Electronic Supplementary Information

EXPERIMENTAL SECTION

Chemicals and materials

The FTO conductive electrode was gained from Zhuhai Kaivo Electronic Components Co. Ltd., China. Strontium hydroxide octahydrate ($Sr(OH)_2 \cdot 8H_2O$), barium nitrate ($Ba(NO_3)_2$), sodium oleate, potassium chromate (K_2CrO_4) and P25 were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$), Sodium hydroxide (NaOH), oleylamine, and oleic acid were purchased from Shanghai Macklin Biochemical Co., Ltd, (Shanghai, China). Protoporphyrin was obtained from Shanghai Jiuding Chemical Technology Co., Ltd (Shanghai, China). N-hydroxy succinimide (NHS) and N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC), and bovine Serum Albumin (BSA) were obtained from Shanghai Medpep Co.,Ltd. (Shanghai, China). Neuron-specific enolase antigen (NSE), brain natriuretic peptide (BNP), amyloid β-protein (Aβ), and procalcitonin (PCT) were both ordered from Sangon Biotech Co.Ltd., (Shanghai, China). All other reagents were of analytical grade and ultrapure water was used throughout the study.

Apparatus

All photoelectrochemical measurements were performed with an electrochemical workstation (Zahner Zennium PP211, Germany). Density functional theory (DFT) calculations were performed using Gaussian 09 program package with B3LYP using 6-31G(d, p) basis set to calculate the energy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of protoporphyrin. The surface morphology of the sample was obtained from scanning electron microscopy (SEM, Gemini 300, Germany Zeiss). Transmission electron micrographs (TEM) were

measured on an H-800 microscope (Hitachi, Japan). X-ray photoelectron spectra (XPS) were elucidated using an ESCALAB 250 electron energy spectrometer (Thermo Fisher Scientific, USA) and the X-ray excitation source was monochromated Al Ka 150 W. UV-vis spectra were obtained on a Shimadzu UV-3101PC spectrometer (Japan). X-ray diffraction (XRD) patterns were obtained by using D8 focus diffractometer (Bruker AXS, Germany).

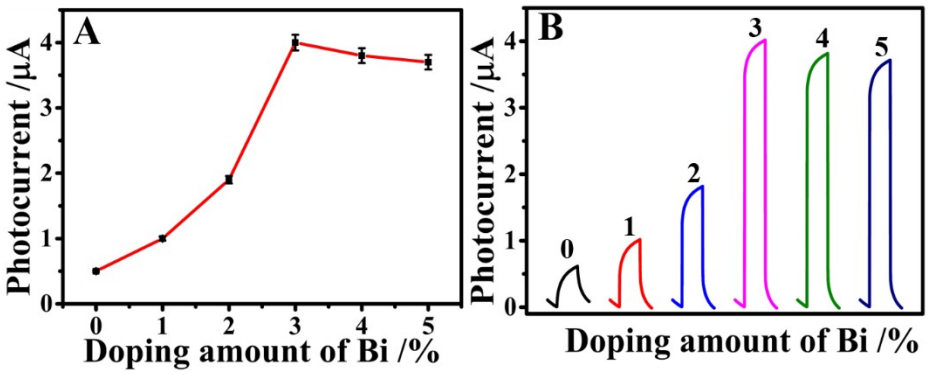

Figure S1. The effect of Bi doping amount to the PEC response of $SrTiO_3$ (A) and the corresponding photocurrent curve (B).

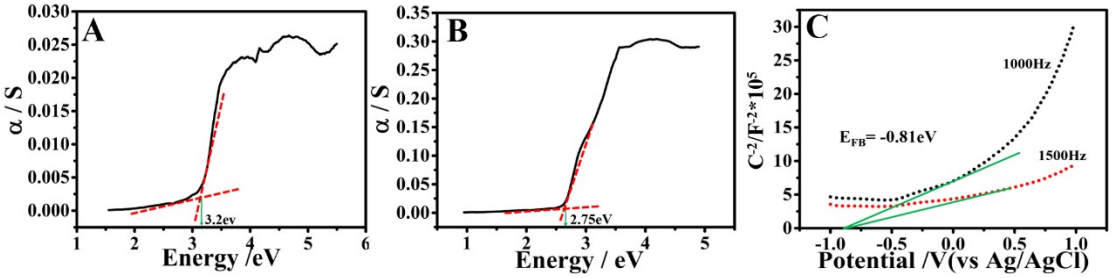

Figure S2. The bang gap analysis image of $SrTiO_3$ (A) and Bi: $SrTiO_3$ (B), and the Mott-Schottky curve of Bi: $SrTiO_3$ (C).

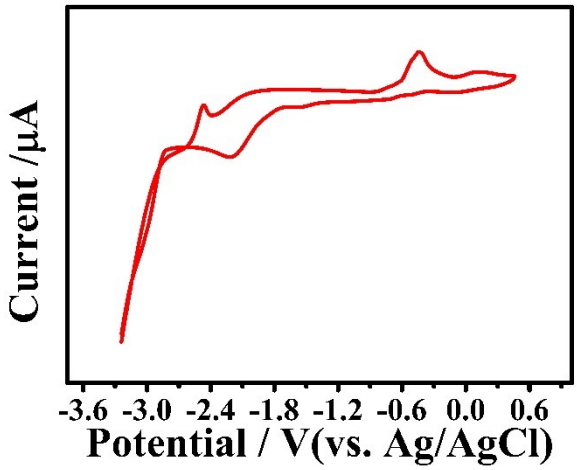

Figure S3. The cyclic voltammetry curve of bare electrode measured in tetrabutylammonium perchlorate acetonitrile solution.

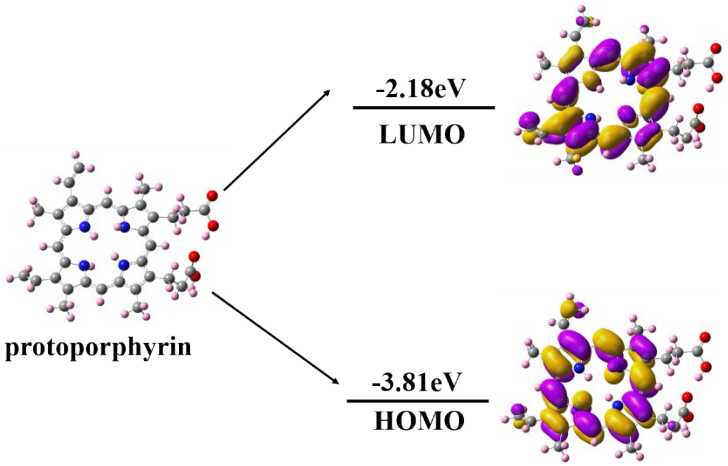

Figure S4. The structure of protoporphyrin and the position of LUMO and HOMO.

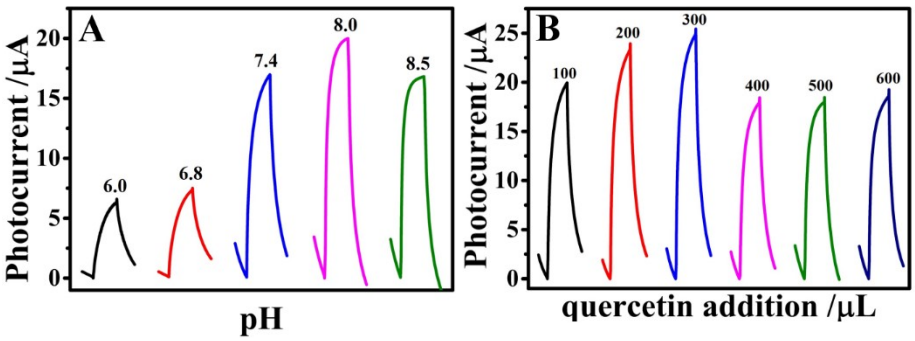

Figure S5. The photocurrent curve of the PEC biosensor in (A) different pH value and (B) different addition amount of quercetin.

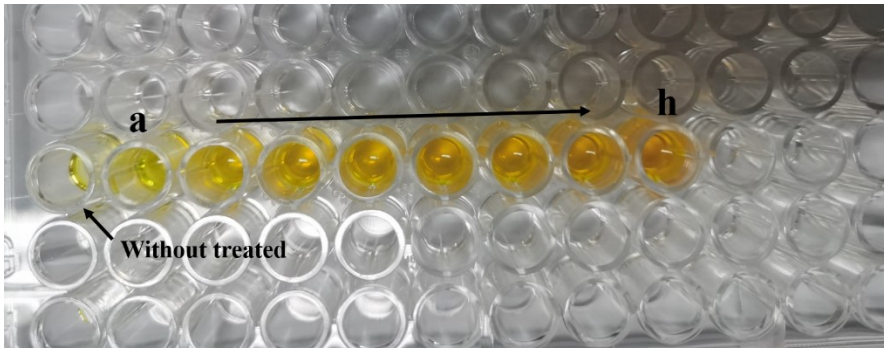

Figure S6. The corresponding colors of 96-well plate with different concentrations of NSE after treated with acid.

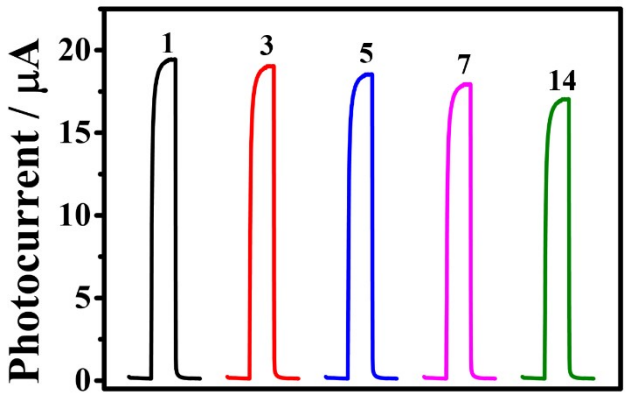

Figure S7. The storge stability results of the PEC biosensor within two weeks.

Table S1. The developed PEC biosensors for detecting NSE compared with other published sensors.

Method	Linear range (ng/mL)	Detection limit (pg/mL)	Reference
chemiluminescence aptasensor	1-100	100	Zheng et al[1]
Fluorescent biosensor	0.0001-1000	0.09	Kalkal et al[2]
Electrochemical sensors	0.00001-100	0.0047	Ma et al[3]
Photothermal immunoassay	0.1-100	53	Zhi et al[4]
Electrochemical sensor	0.048-150	15	Chen et al[5]
This work	0.00007-170	0.025	This work

Table S2. The polarity conversion strategy compared to single polar change strategy for NSE PEC detection.

Photocurrent polarity	Linear range (ng/mL)	Detection limit (pg/mL)	Reference
Single	0.001-100	0.2	Yu et al[6]
Single	0.1-1000	50	Li et al[7]
Single	0.005-1.5	3.5	Liu et al[8]
polarity conversion	0.00007-170	0.025	This work

Table S3. Recovery results of NSE in real serum samples detected by the proposed PEC biosensor (*n*=11)

sample （ng/mL）	Added (ng/mL)	Found (average) (ng/mL))	Recovery (%)	RSD (%)
0.33	0.10	0.428	98.0	2.6
	0.50	0.838	101.6	3.1
	1.00	1.268	103.8	4.3

Reference

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