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# THCH as electron donor in controlled-release system for procalcitonin analysis based on $Bi_2Sn_2O_7$ photoanode

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ABSTRACT

A split-type photoelectrochemical (PEC) sensor for procalcitonin (PCT) detection was successfully prepared. This split-type sensor adopted controlled-release strategy, which separated the two processes of antigen-antibody specific recognition and photoelectric conversion, so that the two processes can be performed independently. In addition, CdS sensitized $Bi_2Sn_2O_7$ is combined for the first time to form a heterojunction as the matrix to provide the basic PEC response, which could effectively absorb visible-light, and reduced electron-hole pair recombination, ensured the stability of the sensor. Distinctly important, the skillfully process was performed in a 96-well plate where the specific reaction was completed proceeded between antigen and antibody. For improving sensitivity of the sensor, acetylcholinesterase (ACHE) connected to $SiO_2$ nanospheres ($SiO_2$ NSs) modified by second antibody ($Ab_2$-ACHE@$SiO_2$ NSs) was designed, the thiocholine (THCH) can be released when acetylthiocholine iodide (ATCH) exists, and the THCH as an electron donor could enhance PEC response. The proposed PEC immunoassay with high-performance photosensitive materials, and the smart electron donor released strategy have a wide detection liner range from 0.0005 to 100 ng/mL with a low detection limit of 0.17 pg/mL, also provide great clinical diagnostic potential for other target proteins.

## 1. Introduction

In the world, a large proportion of patients occupying a mass of medical resources are suffering from sepsis [1–3]. Sepsis is a disease caused by bacterial or fungi, and the incidence of sepsis has increased year by year since the 21st century [4]. Sepsis is mainly divided into three stages according to the degree of inflammation: sepsis, severe sepsis, septic shock. Patients with early sepsis have mild symptoms, and early treatment with antibiotics can be used to achieve effective cure, but if no measures are taken, septic shock can be achieved in just a few hours. At this stage, the patient will have severe shock, and the mortality rate is as high as 70 % [5]. Therefore, if sepsis can be detected early and treated promptly, the mortality of sepsis will be greatly reduced. Procalcitonin (PCT) is the more accurate biomarker for the diagnosis of sepsis so far, and can effectively distinguish between sepsis and other types of infections [4]. Thus, if the concentration of PCT in the body is detected quickly and accurately, the development stage of sepsis can be ascertained, which can help the patient to be treated accurately in time. Also antibiotic was used in moderation to reduce the waste of intensive care unit resources, moreover, prevented from abusing to increase its resistance [6,7].

As a yet, many methods have been developed for the detection of PCT, such as electrochemiluminescence immunoassay [8], chemiluminescence immunoassay [9], fluorescence assay [10] and radioimmunoassay [11]. However, the development of these methods do not go with a swing. Therefore, novel and accurate method for PCT detection is urgently needed. Photoelectrochemical (PEC) immunosensor is an extremely rapid detection technique in recent years due to its special high-efficiency photoelectric conversion units [12], in which it converts into an electric signal by absorbing light signal, the unique signal conversion mode prompts the low background signal for high sensitivity [13,14]. In view of this, a split-type PEC sensor is studied with high sensitivity, great accurate, and satisfactory stability for PCT detection by controlled-release method.

In this work, a novel PEC sensor based on a unique $Bi_2Sn_2O_7$/CdS nanocomposite photoactive conversion unit, and controlled-release strategy of signal amplification was prepared. These two parts are completely separated [15] via 96-well plate, thus, the amplification and

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stability of the photocurrent signal were achieved successfully. And the selection of photoactive materials $Bi_2Sn_2O_7$/CdS was proposed for the first time. Recently, bismuth-based metallic salt materials are particularly prominent in inorganic photoelectric materials due to their first-rate photoelectric properties and good absorption in visible light range, such as $Bi_2O_3$ [16], $BiVO_4$ [17], $BiYWO_6$ [18], $Bi_2WO_6$ [19]. In the process of studying these materials, $Bi_2Sn_2O_7$ was found to be extremely impressive, however, only a single inorganic material cannot meet the needs of sensitivity and stability of photoelectric immunosensor materials, therefore, the combination of CdS (photo sensitizer, ~2.4 eV) matching the band gap of $Bi_2Sn_2O_7$ (~2.76 eV) is introduced to form heterojunction [20]. Based on this, $Bi_2Sn_2O_7$ and CdS are combined to form a heterojunction that will make both stimulated by a photon to form stronger built-in electric field, which promotes the formation and separation of the carrier, as well as prevents the recombination of electron-hole, thus, the signal intensity and stability were increased [21]. Secondly, we innovated a specific reaction carried out in an individual 96-well plate, second antibody ($Ab_2$) was connected to functional carrier $SiO_2$ nanosphere ($SiO_2$ NSs), and with a specific surface for specific recognition of target PCT (Ag), also acetylcholinesterase (ACHE) is used decorated with $SiO_2$ NSs, which is used to catalyze form thiocholine (THCH) [22] after adding its substrate acetylthiocholine iodide (ATCH). The solution containing THCH generated in the microplate is transferred to the detection electrolyte solution, which could act as electron donor [23] for the photo-generated holes of the photoactive materials [24,25], thereby it greatly limited the recombination of the electron-hole pairs, and improved photocurrent [26]. The PEC immunosensor we proposed owns a great photocurrent response due to the dual signal amplification strategy, good stability, and extremely high sensitivity. Based on the above advantages, the sandwich PEC immunoassay can accurate monitor PCT, and has potential development space in clinical medicine.

## 2. Experimental section

### 2.1. Synthesis of $Bi_2Sn_2O_7$

$Bi_2Sn_2O_7$ was prepared according to the previous report with some changings [27]. To begin, 0.90 g of $SnCl_4{\cdot}5H_2O$ was dispersed in 20 mL ultrapure water with stirring for 15 min under room temperature. Subsequently, the pH of the above solution was transformed to 6 by alkaline solution (NaOH, 4 M). After centrifugation, the obtained precipitate and 1.94 g of $Bi(NO_3)_3{\cdot}5H_2O$ were co-dispersed into 40 mL ultrapure water under vigorously stirring. The pH of the resulting suspension was transformed into 12, and subsequently transferred to a Teflon-lined autoclave holding at 180 °C for 24 h. After that, the substance was cleaned with ultrapure water for 3 times. Ultimately, $Bi_2Sn_2O_7$ power was obtained after dried at 60 °C.

### 2.2. Synthesis of $Ab_2$-ACHE@$SiO_2$ NSs

The aminated $SiO_2$ was synthesized according to our previous report [22], and the bioconjugates was prepared as follows: firstly, aminated $SiO_2$ was dissolve into PBS (pH 7.4) buffer solution (5 mg/mL), then 5 mL of glutaraldehyde was added into 2 mL aminated $SiO_2$, and stirred for 6 h at 25 °C. Then, aldehyde-$SiO_2$ was obtained after centrifugation and washed by PBS (pH 7.4) to remove glutaraldehyde. After that, the obtained $SiO_2$ was dissolved in 1 mL PBS with the mixture of 400 μL of $Ab_2$ (12 μg/mL) and 200 μL of ACTH solution (30 μg/mL) added, the above solution was shocked for an hour. The obtained solution was centrifuged and cleaned with buffer solution (pH 7.4), and then scattered into 2 mL PBS, at the same time, 80 μL of 1% BSA solution was joined into with vibrating for another hour to block nonspecific active site. After centrifugation and washed a time with PBS, the obtained product scattered into 5 mL PBS (pH 7.4) solution, and saved at 4°C. Other details for materials synthesis were shown in *Supplementary Materials* file.

### 2.3. Fabrication of immunosensor and photocurrent measurements

ITO slices were incised into 2.0 × 1.0 $cm^2$ pieces, then cleaned by ultrasonic in acetone, ethanol and ultrapure water for 30 min, separately [28]. The ITO substrates were dried in the oven at 70 °C. Firstly, 10 μL of $Bi_2Sn_2O_7$ was dropped onto an ITO, and then dried in air, 10 μL of CdS (5 mg/mL) was dropped onto the obtained electrode to form $Bi_2Sn_2O_7$/CdS modified electrode.

Firstly, 50 μL of capture antibody ($Ab_1$) was dropped into 96-well plate, and placing it at 4 °C overnight to ensure that the $Ab_1$ is firmly bound to the 96-well plate. The unbound PCT $Ab_1$ was carefully washed twice with PBS buffer solution (All the buffer solutions here with a pH of 7.4). Then 25 μL of 1 % BSA prepared in PBS was added into the 96-well plate with incubating for 1 h, then aspirated unbound BSA and washed the 96-well plate. Later, 50 μL of PCT (different concentrations) were dropped into the 96-well plate and incubated for another 1 h. After that, 50 μL of $Ab_2$-ACHE@$SiO_2$ NSs was dropped into the 96-well plate, and incubated at 25°C for 1 h. The plate was washed with PBS carefully after every modification process. Then 100 μL of ATCH (2 mg/mL) was added into the 96-well plate for catalyzing 15 min. Finally, the solution was aspirated from 96-well plate, and injected into 10 mL of PBS buffer solution. The obtained solution containing THCH was transferred into a detection cell, and with the three-electrode system, a white light source between 400–700 nm was used to test the photocurrent signal [22], the wavelength range of the stimulation resource has been shown in the Fig. S1. When the excitation light source illuminates the photosensitive material, the electrons in the valence band absorb the energy of the photon to be excited, and the electrons with energy greater than the width of the forbidden band will be excited to the conduction band to form electron-hole pairs, and the electrons in the excited state will transfer to ITO, the holes left in the valence band will react with the released THCH from the 96-well plate, thus, directional photocurrent is formed. The process is shown in Scheme 1.

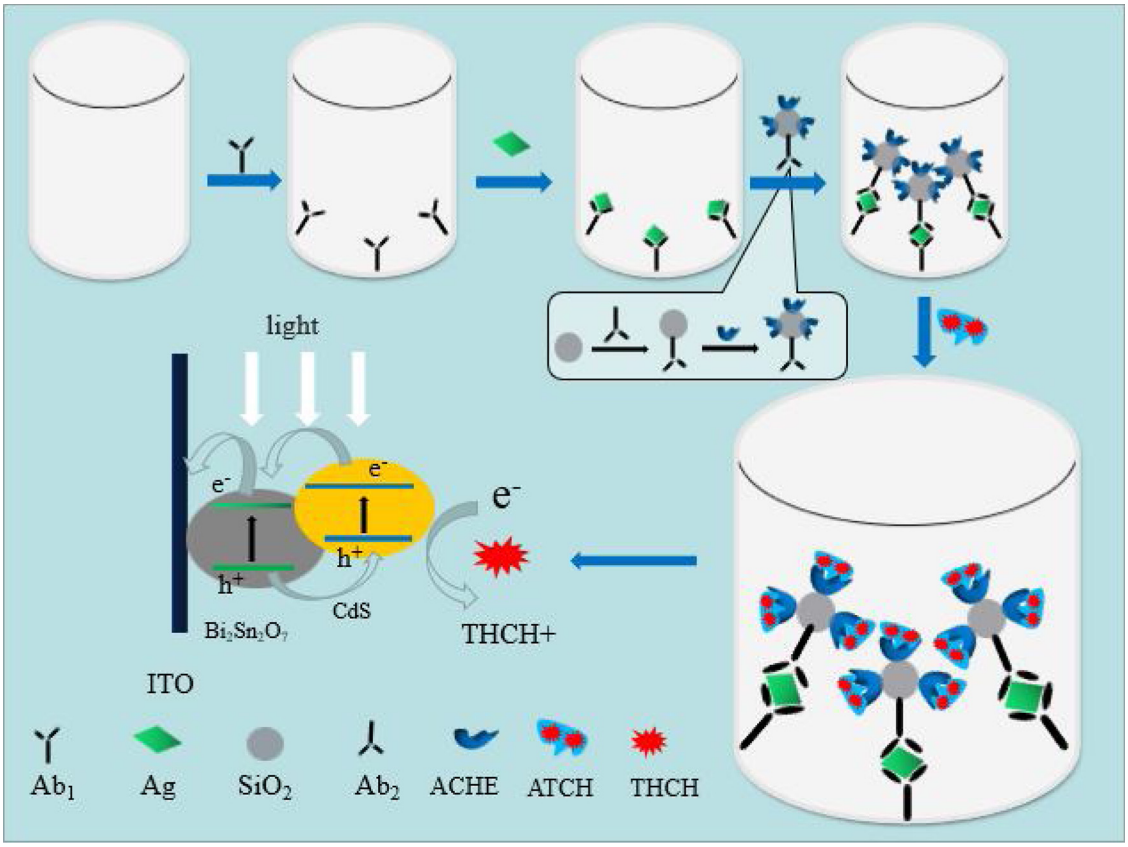
## 3. Results and discussion

### 3.1. Characterization of synthesized materials

The lattice structure of the basic $Bi_2Sn_2O_7$ material was characterized by XRD patterns (Fig. 1A), which proved that the crystal structures of $Bi_2Sn_2O_7$ was more successful and contains no other impurities. In addition, XPS image (Fig. 1B) also proved the purity of this material, further verifying the successful synthesis of $Bi_2Sn_2O_7$. Fig. S2 showed the XPS peaks of Bi and Sn elements, the particular XPS peaks of 1021.3 eV and 1044.25 eV in Fig. S2A fit well with Bi 2p, proving the +3 valence state of Bi, and the peaks of Sn $2p_{1/2}$ (161.75 eV) and S $2p_{3/2}$ (160.65 eV) were assigned to Sn (Fig. S2B) [29,30]. Fig. 1C proved the SEM image of $Bi_2Sn_2O_7$ was in the shape of nanoparticles with a diameter size about 20 nm. Fig. 1D showed the results of the TEM image of CdS, the diameter of CdS particles was about 2 − 5 nm. Fig. 1E demonstrated the SEM of $SiO_2$ NSs, it can be clearly seen from the figure that the functional $SiO_2$ exhibited uniformly textured nanospheres, so that sufficient enough protein molecules can be loaded on the surface of $SiO_2$ NSs. Fig. 1F showed the UV–vis spectrum of $Bi_2Sn_2O_7$, CdS, $Bi_2Sn_2O_7$/CdS, which proved that the combination of heterojunction greatly broadened the absorption of light of different wavelengths, making it absorbable in the visible light region, greatly increases the efficiency of light utilization and further improves the sensor photocurrent response.

### 3.2. Optimization of the experimental conditions

Some efforts have been made to optimize measurement conditions for more sensitive and stable PCT detection in the actual detection




**Scheme 1.** Fabrication Process of Photoelectrochemical Immunosensor.

process [31], including the pH of PBS, and the reaction time between ACHE and its substrate ATCH. The pH of the solution has a vital impact on the activity and specificity of immune molecules, the PBS solutions were prepared with different ladder concentrations (5.3, 5.9, 6.8, 7.4, 8.0), as can be seen from the Fig. 2A, the overall trend of photocurrent gradually increased from a smaller value, and finally fell back, it is obviously showed that the photocurrent reached its optimal value at pH 7.4, and 7.4 was finally took as the ideal pH value of reaction conditions. The work for the reaction time of enzyme and its substrate are also optimized. First of all, we roughly determined the time of the

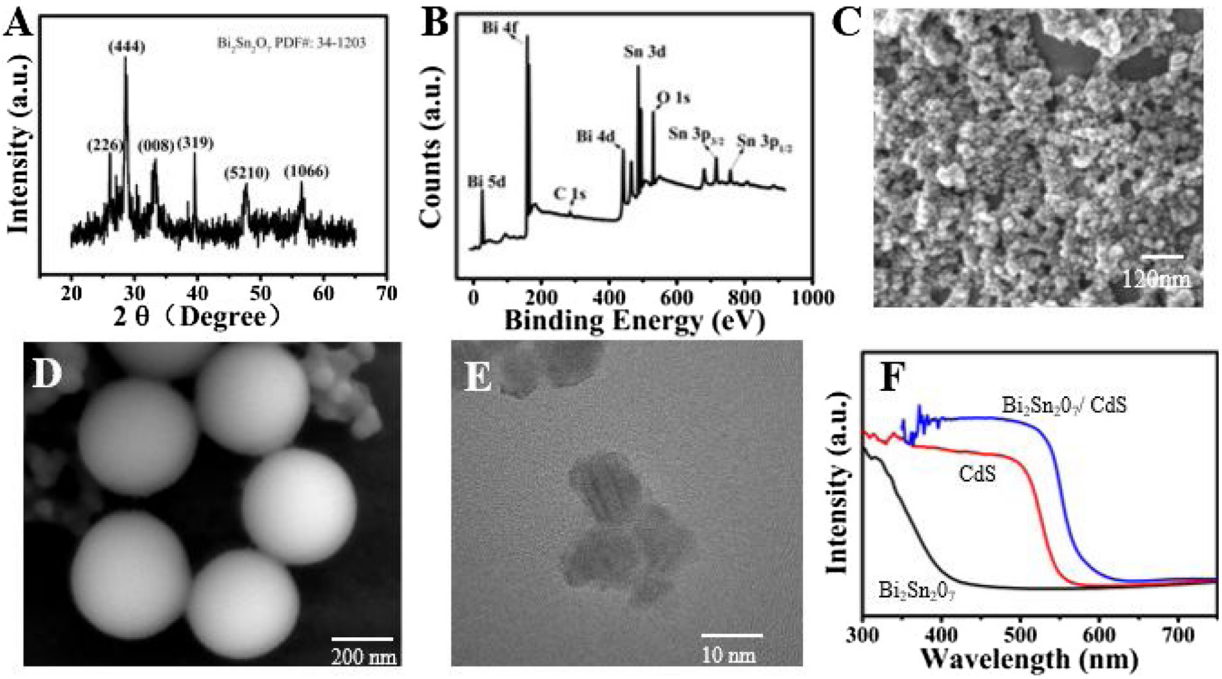



**Fig. 1.** (A) XRD image of $Bi_2Sn_2O_7$, (B) XPS image of $Bi_2Sn_2O_7$, (C) SEM image of $Bi_2Sn_2O_7$, (D) TEM image of CdS, (E) SEM image of $SiO_2$, (F) UV–vis diffuse reflectance spectra of $Bi_2Sn_2O_7$, CdS, $Bi_2Sn_2O_7$/CdS.

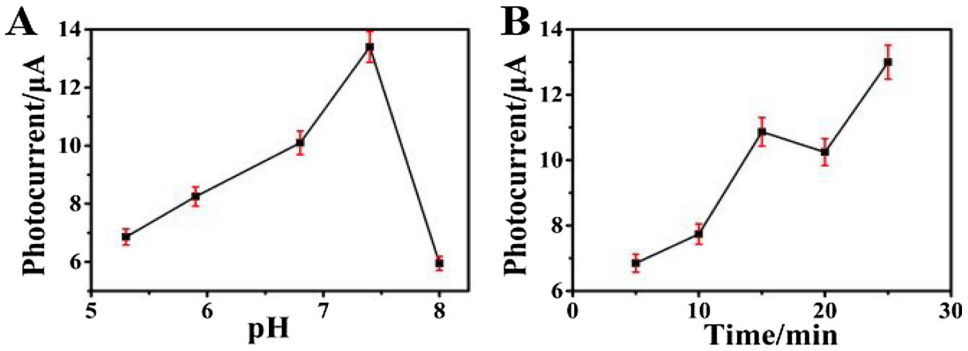



**Fig. 2.** (A) The effect of pH value of PBS solution; (B) The effect of the reaction time of ATCH. Error bars = SD ($n$ = 3).

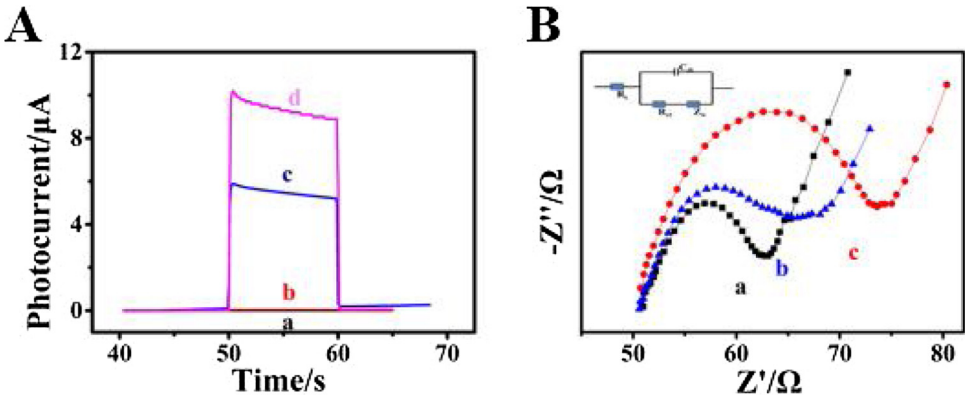



**Fig. 3. (A)** PEC signal and (B) Nyquist diagrams of (a) the bare ITO electrode, (b) $Bi_2Sn_2O_7$/ITO, (c) $Bi_2Sn_2O_7$/CdS/ITO (PBS solution), (d) $Bi_2Sn_2O_7$/CdS/ITO (PBS solution containing released THCH from 96-well plate, $c_{PCT}$ = 0.05 ng/mL). Inset in B: equivalent circuit for EIS.

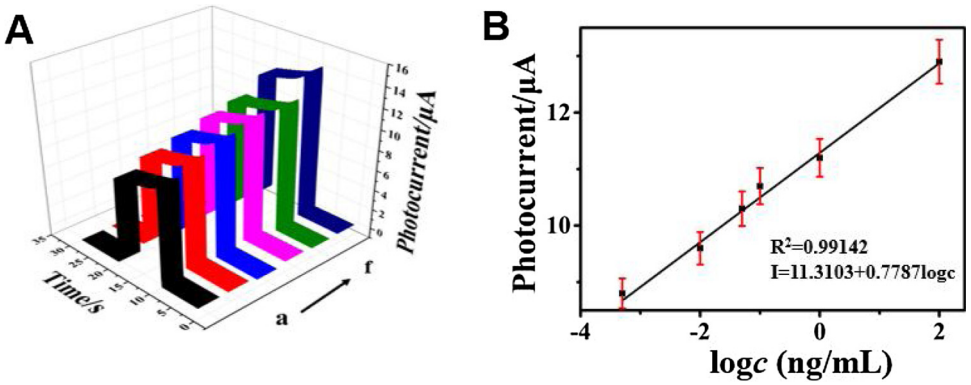



**Fig. 4.** (A) PEC response and (B) Calibration plot of ITO/$Bi_2Sn_2O_7$/CdS electrode toward PCT at different concentrations: (a-f): 0.0005, 0.01, 0.05, 0.1, 5, 100 ng/mL. Error bars = SD ($n$ = 3).

release of THCH within 30 min, then choose node for every 5 min, and at different time points (5 min, 10 min, 15 min, 20 min, 25 min) to select solution containing THCH in 96-well plate for photocurrent testing. From the Fig. 2B, photocurrent signal was gradually enlarged within 15 min, meanwhile, the photocurrent signal was reduced the next time, also extremely unstable, so 15 min was selected for the later measurement.

### 3.3. Characterization of the immunosensor

This part of the work demonstrated the successful construction of the immunosensor. These experiments were carried out in PBS solution [32]. As shown in Fig. 3A, curve a reflected the unmodified working electrode has no photocurrent response, and then curve b verifies when $Bi_2Sn_2O_7$ was modified onto ITO, the photocurrent was enhanced. After CdS was loaded onto the $Bi_2Sn_2O_7$ electrode, the photocurrent was further enhanced due to the formation of $Bi_2Sn_2O_7$/CdS heterojunction (curve b). After the released THCH was dripped into PBS solution, the electron donor (THCH) promoted the photocurrent increased significantly (curve d). The results of these curves showed that the layer-by-layer modification of the sensor electrode is extremely successful. In addition, in order to further verify the success of electrode modification, electrochemical impedance spectrum (EIS) was applied to characterized the above processes. It can be seen from the Fig. 3B, the resistance value of the modified electrode increased each layer in different degrees, which is also in line with the characteristics of the electrode of successful modification.

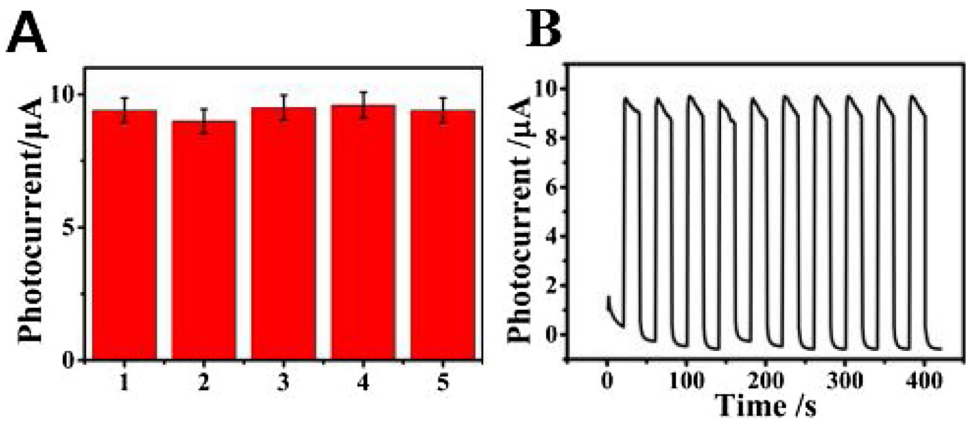



**Fig. 5.** (A) The reproducibility and ($c_{PCT}$ = 0.05 ng/mL) (B) stability test of the sensor. ($c_{PCT}$ = 0.005 ng/mL) Error bars = SD ($n$ = 3).

### 3.4. PCT analysis

In order to test the performance of the invented split-type sensor for the quantitative analysis of PCT, the following work was completed. The addition of different concentrations of PCT in a 96-well plate further resulted in different amounts of binding of ACHE and ATCH, further leading to the difference in THCH released by the combination of the two. In the process of PEC signal test, THCH as an electron donor generated in the 96-well plate further improved the PEC response, and the sensitivity of the sensor. Fig. 4A showed the minimum concentration of the antigen obtained the smallest photocurrent, as the antigen concentration increasing, the photocurrent also increased in order. Finally, we reached the antigen in the range of 0.0005 − 100 ng/mL, and the relationship linear equation between the concentration and photocurrent is $I = 11.31 + 0.7787\log c$ (ng/mL) with a correlation coefficient of 0.9914, and the limit of detection (LOD) was experimentally found as 0.17 pg/mL. It can be seen that by using this type of sensor, the antigen concentration was accurately obtained based on the magnitude of the obtained photocurrent. In order to prove the superiority of this detection method in biological detection, we made a corresponding comparison, and the comparison results were listed in detail in Table S1, it can be concluded that this detection method of controlled-release strategy has strong superiority.

### 3.5. Reproducibility and stability of the PEC immunosensor

For the determination of disease marker in clinical medicine, in addition to the quantitative relationship between signals and antigens, stability and repeatability are also extremely important aspects. Fig. 5A showed the same construction procedure for PEC detection and ($c_{PCT}$ = 0.05 ng/mL) the RSD was 4.7 %, which was a good proof of the reproducibility of the immunosensor. Fig. 5B displayed the relationship between the photocurrent signal and time after the light was turned or off for several cycles, the stability of such sensors was demonstrated.

### 3.6. Real samples detection

All of the detection models were developed for better clinical application, in order to test the reliability of the actual application of the sensor, real samples were tested using the standard addition method. Different concentrations of PCT (0.02, 0.20, 2.00 ng/mL) in human serum (0.15, 1.25, 3.75 ng/mL) were detected, and the data obtained were listed in Table S2. As can be seen from the Table S2, RSD was in the range of 2.52–4.33 %, and the recovery rate was in the range of 97–103 %. According to the data obtained, this sensing detection model has great clinical detection potential.

## 4. Conclusion

A split-type immunosensor based on electron donor controlled-release strategy was successfully prepared. The significant advantage of this split-type sensor was that it separated the two processes of immunoreaction and PEC measurement, eliminating the interfering with each other. The outstanding electrode used for signal testing was modified with inorganic material heterojunction, and the THCH as electron donors were completely controlled released in 96-well plate, owing a very low detection limit, and exhibits good stability, reproducibility, and anti-interference. In addition to the above advantages, the developed sensor can achieve advance storage, so that the pursuit of rapid detection in clinical medicine can be realized.

## CRediT authorship contribution statement

**Dongquan Leng:** Conceptualization, Data curation, Writing - original draft. **Jingshuai Li:** Methodology, Data curation. **Rui Xu:** Methodology, Data curation. **Lei Liu:** Methodology, Writing - review & editing. **Xuejing Liu:** Methodology, Writing - review & editing. **Dawei Fan:** Writing - review & editing. **Huan Wang:** Formal analysis, Project administration. **Qin Wei:** Supervision, Funding acquisition, Formal analysis. **Huangxian Ju:** Formal analysis.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.snb.2020.128509.

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