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Near-infrared photoactive Yb-MOF functionalized with large conjugate ionic liquid: Synthesis and application for photoelectrochemical immunosensing carcinoma embryonic antigen

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1. Materials and reagents

1,6-Dibromo-pyrene, imidazole, methyl 4-bromomethyl benzoate, $YbCl_3 \cdot 6H_2O$ are all purchased from Shanghai Saen Chemical Technology Co., Ltd (Shanghai, China), potassium hydroxide, chloroauric acid, ascorbic acid, glutaraldehyde (GLD) (25% aqueous solution) and Human Epididymal protein 4 (HE4) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Bovine serum albumin (BSA) and glutamic acid (Glu) are brought from Shanghai Ruji Biotechnology Co., Ltd (Shanghai, China). Immunoglobulin G (IgG) was acquired from Beijing Solarbio Science & Technology Co., Ltd (Beijing, China). Human serum albumin (HSA) was provided by Shanghai Pufei Biotech Co. Ltd (Shanghai, China). Neuron Specific Enolase (NSE) was bought from Beijing Biosynthesis Biotechnology Co., Ltd (Beijing, China). All other reagents were of analytical grade and were used as received. All solutions were prepared by using ultra-pure water. Human serum samples were kindly supplied by the Central Hospital of Wuhan (Wuhan, China).

2. Apparatus

^1H NMR spectrum is obtained from AVANCE III 600 NMR system (Bruker, German). FT-IR analysis is carried out with Nexus470 FTIR spectrometer (Nicolet, USA). Mass spectrum is conducted on the auto flex speed MALDI-TOF(TOF) mass spectrometer (BRUKER, Germany). Fluorescence spectrum is gained from Hitachi F-7000 fluorescence spectrophotometer (Hitachi, Japan). UV-Vis-NIR spectrum is measured on Cary 5000 spectrophotometer (Agilent Technologies, USA). Transmission electron microscopic (TEM) images are obtained from Talos F200X

instrument (Thermo Fisher, USA) at an acceleration voltage of 20 to 200 kV. Field emission scanning electron microscope (FESEM) is conducted on SU8010 (Hitachi, Japan). XPS analysis is carried out with MULT1LAB2000 X-ray photoelectron spectrometer (XPS) (VG, USA). X-ray diffraction (XRD) patterns are acquired by D8 ADVANCE (BRUKER, Germany). The porosity and total surface area of the materials are determined by N_2 adsorption-desorption isotherms using a Micromeritics TriStar II 3flex system (Micromeritics, America). Atomic force microscope (AFM) was detected from SPM-9700HT (Hitachi, Japan).

3. Synthesis of DDPDBCBIm(Br)$_2$ ionic liquid

The synthesis process of DDPDBCBIm(Br)$_2$ ionic liquid is shown in **Scheme S 1**. A mixture of 1,6-Dibromopyrene (500 mg, 1.39 mmol, 1eq), imidazole (378 mg, 5.56 mmol, 4eq), potassium carbonate (K_2CO_3, 1535 mg, 1.12 mmol, 8 eq), cuprous iodide (CuI, 106.4 mg, 0.56 mmol, 0.4 eq) and DMF (64 mL) was heated in a Teflon-lined stainless vessel at 160 °C for 48 h under N_2.[1] After being cooled down to room temperature, the suspension was mixed with water, then the solvent was removed by vacuum suction filtration. The obtained filter cake was thoroughly washed with water to yield a green solid product. Secondly, the dried product was reacted with methyl 4-bromomethylbenzoate in acetonitrile at 82 °C for 24 h with constant stirring to confirm the completion of the reaction. Then, adding anhydrous ether to the resulting yellow transparent solution until a reseda precipitate is formed. After vacuum suction filtration, the gained dried product was re-dissolved in the mixture solution of ethanol and ultrapure water (v/v = 4:1). KOH was added to the product solution successively. The mixture was heated at 80 °C for 4 h. The pH value of the solution was adjusted to 2.0 by adding HCl solution while maintaining the reaction mixture at room temperature.[2]

Subsequently, the mixture was separated by vacuum filtration and the crude product was washed with ultrapure water, and dried under vacuum to give the desired product: DDPDBCBIm$(Br)_2$ ionic liquid (yield: 95 %). The product was characterized by 1H-NMR, FTIR and MALDI-TOF-MS. All results are shown in **Figure S 1**.

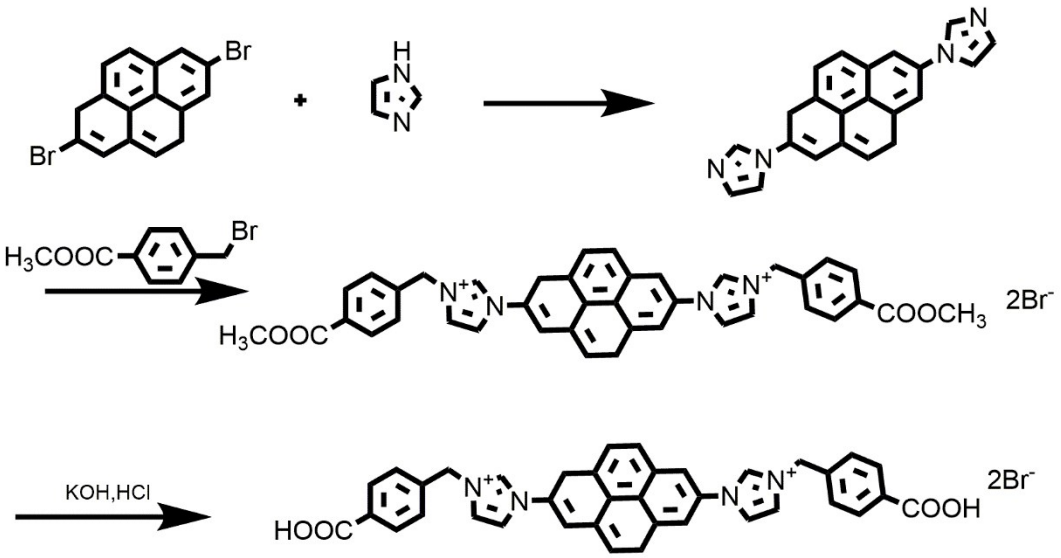
4. Synthesis of Yb-MOF

$YbCl_3 \cdot 6H_2O$ (44 mg), DDPDBCBIm $(Br)_2$ ionic liquid (40 mg), and DMF (64 mL) were mixed in a 250 mL beaker with ultrasonic dissolution. A volume of 60 μL of HCl aqueous solution (1 M) was added to the mixture and dissolved evenly under an ambient condition. Then the resultant mixture was transferred to a 100 mL Teflon-lined stainless vessel and heated at 100 °C for 72 h.[3, 4] After cooling to room temperature, the obtained dark green solid was collected by centrifugation, followed by thorough washing with DMF and deionized water. Finally, the products were dried at 60 °C under vacuum.

5. Synthesis Yb-MOF@Au-NPs nanocomposites

The synthesis method of the Yb-MOF@Au-NPs composites is improved according to the previously reported.[5] Yb-MOF (8 mg) was treated in vacuum for an hour at a negative pressure. The $HAuCl_4$ (10 mL, 20 mmol L^{-1}) was injected into the sealed system. The mixture was kept in an ice bath for 3 h in air. Subsequently, Yb-MOF was separated from the mixture at a centrifugation rate of 10000 rpm for 6 min. After that, Yb-MOF was dispersed in the ultrapure water. Adding 2 mL of 0.01 M $NaBH_4$ solution dropwise to it under vigorous stirring, 5 minutes later, the reaction was completed. The product was collected by centrifuging at a speed of 10000 rpm for 10 min and washed 3 times with ultrapure water. Then, dried in vacuum to yield Yb-MOF@Au-NPs nanocomposites.

Some data in **Figure S 1a** are presented as following: 1H NMR (400 MHz, DMSO-d6) δ 8.34 (s, 2H, number 9 and 12), 8.00 (s, 8H, number 1-8), 7.84 (s, 2H, number 10 and 11), 7.55 - 7.27 (m, 6H, number 13, 14, 16 ,17, 18 and 19), 6.92 (s, 4H, number 20 and 21), 6.51 (s, 2H, number 22 and 23), 4.98 (s, 4H, number 15). The FT-IR spectrum of the DDPDBCBIm$(Br)_2$ ionic liquid is illustrated in **Figure S 1b**. The characteristic peak at 3450 cm^{-1} corresponds to the stretching vibration of O-H on H_2O. The absorption bands due to stretch of carboxylate group (COOH) was observed in the expected position at 1717 cm^{-1}. Three bands at 1663, 1500, and 1462 cm^{-1} are the characteristic vibration peaks of benzene ring. Other two bands at 835 and 749 cm^{-1} are ascribed to the vibration peaks of C=C and C=N on the imidazole ring, respectively.[6] The MALDI-TOF-MS spectrum (**Figure S 1c**) indicates that the *m/z* of $DDPDBCBIm^{2+}$ is 634.526 ($[M + CHO]^+$).The results show that DDPDBCBIm$(Br)_2$ ionic liquid has been successfully synthesized.



Scheme S1. Scheme for the synthesis of DDPDBCBIm$(Br)_2$ ionic liquid.

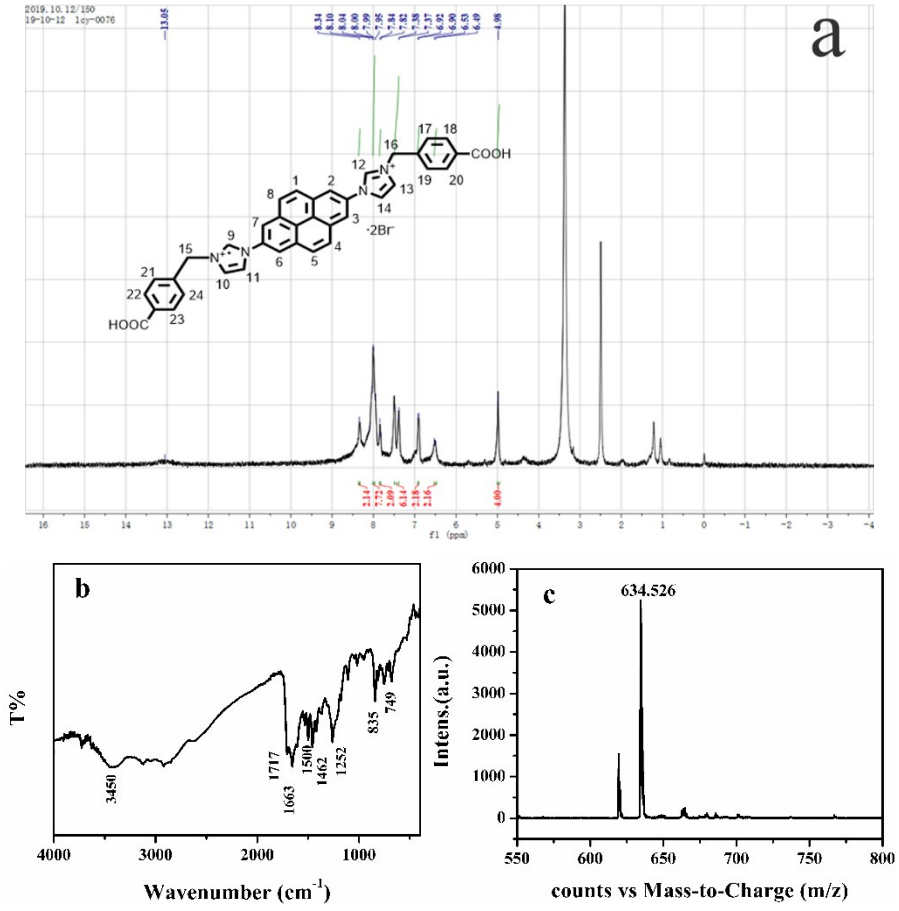


Figure S 1. ^{1}H NMR (a), FTIR (b), and MALDI-TOF-MS (c) spectra of DDPDBCBIm(Br)$_2$ ionic liquid.

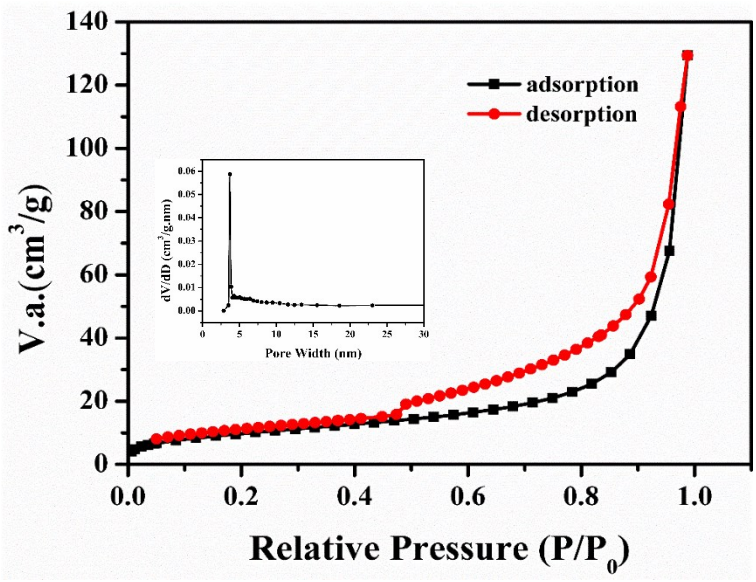


Figure S 2. BET adsorption-desorption isotherms of Yb-MOF. The inset is the corresponding pore size distribution

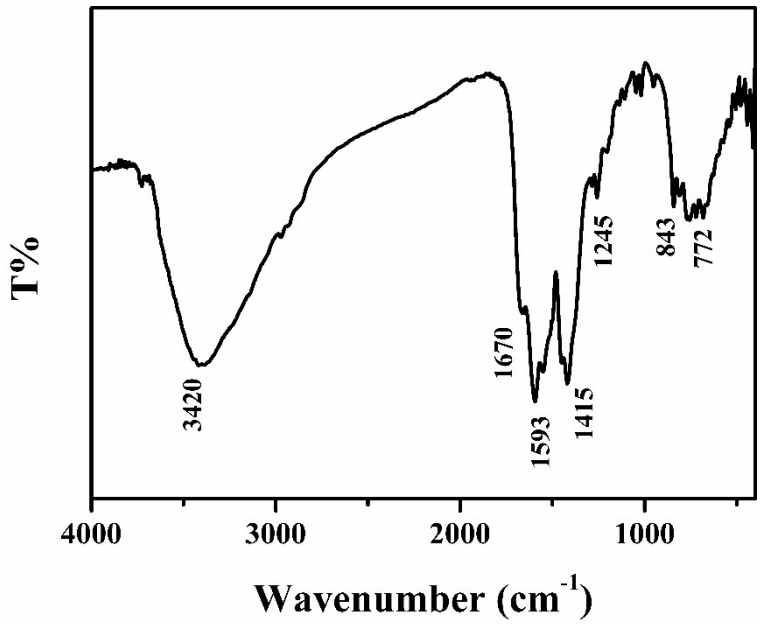


Figure S 3. FT-IR spectrum of Yb-MOF nanosphere.

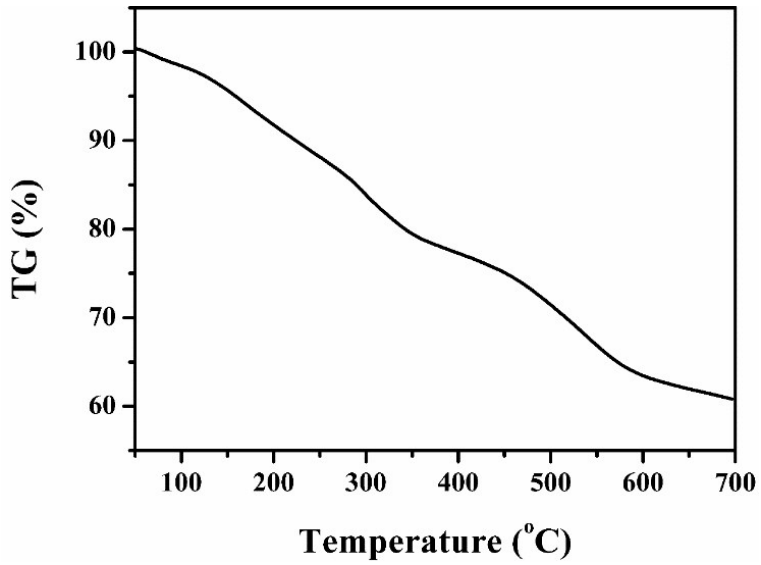


Figure S 4. TG curve of Yb-MOF nanosphere.

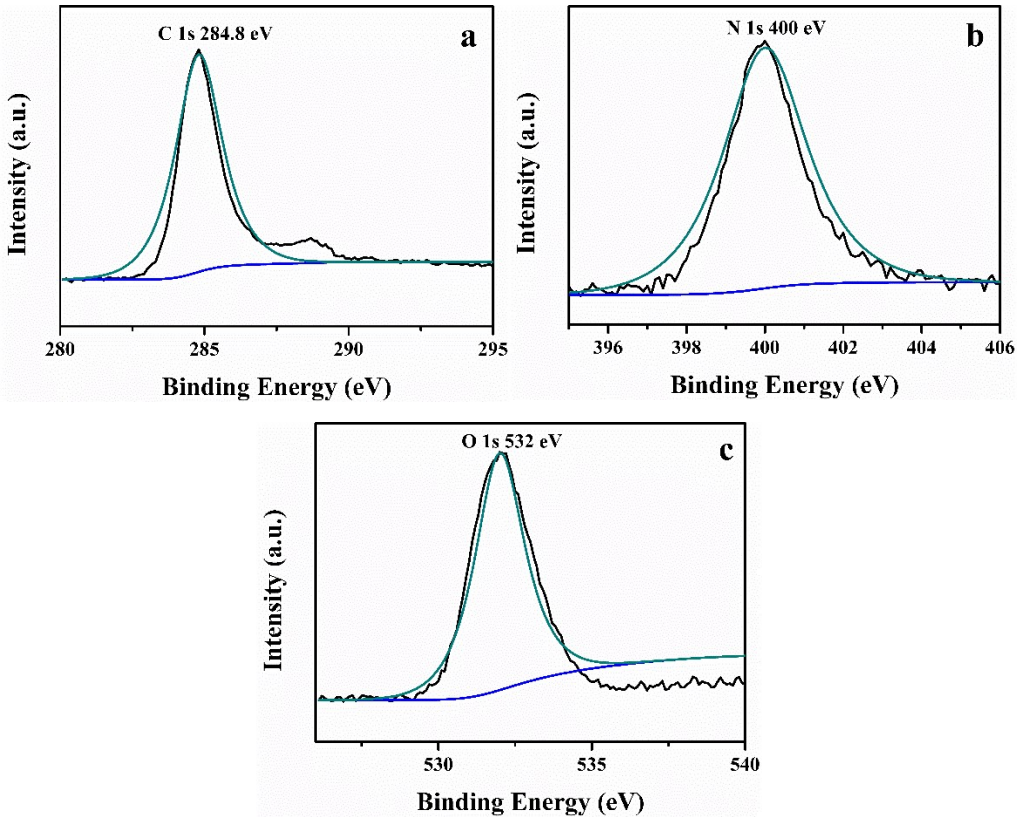


Figure S 5. High-resolution XPS spectra of C 1s (a), N 1s (b) and O 1s (c).

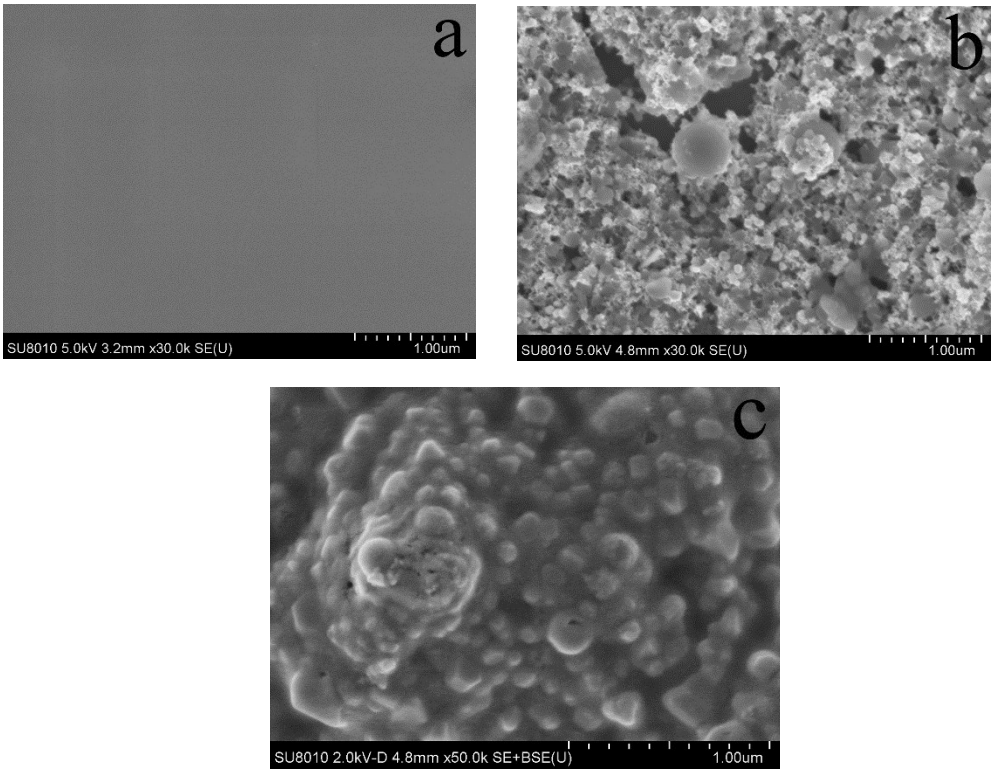


Figure S 6. SEM images of a bare GCE (a), a Yb-MOF@Au-NPs/GCE (b) and an anti-CEA/Yb-MOF@Au-NPs/GCE (c).

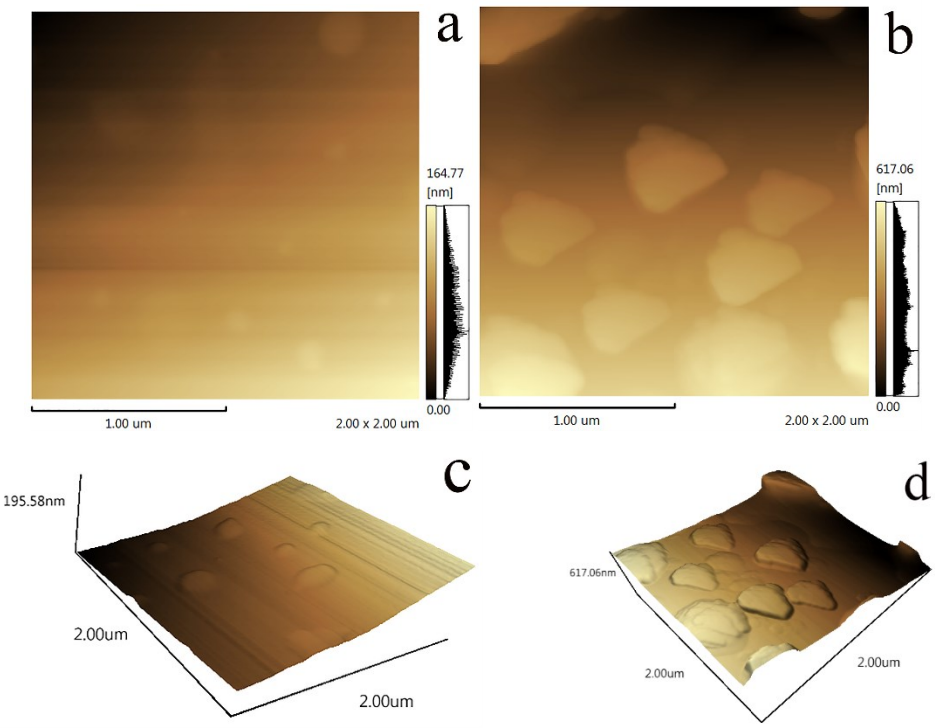


Figure S 7. AFM images of an Yb-MOF@Au-NPs/GCE (a) and an anti-CEA/ Yb-MOF@Au-NPs/GCE (b); 3D images of Yb-MOF@Au-NPs/GCE(c) and anti-CEA/ Yb-MOF@Au-NPs/GCE (d).

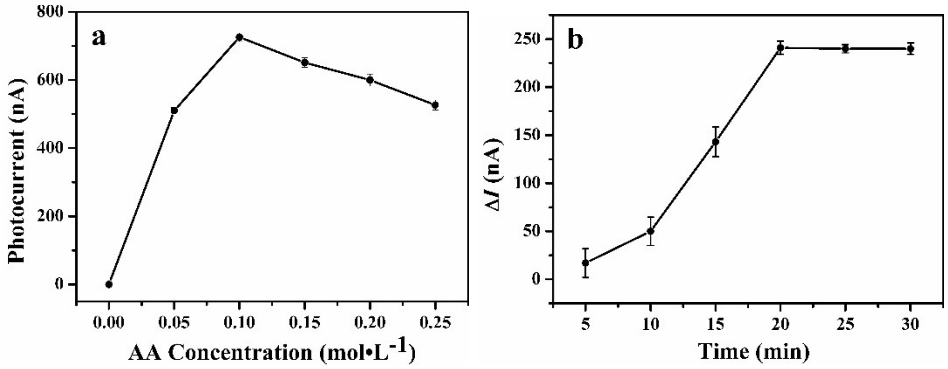


Figure S 8. Effects of the ascorbic acid concentration (a) and the incubation time (b) on the photocurrent response of 1.0 ng mL^{-1} CEA.

Table S 1. Simulation parameters of the equivalent circuit components

Electrode	R_s (Ω)	R_{ct} (Ω)	*Cdl* (F)	Z_w
GCE	118.3	60.15	7.313E-7	0.006688
Yb-MOF@Au-NPs/GCE	113.3	850.7	5.371E-6	0.003922
Anti-CEA/Yb-MOF@Au-NPs/GCE	230	1375	2.274E-6	0.002912
BSA/Anti-CEA/Yb-MOF@Au-NPs/GCE	174.1	2743	1.616E-5	0.004369
CEA/BSA/Anti-CEA/Yb-MOF@Au-NPs/GCE	369.3	4151	1.928E-6	0.004005

Table S 2. Merits of the PEC immunosensor for CEA determination.

Method	Linear range	Detection limit	Ref.
Electrochemical sensor	0.03-6.00 ng/mL	5.38 pg/mL	7
Electrochemiluminescence sensor	1.0 pg/mL-5.0 ng/mL	0.3 pg/mL	8
Fluorescence immunoassay	0.1-80 ng/mL	74.5 pg/mL	9
Photoelectrochemical sensor	0.1-20 ng/mL	0.05 ng/mL	10
Photoelectrochemical sensor	0.01-10 ng/mL	1 pg/mL	11
Electrochemical impedance spectroscopy	2.5ng/mL-1.5 μg/mL	3 ng/mL	12
Enzyme-linked immunosorbent assays	1-250 ng/mL	3 ng/mL	13
Photoelectrochemical sensor	0.005-15 ng/mL	0.25 pg/mL	This method

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