

An ultrasensitive label-free photoelectrochemical sensor based  
on Ag<sub>2</sub>O sensitized WO<sub>3</sub>/TiO<sub>2</sub> acicular composite for detection  
of AFB1

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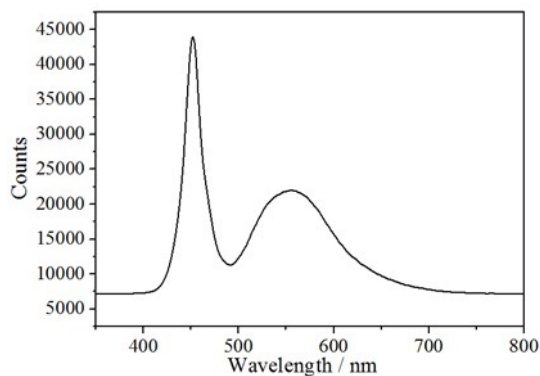
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## 1. Materials and reagents

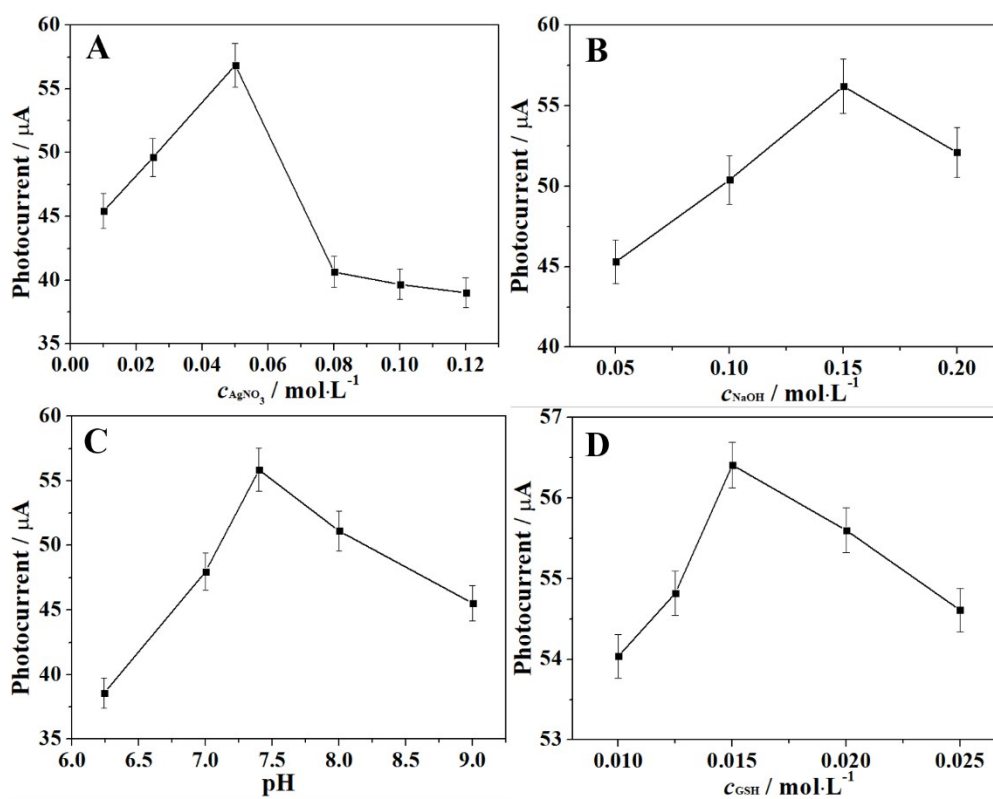
Fluorine-doped SnO<sub>2</sub> transparent conductive glass (FTO) was obtained from Zhuhai Kay-woo Electronic Components Co., Ltd., China. Bovine serum albumin (BSA) was obtained from Sigma-Aldrich (Beijing, China). Thioglycolic acid (TGA) was obtained from Tianjin Kermel Chemical Reagent Co., Ltd. 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS) were obtained from Aladdin Reagent Database Inc (Shanghai, China). Phosphate buffered saline (PBS, 1/15 mol/L KH<sub>2</sub>PO<sub>4</sub> and 1/15 mol/L Na<sub>2</sub>HPO<sub>4</sub>) containing GSH was used as an electrolyte for the PEC measurements.

## 2. Apparatus

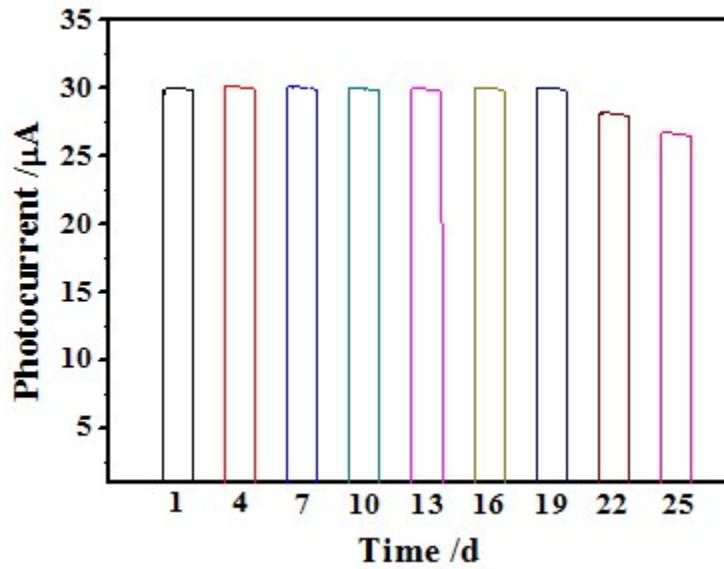
Electrochemical impedance spectroscopy (EIS) analysis was performed on an RST5200F electrochemical workstation (Zhengzhou Shiruisi Technology Co., Ltd, China) with a three-electrode system in a 5.0 mmol/L [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> solution containing 0.10 mol/L KCl. Scanning electron microscope (SEM) images and energy dispersive spectrometry (EDS) were obtained using a field emission SEM (Zeiss, Germany). X-ray diffraction (XRD) patterns were collected on a D8 advance X-ray diffractometer (Bruker AXS, Germany). UV-vis spectra were obtained on a Shimadzu UV-3101PC spectrometer (Japan).



**Fig. S1.** Wavelength range of the LED lamp resource.



**Fig. S2** Effects of concentration of (A)  $\text{AgNO}_3$  and (B)  $\text{NaOH}$ , (C) pH and (D) concentration of GSH in the PBS buffer solution on the photocurrent response of the  $\text{FTO}/\text{WO}_3/\text{TiO}_2/\text{Ag}_2\text{O}$  electrode



**Fig. S3.** The life time of the label-free PEC sensor.

**Table S1** Simulation parameters of the equivalent circuit components

Electrode	$R_s$ ( $\Omega$ )	$R_{et}$ ( $\Omega$ )	$C_{dl}$ (F)	$Z_w$
FTO	56.43	123	$5.849 \times 10^{-6}$	0.008091
FTO/ $WO_3$	57.76	515.4	$6.716 \times 10^{-6}$	0.001232
FTO/ $WO_3$ / $TiO_2$	58.34	938	$3.189 \times 10^{-5}$	0.005060
FTO/ $WO_3$ / $TiO_2$ / $Ag_2O$	56.12	979.4	$6.758 \times 10^{-6}$	0.001867
FTO/ $WO_3$ / $TiO_2$ / $Ag_2O$ /TGA	55.27	1220	$3.083 \times 10^{-6}$	0.002619
FTO/ $WO_3$ / $TiO_2$ / $Ag_2O$ /TGA/(EDC/NHS)	55.89	2062	$2.873 \times 10^{-5}$	0.001579
FTO/ $WO_3$ / $TiO_2$ / $Ag_2O$ /TGA/(EDC/NHS)/ $Ab_1$	57.92	3364	$2.981 \times 10^{-5}$	0.003279
FTO/ $WO_3$ / $TiO_2$ / $Ag_2O$ /TGA/(EDC/NHS)/ $Ab_1$ / BSA	56.47	3374	$2.792 \times 10^{-5}$	0.001204
FTO/ $WO_3$ / $TiO_2$ / $Ag_2O$ /TGA/(EDC/NHS)/ $Ab_1$ / BSA/ AFB1	58.89	5121	$2.847 \times 10^{-5}$	0.002315