

Supplementary Information

Photoelectrochemical battery for efficient energy recovery

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Experiment section

Reagents: Titanium foil (purity > 99.7%) was bought from Aldrich. Hydrofluoric acid, nitric acid, acetone, absolute ethanol, ethylene glycol and sodium hydrate were of analytical grade from Beijing Chemical Reagent Company (China) without further purification. Ultrapure water from Water Purifier (Sichuan Water Purifier Co., Ltd., China) was used in all the experiments.

Preparation of TiO₂ nanotubes (TNTs) photoanode: Titanium foil was first chemically etched in a mixture of HF and HNO₃ (volume ratio of HF:HNO₃:H₂O in 1:4:5) for 40 s. Then the titanium foil was rinsed with acetone, absolute ethanol and water for 10 min, respectively. TNTs was prepared by a potentiostatic anodization in a two-electrode electrochemical cell, in which rinsed titanium foil was used as working electrode and platinum foil served as counter electrode. The TNTs was formed by anodizing titanium foil in 40 mL of 0.5 wt% HF solution at 20 V for 20 min. The obtained titanium foils were annealed at 500 °C for 3 h in air atmosphere, heating rates was kept at 1 °C min⁻¹. The obtained TNTs possess highly crystalline TiO₂ with a mixture of anatase and rutile phases, proved by X-ray diffraction (XRD) (Fig S1) and scanning electron microscope (SEM) (Fig. S2).

Preparation of Ag/Ag₂O cathode: Silver foil was used as the working electrode. Prior to anodization, silver foil was washed with 0.1 M HNO₃ in ultrasonic bath sequentially. Then Ag₂O/Ag electrode was prepared through the anodization of silver foil in 1 M NaOH under constant potential 0.2 V (Fig. S3). After 1 h electrochemical

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oxidation, Ag_2O was formed, proved by its XRD result with typical (111) peak of Ag_2O (Fig. S4). The surface morphology of $\text{Ag}_2\text{O}/\text{Ag}$ electrode examined by SEM presents irregular micro/nanoparticles with the size of 500 nm (shown in Fig. S5).

Apparatus: SEM images were taken with a XL30 field-emission scanning electron microscope at an accelerating voltage of 15 kV. XRD patterns were collected by a D8 ADVANCE (Germany) with Cu $K\alpha$ radiation ($\lambda=1.54056 \text{ \AA}$) in the range of $20\text{-}80^\circ$ (2θ). Photoelectrochemical (PEC) studies were performed in a conventional three electrode system with a platinum foil as the counter electrode and Ag/AgCl (saturated KCl) as the reference electrode. Photoelectrochemical battery (PEB) were carried out using a two electrode system with a TNTs photoanode and $\text{Ag}/\text{Ag}_2\text{O}$ cathode. All electrochemical measurements were recorded by a CHI 832C electrochemical workstation (Chenhua Co., Shanghai).

Figure

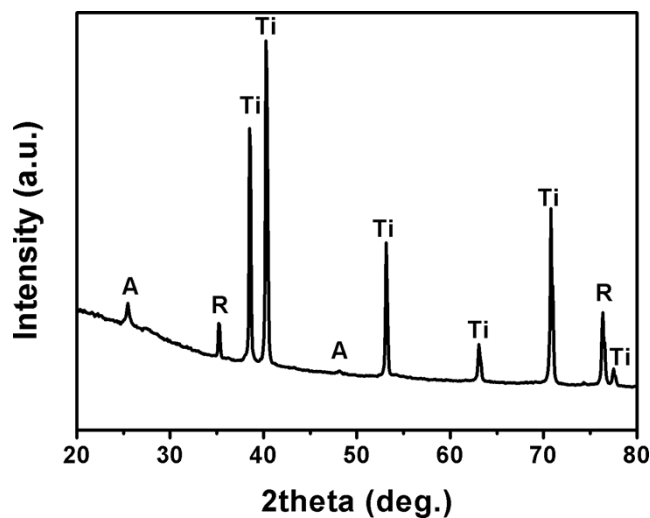


Fig. S1 The typical XRD pattern of the as-prepared TNTs.

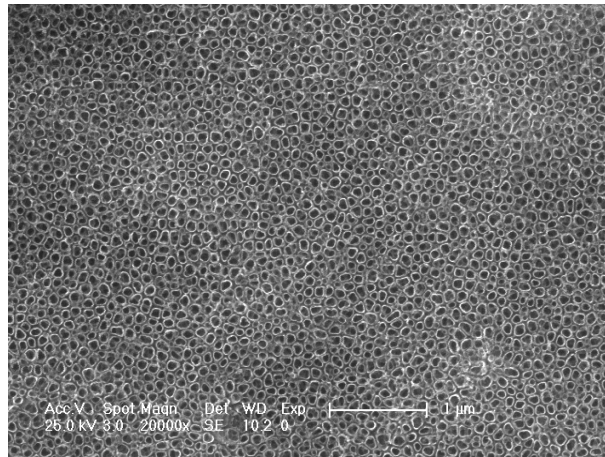


Fig. S2 The typical SEM image of the as-prepared TNTs.

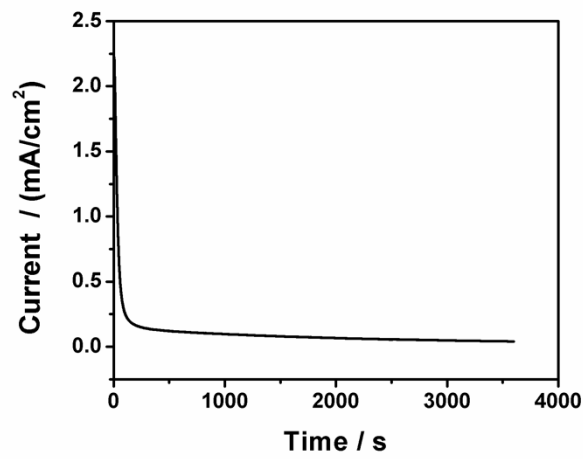


Fig. S3 The chronoamperometry curve of the as-prepared $\text{Ag}_2\text{O}/\text{Ag}$.

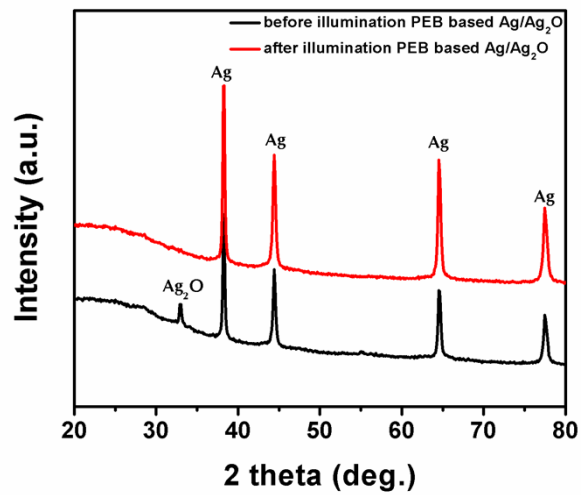


Fig. S4 The typical XRD pattern of the as-prepared $\text{Ag}_2\text{O}/\text{Ag}$ through the anodization of silver foil in 1 M NaOH under constant potential 0.2 V.

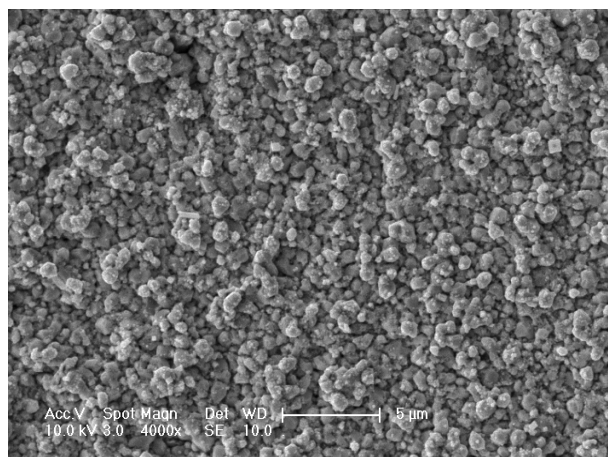


Fig. S5 The typical SEM image of the as-prepared $\text{Ag}_2\text{O}/\text{Ag}$.

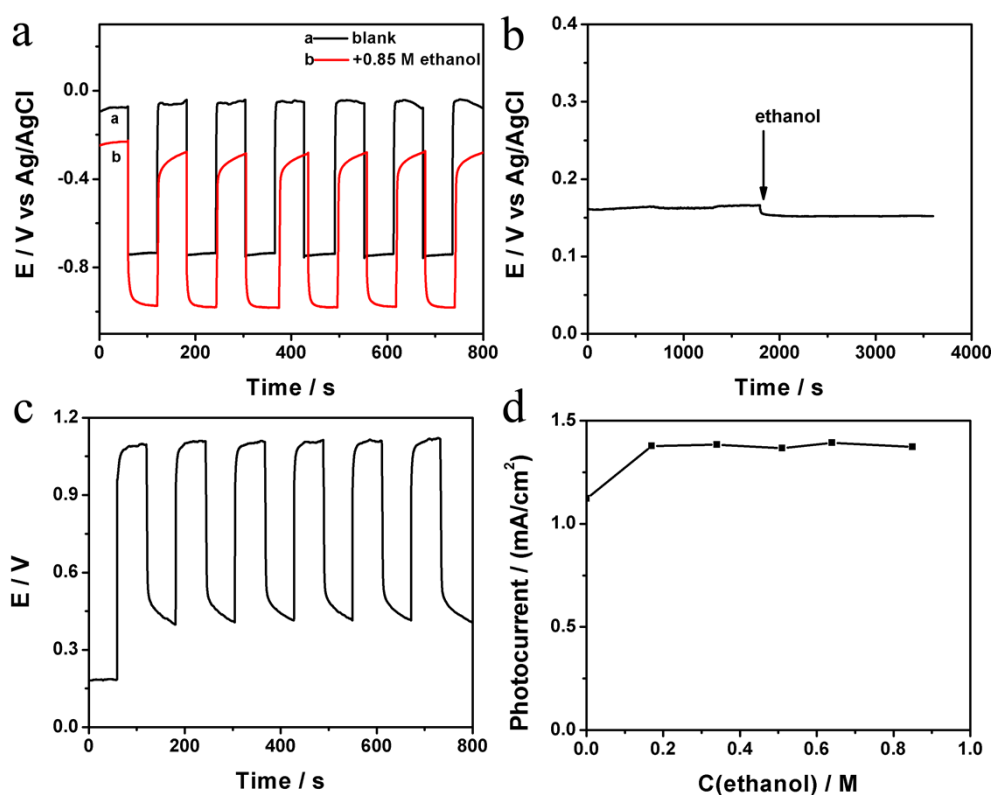


Fig. S6 (a) light-induced potential change collected from TNTs photoanode, (b) potential change of $\text{Ag}_2\text{O}/\text{Ag}$ cathode collected from $\text{Ag}_2\text{O}/\text{Ag}$ cathode, and (c) potential change of PEB in 1.0 M NaOH in the absence (blank) and presence of ethanol (0.85 M), respectively; (d) the effect of the concentration of ethanol on the photocurrent response of TNTs photoanode at a bias of -0.4 V vs Ag/AgCl .

Fig. S6a depicts the light-induced potential change of TNTs photoanode in 1.0 M NaOH in the absence and presence of 0.85 M ethanol. Instant photoresponses at a photovoltage of about -0.74 V and -0.97 V vs Ag/AgCl are observed in the absence and presence of ethanol upon UV illumination, which are accordance with LSV results. As can be seen in Fig. S6c, an obvious constant potential of 1.10 V based on TNTs photoanode and $\text{Ag}_2\text{O}/\text{Ag}$ cathode can be observed upon UV illumination. To maximize

the performance of PEB, the effect of ethanol concentration on the photocurrent response of TNTs photoanode was also investigated. As depicted in Fig. S6d, the photocurrent density in the presence of ethanol was higher than that without ethanol whereas the photocurrent density remains unchanged as the ethanol concentration increases upon the addition of ethanol. Herein we choose 0.85 M ethanol for PEB operation later.

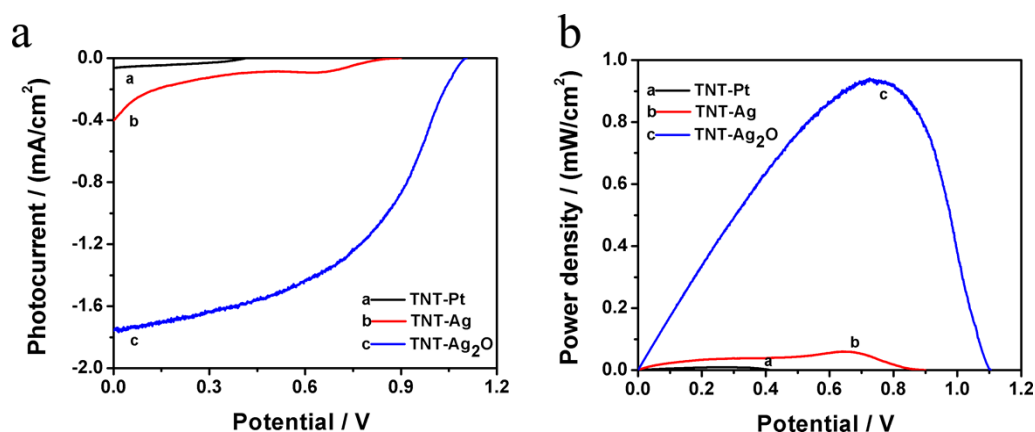


Fig. S7 (a) LSVs and (b) the power density as a function of potential collected from PEFCs based on Pt cathode (black), Ag cathode (red) and Ag₂O/Ag cathode (blue) in 1.0 M NaOH containing 0.85 M ethanol.

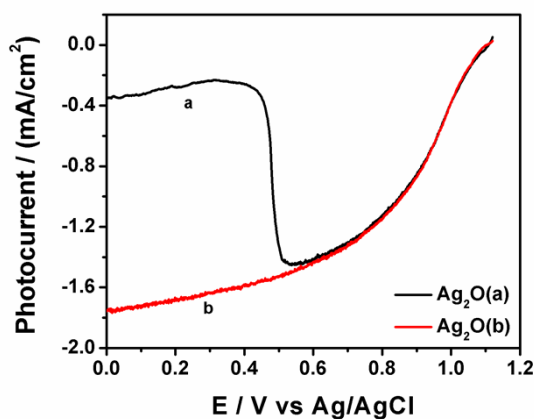


Fig. S8 The effect of the electrochemical oxidation time for the preparation of Ag₂O/Ag on the performance of PEB: 0.5 h (a) and 1 h (b).

It can be found that the electrochemical oxidation time for Ag foil only affected the capacity of Ag₂O/Ag electrode (the working time of PEB) but had no effect on the performance of PEB (Fig. S8). Thus, by controlling the area of Ag electrode and electrochemical oxidation times, we can easily tune the working time of our PEFCs.

Table 1. The comparisons between our work and conventional PEFCs.

<i>Photoanode</i>	<i>Cathode</i>	<i>Membrane</i>	<i>Open circuit voltage</i>	<i>Maximum power density</i>
Zinc chlorin-e6 sensitized TiO ₂ nanoparticles ¹	Pt	No	0.415 V	0.028 μW/cm ²
Porphyrin-sensitized TiO ₂ nanoparticles ²	Hg/ Hg ₂ SO ₄	Yes	1.10 V	37 μW/cm ²
Porphyrin-sensitized TiO ₂ nanoparicles ³	Pt black	Yes	0.74 V	33.94 μW/cm ²
Porphyrin-sensitized SnO ₂ nanoparticles ⁴	Hg/ Hg ₂ SO ₄	Yes	0.75 V	19 μW/cm ²
TiO ₂ nanotube arrays ⁵	Pt	No	1.42 V	0.67 mW/cm ²
TiO ₂ nanotube arrays ⁶	Pt black	No	1.30 V	0.27 mW/cm ²
TiO ₂ nanotube arrays ⁷	bilirubin oxidase	No	1.0 V	47 μW/cm ²
TiO ₂ nanotube arrays*	Ag ₂ O/ Ag	No	1.10 V	0.94 mW/cm ²

[*] Our present work.

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