Supplementary Material

A label-free photoelectrochemical immunosensor for carcinoembryonic antigen detection based on a g-C_3N_4/CdSe nanocomposite

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1. Materials and Reagents

Selenium (Se), cadmium chloride ($CdCl_2$), Melamine and L-Cysteine were purchased from Aladdin Reagent Co. Ltd (Shanghai, China). Sodium sulfite anhydrous (Na_2SO_3) was purchased from Guangfu Chemical Reagent Co. Ltd (Tianjin, China). Interleukin-6 (IL-6), cytochrome C (Cyt C), anti-CEA antibody and carcinoembryonic (CEA) were obtained from Beijing Biosynthesis Biotechnology Co., Ltd (Beijing, China). Ascorbic acid (AA) and bovine serum albumin (BSA) were provided by Shanghai Sangon Biological Engineering Technology Co., Ltd (Shanghai, China). Poly (diallyldimethylammonium chloride) (PDDA, Mw 200000-350000, 20 wt% in H_2O), ethyl-(3-methyl-propyl)carbodiimide amine hydrochloride (EDC) and N-Hydroxysuccinimide (NHS) were acquired from Sinopharm Chemical Reagent Co. Ltd. (Beijing, China). All reagents were analytically pure and without further purified before used. Ultra-pure water (18 MΩ/cm) was utilized through the whole work. Electrolyte which used in the whole photoelectrochemical measurement was 100 mM phosphate buffered saline (PBS, pH 7.4) containing 100 mM AA. The preparation of IL-6, Cyt C, CEA, anti- CEA and washing solution were used with 10

mM phosphate buffered saline (PBS, pH 7.4), and 1% (w/v) BSA which dissolved in 10 mM PBS was used as the blocking agent.

2. Instrumentations

High resolution transmission electron microscopy (HRTEM) and transmission electron microscopy (TEM) images were made at a JEM-2100 transmission electron microcopy (JEOL Ltd., Japan). Ultraviolet-visible (UV-vis) absorption spectra were performed on a UV-3600 UV spectroscopy (Shimadzu Ltd, Japan). Photoluminescence (PL) spectra were obtained on photoluminescence spectrometer (F-2500, Hitachi, Japan). X-ray powder diffractions (XRD) were performed on an X-Ray diffractometer (Rigaku D/max-rA, Japan). The photoelectrochemical measurements were made at the CHI 660D electrochemical workstation (CH Instruments, China) using a traditional three-electrode system: the working electrode was a modified FTO, auxiliary electrode was a Pt electrode, and the reference electrode was a Ag/AgCl (saturated KCl). A xenon lamp was used as light source (Nanjing, China). Electrochemical impedance spectroscopy (EIS) was carried out with a Thales electrochemical workstation (Zahner-elektrik GmbH & Co., Germany) using a traditional three-electrode system which same as above. The electrolyte was 0.01 M of PBS (pH 7.4) including 0.1 M of KCl and 2 mM of $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1), the frequency is ranged from 100 mHz to 100 KHz, and the amplitude was 5 mV.

3. ***The detection limit of the immunsensor***

The detection limit was calculate as $3\sigma/S$, where σ is the standard deviation of three independently blank samples response and the S is the slope of the analytical curve. The standard deviation of three independently blank samples response of the immunosensor was 0.5, and the slope of the analytical curve was 7.0407, thus the detection limit of the immunsensor was $3\sigma/S=3\times0.5/7.0407=0.21$ ng·mL^{-1}.

4. Table S1.

Electrode description	Method	Analytical range (ng/mL)	References
Au	Surface acoustic wave	0.5-30	1

Ag_2S@ZnO/Au	Colorimetry	0.1-20	2
NCMTs@Fe3O4@Cusilicate@Con A	Electrochemistry	0.03-6	3
AuNPs-CysA-GA	Electrochemistry	1-5000	4
MBs	Liquid crystal sensors	0.46-3	5
GO/QDs	FRET	0.5-70	6
Fe2O3@PEDOT:PSS	Electrochemistry	4-25	7
CNT@AgNPs	Electrochemistry	25-1000	8
g-C3N4/CdSe	Photoelectrochemistry	10-100000	This work

Table S1. Comparison of various methods for target CEA detection.

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