Supplementary materials

Article

Ultrasensitive Photochemical Immunosensor Based on Flowerlike $SnO_2/BiOI/Ag_2S$ Composites for Detection of Procalcitonin

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1. Materials and apparatus

Thioglycolic acid (TGA) was obtained from Macklin Reagent Co., Ltd. (Shanghai, China). 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS) were obtained from Aladdin Reagent Database Inc. (Shanghai, China). Tin (IV) chloride pentahydrate ($SnCl_4$), thioacetamide, potassium iodide (KI), Bismuth nitrate pentahydrate ($Bi(NO_3)_3·5H_2O$), sodium sulfide (Na_2S), silver nitrate ($AgNO_3$), ascorbic acid (AA), absolute ethanol, isopropyl alcohol and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Phosphate buffered solution (PBS, 1/15 $mol·L^{-1}$ KH_2PO_4 and 1/15 $mol·L^{-1}$ Na_2HPO_4) containing AA was used as an electrolyte for the PEC measurements. All other chemicals in the experiment were analytical grade and were used as received without further purification.

2. Apparatus

Scanning electron microscope (SEM) images and energy dispersive spectroscopy (EDS) were obtained by using a field-emission SEM (Zeiss, Gemini 300, Germany). Electrochemical impedance spectroscopy (EIS) analysis was performed with an RST5200F electrochemical workstation (Zhengzhou Shiruisi Technology Co., Ltd, China) with a three-electrode system in a 5.0 $mmol·L^{-1}$ $[Fe(CN)_6]^{3-/4-}$ solution containing 0.10 $mol·L^{-1}$ KCl. UV-vis diffuse reflectance spectrum measurements were performed with a Shimadzu UV-3101PC spectrometer (Japan). All PEC experiments were measured on a CHI760E electrochemical workstation (Chenhua Instrument Shanghai Co., Ltd, China) by using a conventional three-electrode system comprising of a saturated calomel electrode as reference electrode, a platinum wire as a counter-electrode, and the as-prepared $SnO_2/BiOI/Ag_2S$ modified ITO electrode ($2.5×1.0\ cm^2$) as working electrode.

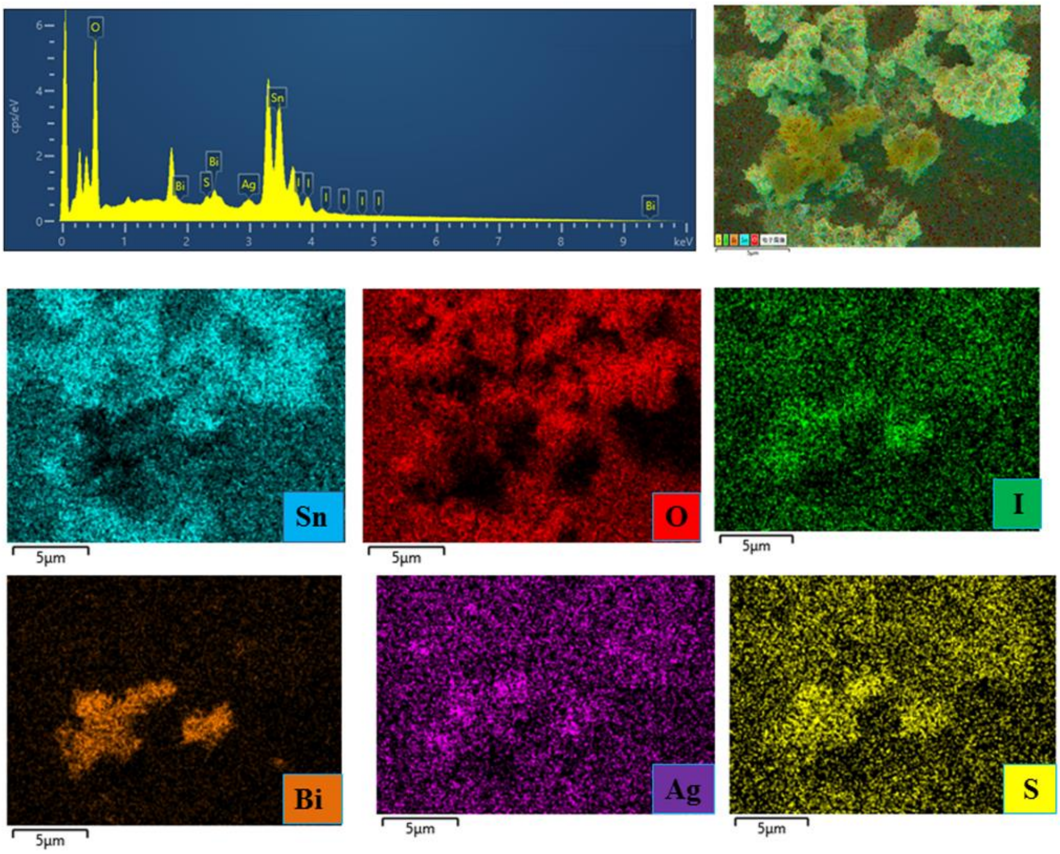

Figure S1 The EDS mapping images of SnO_2/BiOI/Ag_2S composites.

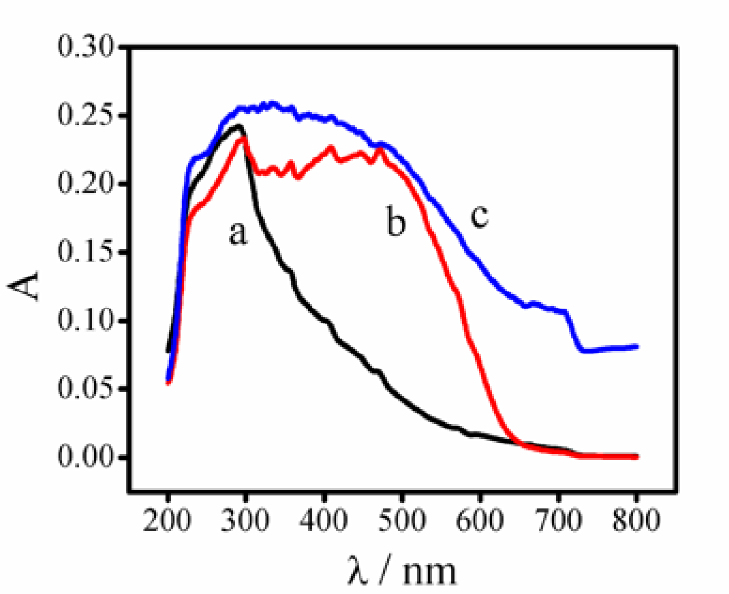

Figure S2 UV-Vis diffuse reflectance spectra of SnO_2 (a), SnO_2/BiOI (b) and SnO_2/BiOI/Ag_2S (c).

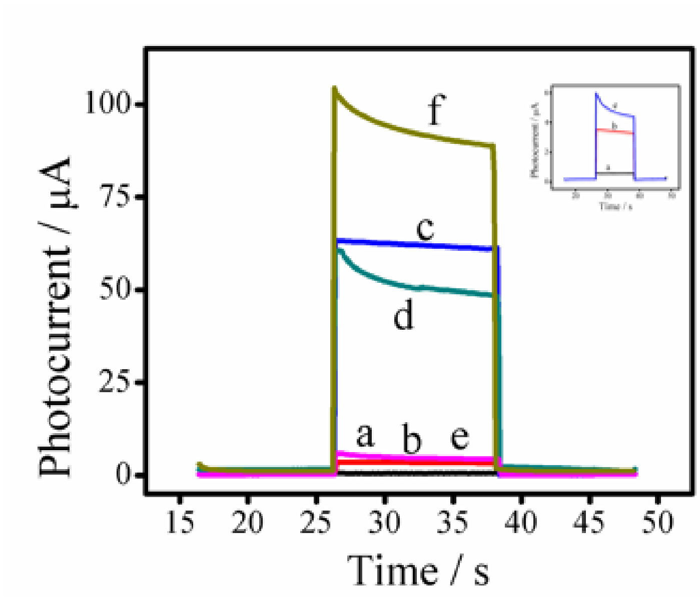

Figure S3 Time-based photocurrent response curves of SnO_2(a), BiOI(b), SnO_2/BiOI(c), SnO_2/Ag_2S(d), BiOI/Ag_2S(e) and SnO_2/BiOI/Ag_2S(f).

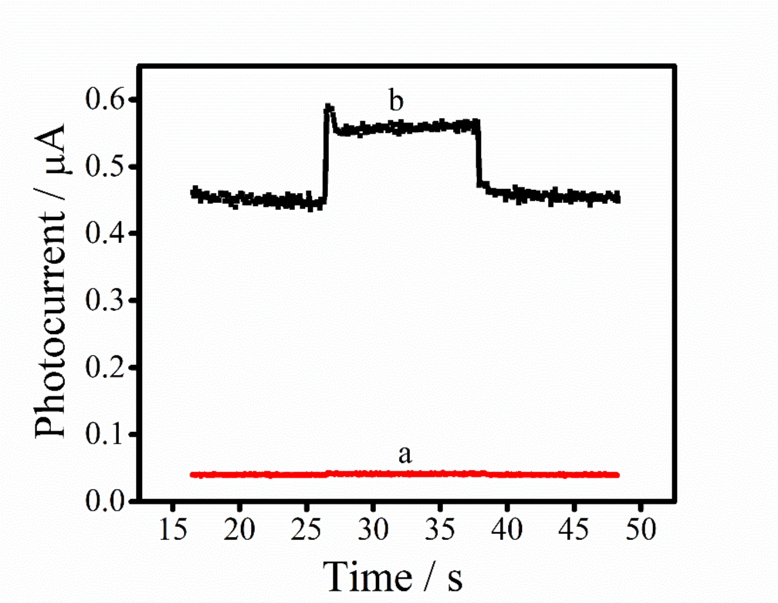

Figure S4 Time-based photocurrent response curves of ITO electrode (a) and ITO/SnO_2 (b)

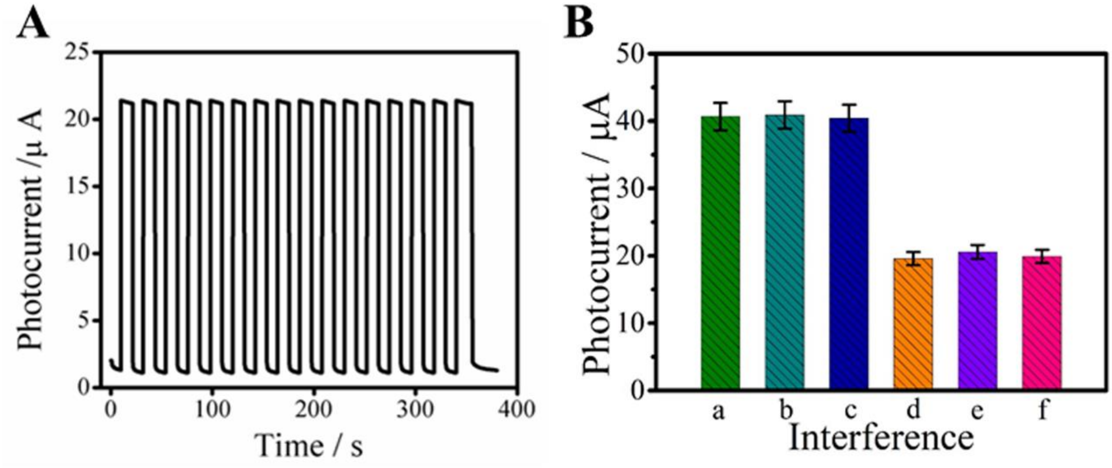

Figure 5. Stability curve of chronocurrent (A); Selectivity of the PEC immunosensor for detecting PCT (B) : (a) Blank , (b) Blank+100 ng·mL^{-1} CEA, (c) Blank+100 ng·mL^{-1} PSA, (d) 1.0 ng·mL^{-1} PCT, (e) 1.0 ng·mL^{-1} PCT+100 ng·mL^{-1} CEA, (g) (f) 1.0 ng·mL^{-1} PCT+100 ng·mL^{-1} PSA. The applied potential was 0 V. Error bars = SD (*n* = 5).

Table S1 Comparison of the performance of the proposed PEC immunosensor for PCT detection and those of other reports.

Detection method	Liner range ($pg\cdot mL^{-1}$)	Detection limit ($pg\cdot mL^{-1}$)	References
Chemiluminescence immunoassay	$44 - 1.0 \times 10^5$	44	1
Eelectrochemical immunosensor	$1.0 - 5.0 \times 10^4$	0.36	2
Ratiometric electrochemical immunosensor	$1.0 - 1.0 \times 10^5$	0.30	3
Immunosorbent assay	$1.0 - 1.0 \times 10^5$	0.095	4
Immunochromatographic assay	$62.5 - 4.0 \times 10^5$	62.5	5
SERS-based immunochromatographic assay	$10 - 1.0 \times 10^7$	8.017	6
Time-resolved digital immunoassay	$4.2 - 1.25 \times 10^4$	2.8	7
Electrochemical paper-based analytical device	$0.50 - 2.5 \times 10^5$	0.27	8
Lateral flow immunoassay	$12 - 1.0 \times 10^4$	31	9
Capillary immunosensor	$0.10 - 1.0 \times 10^5$	0.01	10
Electrochemiluminescence immunosensor	$0.10 - 1.0 \times 10^4$	0.0257	11
Electrochemiluminescence immunosensor	$0.10 - 1.0 \times 10^5$	0.01258	12
Electrochemiluminescence immunosensor	$0.010 - 1.0 \times 10^5$	0.00365	13
Electrochemiluminescence immunosensor	0.005 - 100	0.0021	14
Electrochemiluminescence immunosensor	$0.10 - 5.0 \times 10^4$	0.054	15
Electrochemiluminescence immunosensor	$0.05 - 1.0 \times 10^5$	0.017	16
Photoelectrochemical immunosensor	$0.10 - 5.0 \times 10^4$	0.020	17
Photoelectrochemical immunosensor	$0.10 - 1.0 \times 10^5$	0.030	18
Photoelectrochemical immunosensor	$0.50 - 1.0 \times 10^5$	0.17	19
Photoelectrochemical immunosensor	$1.0 - 1.0 \times 10^5$	0.42	20
Photoelectrochemical immunosensor	$0.50 - 1.0 \times 10^5$	0.14	This work

Table S2. The results of the PCT determination in human serum samples

Content in samples ($ng \cdot mL^{-1}$)	Added content ($ng \cdot mL^{-1}$)	Average content (*n*=11) ($ng \cdot mL^{-1}$)	RSD (*n*=11, %)	Recovery (%)
0.0400	0.0100	0.0512	8.4	103%
	1.00	1.04	7.6	100%
0.800	1.00	1.79	4.7	98.8%
	10.0	10.8	2.2	100 %

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