

Solar driven electrochromic photoelectrochemical fuel cell for simultaneous energy conversion, storage and self-powered sensing

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Table S1 and S2;

Reference.

Abbreviations

PFC	photoelectrochemical fuel cell
ZnO	zinc oxide
NRA	nanorod arrays
BiOI	bismuth oxyiodide
V_{oc}	open-circuit voltage
P_{max}	maximum power output density
PB	Prussian blue
SILAR	successive ionic layer adsorption and reaction
PW	Prussian white
FTO	fluorine-doped indium tin oxide
PEC	phototoelectrochemical
SEM	scanning electron microscopy
TEM	transmission electron microscopy
HRTEM	high-resolution TEM
EDS	energy-dispersive X-ray spectroscopy
XRD	X-ray diffraction
ITO	indium tin oxide
CV	cyclic voltammetric
PBS	Phosphate-buffered saline
LSV	linear sweep voltammograms
CB	conduction band
VB	valence band
PPi	pyrophosphate ion
ALP	alkaline phosphatase

1. Supporting Text

Materials and reagents

All chemicals used were of analytical reagent grade without further purification. The following materials were used: zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 99.99%, Sigma-Aldrich Co., Ltd.); zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98 %, Sigma-Aldrich Co., Ltd.); hexamethylenetetramine (HMTA) ($\text{C}_2\text{H}_{12}\text{N}_4$, 99%, Sigma-Aldrich Co., Ltd.); bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 98 %, Sinopharm Chemical Reagent Co., Ltd), potassium iodide (KI, 98 %, Sinopharm Chemical Reagent Co., Ltd). Fluorine tin oxide (FTO) glass (a thickness of FTO layer of 150 nm and resistance about 15 Ω /square; thickness of glass: 1.1 mm) was obtained from Xiamen FTO Photoelectricity Industry (Xiamen, China). Indium tin oxide (ITO) slices (ITO coating about 180 nm, sheet resistance about 10 Ω /square) were purchased from Weiguang Corp. (China). KCl, HCl, $\text{K}_3[\text{Fe}(\text{CN})_6]$, FeCl_3 , NaOH were bought from Beijing Reagent Company. All aqueous solutions were prepared using ultrapure water (Milli-Q, Millipore).

Preparation of Prussian Blue (PB) film

The PB was prepared according to previous work.^[1] The ITO chips were firstly treated with acetone, ethanol, and water sequentially under ultrasonic bath, followed by immersing in a solution containing of ethanol/NaOH (1 M) with volume ratio 1:1 for 30 min. Then the ITO electrode was rinsed with ultrapure water and dried under N_2 flow. The electropolymerization was performed on a CHI600D three-electrode electrochemical system (Chenhua Instruments Co. Shanghai) with the Ag/AgCl electrode used as a reference electrode and Pt wire employed as the counter electrode, the ITO substrate as working electrode. The PB electropolymerization was carried out in a freshly solution containing 0.1 M KCl, 0.1 M HCl, 2.5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$, and 2.5 mM FeCl_3 by applying a controlled potential of 0.4 V for 480 s. After that, the resulting electrodes was thoroughly rinsed with water to remove the physically adsorbed species, and then dried in 100 °C overnight. The ITO-PB electrode (cathode) was obtained successfully.

Optimization of Detection Conditions

To monitor the practical application of this platform, some factors influencing the signal response were optimized. As shown in Figure S3a, the power output decreased with the increasing amounts of Cu^{2+} , and could reach the constant responses up to 200 μM . Thus, this concentration of Cu^{2+} was used in the following experiments. Moreover, the absorption time of photoanode toward Cu^{2+} was explored. Obviously, the shift of power output decreased with the increasing absorption time and tended to be steady after 30 min (Figure S3b). In order to obtain a wider dynamic range toward PPI sensing and best response at low concentration, 30 min of absorption time was adopted. Due to the strong binding capacity of PPI toward Cu^{2+} , the reaction time between PPI and Cu^{2+} processed photoanode was also optimized (Figure S3c), using 50 μM PPI as a model. The power output increased with the increasing reaction time that could reach the constant responses up to 5 min. The dissociative PPI in the solution have completely chelated with Cu^{2+} . Herein, 5 min was adopted as the optimal reaction time between PPI and Cu^{2+} processed photoanode.

Selectivity

To validate the specificity toward PPI, several targets containing ATP (Adenosine Triphosphate), ADP (Adenosine Diphosphate), AMP (Adenosine Monophosphate), PO_4^{3-} , H_2PO_4^- , HPO_4^{2-} , SO_3^{2-} , SO_4^{2-} , CO_3^{2-} , and HCO_3^- considered to possibly interfere with the PPI sensing were incubated with Cu^{2+} treated photoanode, and the signal response was recorded. As exhibited in Figure S4a and b, no significant effect on the signal response is observed in the presence of the interferences compared with the blank test (in the absence of PPI). The satisfactory selectivity can be ascribed to the specific and high affinity of Cu^{2+} and PPI. Therefore, the proposed method has demonstrated an excellent selectivity toward PPI, showing its potential application for practical application in complex samples.

Reproducibility and Stability

The reproducibility of the proposed time read-out PEC technique was examined by detecting 50 μM PPI with five different sensors, respectively. The relative standard deviation (RSD) toward PPI was 3.7 % obtained confirming the good precision and

reproducibility for our method. Furthermore, the signal response (power output and discolourization time) has almost no change after stored at 4 °C for 4 weeks, validating that the developed method had good storage stability that could be suitable for long distance transport in remote regions and developing countries.

Practical application

To further demonstrate the potential of application of our detection method for PPI assay in real sample, PPI in diluted human serum specimen was performed. As can be seen from Table S2, four serum samples with different concentrations of PPI were measured using the developed method respectively. The results revealed that satisfactory recoveries in the range between 92.7 % and 103.8 % were obtained, indicating the potential of the developed method for analysis of real complicated biological samples.

2. Supporting Graph

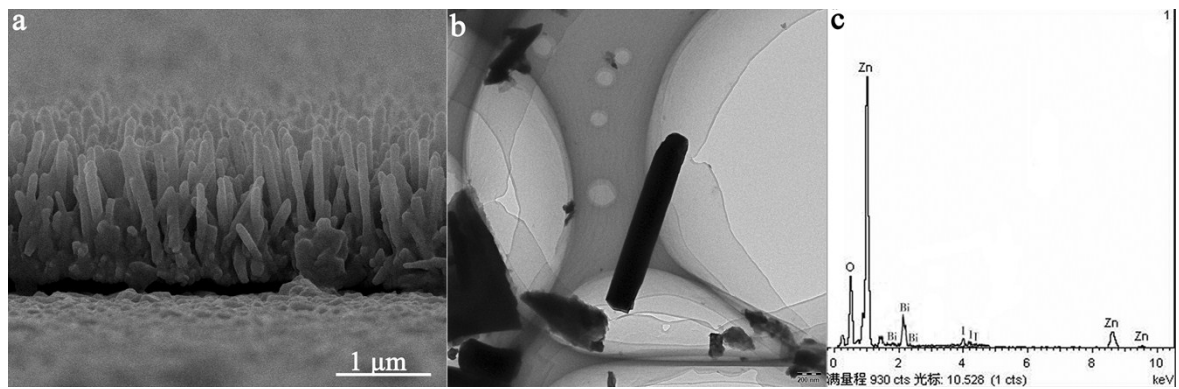
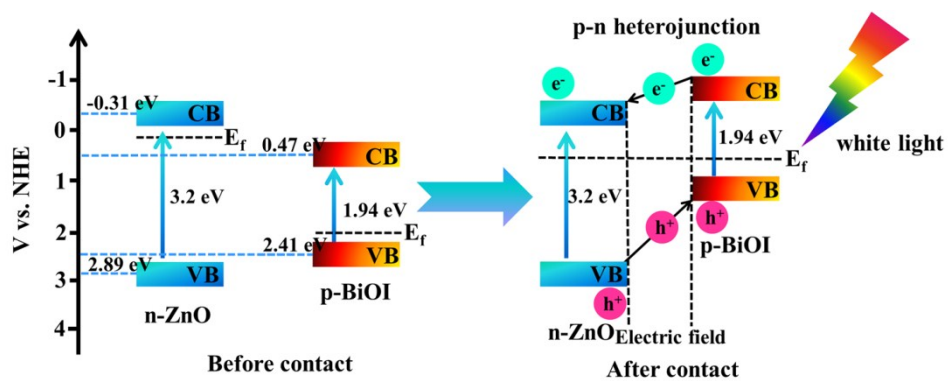


Figure S1. Cross section (a) and TEM image (b) of ZnO nanorods, (c) EDS data of BiOI@ZnO core/shell heterostructure.



Scheme S1. Schematic diagrams of the band energy of p-BiOI and n-ZnO before and after contact, and proposed electron-hole pair separation and transfer paths of BiOI@ZnO under illumination.

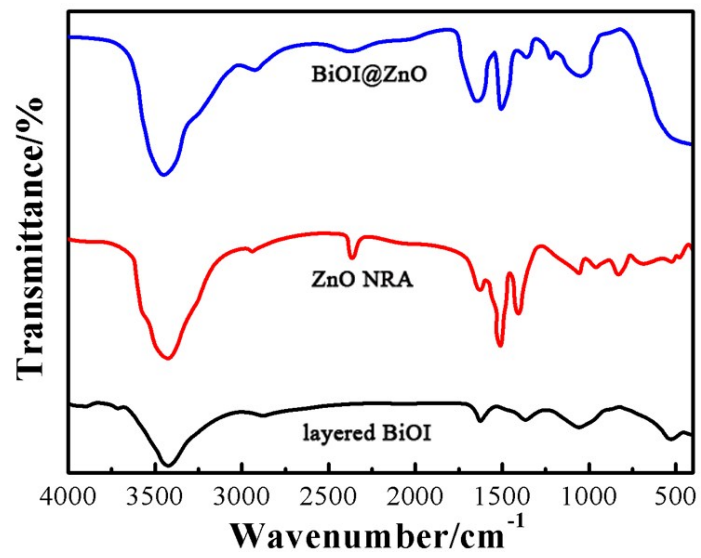
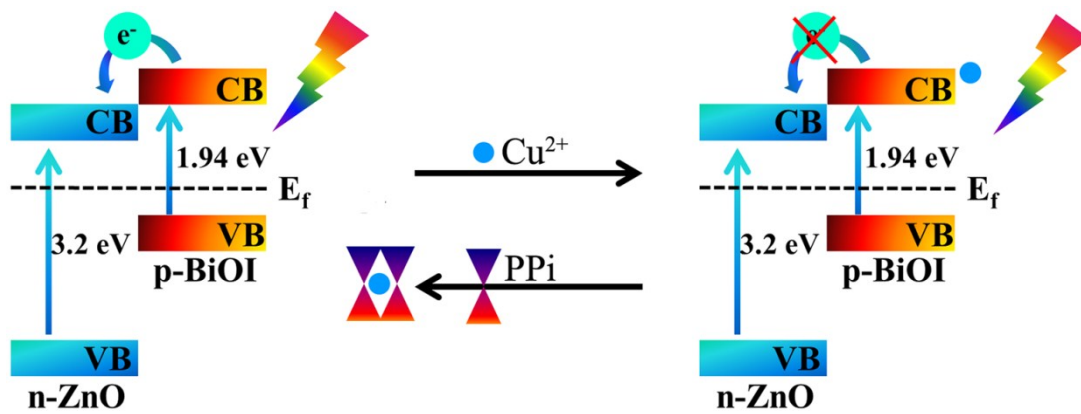
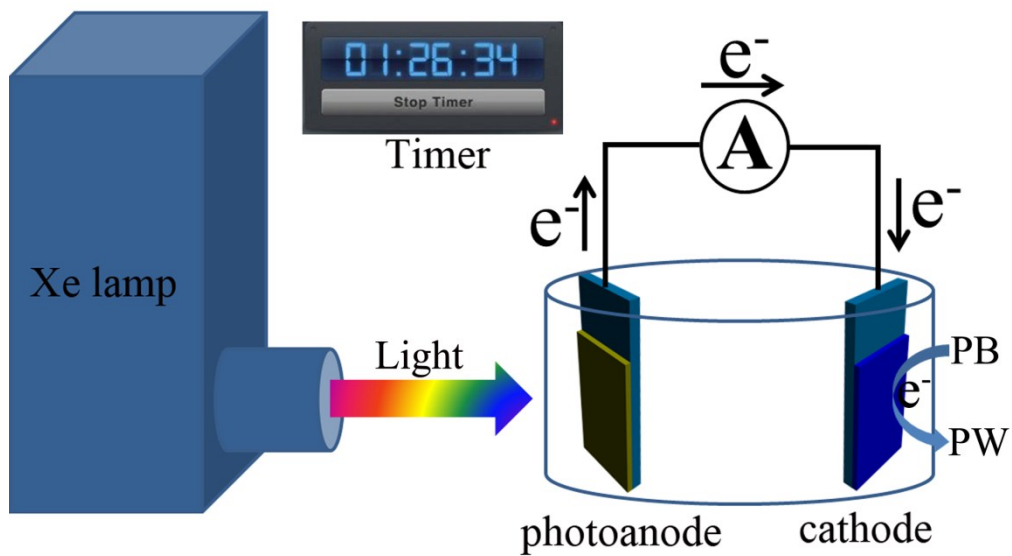


Figure S2. FTIR of ZnO NRA, layered BiOI NPs, and BiOI@ZnO.



Scheme S2. Schematic Illustration of PPI Assay.



Scheme S3. Schematic illustrates the PFC technique.

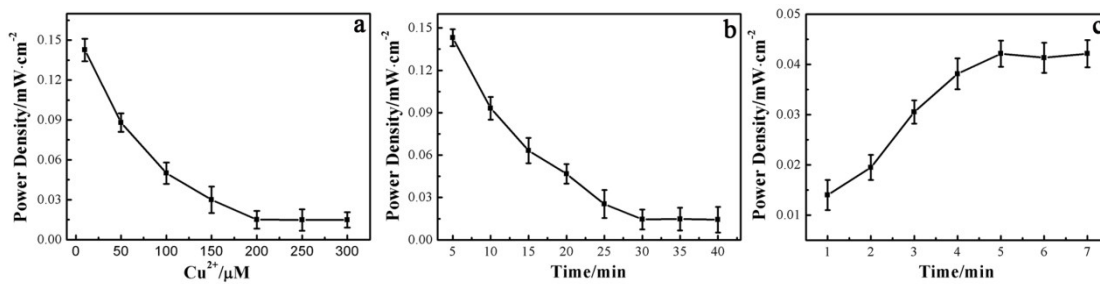


Figure S3. The optimization of effects of Cu²⁺ concentration (a), absorption time of photoanode toward Cu²⁺ (b), reaction time of Cu²⁺ and PPI (c) toward power output intensity.

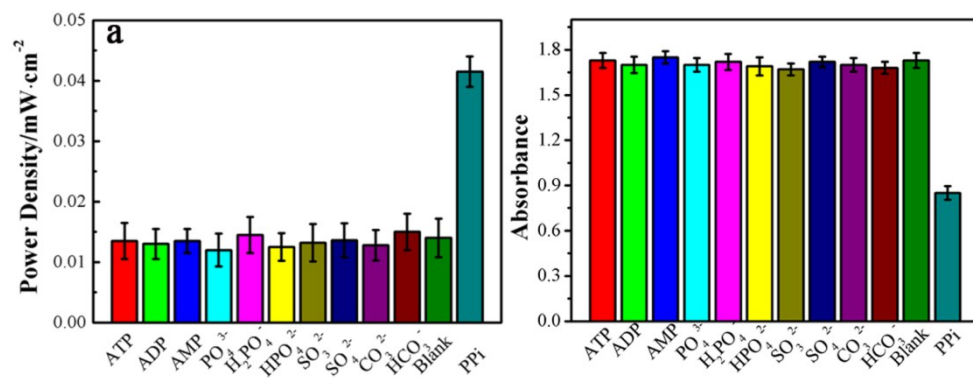


Figure S4. Selectivity of the developed assay for PPI detection over other interferents.

The concentration of PPI and interferents used for selectivity is 50 μ M.

3. Supporting Table

Table S1. Comparison of analytical properties of different methods toward PPI.

Method	Linear range (μM)	Detection limit (nM)	References
fluorescence	3.3-85.8	300	[2]
colorimetric	20-350	-	[3]
fluorescence	0-100	113	[4]
fluorescence	0.04-40	40	[5]
Photoelectrochemical fuel cell	0.1-150	67.3	This work

Table S2. Detection of results of PPI in human serum specimen by the proposed method.

Sample	1	2	3	4
Added/(μM)	10.00	50.00	100.00	120.00
Found/(μM)	9.63	51.9	93.52	122.14
RSD/%	4.03	3.84	4.26	3.57
Recovery/%	96.3	103.8	93.52	101.78

^a The average value of eleven successive determinations.

4. Reference

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