise to a further  
 20 increase in the photocurrent, reaching  $1.3 \text{ mA cm}^{-2}$  at 1.23 V vs. RHE for m-H-  
 21  $\text{WO}_3/\text{TiO}_2$ . The much higher photocurrent density of m-H- $\text{WO}_3/\text{TiO}_2$  in comparison to  
 22 m-H- $\text{WO}_3$  and m- $\text{WO}_3/\text{TiO}_2$  validates the synergistic effect between oxygen defects

1 and heterostructured interface for charge separation. The improved charge transfer  
2 kinetics of interface-modulated nanojunction was further evaluated by EIS  
3 measurements. Profiting from the good conductivity of carbon support, all the  
4 microfluidic photoanodes possess low series resistance of less than 5  $\Omega$  (Fig. 3b). In the  
5 Nyquist curves, m-H-WO<sub>3</sub>/TiO<sub>2</sub> exhibits the smallest arc radius compared to the other  
6 photoanodes, demonstrating the remarkably decreased charge transfer resistance. The  
7 important contribution of oxygen defects to the photostability of microfluidic  
8 photoanodes was thereafter evaluated by the time course of photocurrent, where both  
9 m-WO<sub>3</sub> and m-WO<sub>3</sub>/TiO<sub>2</sub> photoanodes experience obvious decrease in photocurrent  
10 density during 1 h operation (Fig. 3c). XPS results indicate that one of the O 1s peaks  
11 of m-WO<sub>3</sub> located at relatively high binding energy almost disappeared after the  
12 polarization treatment (Fig. S6), which corresponds to the passivation of surface states.  
13 We can therefore draw a conclusion that the PEC reactive sites of WO<sub>3</sub> are strongly  
14 correlated with the surface oxygen-related defects [25,53]. Indeed, m-H-WO<sub>3</sub> and m-  
15 H-WO<sub>3</sub>/TiO<sub>2</sub> with massive surface defects show excellent photostability, further  
16 indicating the pivotal contribution of interface modulation to the high performance of  
17 microfluidic photoanodes. Furthermore, the wavelength-dependent incident photon to  
18 current efficiency (IPCE) measurements of m-H-WO<sub>3</sub> and m-H-WO<sub>3</sub>/TiO<sub>2</sub> were  
19 conducted and displayed in Fig. 3d, where the enhancement factors contributed by TiO<sub>2</sub>  
20 were also calculated and shown. To circumvent the problem of different reaction  
21 kinetics on WO<sub>3</sub> and TiO<sub>2</sub> surface, glycerol was added to the electrolyte to scavenge  
22 holes. It can be observed that TiO<sub>2</sub> contributes to about 1.5-fold IPCE enhancement  
23 factor in both UV and visible region, with the highest IPCE reaching nearly 75% for m-  
24 H-WO<sub>3</sub>/TiO<sub>2</sub>. The excellent performance of TiO<sub>2</sub> decoration throughout the entire  
25 photoresponse region suggests that the accelerated charge separation induced by TiO<sub>2</sub>,  
26 rather than the enhanced light absorption, may be the main reason for its high photon  
27 utilization efficiency.

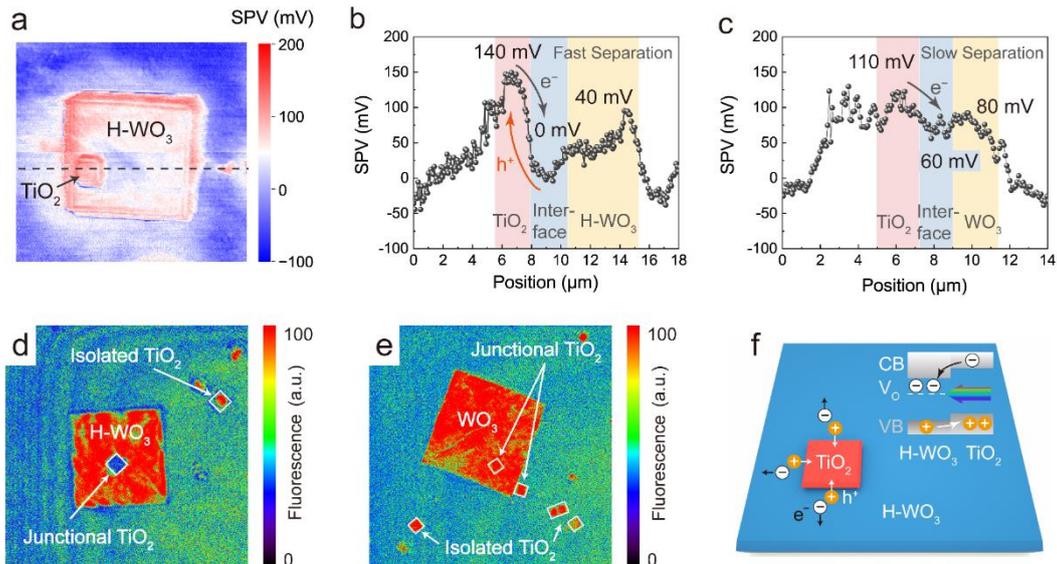


1  
2 **Fig. 3.** (a) Chopped J–V curves, (b) EIS Nyquist plots, and (c) photocurrent-time curves  
3 of different microfluidic photoanodes. The electrolyte is 0.5 M Na<sub>2</sub>SO<sub>4</sub> buffered by 0.1  
4 M borate solution (pH = 6) The steps or abrupt increase appearing in the solid line in  
5 panel c are due to the abrupt burst of oxygen bubbles that formed and adhered to the  
6 Teflon electrode holder. (d) IPCE spectra of m-H-WO<sub>3</sub> and m-H-WO<sub>3</sub>/TiO<sub>2</sub> measured  
7 at 1.23 V vs. RHE with the existence of 0.1 M glycerol.

8 To achieve a fundamental insight into the charge transfer process in the interface-  
9 modulated nanojunction, KPFM, a powerful tool to measure the surface potential with  
10 high spatial resolution, was utilized to visibly probe the charge separation at WO<sub>3</sub>/TiO<sub>2</sub>  
11 interface. A model heterostructure, with anatase TiO<sub>2</sub> crystal deposited onto defective  
12 WO<sub>3</sub> microplate (H-WO<sub>3</sub>), was assembled onto the graphite substrate (Fig. S7). This  
13 model structure with the WO<sub>3</sub>/TiO<sub>2</sub> interface and oxygen defects exhibits enhanced  
14 PEC activity in a similar manner with the microfluidic photoanode, as demonstrated in  
15 Fig. S8. Therefore, it is reasonable to utilize this modeled photocatalyst to probe the  
16 spatial charge transfer and separation at the nanometer scale. By subtracting the surface  
17 potential measured under dark from that under light conditions (Fig. S9), we obtained  
18 the surface photovoltage (SPV) image of H-WO<sub>3</sub>/TiO<sub>2</sub> heterojunction as depicted in

1 Fig. 4a. The representative cross-sectional SPV profiles associated with the dashed line  
2 in Fig. 4a are shown in Fig. 4b. It can be observed that TiO<sub>2</sub> and the major part of H-  
3 WO<sub>3</sub> show positive SPV signals of about 140 mV and 40 mV, respectively, indicating  
4 the presence of photogenerated holes on both H-WO<sub>3</sub> and TiO<sub>2</sub> [54]. The SPV value  
5 around the heterojunction interface decreases to 0 mV, which suggests the migration of  
6 electrons from TiO<sub>2</sub> to WO<sub>3</sub> and the accompanied holes migration from WO<sub>3</sub> to TiO<sub>2</sub>  
7 (Fig. 4b). In comparison, a much higher SPV value (60 mV) was observed in the  
8 interfacial region of WO<sub>3</sub>/TiO<sub>2</sub> nanojunction without defect modulation (Fig. 4c and  
9 S10). Meanwhile, the SPV value of TiO<sub>2</sub> deposited on defect-free WO<sub>3</sub> was about 110  
10 mV, which is much smaller than that on H-WO<sub>3</sub>. The relative small potential difference  
11 across the WO<sub>3</sub>/TiO<sub>2</sub> interface visually demonstrates its slow charge separation process.  
12 On the contrary, the charge separation on defective WO<sub>3</sub>/TiO<sub>2</sub> nanojunction is faster,  
13 evidencing the important role of defects on interfacial charge transfer.

14 The unique feature of defective WO<sub>3</sub>/TiO<sub>2</sub> interface was further confirmed by  
15 spatially resolved photoluminescence (PL) measurements using a similar model  
16 structure on glass, as the PL emission is directly associated with the electron-hole  
17 recombination [52,55]. Compared to the isolated one, junctional TiO<sub>2</sub> nanocrystal on  
18 defective WO<sub>3</sub> plate exhibits almost no fluorescence (Fig. 4d and S11), indicating the  
19 inhibited recombination of electrons and holes. In contrast, the integration of TiO<sub>2</sub> and  
20 defect-free WO<sub>3</sub> results in a negligible change in the fluorescence intensity (Fig. 4e). It  
21 can therefore be deduced that defect engineering can provide more opportunity for  
22 efficient charge separation in nanojunctions, which is in accordance with the KPFM  
23 results. As illustrated in Fig. 2f and 4f, WO<sub>3</sub> and TiO<sub>2</sub> form type-II heterostructure  
24 based on their energy band alignment, where the oxygen vacancies (V<sub>O</sub>) in WO<sub>3</sub>  
25 introduce intraband state for charge reservation. The intraband V<sub>O</sub> state with the  
26 fundamental role as an electron mediator can unambiguously enhance the charge  
27 separation in WO<sub>3</sub>/TiO<sub>2</sub> nanojunction [52]. With accelerated electrons transfer from  
28 TiO<sub>2</sub> to H-WO<sub>3</sub>, more photogenerated holes can accumulate on the surface of TiO<sub>2</sub>,  
29 thereby speeding up the oxidation reaction (Fig. 4f).

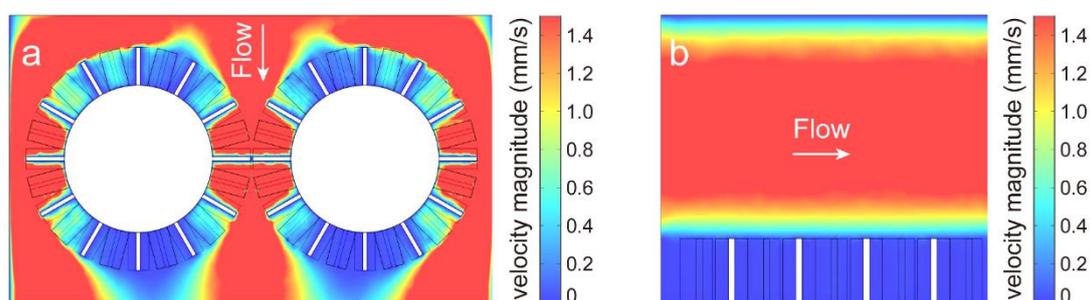


1 **Fig. 4.** (a) SPV image of H-WO<sub>3</sub>/TiO<sub>2</sub> and (b) the representative cross-sectional SPV  
 2 profiles associated with the dashed line in panel a. (c) The representative cross-sectional  
 3 SPV profiles of defect-free WO<sub>3</sub>/TiO<sub>2</sub> heterostructure. Spatially resolved PL images of  
 4 (d) defective and (e) defect-free WO<sub>3</sub>/TiO<sub>2</sub> heterostructure. (f) Schematic diagram of  
 5 charge separation across the defective WO<sub>3</sub>/TiO<sub>2</sub> interface. The energy band alignment  
 6 and defect state induced by oxygen vacancies are also shown.  
 7

### 8 3.3. Flow field simulation

9 Apart from the photon utilization efficiency, the mass transfer of reactants on the  
 10 photoelectrode surface is also of great significance. Therefore, the impact of  
 11 microfluidic channels on the flow velocity and mass diffusion of reactants was  
 12 investigated by computational fluid dynamics (CFD) simulation. A reaction box with  
 13 the modeled structure in it was constructed, where the solution was allowed to pass  
 14 through the catalyst with an initial velocity. For comparison, the planar structure with  
 15 a liquid flow direction parallel to the electrode was also modeled and tested. Fig. 5  
 16 shows the liquid velocities of microfluidic and planar electrodes in the cross-sectional  
 17 area, respectively. It can be observed that the spacings of carbon fibers provide unique  
 18 microchannels for the liquid to flow through. As a consequence, the liquid flow rate  
 19 near the catalyst surface is almost identical to that in the bulk, significantly compressing  
 20 the diffusion layer and enabling the rapid diffusion of reactants and products in the  
 21 microfluidic electrode (Fig. 5a) [41]. In contrast, the liquid velocity on the surface of  
 22 planar electrode is almost zero, with an obvious laminar layer setting between the  
 23 catalyst and bulk electrolyte (Fig. 5b). To have a closer look at the hydrodynamic

1 characteristics of planar electrode, a similar model with the inflow direction  
2 perpendicular to the electrode was constructed (Fig. S12). The planar electrode indeed  
3 acted as a physical barrier against the water flow and resulted in a 90° turn in the fluid  
4 direction. In this context, the outflow direction is always parallel to the planar electrode  
5 no matter what the inflow direction is, with a relatively low liquid velocity and limited  
6 mass transfer on the surface of planar electrode. The slow reactant diffusion would  
7 cause great restraint on the surface reaction, unavoidably leading to low hole utilization  
8 efficiency and overoxidation of organic molecules. This comparison indicates that the  
9 microfluidic architecture should possess fast reaction kinetics and high solar-to-  
10 chemical efficiency for PEC upgrading reactions.



11 **Fig. 5.** CFD simulations of the flow velocity distribution in (a) microfluidic and (b)  
12 planar electrode.  
13

#### 14 3.4. PEC chemicals upgrading

15 Considering the fast reactants diffusion and nanojunction-enhanced hole accumulation  
16 on the surface of TiO<sub>2</sub>, our 3-D hierarchical structure should be an ideal platform for  
17 PEC chemicals upgrading with high efficiency. To verify this hypothesis, microfluidic  
18 photoelectrodes were employed to upgrade glycerol into value-added fine chemicals  
19 [5]. For a reasonable comparison, planar WO<sub>3</sub> photoanodes with and without TiO<sub>2</sub>  
20 decoration were prepared on FTO conductive glass and referred to as pl-H-WO<sub>3</sub>/TiO<sub>2</sub>  
21 and pl-H-WO<sub>3</sub>, respectively. As a consequence of PEC oxidation, the addition of  
22 glycerol into the electrolyte solution leads to a significant increase of photoresponse  
23 (Fig. S13). The photocurrent density of m-H-WO<sub>3</sub>/TiO<sub>2</sub> reaches 2.89 mA cm<sup>-2</sup> at 1.23  
24 V vs. RHE, which is much higher than those of pl-H-WO<sub>3</sub> and pl-H-WO<sub>3</sub>/TiO<sub>2</sub> (Fig.  
25 6a). This well demonstrates the synergistic contribution of charge separation and mass  
26 transfer to the photon utilization in m-H-WO<sub>3</sub>/TiO<sub>2</sub> photoanode. PEC glycerol  
27 oxidation was thereafter conducted at different applied potentials (0.6, 0.9, and 1.2 V  
28 vs. RHE) and the products were analyzed by HPLC and <sup>1</sup>H NMR methods (Fig. S14

1 and S15). The glycerol consumption and product yields are listed in Table 1, with the  
 2 generation rates of oxidation products on pl-H-WO<sub>3</sub> and m-H-WO<sub>3</sub>/TiO<sub>2</sub> shown in Fig.  
 3 6b. It can be concluded that the microfluidic photoanodes can efficiently convert  
 4 glycerol into value-added glyceraldehyde (GLAD) and 1,3-dihydroxyacetone (DHA),  
 5 with a small amount of formic acid (FA), glycolic acid (GA), and CO<sub>2</sub> as by-products.  
 6 For m-H-WO<sub>3</sub>/TiO<sub>2</sub> photoanode, the generation rate of valuable products (GLAD +  
 7 DHA) reaches 35.3 μmol cm<sup>-2</sup> h<sup>-1</sup> at 1.2 V vs. RHE, with a selectivity of 85% (Fig. 6c)  
 8 and faradaic efficiency (FE) of 70% (Fig. 6d). The production rate is about 3 times  
 9 higher than that of conventional planar photoanode (pl-H-WO<sub>3</sub>, 13.3 μmol cm<sup>-2</sup> h<sup>-1</sup>).  
 10 Meanwhile, the selectivity and faradaic efficiency of pl-H-WO<sub>3</sub> toward (GLAD + DHA)  
 11 generation are 61% and 42% at 1.2 V vs. RHE, respectively, which are much smaller  
 12 than those of m-H-WO<sub>3</sub>/TiO<sub>2</sub>. Profited from the enhanced diffusion of glycerol  
 13 molecules and their oxidation derivatives in microflow channels, the microfluidic  
 14 platform not only exhibits exceedingly high activity over the entire range of potentials  
 15 (0.6–1.2 V vs. RHE), but also inhibits the overoxidation of glycerol into by-products  
 16 such as formic acid and glycolic acid (entry 1–6 in Table 1 and Fig. 6b–d) [56]. It should  
 17 also be noted that CO<sub>2</sub>, the complete oxidation product of glycerol, only accounts for  
 18 less than 6% of the total carbonaceous products in the microfluidic systems, while those  
 19 values for the planar systems are about 20% (Table 1). No difference in product  
 20 compositions is observed for m-H-WO<sub>3</sub> and m-H-WO<sub>3</sub>/TiO<sub>2</sub>. Thus, the type of  
 21 semiconductors presents little impact on the reaction selectivity. Finally, to rule out the  
 22 possible generation of toxic compounds, cytotoxicity tests were conducted on the  
 23 glycerol solutions before and after PEC oxidation on m-H-WO<sub>3</sub>/TiO<sub>2</sub>. The glycerol  
 24 sample after PEC oxidation showed a promoting effect on the cell viability (Fig. S16),  
 25 demonstrating that the oxidation products of glycerol are rather nutrient than toxicant.  
 26 All these results demonstrate the inherent advantages of microfluidic platform,  
 27 contributing to the state-of-the-art PEC performance of m-H-WO<sub>3</sub>/TiO<sub>2</sub> photoanode for  
 28 glycerol upgrading [56-58].

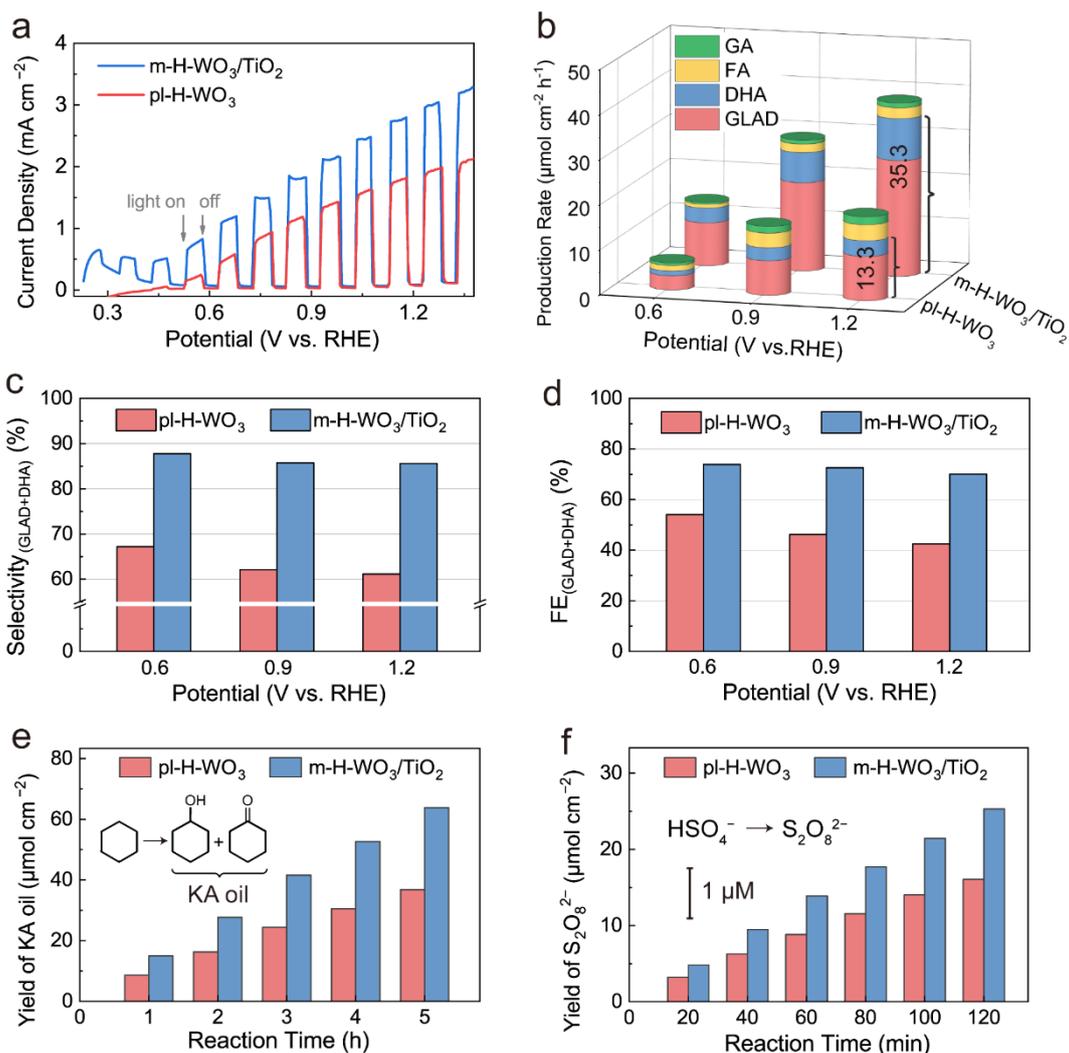
29 **Table 1** PEC glycerol consumption and product yields on different photoanodes

Entry	Photoanode	Potential [V vs. RHE]	Charge [C]	Glycerol Consumption [μmol]	Products [μmol]					Carbon Balance	CO <sub>2</sub> Yield
					GLAD	DHA	FA	GA	CO <sub>2</sub>		
1	m-H-WO <sub>3</sub> /TiO <sub>2</sub>	0.6	10.2	44.4	29.1	9.9	2.7	1.2	6.5	96.5%	4.9%

2	m-H-WO <sub>3</sub> /TiO <sub>2</sub>	0.9	21.2	93.0	59.4	20.1	5.7	2.7	13.2	94.2%	4.7%
3	m-H-WO <sub>3</sub> /TiO <sub>2</sub>	1.2	29.2	123.6	77.7	28.2	7.2	3.3	21.7	95.3%	5.9%
4	m-H-WO <sub>3</sub>	0.6	4.1	18.3	12.0	4.2	1.2	0.3	3.3	97.8%	6.0%
5	m-H-WO <sub>3</sub>	0.9	12.4	54.9	34.8	12.3	3.3	1.8	6.8	94.1%	4.1%
6	m-H-WO <sub>3</sub>	1.2	17.5	75.9	50.1	15.9	4.8	2.4	8.4	94.9%	3.7%
7	pl-H-WO <sub>3</sub> /TiO <sub>2</sub>	0.6	7.3	25.5	12.6	4.8	5.4	2.7	10.8	96.5%	14.1%
8	pl-H-WO <sub>3</sub> /TiO <sub>2</sub>	0.9	15.3	54.6	25.2	9.0	11.4	5.4	33.4	96.6%	20.4%
9	pl-H-WO <sub>3</sub> /TiO <sub>2</sub>	1.2	24.2	81.6	36.3	12.9	12.6	6.0	53.5	92.2%	21.9%
10	pl-H-WO <sub>3</sub>	0.6	4.5	18.9	9.5	3.2	3.7	1.8	8.9	95.8%	15.7%
11	pl-H-WO <sub>3</sub>	0.9	13.3	51.2	23.1	8.7	9.8	4.5	30.2	94.0%	19.7%
12	pl-H-WO <sub>3</sub>	1.2	18.1	65.4	29.6	10.4	10.7	5.3	45.6	95.3%	23.2%

1 Reaction conditions: 20 mL 0.5 M Na<sub>2</sub>SO<sub>4</sub>, 0.1 M borate buffer, and 0.1 M glycerol,  
2 pH = 6, electrode area = 3 cm<sup>2</sup>, 30°C.

3 We then employed cyclohexane and HSO<sub>4</sub><sup>-</sup> as the representative hydrocarbon and  
4 inorganic substrates to verify the versatility of this microfluidic PEC electrode.  
5 Selective oxidation of cyclohexane is intrinsically important in the chemistry of C-H  
6 activation and the commercial synthesis of Nylon [59]. As shown in Fig. 6e, m-H-  
7 WO<sub>3</sub>/TiO<sub>2</sub> photoanode can efficiently and selectively transform cyclohexane into  
8 value-added KA oil (cyclohexanol and cyclohexanone). The yield of KA oil on m-H-  
9 WO<sub>3</sub>/TiO<sub>2</sub> reaches 64 μmol cm<sup>-2</sup> after 5 h reaction, which is nearly 2 times higher than  
10 that of pl-H-WO<sub>3</sub>. Benefitting from the numerous reaction sites, m-H-WO<sub>3</sub>/TiO<sub>2</sub>  
11 maintains a relatively high faradaic efficiency in comparison to its planar counterpart  
12 (Fig. S17). Similar results can be observed for the oxidation of HSO<sub>4</sub><sup>-</sup> to S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, where  
13 99% faradaic efficiency can be realized by m-H-WO<sub>3</sub>/TiO<sub>2</sub> in the first 20 minutes of  
14 oxidation (Fig. 6f and S17). As a strong oxidant, S<sub>2</sub>O<sub>8</sub><sup>2-</sup> is of great value and widely  
15 used for many chemical and environmental reactions [9]. About 4 mM S<sub>2</sub>O<sub>8</sub><sup>2-</sup> can be  
16 obtained by m-H-WO<sub>3</sub>/TiO<sub>2</sub> after PEC oxidation for 2 hours, which is much higher than  
17 that of pl-H-WO<sub>3</sub> (2.4 mM) (Fig. 6f). In this context, the nanojunction-enhanced  
18 microfluidic PEC platform offers more opportunity for PEC oxidative upgrading of  
19 various chemicals.

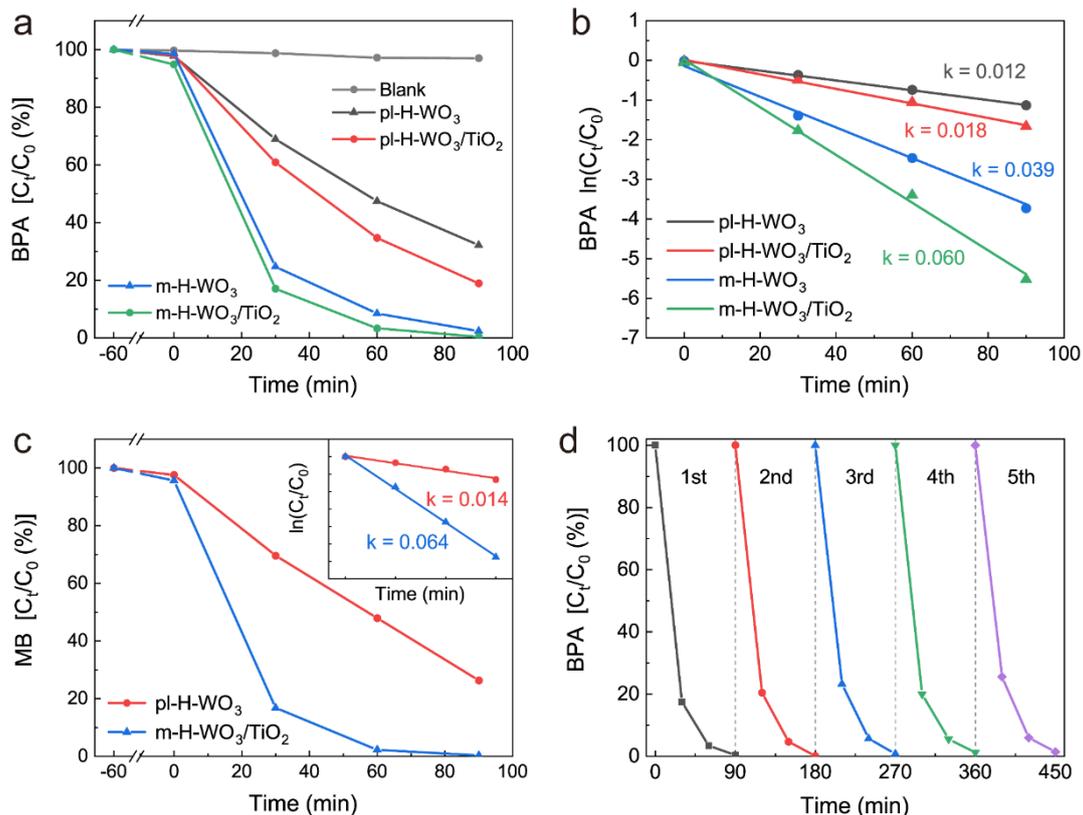


**Fig. 6.** (a) Chopped J–V curves of pl-H-WO<sub>3</sub> and m-H-WO<sub>3</sub>/TiO<sub>2</sub> photoanodes. (b) PEC production rates of glycerol oxidative products. (c) Selectivities and (d) faradaic efficiencies of pl-H-WO<sub>3</sub> and m-H-WO<sub>3</sub>/TiO<sub>2</sub> for the production of valuable products (GLAD + DHA). The electrolyte for panel a–d is a mixture of 0.5 M Na<sub>2</sub>SO<sub>4</sub>, 0.1 M glycerol, and 0.1 M borate buffer (pH = 6). (e) Generation of KA oil in the PEC oxidation of cyclohexane. Electrolysis was conducted at 0.8 V vs. Ag/Ag<sup>+</sup>. The electrolyte was a mixture of 18 mL cyclohexane, 12 mL t-BuOH, and 2 mL HNO<sub>3</sub>. (f) Generation of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> in the PEC oxidation of HSO<sub>4</sub><sup>-</sup>. Electrolysis was conducted at 1.2 V vs. RHE in 20 mL 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.

### 3.5. PEC pollutants degradation

With numerous flow channels and oxidation sites, m-H-WO<sub>3</sub>/TiO<sub>2</sub> should also be a good candidate for the PEC degradation of organic pollutants. Bisphenol A (BPA), a representative environmental contaminant with adverse effects on endocrine systems of human and aquatic organisms, was used to evaluate the potential of this microfluidic

1 photoanode for pollutant removal. Before photoelectrocatalytic degradation, the  
2 photoanodes were immersed into BPA solution for 60 min under dark conditions to  
3 reach the adsorption-desorption equilibrium. Compared to planar electrodes, the  
4 adsorption capacities of BPA on microfluidic electrodes are much higher, verifying  
5 their ample reaction sites (Fig. 7a). Upon illumination, more than 99% of BPA was  
6 decomposed over m-H-WO<sub>3</sub>/TiO<sub>2</sub> after 90 min, while the degradation efficiency of pl-  
7 H-WO<sub>3</sub> was only 67%. Both TiO<sub>2</sub> decoration and construction of microflow channels  
8 contribute to the fast BPA elimination, with the BPA degradation efficiencies of pl-H-  
9 WO<sub>3</sub>/TiO<sub>2</sub> and m-H-WO<sub>3</sub> being 81% and 98%, respectively. It can be therefore deduced  
10 that in comparison to charge separation on photoanode, the mass transfer of BPA is  
11 more important for its fast PEC degradation. To have a quantitative analysis on BPA  
12 degradation process, pseudo-first-order kinetics was employed to simulate all the PEC  
13 degradation plots (Fig. 7b). It can be observed that m-H-WO<sub>3</sub>/TiO<sub>2</sub> exhibits an apparent  
14 rate constant ( $k$ ) of 0.060 min<sup>-1</sup> for BPA degradation, which is 5-fold higher than that  
15 of pl-H-WO<sub>3</sub> (0.012 min<sup>-1</sup>). Furthermore, the rate constant of m-H-WO<sub>3</sub> (0.039 min<sup>-1</sup>)  
16 is relatively higher than that of pl-H-WO<sub>3</sub>/TiO<sub>2</sub> (0.018 min<sup>-1</sup>). This proves the  
17 significant contribution of mass transfer in microflow channels to the fast PEC  
18 degradation. The decolorization of methylene blue (MB) was also tested to investigate  
19 the versatility of m-H-WO<sub>3</sub>/TiO<sub>2</sub> photoanode. As shown in Fig. 7c, the solution was  
20 totally decolorized over m-H-WO<sub>3</sub>/TiO<sub>2</sub> after 90 min, with nearly 5-fold higher reaction  
21 kinetics ( $k = 0.064 \text{ min}^{-1}$ ) than pl-H-WO<sub>3</sub> ( $k = 0.014 \text{ min}^{-1}$ ). The extraordinary  
22 performance of microfluidic photoanode in BPA and MB elimination suggests its  
23 potential applicability for environmental remediation. More importantly, m-H-  
24 WO<sub>3</sub>/TiO<sub>2</sub> shows a negligible decrease of activity during five cycling runs, indicating  
25 its good photostability (Fig. 7d). In this regard, the nanojunction-enhanced microfluidic  
26 PEC platform demonstrates great potential for the fast elimination of various aquatic  
27 pollutants.



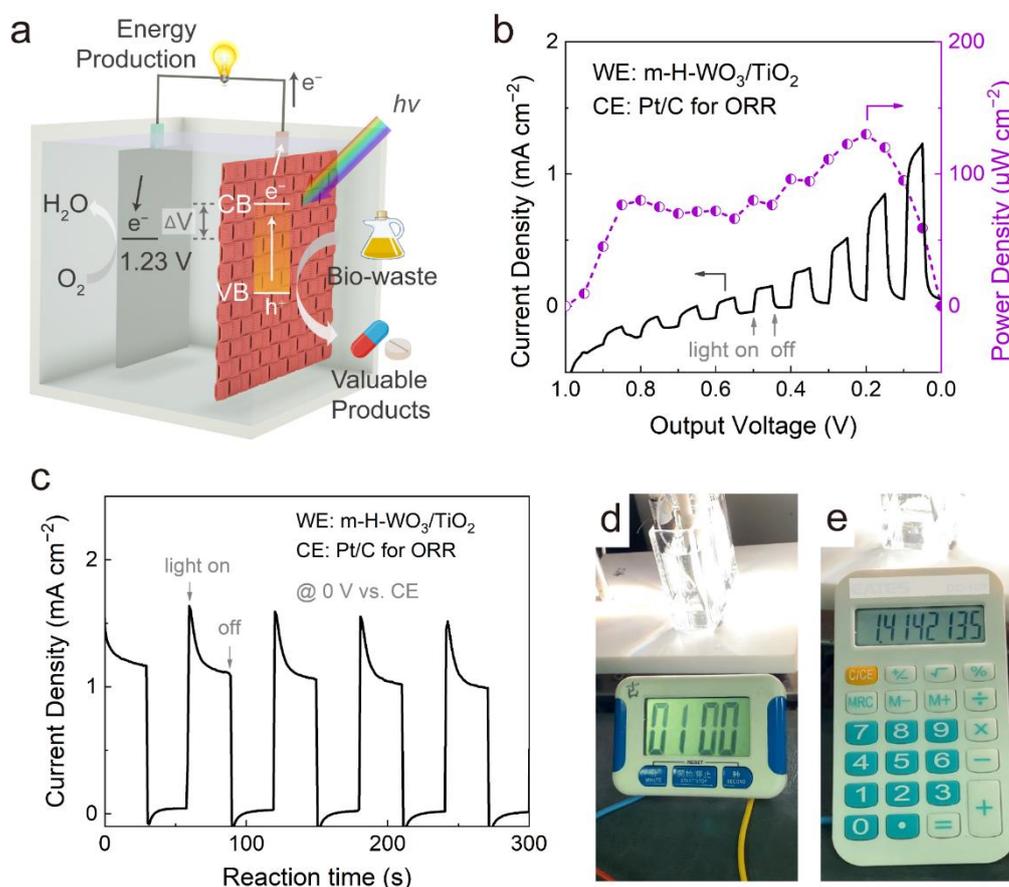
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2 **Fig. 7.** (a) PEC degradation of BPA and (b) the corresponding kinetics plots over  
 3 different photoanodes. (c) PEC degradation of MB and the corresponding kinetics plots.  
 4 (d) Cycling degradation of BPA over m-H-WO<sub>3</sub>/TiO<sub>2</sub>. The degradation experiments  
 5 were conducted at 1 V vs. RHE in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution containing 10 mg L<sup>-1</sup>  
 6 pollutants (pH = 6) under simulated solar-light irradiation (AM 1.5 G, 100 mW cm<sup>-2</sup>).

### 7 3.6. Photocatalytic fuel cell

8 Having demonstrated the extraordinary performance of microfluidic photoanode for  
 9 oxidative chemicals upgrading, we attempted to design a bias-free PEC system for self-  
 10 sustained organic synthesis. As illustrated in Fig. 8a, a two-electrode photocatalytic fuel  
 11 cell (PFC) was constructed by using m-H-WO<sub>3</sub>/TiO<sub>2</sub> as the photoanode and Pt/C coated  
 12 carbon paper as the cathode for oxygen reduction reaction (ORR) [60]. When glycerol  
 13 is employed as the organic source, an open-circuit potential of 0.9 V and a short-circuit  
 14 current of 1.2 mA cm<sup>-2</sup> are realized using such an integrated device (Fig. 8b).  
 15 Correspondingly, a maximum output power density of 130 μW cm<sup>-2</sup> is obtained, which  
 16 is among the highest values reported to date (Table S1). Besides, this photocatalytic  
 17 fuel cell can maintain a stable current of ~1.2 mA cm<sup>-2</sup> at 0 V vs. CE (i.e. without  
 18 external electric bias), demonstrating its good stability for electricity generation (Fig.

8c). By connecting two of above photocatalytic fuel cells in series, a higher output voltage can be easily realized, which is sufficient to power common electronic devices with the nominal voltage of 1.5 V, such as electronic timer (Fig. 8d and Video S1) and calculator (Fig. 8e and Video S2). The above results demonstrate that we can simultaneously obtain value-added chemicals and electricity by this PFC system.



**Fig. 8.** (a) Schematic diagram of the PFC system with microfluidic photoanode and ORR cathode. (b) Chopped J–V curve of the PFC system. The output power density is also shown and calculated by multiplying the photocurrent density by the output voltage. (c) Chopped photocurrent-time profiles of the PFC system at short circuit. Photographs showing (d) an electronic timer and (e) an electronic calculator powered by two of the PFC cells connected in series.

#### 4. Conclusion

In conclusion, we demonstrated an efficient photoelectrochemical platform based on  $\text{WO}_3/\text{TiO}_2$  nanojunction with engineered defects and microfluidic structure. Profiting from the nanojunction-enhanced charge separation and microchannel-facilitated mass transfer, this 3-D nanoarchitecture exhibited unprecedented activity and selectivity for

1 chemical upgrading of various organic and inorganic compounds. The impressive  
2 production rates of high value-added chemicals by glycerol oxidation ( $35.3 \mu\text{mol cm}^{-2}$   
3  $\text{h}^{-1}$ ) and cyclohexane activation ( $12.8 \mu\text{mol cm}^{-2} \text{h}^{-1}$ ) were nearly 3 and 2 times higher  
4 than those of conventional planar system. The interface-modulated photoanode also  
5 contributed to 5-fold higher degradation kinetics for the removal of two representative  
6 organic pollutants (BPA and MB). A highly efficient photocatalytic fuel cell with high  
7 open-circuit potential (0.9 V) and short-circuit current ( $1.2 \text{ mA cm}^{-2}$ ) was finally  
8 constructed based on this nanojunction-enhanced microfluidic photoanode. We thus  
9 can simultaneously obtain value-added chemicals and electricity by this two-in-one  
10 photocatalytic fuel cell system. Thus, this work not only provides an inspiring approach  
11 to visualize the charge separation in heterostructured architectures, but also  
12 demonstrates the great potential of microfluidic PEC system for solar energy utilization  
13 toward a sustainable and low-carbon society.

#### 14 **Acknowledgments**

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18 her help in glycerol oxidation products analysis. We also thank Dr. William A. Jefferson  
19 for proofreading this manuscript.

#### 20 **Supplementary data**

21 Experimental procedures, SEM and TEM images, O 1s XPS spectra, KPFM results,  
22 spatially resolved photoluminescence image, identification of reaction products,  
23 faradaic efficiencies for the production of KA oil and  $\text{S}_2\text{O}_8^{2-}$ , cytotoxicity results,  
24 performance comparison of photocatalytic fuel cells.

25 Assembly of two photocatalytic fuel cells to power common electric devices (Videos).

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