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A novel sandwich-type photoelectrochemical sensor for SCCA detection based on Ag_2S sensitized BiOI matrix and $Au_{core}Pd_{shell}$ nanoflower label for signal amplification

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1. Materials and reagents

Disodium tetrachloropalladate (Na_2PdCl_4), $Bi(NO_3)_3 \cdot 5H_2O$ and ascorbic acid ($C_6H_8O_6$) were obtained from Shanghai McLean biochemical technology Co., Ltd. Glacial acetic acid (CH_3COOH) was obtained from yao shun import and export Co., Ltd, China. KI was obtained from Tianjin Damao chemical reagent factory. $HAuCl_4 \cdot 6H_2O$ was purchased from Alfa Aesar. Trisodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) was obtained from Tianjin Guangcheng chemical reagent Co., Ltd. Polyvinyl pyrrolidone (PVP) was obtained from SIGMA-ALDRICH. Hydroquinone ($C_6H_6O_2$) was obtained from pharmaceutical Shanghai chemical reagent Co., Ltd, China. $AgNO_3$ was obtained from Shanghai reagent factory of China. $Na_2S \cdot 9H_2O$ was obtained from Fine chemical plant of laiyang economic and technological development zone. 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_2PO_4 and 1/15 mol/L Na_2HPO_4) containing AA was used as an electrolyte for the PEC measurements. Indium tin oxide (ITO) glass was obtained from Zhuhai Kaivo Electronic Components Co., Ltd, China.

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 $[Fe(CN)_6]^{3-/4-}$ 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). Transmission electron micrographs (TEM) were measured on an H-800 microscope (Hitachi, Japan). 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). Photoluminescence (PL) emission spectra were acquired under excitation at 310 nm using an Edinburgh Instruments FLS920 spectrometer (Edinburgh Instruments, UK).

3. Optimization of experimental conditions

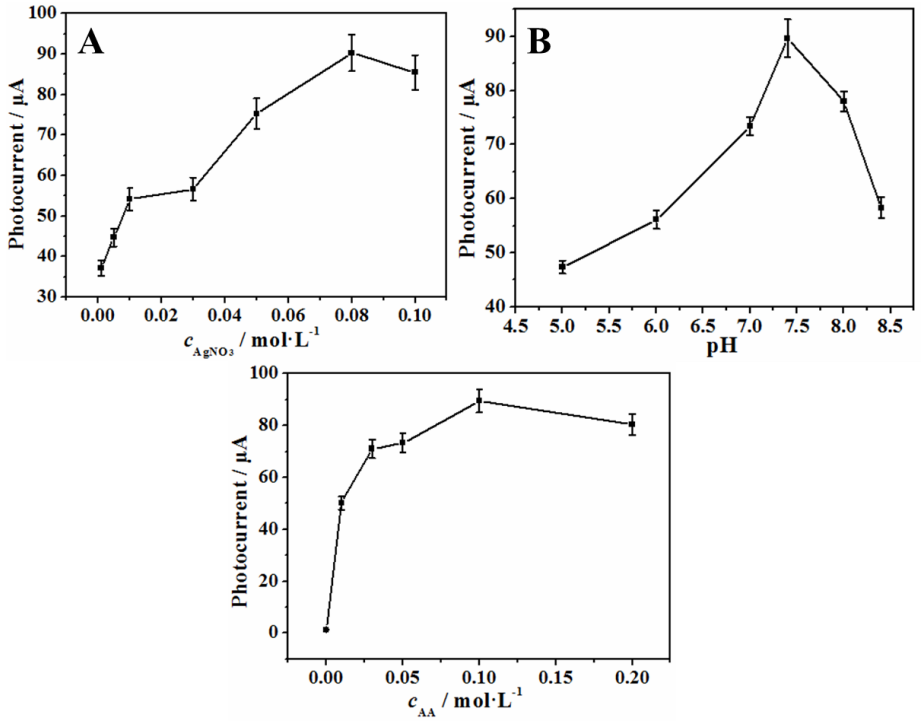

Fig. S1. Effects of concentration of $AgNO_3$ (A), pH (B) and concentration of AA in the PBS buffer solution (C) on the photocurrent response of the ITO/BiOI/Ag_2S electrode. The potential was 0 V.

4. Simulation parameters of the equivalent circuit components

Table S1. Simulation parameters of the equivalent circuit components

Electrode	R_s (Ω)	R_{et} (Ω)	C_{dl} (F)	Z_W
ITO	87.0	14.85	4.594×10^{-7}	0.00782
ITO/BiOI	87.3	32.78	7.514×10^{-6}	0.01137
ITO/BiOI/Ag_2S	81.3	39.36	4.188×10^{-6}	0.00729
ITO/BiOI/Ag_2S/TGA	84.9	45.35	4.321×10^{-6}	0.00764
ITO/BiOI/Ag_2S/TGA/(EDC/NHS)	82.1	59.57	6.469×10^{-6}	0.00749
ITO/BiOI/Ag_2S/TGA/(EDC/NHS)/Ab_1	83.5	70.50	4.561×10^{-6}	0.00696
ITO/BiOI/Ag_2S/TGA/(EDC/NHS)/Ab_1/SCCA	87.0	10.89	4.191×10^{-6}	0.00545
ITO/BiOI/Ag_2S/TGA/(EDC/NHS)/Ab_1/SCCA /Au_cPd_s@Ab_2	85.3	105.1	3.807×10^{-6}	0.00498

5. Comparison of various methods for SCCA detection

Table S2. Comparing different methods of detecting SCCA

Methods	Linear range ($pg\cdot mL^{-1}$)	LOD ($pg\cdot mL^{-1}$)	Reference
Electrochemiluminescence immunosensor	1-10000	0.4	[1]
Electrochemical immunosensor	0.1-80000	33000	[2]
Photoelectrochemical immunoassay	0.8-80000	0.21	[3]
Immunosensor	100-5000	0.3	[4]
Electrochemiluminescence immunosensor	1-100000	0.33	[5]
Photoelectrochemical immunoassay	0.01-100000	0.0016	This work

From Table S2, it can be seen that the detection limit and linear range using PEC sensor based on Ag_2S sensitized BiOI matrix and Au_cPd_s nanoflower label for signal amplification is better or comparable to the results reported for the detection of SCCA. The reasons why the sensor has the low detection limit are as follows: Firstly, the surface of BiOI is uneven accompanied by a mass of holes structure, which is conducive to load nanoparticles to manufacture nanocomposites with superior

performance; secondly, the Ag_2S improved the absorption of BiOI in the visible light region and promoted the photocurrent production distinctly; in addition, the signal amplification strategy is fulfilled by utilizing Au_cPd_s as the label anchored secondary antibodies due to the absorption competition of visible-light resource and the efficient energy transfer between Au_cPd_s and $BiOI/Ag_2S$ matrix; and lastly, the excellent PEC sensor based on sensitization and signal amplification protocols contributes to the ultrasensitive detection of SCCA.

6. The results of the SCCA determination in human serum sample

Table S3. The results of the SCCA determination in human serum sample

Content of SCCA in the serum ($ng \cdot mL^{-1}$)	The addition content ($ng \cdot mL^{-1}$)	The detection content ($ng \cdot mL^{-1}$, $n = 5$)	RSD (%, n = 5)	Recovery (%)
0.14	0.50	0.69,0.66,0.65,0.69,0.68	2.70	107
	1.00	1.10,1.11,1.09,1.15,1.14	2.30	97.8
	2.00	2.20,2.16,2.23,2.18,2.10	2.24	102

7. Comparison between the proposed PEC sensor and the ELISA method

Table S4. Human serum sample analysis using the proposed method and the ELISA method

Serum sample	ELISA ($ng\ mL^{-1}$)	Average ($ng\ mL^{-1}$)	*s*	RSD (%)	This method ($ng\ mL^{-1}$)	Average ($ng\ mL^{-1}$)	*s*	RSD (%)	Relative errors (%)	F^a value
1	0.74 0.75 0.69 0.71 0.67	0.71	0.033	4.7	0.69 0.73 0.75 0.76 0.71	0.73	0.029	3.93	2.8	1.29
2	1.83 1.87 1.91	1.88	0.041	2.2	1.89 1.82 1.83	1.82	0.043	2.4	-3.2	1.10

1.93	1.78
1.85	1.79

[a] The F values refer to comparison of the proposed method with ELISA method. The theoretical values at 95% confidence limits: $F = 6.39$, $F = \frac{s^2_{max}}{s^2_{min}}$

Reference

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