Technical Note

A sunlight powered portable photoelectrochemical biosensor based on potentiometric resolve ratiometric principle

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A sunlight powered portable photoelectrochemical biosensor based on potentiometric resolve ratiometric principle

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Abstract

As a new analysis tool, photoelectrochemical (PEC) biosensors have been widely studied in recent years. However, common PEC biosensors usually require a high stable light source to excite the electrical signal and an electrochemical workstation to collect and process the signal data, which limited the development of portable PEC devices. Herein, we propose the design of a sunlight powered portable PEC biosensor that use sunlight as the light source. The sunlight intensity changes over time and weather and bring varied background PEC currents. To eliminate the interference caused by unstable excitation light, the potentiometric resolve ratiometric principle was introduced. Coupled with a miniature electrochemical workstation and a laptop, a sensitive and portable PEC sensing platform was successfully developed. The detection may be achieved under the irradiation of sunlight and no longer need an extra light source. In a proof of concept experiment, this platform was successfully applied in Aflatoxin B1 analysis, which was promising in the development of portable biosensors.

Keywords: photoelectrochemical biosensor; portable; sunlight; mycotoxin

1. Introduction

As a newly developed technique, photoelectrochemical (PEC) analysis has attracted great interests due to the advantages of high sensitivity, low cost and easy operation[1]. In the PEC process, the electrical signals were generated by PEC active materials modified on the electrode under light irradiation[2-5]. And target concentrations may be quantified based on the electrical signal change with the assistant of recognition probes[6,7]. The combination of PEC processes and electrochemical bioanalysis has been extensively studied[8-11]. Among those considerable efforts to improve PEC sensing, various novel materials with excellent PEC activity have been prepared. Many signal transformation principles, such as enzyme catalysis[12-14] and energy transfer[15-17], have been well studied. And PEC biosensors have been widely applied in fields of DNA analysis[11,18], immunoassays[19-21], enzymatic sensing[10,22,23], cell-associated detection[24-28], food safety[29,30] and environmental monitoring[31,32], etc. However, the development of portable PEC biosensors is still at an early stage. Portability is crucial for demands of on-site detection, such as point-of-care testing or anti-terrorism. Most PEC biosensors lack enough portability, which seriously limited their practical application ranges.

In traditional PEC instruments, there're two main components, the light source to excite the electrical signal and the electrochemical workstation to collect and process the signal data. With the fast development of electronic technology, the miniaturization of electrochemical work station has been realized, which facilitated the advent of portable electrochemical sensing device. But it's difficult to reduce the

volume of light source because of the requirement of long-term stability. A highly stable light source is necessary because the PEC current is directly related with the light intensity. The instability of light source may bring a false positive or negative detection result[33,34]. In previous efforts to develop portable PEC sensing platform, an approach is to use chemiluminescence (CL), the emission of light generated in chemical reactions to excite PEC active materials in the replacement of conventional external light device[35]. For example, Ding et al. reported a new PEC strategy or the determination of physiological thiols in cancer cells with the utilization of the isoluminol–H_2O_2–Co^{2+} CL system as a light source for the first time[36]. On this base, CL system can further be combined with microfluidic paper-based analytical devices (μPADs) as an integrated internal CL light source to fabricated disposable and cost-effective microfluidic PEC origami device[37]. These works about self-illuminated light by CL system have conducted meaningful explorations. However, it's obvious that the CL intensity is much weaker than common light source, such as xenon lamp or mercury lamp. In CL sensing, the CL signal often need to be amplified by photomultiplier tube to achieve sensitive detection, which indicates the PEC signal generated under CL irradiation would be much weaker than usual values. Of course, the weak PEC signal also can be collected and quantified. But it will be better if the PEC current can keep similar values while getting rid of cumbersome light source devices.

To solve this problem, here we propose a feasible method that use sunlight to excite PEC signals. As a strong and unstable light source, the sunlight intensity

changes over time and weather, which cannot be used in traditional PEC biosensors due to the varied background current. In this work, the interference caused by unstable excitation light was eliminated through the potentiometric resolve ratiometric principle. Coupled with a miniature electrochemical workstation and a laptop, a sensitive and portable PEC sensing platform was successfully developed. The detection may be achieved under the direct irradiation of sunlight and no longer need an extra light source. Aflatoxin B1 (AFB1) is a highly toxic carcinogen and mainly found in agricultural and sideline products such as cereals and dairy products. In a proof of concept experiment, this portable platform was applied in AFB1 detection and showed an excellent performance with a wide linear range (1.0 pg·mL^{-1} to 100.0 ng·mL^{-1}) and a lower detection limit of 0.25 pg·mL^{-1} (S/N=3).

2. Experimental

2.1. Reagents and Chemicals

Graphene oxide (GO, 2.0 mg·mL^{-1}) solution was obtained from Nanjing XFNANO Materials Tech Co., Ltd. Amino-functionalized AFB1 aptamer was purchased from Sangon Biotech Co., Ltd (Shanghai, China), and the sequence as following: 5'-NH_2-C_6-GTT GGG CAC GTG T TG TCT CTC TGT GTC TCG TGC CCT TCG CTA GGC CCACA-3'. Chitosan (CS) and bovine serum albumin (BSA) were offered from Sigma-Aldrich Co. (St. Louis, MO, USA). In addition, $Ti(SO_4)_2$, glycine (Gly), $AgNO_3$, N, N-dimethylformamide (DMF), sodium hydroxide (NaOH), sodium dihydrogen phosphate ($NaH_2PO_4 \cdot 2H_2O$), disodium hydrogen phosphate ($Na_2HPO_4 \cdot 12H_2O$) and ethanol were provided from Sinopharm Chemical Reagent Co.,

Ltd. Phosphate buffer solutions (PBS, 0.1 $mol \cdot L^{-1}$) were prepared from NaOH, Na_2HPO_4, and NaH_2PO_4. All other chemicals were of analytical grade, and the aqueous solutions were prepared with ultra-pure water.

2.2. Preparation of materials and sensors

Preparation of Ag/TiO_2/3DNGH hydrogels: Firstly, 100.0 mg Glycine (Gly), 0.24 g $Ti(SO_4)_2$ as well as 30.0 mg silver nitrate were added into 10.0 mL GO solution and sonicated for 1 h[38]. Then, the above suspension was transferred into a Teflon-sealed autoclave, which was maintained at 180 °C for 12 h. At this point, Ag/TiO_2/3DNGH hydrogels were successfully prepared. Finally, the above hydrogels were washed with ultra-pure water and then were freeze dried for 2 days.

Carbon nitride nanosheet (CNNS) was prepared according to the literature method[39], details were provided in the supplementary material.

Fabrication of the ratiometric PEC aptasensor for AFB1: 20.0 μL of Ag/TiO_2/3DNGH hydrogels dispersion (2.0 $mg \cdot mL^{-1}$) and 20.0 μL of the prepared CNNS suspension were coated on adjacent area independently on the ITO electrode and dried in the air. Then, 10.0 μL of chitosan solution was coated on the Ag/TiO_2/3DNGH modified area and dried at room temperature to improve the stability. Afterward, Ag/TiO_2/3DNGH modified area was covered with 10.0 μL of 2.0 $\mu mol \cdot L^{-1}$ AFB1 aptamer (as shown in Fig. S6 A) overnight at 4 °C to fully immobilize the aptamer through covalent bond. And then the electrode was washed several times with PBS to remove unreacted aptamers. Finally, the electrode was coated with 10.0 μL 1% bovine serum albumin (BSA) for 60 min at 4 °C to block unbound active sites.

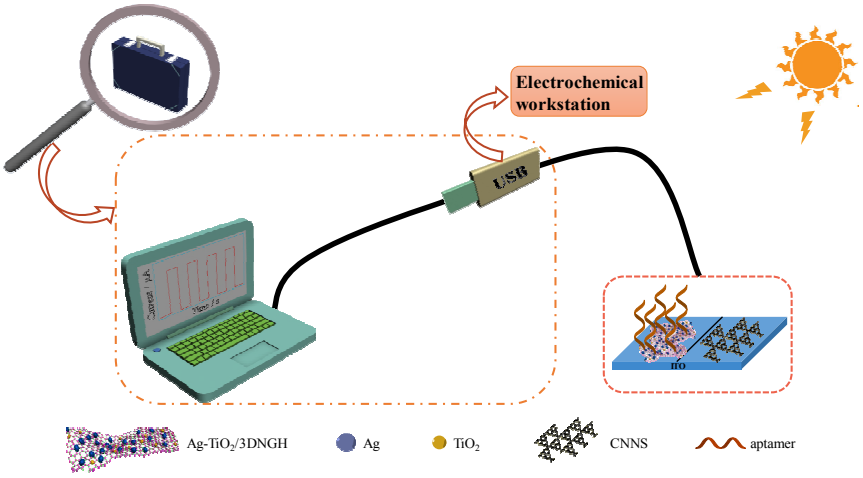
So far, the ratiometric PEC aptasensor for AFB1 was successfully obtained and stored at 4 °C. In the detection process, the modified electrode was incubated in the AFB1solution at 37 °C for 40 minutes (Fig. S6 B).

3. Results and discussion

3.1. Working principle of sunlight powered portable PEC biosensor

Herein, we report a sunlight powered portable PEC device. As shown in scheme 1, this device was consisted of a laptop computer, a miniature electrochemical workstation with a similar size of USB flash disk and a three-electrode system. The laptop was used to display detection result and the electrochemical workstation was used to collect and process data, which was just the scaled-down version of traditional PEC device. The core mechanism of this device was the potentiometric resolve ratiometric principle, which may eliminate the interference caused by unstable sunlight intensity. In brief, two nanomaterials Ag/TiO_2/3DNGH and CNNS were prepared and separately modified on the two adjacent areas of one ITO electrode (Detailed experimental protocols and characterizations were provided in the supporting information). Then AFB1 aptamer was modified onto the surface of Ag/TiO_2/3DNGH area. The magnitude and direction of photocurrents generated by these two nanomaterials were adjustable by the bias voltage. Under the irradiation of sunlight, when the bias voltage was set to 0.15 V (the critical potential of CNNS), the photocurrent from CNNS was zero and the cathodic photocurrent was generated from the Ag/TiO_2/3DNGH. While the bias potential was set to the critical potential of Ag/TiO_2/3DNGH -0.235 V, the anodic photocurrent was completely generated by the

CNNS. So PEC currents from two nanomaterials can be clearly distinguished. The anodic photocurrent at -0.235 V was in direct proportion to the sunlight intensity. For the cathodic photocurrent at 0.15 V, it decreased as the concentration of AFB1 increased due to the captured analyte while it was also affected by the sunlight intensity. Therefore, the anodic photocurrent at -0.235 V was not influenced by AFB1 and can provide a stable reference for evaluating the excitation light intensity. And the target concentration may be obtained through the ratio of two photocurrents no matter how the sunlight intensity changed.



Scheme 1. Schematic diagram for the detection of AFB1 with the portable ratiometric PEC aptasensor.

3.2. Detection performance

Fig.1 A and Fig.1 B represented the photocurrent responses of CNNS and Ag/TiO_2/3DNGH at different potentials, respectively. From the figure, it can be seen that when the applied potential changed from 0 V to 0.25 V, the photocurrent of CNNS changed from the anodic photocurrent to the cathodic photocurrent (Fig.1 A). Similarly, the photocurrent of Ag/TiO_2/3DNGH was also changed from anodic

photocurrent to cathodic photocurrent in the range of -0.3 to -0.2 V (Fig.1 B). And 0.15 V and -0.235 V were the critical potentials of CNNS and Ag/TiO_2/3DNGH that photocurrents decreased to zero during the anodic photocurrent changed to the cathodic photocurrent. In addition, it was also verified whether the dual modified electrodes interfere with each other at their respective critical potentials. As displayed in Fig.1 C, at -0.235 V (the critical voltage of Ag/TiO_2/3DNGH), the Ag/TiO_2/3DNGH-modified electrode had almost no photocurrent response (curve a), and CNNS-modified electrode exhibited a strong anodic photocurrent response (curve b), whereas the Ag/TiO_2/3DNGH and CNNS dual modified electrode showed a similar anodic photocurrent compared with that of a CNNS-modified electrode (curve c). In Fig.1 D, the bias potential was set to the critical potential of CNNS (0.15 V), the photocurrent of the CNNS-modified electrode was close to zero (curve a). At this time, the Ag/TiO_2/3DNGH and CNNS dual modified electrodes (curve c) produced a cathodic photocurrent, which was nearly the same as to that of the modified Ag/TiO_2/3DNGH electrode (curve b). In summary, the photocurrents from two materials could be easily distinguished by changing the bias potential.

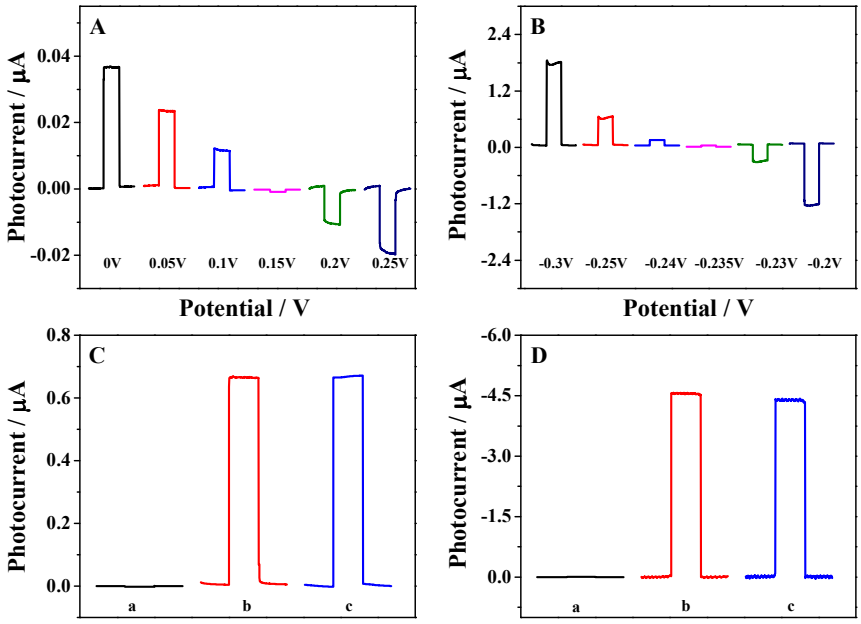


Fig. 1 Photocurrent of CNNS (A) at 0V, 0.05V, 0.1V, 0.15V, 0.2V, 0.25V and Ag/TiO_2/3DNGH (B) at -0.3V, -0.25V, -0.24V, -0.235V, -0.23V, -0.2V; Photocurrent of (C) CNNS(a), Ag/TiO_2/3DNGH (b) and CNNS & Ag/TiO_2/3DNGH (c) at -0.235V as well as (D) Ag/TiO_2/3DNGH (a), CNNS (b) and CNNS & Ag/TiO_2/3DNGH (c) at 0.15V.

As discussed above, this biosensor was designed to work under unstable sunlight, which changes over time and weather. To verify the feasibility, the photocurrents at different time were tested. As can be seen from Fig.2 A, the photocurrent intensities of the proposed biosensor at V_1 (-0.235 V) and V_2 (0.15 V) both changed significantly from 8 a.m. to 4 p.m. due to the greatly varied sunlight. However, the impacts of excitation light intensity on the photocurrents at two potentials were the same. So the ratio of two photocurrents remained almost constant (Fig.2 B). This result demonstrated that this sensor can eliminate the interference of unstable sunlight and can be used in outdoor detection.

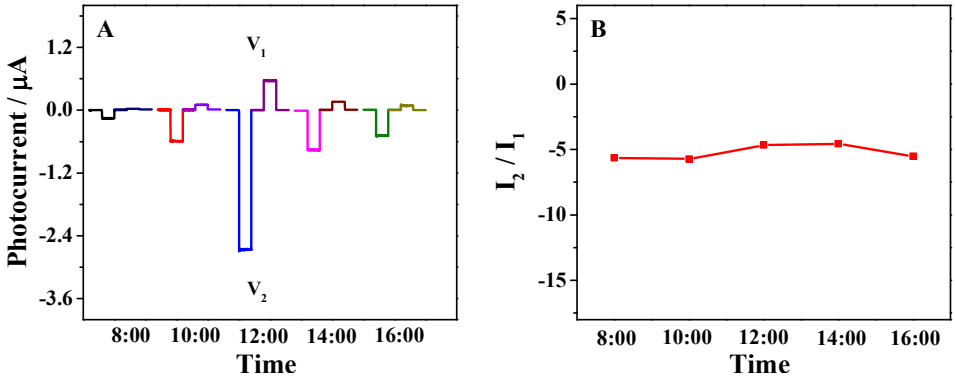


Fig. 2 (A) Photocurrents of CNNS & Ag/TiO_2/3DNGH dual modified ITO electrodes at different time on the same day at -0.235V (V_1) and 0.15V (V_2), respectively. (B) Ratios of photocurrents at different time on the same day (I_1 was the photocurrents of CNNS & Ag/TiO_2/3DNGH dual modified ITO electrodes at V_1 (-0.235 V); I_2 was the photocurrents of CNNS & Ag/TiO_2/3DNGH dual modified ITO electrodes at V_2 (0.15 V)).

The analysis performance of the developed biosensor was examined by detecting various concentrations of AFB1. To better show the effect of sunlight change, the detection time was extended to 4 hours in the morning. The cathodic photocurrent intensity of dual modified electrode at 0.15 V should decrease with the increase of the concentration of AFB1 due to the enhanced steric hindrance[40]. But as shown in Fig.3 A, the anodic and cathodic photocurrents both increased because of the enhanced sunlight. So the quantification of AFB1 cannot be achieved based a single photocurrent change. Meanwhile, a good linear relationship was shown in Fig.3 B. That was a linear about correlation curve between the ratio of I_2 (the cathodic photocurrent at 0.15 V) to I_1 (the anodic photocurrent at -0.235 V) and the logarithmic values of the concentration of AFB1 from 1.0 pg·mL^{-1} to 100.0 ng·mL^{-1}. The I_1 value

was in direct proportion to light intensity. So the interference of sunlight change on I_2 can be eliminated after divided by I_1. As can be seen from the figure, the ratio decreased with the increased concentrations of AFB1, which was corresponding to the steric hindrance mechanism. After the concentration reached 100.0 ng·mL^{-1}, the ratio of the photocurrent remained substantially constant while the concentration is further increased. This phenomenon was due to saturation of the target recognition site on the electrode surface and could not continue to capture the target.

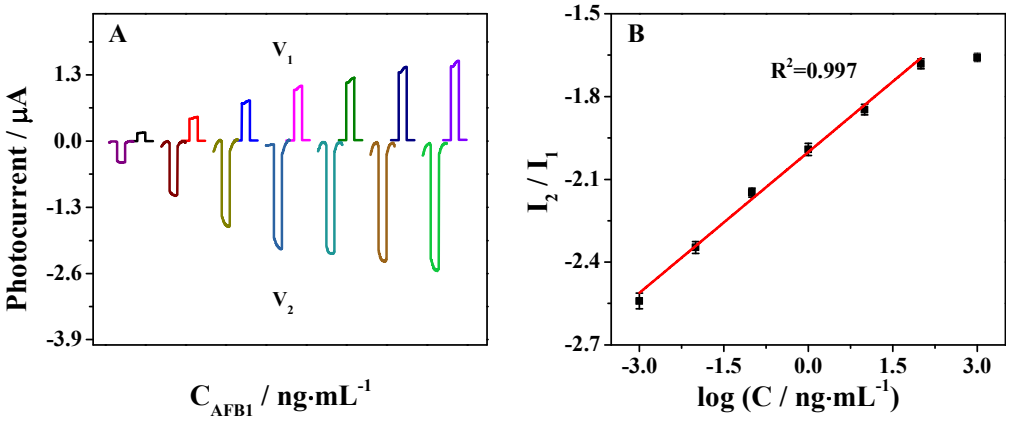


Fig. 3 (A) Photocurrents of CNNS & Ag/TiO_2/3DNGH in the presence of 1.0×10^{-3}, 1.0×10^{-2}, 1.0×10^{-1}, 1.0, 1.0×10^{1}, 1.0×10^{2}, 1.0×10^{3} ng/mL AFB1 at -0.235V (V_1) and 0.15V (V_2), respectively. (B) Linear calibration curve of the ratio of I_2 / I_1 for different concentrations of AFB1 (I_1 and I_2 were the photocurrents of the CNNS & Ag/TiO_2/3DNGH double-modified electrodes at -0.235V and 0.15V, respectively.).

3.3. Selectivity, reproducibility and stability of the aptasensor

As well known, selectivity, reproducibility and stability were important parameters to evaluate the detection performance. In order to explore the selectivity of the established method in this work, three toxins (AFB1 (1.0 ng·mL^{-1}), FB1

(Fumonisin B1, 100.0 ng·mL^{-1}) and OTA (Ochratoxin A, 100.0 ng·mL^{-1})) were tested. As shown in Fig. S7, significant photocurrent intensity changes only occurred in AFB1 and mixed solutions while the other two similar interferents had no obvious signal changes. The result confirmed that the proposed PEC biosensor had good selectivity toward AFB1. In order to evaluate the reproducibility, six modified electrodes were used for the detection of 1.0 ng·mL^{-1} AFB1 under the same experimental conditions. The relative standard deviations (RSD) of photocurrents at -0.235 V and 0.15 V were 1.4% and 1.3%, respectively, which indicated a good reproducibility (Fig. S8A). Fig. S8B presented the photocurrents after being stored at 4 °C for 7 days and 30 days. The PEC response at -0.235 V retained 98.9% after 7 days and retained 94.2% after 30 days. At the same time, the PEC response at 0.15 V retained 99.1% after 7 days and 94.6% after 30 days. These results suggested that this biosensor had a high stability.

3.4. Real sample analysis

For the verification of the practicality of the proposed biosensor in this work, AFB1 was analyzed in 10-fold-diluted soy milk samples. Based on the designed ratiometric aptamer sensing strategy, the recoveries of three known concentrations of AFB1 in soy milk samples were investigated. The experimental results were shown in Table S1, the obtained recoveries value ranged from 97.92% to 102.60% and the relative standard deviations (RSDs) were varied from 2.48% to 3.27%. The results show that this biosensor is suitable for the actual application of AFB1 detection. Furthermore, compared with other detection methods summarized in Table S2, the

proposed method has a wider linear range and lower detection limit.

4. Conclusions

In summary, we successfully developed a sunlight powered portable PEC biosensor. Sunlight is a strong and unstable light source. Through the potentiometric resolve ratiometric principle, the interference of excitation light intensity variation may be eliminated by the ratio of photocurrents at two bias potentials. The proposed PEC biosensor can provide a comparable performance with traditional PEC devices while getting rid of the cumbersome equipment. The main components contain only a laptop and a miniature electrochemical workstation with a similar size of USB flash disk, which guarantees that this device has a good portability and is very suitable for outdoor operation. In a proof of concept experiment, this biosensor was applied in AFB1 detection and displayed excellent sensitivity, stability, and reproducibility. This design provides a universal PEC platform and has great potentials in various fields, such as food safety and environmental monitoring that require portability and in field detection.

Associated Content

Supporting information

Instruments used in the experiment, preparation of CNNS, and characterization of nanomaterials were provided in supplementary materials.

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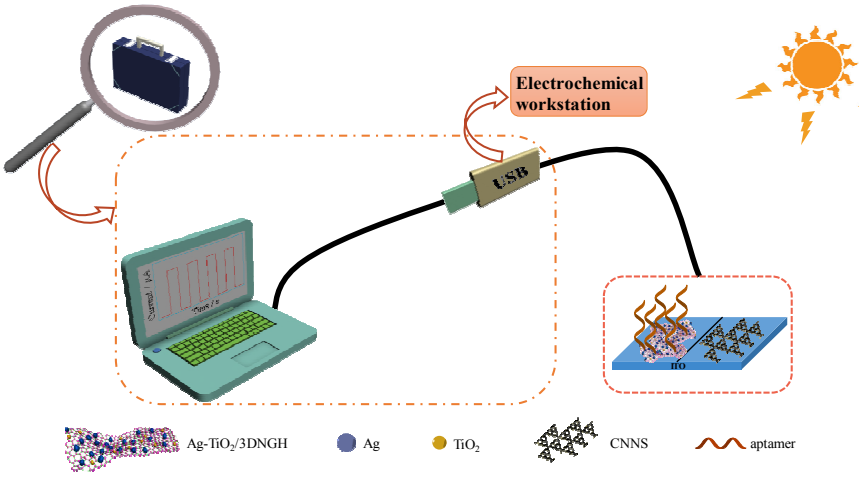
For TOC only:



A sunlight powered portable photoelectrochemical biosensor based on potentiometric resolve ratiometric principle was successfully developed.