A photoelectrochemical aptasensor for sensitively monitoring chloramphenicol using plasmon-driven AgNP/BiOCl composites

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Experimental reagents

All chemicals used to prepare the samples were analytical grade without no further processing. Sodium hydroxide (NaOH), Potassium chloride (KCl), Sodium hydrogen phosphate(Na₂HPO₄), Sodium dihydrogen phosphate (NaH₂PO₄), Potassium ferricyanide (K₃Fe(CN)₆), Potassium ferrocyanide (K₄Fe(CN)₆·3H₂O), Trisodium citrate (C₆H₅Na₃O₇·2H₂O), Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O) and Silver nitrate (AgNO₃) were purchased from Sinopharm Chemical Reagent Corporation. 1-hydroxyethyl-3-methylimidazolium chloride ([HOEmim]Cl) were purchased from Shanghai Chengjie Chemical Co. Ltd. The CAP-aptamer for constructing PEC aptasensor was bought from Sangon Biotech (Shanghai) Co., Ltd. The sequences of CAP-aptamer: 5'-ACTTCAGTGAGTTGTCCCACGGTCGGCGAGTCGGTGGTAG-3'.

Preparation process

Synthesis of silver nanoparticle (AgNP)

According to reference,¹ AgNPs were prepared with subtle changes: 2 mL AgNO₃ solution (20 mM) was transfer to a clean round-bottomed flask and evenly distributed 90 mL water. The solution was boiling in the oil bath (stirring in the whole process) with the addition of 8 mL 2 wt% $C_6H_5Na_3O_7\cdot 2H_2O$ solution drop by drop. The mixtures were carried out continuous stirring in 20 min under electromagnetic stirring to obtain the brown AgNPs colloid solution.

Synthesis of AgNP/BiOCl composites

In the typical synthesis, BiOCl was synthesized by ionic liquid assisted hydrothermal method. 1mmol [HOEmim]Cl and 1mmol Bi(NO₃)₃·5H₂O was mixed in 20 mL H₂O and stirred until uniform. Subsequently, the mixture was transferred into Teflon-lined hydrothermal reaction vessel and heated at 160 °C for 24 h. The final product was collected by centrifugation and washed with ethanol and distilled water for many times. 66 mg BiOCl was suspended into 60 mL of distilled water at room temperature. 20 mL AgNPs colloid solution was added into the suspension in the beaker keeping 4 h electromagnetic stirring to obtain AgNP/BiOCl composites. AgNP/BiOCl composites was collected by centrifugation and washed with ethanol for many times, dried in the vacuum drying oven at 60 °C.

Apparatus

The crystallographic structure of the prepared specimens was tested by XRD6100 X-ray powder diffraction (Shimadzu, Japan) operated at 30 kV and 30 mA. Transmission electron

microscope (TEM) images were performed using JEM-2100F (JEOL, Japan) worked at 200 kV. The composition and valence of implanted element in the prepared specimens were analyzed by X-ray photoemission spectroscopy (XPS) measurements (Thermo ESCALAB 250XI system, America). UV-Vis diffuse reflectance spectroscopy was measured on UV-2600 spectrophotometer (Shimadzu Corporation, Japan). With a universal three electrode system, all the PEC experiments were tested at room temperature: modified tin oxide conductive (ITO) glass functioned as a working electrode, a Ag/AgCl electrode worked as the reference electrode and a Pt-wire auxiliary electrode as counter electrode. The PEC experiment (except single-color light excited PEC experiments) were carried out in a photoelectrochemical (PEC) system constituted with the CHI660E electrochemical workstation and a 300 W xenon high brightness source (PLS-SXE300, Beijing Perfectlight) as the light source. The single-color light excited PEC experiments were carried on by PLS-LED100B high power LED light sources (Beijing Perfectlight) with 365 nm and 450 nm monochromatic light sources, respectively. The electrochemical impedance spectroscopy (EIS) analysis was carried out at 0.24 V in the electrolyte made up of 5 mM [Fe(CN)₆]^{3-/4-} equimolar and 0.1 M KCl, and the frequency range was from 0.1 Hz to 100 KHz.

The band gap of BiOCl can be evaluated (Fig. S1) by the mentioned below formula: $\alpha hv = A(hv - E_g)^{n/2}$,² where α , h, v, A and E_g represents absorption coefficient, Planck constant, incident optical frequency, semiconductor band gap and ratio constant, respectively. The E_g of BiOCl was calculated to be 3.28 eV. For BiOCl, the conduction band (CB) position was calculated by the following empirical equation: $E_{CB} = X - E_e - 0.5E_g$,³ where X is semiconductor electronegativity (the geometric average of constituent atomic electronegativity), E_e represents free electrons energy on the hydrogen atomic-scale (4.5 eV), E_{CB} represents CB potential. The E_{CB} valve of BiOCl was measured to be 0.09 eV.



Fig. S1 Band gap value of BiOCl estimated from the plotted curve.

Owing to the promoting effect of bias potential on the photogenerated electrons separation, the photocurrent response increases with change of bias potential in the range from 0.2 V to –0.3 V (Fig. S2).^{4,5} Nevertheless, high bias potential usually brings out other side reactions originated from the other interferences in the sample.⁶ It is obviously shown that the enhancement of photocurrent markedly slowed down when the bias potential exceeds –0.2 V. Thus –0.2 V was chosen as the appropriate bias potential in the construction of the PEC aptasensor to diminish interference caused by high bias potential. Generally, the pH value can impact the charge properties of the AgNP/BiOCI composites interface in the buffer solution. As a turning point, the pH value 7 is chosen to further assemble PEC aptasensor owing to the remarkable photocurrent response (Fig. S3). The aptamer are not only specific active sites, but also possess large steric hindrance. Consequently, it is necessary to choose appropriate aptamer concentration to construct PEC aptasensor. With the increase of CAP concentration, the photocurrent response of the aptamer/AgNP/BiOCI/ITO gradually decrease, demonstrating the photocurrent change is related to aptamer concentration (Fig.

S4). Give consideration to photocurrent change and the amount of aptamer dosage, 2 μ M CAPaptamer was used as the optimum concentration for the construction of the PEC CAP aptasensor.



Fig. S2 Effects of bias potential on photocurrent response of aptamer/AgNP/BiOCl/ITO electrodes.



Fig. S3 Effects of pH of the electrolyte on photocurrent response of aptamer/AgNP/BiOCl/ITO electrodes.



Fig. S4 Effects of aptamer concentration on photocurrent response of aptamer/AgNP/BiOCl/ITO electrodes in 0.2 pM CAP.



Fig. S5 Photocurrent response of the aptamer/AgNP/BiOCl/ITO electrode in 0.5 pM CAP under continuous illumination.

For investigating the reproducibility of the PEC aptasensor, the photocurrent response of the six aptamer/AgNP/BiOCl/ITO electrodes were tested in the presence of 10 nM CAP. The photocurrent response valve is 0.344, 0.368, 0.350, 0.355, 0.364 and 0.356 μ A, respectively. Consequently, the RSD value was 2.49%. Calculation formula

$$SD = \sqrt{\frac{\Sigma(x_i - x)^2}{n - 1}}$$

$$RSD = \frac{SD}{x_i} * 100$$

$$x_1 = 0.344, x_2 = 0.368, x_3 = 0.350,$$

$$x_4 = 0.355, x_5 = 0.364, x_6 = 0.356$$

$$x = 0.356,$$

$$SD = \sqrt{\frac{\Sigma(x_i - x)^2}{n - 1}} = 0.00886,$$

$$RSD = \frac{SD}{x_i} * 100$$

$$RSD = \frac{SD}{x_i} * 100$$



Fig. S6 Reproducibility of aptamer/AgNP/BiOCl/ITO electrodes in 10 nM CAP.

Sample	Added (nM)	Found (nM)	Recovery	RSD (%, n=3)
1	0.100	0.0972	97.20%	2.30%
2	2.000	1.983	99.15%	1.40%
3	5.000	5.267	105.34%	5.70%
4	10.000	10.253	102.53%	4.50%

Table. S1 The determination of CAP in real water using the PEC aptasensor.

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