

Construction of a Photoelectrochemical Sensor Based on FeTCPc@ZnO for the Detection of Oxytetracycline

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This paper proposes a photoactive nanomaterial of zinc oxide (ZnO) sensitized with iron (III) tetracarboxy phthalocyanine (FeTCPc), and develops a photoelectrochemical (PEC) method for the rapid and trace determination of oxytetracycline hydrochloride. In the preparation process, a simple one-step hydrothermal method is used to compound FeTCPc@ZnO/ITO, followed by fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and x-ray diffraction (XRD) and other characterization methods to confirm the composition and morphology of ZnO and FeTCPc. Take various methods to study the photocurrent response of oxytetracycline on bare/ITO, FeTCPc@ZnO/ITO, FeTCPc/ITO, ZnO/ITO and CTS/ITO respectively, and optimize each detection condition, make it show the strongest response. Apparently, the photoelectric response for detection of hygromycin was most significant when FeTCPc was used in combination with ZnO. The results show that under optimal conditions, the photocurrent response intensity of the constructed PEC is inversely proportional to the concentration of oxytetracycline, and the logarithmic range of 0.5 nM ~ 0.25 mM has a good linear relationship and linear regression. In addition, the PEC has excellent reproducibility and stability. The proposed photoelectrochemical sensor was applied to the detection of actual drug oxytetracycline, and the result is close to the drug labeling amount, which is relatively satisfactory.

Keywords: photoelectrochemical sensor; zinc oxide; oxytetracycline hydrochloride; iron (III) tetracarboxy phthalocyanine

1. INTRODUCTION

In recent years, with the rapid development of animal husbandry and aquaculture, tetracycline antibiotics with good bacteriostatic effects have been widely used to inhibit biological infections[1]. There are many types of tetracycline antibiotics, at present, the more common ones on the market are

oxytetracycline, chlortetracycline, and tetracycline, among them, oxytetracycline has a wide range of uses, which has become the largest tetracycline antibiotic in each country, and it has a rising trend year by year [2]. Oxytetracycline (OTC), also known as Geotrichum, is a tetracycline broad-spectrum antibiotic metabolized by *Streptomyces rimosus* and is a fast bacteriostatic agent [3]. This product has a strong inhibitory effect on infections caused by gram-positive bacteria and gram-negative bacteria [4]. In addition, OTC is also a growth promoter, adding OTC to the feed can increase the survival rate of seedlings, reduce the cost of the growth cycle, and can achieve the effect of inhibiting fungi and enhance the disease resistance and adaptability of livestock [5], has a good control effect on livestock and poultry diseases, so OTC is often used in large quantities in livestock feed additives. However, OTC cannot be completely absorbed by organisms, and a large part of it will be excreted by organisms, which will pollute water and soil [6,7]. At present, people's abuse or irregular use of OTC has had a potential impact on food safety. If food with OTC residues is consumed for a long time, it may cause a large amount of OTC to accumulate in the body, thereby causing damage to the organism and causing toxic effects [7]. Furthermore, the residue of OTC may also cause microorganisms to produce various resistance genes, thereby enhancing their drug resistance [8], therefore, it is an indispensable measure to detect and monitor the content of OTC in food and drugs.

At present, there are many detection methods for OTC, such as fluorescence-based biosensor [9], enzyme-linked immunosorbent assay [10], high performance liquid chromatography [11], liquid chromatography-mass spectrometry [12], and so on. These analytical methods have their own advantages, but they generally have problems such as complicated sample preparation, high instrument operation cost, and long time-consuming. Therefore, finding a more convenient and low-cost method has become a current research hotspot.

Photoelectrochemical (PEC) [13,14] analysis method is a new detection method developed by combining the advantages of both electrochemical and photochemical analysis techniques. Because of its simple operation, low background signal, high sensitivity, and easy miniaturization, it has great development potential in the future [13–16]. Under the irradiation of light, the light is absorbed by the photosensitive material, and the electrons in the material are excited by the energy to produce charge transfer, which is reflected in the conversion of light energy, electrical energy and chemical energy [17–19]. PEC sensor occupies an extremely important position in environmental detection, food safety monitoring, and so on [20]. Therefore, this paper uses a PEC sensor to detect OTC, and this method is simple, fast, convenient, with wide detection limits and high accuracy.

For the preparation of PEC sensors, it is very important to select photoelectrically active materials. For example, quantum dots [21,22], semiconductor materials [23,24], conductive polymers and other substances are currently ideal materials for constructing PEC sensors [25,26]. Metal phthalocyanine compound is a kind of organic semiconductor material with good electrocatalysis and photoelectric performance [27,28]. Carbon nanomaterials such as graphene, carbon nanotubes were often used as electrode material for electrochemical sensing [29–31]. Phthalocyanine and graphene oxide covalent compound can be widely used in electrochemical sensing, owing to the synergistic effect with highly conductive sensing element, highly surface area and adsorption capacity [15,26]. Zinc oxide (ZnO), with stable physical and chemical properties, good magnetic, electrical, optical and other properties, is a new wide band gap semiconductor oxide material ($E_g=3.37$ eV at room

temperature), compared with other wide band gap semiconductors, its exciton binding energy can be as high as 60 meV [32,33]. And zinc oxide raw materials are easily available, so it has huge development prospects. However, the recombination probability of photogenerated electron-hole pairs generated by zinc oxide after excitation is relatively large, which greatly limits the application of zinc oxide in PEC sensors [34,35]. However, under the action of FeTCPc, the zinc oxide particles have a hollow structure. The results show that FeTCPc as a structural modifier greatly promotes the photoelectric properties of zinc oxide.

In this study, we synthesized and used soluble iron (III) tetracarboxy phthalocyanine to sensitize zinc oxide by doping to prepare FeTCPc@ZnO nanocomposite material, and modified it on the ITO glass conductive electrode to construct a new type of PEC sensor for detecting OTC hydrochloride. The constructed PEC sensor has low detection limit and good stability, which can be applied to actual detection.

2. EXPERIMENTAL SECTION

2.1. Reagents and instruments.

The methanol and acetone used in this experiment were purchased from Chengdu Kelong Chemical Co., Ltd., diethylene glycol was obtained from Tianjin Guangfu Fine Chemical Research Institute, and phosphoric acid and boric acid were obtained from Taicang Lu Test Agent Co., Ltd. and Tianjin Bodi respectively. Zinc acetylacetonate and ethanol were supplied by Macleans and Sinopharm Chemical Reagent Co., Ltd. The water used in the experiments is double distilled unless otherwise stated.

The materials have been characterized by Fourier infrared (FTIR, Spectrum 65, USA), scanning electron microscopy (SEM, ZEISS, Japan), and X-ray diffraction (XRD, BrukerD8 advanced, Germany). The photoelectrochemical measurements have been performed using CHI760E electrochemical workstation (Tsinghua Instruments Co., Ltd., Shanghai, China).

2.2 Preparation of FeTCPc@ZnO and monomer ZnO

According to previous references [28], a simple one-step hydrothermal method was used to synthesize iron (III) tetracarboxy phthalocyanine (FeTCPc), which was further combined with zinc oxide (ZnO) nanoparticles to obtain FeTCPc@ZnO. Accurately weigh 0.5 g of FeTCPc solid, grind it evenly in a mortar, and then dissolve it in 100 mL of ethanol/diethylene glycol (the volume ratio is 1:1) mixed solution, 5.0 g of zinc acetylacetonate solid was added to the mixed solution. After 30 min of magnetic stirring until the mixture was fully mixed, it was transferred to a 100 mL autoclave lined with polytetrafluoroethylene. The autoclave was placed in a vacuum drying box at 150°C for a hydrothermal reaction for 18 h. After the reaction, the product was centrifuged and washed twice with absolute ethanol. The obtained solid was dried in vacuum drying box drying oven for 24 h, and finally a blue FeTCPc@ZnO nanocomposite was obtained. ZnO nanoparticles were synthesized by the same method without adding FeTCPc.

2.3 Preparation of working electrode

The ITO glass working electrode was ultrasonically cleaned in acetone, absolute ethanol and water for 20 min, and then dried under infrared light for standby.

The 4.0 mg FeTCPc@ZnO nanocomposite was ultrasonically dispersed into 1 mL water to obtain 4.0 mg/mL modified solution. Then 30 μ L FeTCPc@ZnO modified liquid was transfer to the conductive surface of ITO glass, and dry under infrared light. In order to prevent the material from falling off, 2 μ L of 1% chitosan solution (CTS) was dropped evenly on the surface of the formed light blue film, and let it dry naturally at room temperature, waiting for later use. For comparison, FeTCPc/ITO, ZnO/ITO, CTS/ITO and bare/ITO were prepared in the same way.

2.4 Pretreatment of actual samples

10 OTC tablets were fully ground to powder, and then the mass of 1 tablet was weighed and dissolved in water, ultrasonicated for 5 min to make it completely dissolved, and finally fixed to 250 mL volumetric flask, waiting for use.

2.5 Detection of OTC

BBS (borax and boric acid) with a concentration of 0.1 M was used as the supporting electrolyte, the Ag/AgCl electrode and the platinum wire electrode were the reference electrode and the auxiliary electrode, respectively, and FeTCPc@ZnO/ITO was the working electrode to form three-electrode system. The excitation light source selects an ultraviolet filter, the time-current method (i-t) was used as the detection method, and the concentration of the OTC standard solution of the substance to be tested is 0.5 μ M. Setting parameters: the bias voltage is 0 V, and the illumination time is 20 s. All experiments were carried out at room temperature.

3. RESULTS AND DISCUSSION

3.1 Morphology and spectral characterization

Fig.1 (A, B, C and D) are the SEM images of ZnO and FeTCPc@ZnO. The successful preparation of FeTCPc@ZnO nanocomposites was confirmed by the observation of ZnO particles attached to FeTCPc in the upper part of the composite under the microscope in Fig.1 (C, D), and the rounded spherical shape of ZnO particles morphology. From the SEM images in Fig.2 (A, B), it can be seen that the morphology of pure ZnO nanoparticles is spherical and aggregated [28].

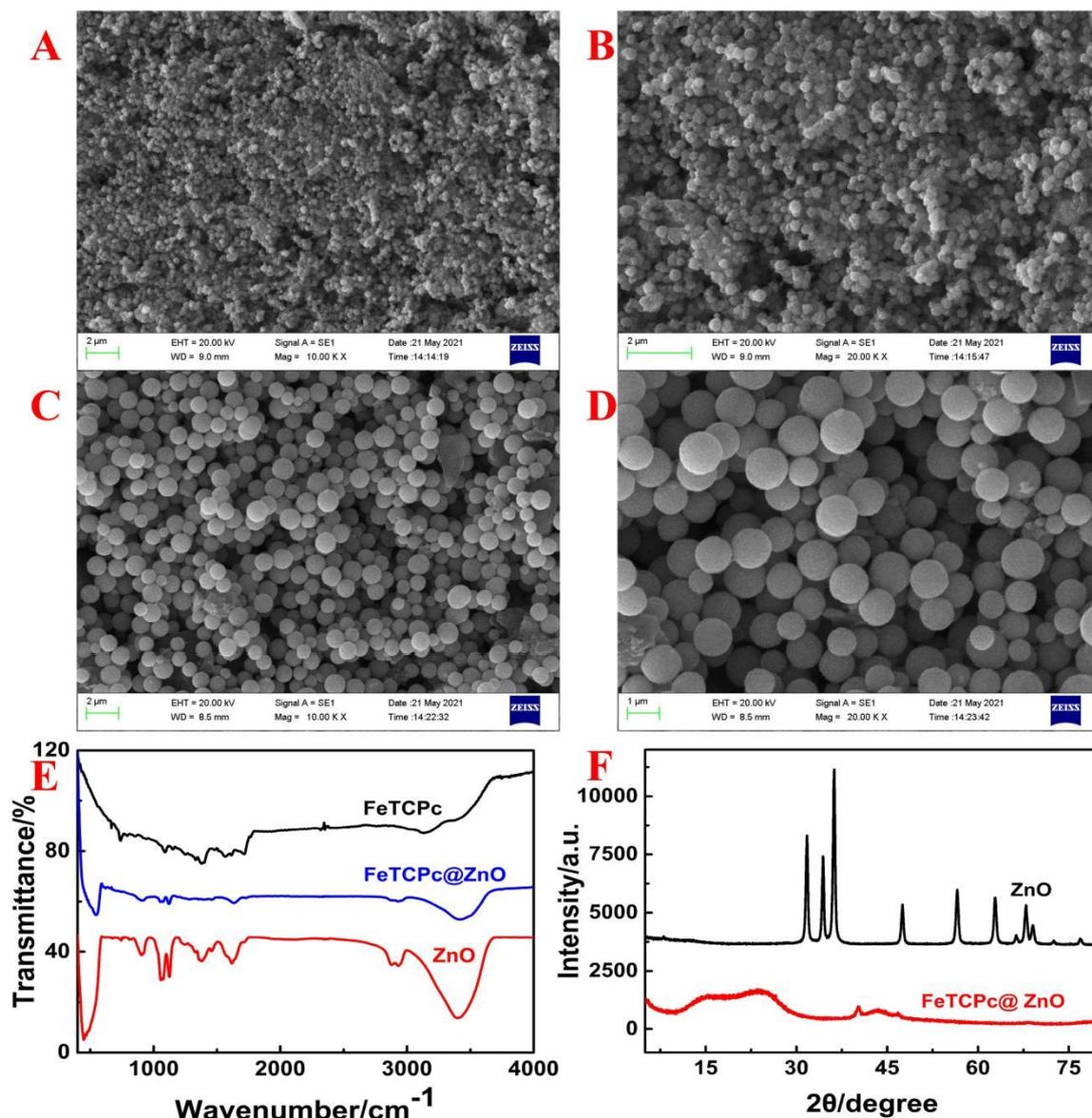


Figure 1. SEM images of (A, B) ZnO and (C, D) FeTCPc@ZnO, (E) FTIR and (F) XRD of FeTCPc, FeTCPc@ZnO, and ZnO;

The infrared spectrum information of FeTCPc, FeTCPc@ZnO, and ZnO are included in the Fig.1 (E). The FTIR of FeTCPc shows an absorption peak near 3133 cm⁻¹ that is characteristic of the -COOH, indicating the existence of characteristic structure of -COOH [36]. The peaks were observed near 1251 cm⁻¹, 942 cm⁻¹ and 792 cm⁻¹ are the structure of the phthalocyanine macrocyclic skeleton. 2318 cm⁻¹ is the stretching vibration absorption peak of -C=N, 1715 cm⁻¹ is the characteristic absorption peak of -C=O stretching vibration [37], and 1331 cm⁻¹ is the stretching vibration peak of the carboxylic acid group -CO-, 1089 cm⁻¹ is the C-H stretching vibration absorption peak on the phthalocyanine macrocycle, and 739 cm⁻¹ is the absorption vibration peak of the substituted benzene ring [37]. For ZnO, the strong absorption peak at 539 cm⁻¹ is the characteristic absorption peak of zinc oxide [28]. It can be seen that there is an absorption peak near 3423 cm⁻¹, which is the absorption peak

of -OH [38]. It may be because the sample itself contains crystal water or the sample absorbs moisture, or the pre-dried potassium bromide is not sufficiently dried or absorbs moisture and contains moisture. Compared with the FTIR of FeTCPc and ZnO, it can be seen that the absorption peak is weakened and the red shift occurs, indicating FeTCPc and ZnO were successfully doped, confirming the successful preparation of the composite. In addition, the strong absorption peak observed at the vicinity of 3400 cm^{-1} of the composite may be derived from the absorption peak of water, which indicates that the composite may not be sufficiently dried or contain crystal water. The above data are similar to the results presented in references, which verifies that FeTCPc has been successfully prepared.

Fig.1 (F) is the image of the XRD test performed on ZnO and FeTCPc@ZnO. It can be seen from the figure that the characteristic diffraction peaks of pure ZnO are 31.8, 34.4, 36.3, 47.5, 56.6, 62.9, 66.6, 68.1 and 69.2, indicating the formation of wurtzite structure ZnO with high grain size [28]. For FeTCPc@ZnO composite materials, after sensitizing with FeTCPc, no obvious peaks are observed at the peak positions of FeTCPc and ZnO. The possible reason is that the crystallinity of the composite material is not strong.

3.2 Electrochemical impedance analysis

In this experiment, five ITO glass conductive electrodes were prepared as working electrodes, namely FeTCPc@ZnO/ITO, FeTCPc/ITO, ZnO/ITO, CTS/ITO and bare/ITO, based on electrochemical impedance technology (EIS) to evaluate the conductivity of these five modified electrodes. The electron transfer ability was studied in 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solution containing 0.1 M KCl. The electrochemical impedance spectrum is shown in Fig.2 (A). Each curve is composed of a semicircle in the high-frequency area at the front end and an oblique line in the low-frequency area at the tail. The high-frequency area represents the electron transfer process [29]. In Fig.2 (A), the order of the resistance of each electrode is: FeTCPc/ITO < FeTCPc@ZnO/ITO < CTS/ITO < bare/ITO < ZnO/ITO. The largest semi-circle diameter is ZnO/ITO, which means that the resistance of ZnO material is large and its charge transfer rate is low. It can be clearly seen that the bare/ITO and the CTS/ITO are almost overlapped, indicating that the conductivity of the two is close, and the conductivity is only better than that of the semiconductor ZnO. The semicircular part of FeTCPc is the smallest, which means that the electron transfer resistance of all materials is the smallest. When FeTCPc is compounded with ZnO, it is second only to the conductivity of FeTCPc, and the conductivity is quite excellent compared with the monomer ZnO, indicating that the modification of FeTCPc is successful.

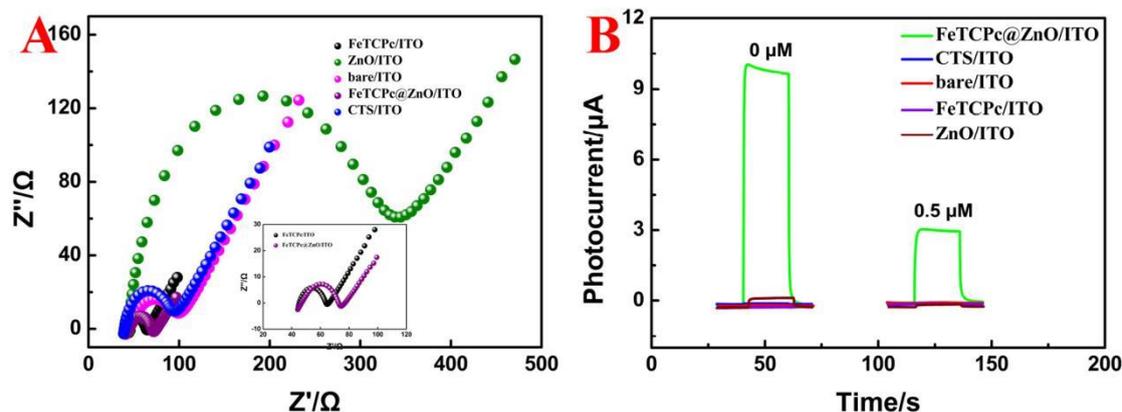


Figure 2. EIS spectra of different electrodes(A) and i-t curve graph(B)

3.3 PEC characterization of different modified electrodes

Under the irradiation of ultraviolet light, the photoelectric response of FeTCPc@ZnO/ITO, FeTCPc/ITO, ZnO/ITO, CTS/ITO and bare/ITO were studied in BBS solution (pH=8.0). As shown in Fig.2 (B), FeTCPc/ITO, bare/ITO and CTS/ITO in the blank electrolyte solution and 0.5 μM OTC showed no significant changes in the photocurrent. Compared with the blank electrolyte solution, the photocurrent of FeTCPc@ZnO/ITO in 0.5 μM OTC dropped sharply, and both were much larger than ZnO/ITO. The reason for this phenomenon may be that when OTC was added, the active sites on the modified electrode were occupied by it, which hinders the transport of photoelectrons, which is ultimately expressed as a significant reduction in photocurrent. This result also shows that the sensor was successfully prepared. Therefore, it is feasible to use FeTCPc@ZnO composite material to modify ITO conductive glass electrode to detect OTC.

3.4 Optimization of experimental conditions

In order to obtain the best detection sensitivity of OTC and PEC signal intensity, the concentration, coating amount, electrolyte solution and pH of FeTCPc@ZnO modification solution were optimized. Fig.3 (A) shows the effect of FeTCPc@ZnO concentration on PEC response. It can be observed from Fig.3 (A) that the PEC sensor has the greatest response to OTC when the concentration of FeTCPc@ZnO is 4.0 mg/mL. When the concentration of FeTCPc@ZnO increases, the PEC current response decreases due to the saturation of the FeTCPc@ZnO composite on the surface of the glass conductive electrode. It can be concluded that the optimal concentration of the prepared FeTCPc@ZnO modification solution is 4.0 mg/mL. Fig.3 (B) is to investigate the effect of FeTCPc@ZnO coating amount on PEC response. It can be observed from Fig.3 (B) that when the coating amount of FeTCPc@ZnO is 30 μL , the PEC sensor has the greatest response to OTC. An increase in the amount of modification will result in a decrease in the photocurrent value. This may be due to the excessive thickness of the FeTCPc@ZnO film on the electrode surface, which hinders the transfer of electrons, thereby reducing the photocurrent; and a small amount of FeTCPc@ZnO cannot

meet the needs of the photoelectrocatalytic process, so the photocurrent is smaller when there is less modification. In Fig.3 (C) shows the detected photocurrent signal of FeTCPC@ZnO/ITO in different electrolyte solutions (PBS, BBS, B-R, MBS, HAc-NaAc, pH=7), the photoelectric response of OTC detected in the BBS electrolyte solution is the largest and the effect is the best.

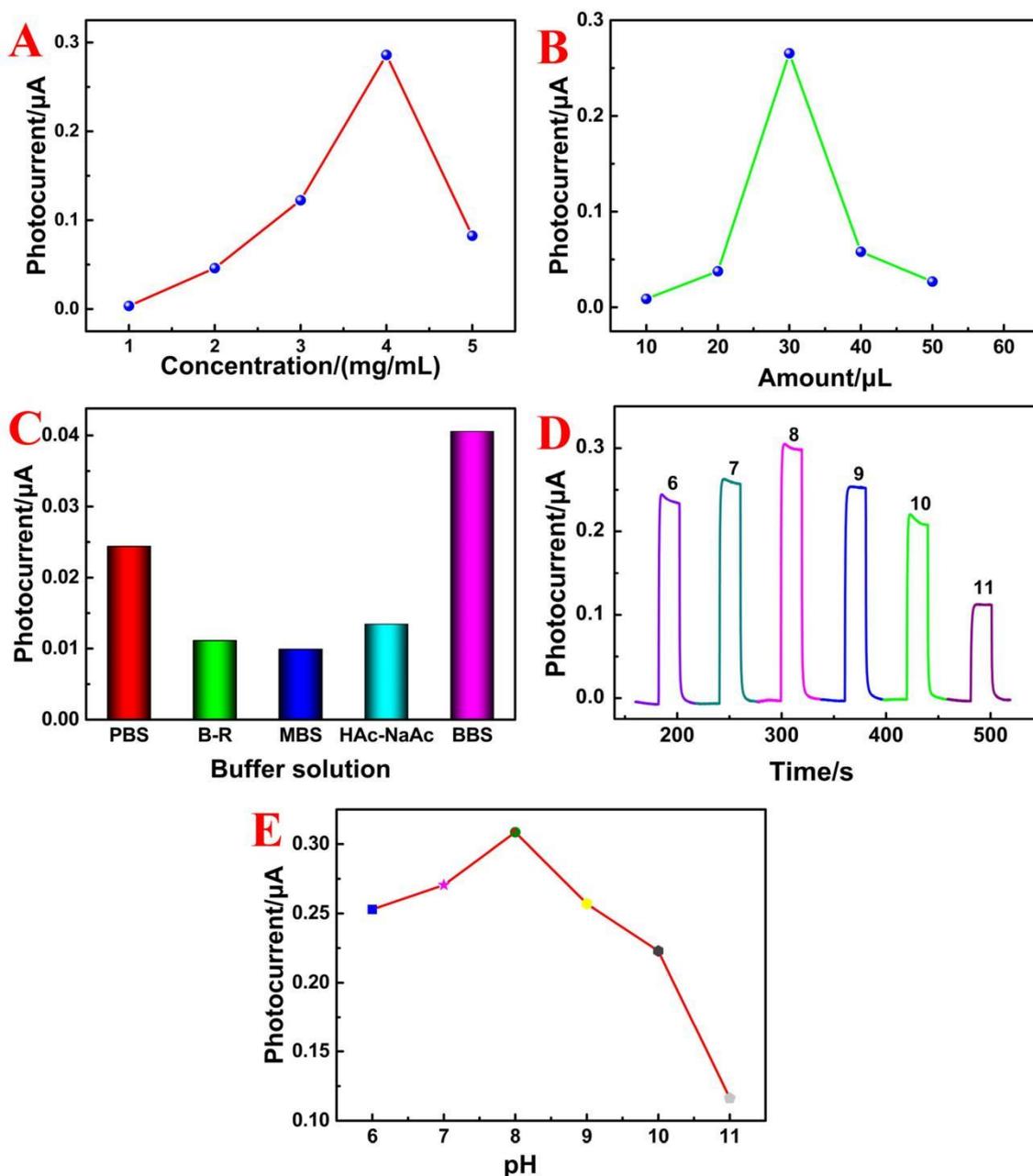


Figure 3. The influence of different concentration (A), modification amount (B), buffer solution (C), pH (D and E) on photocurrent

In addition, the influence of the pH (6.0, 7.0, 8.0, 9.0, 10.0, 11.0) of the BBS electrolyte solution on the photocurrent intensity of the PEC sensor was also studied. It can be seen from Fig.3 (D)

that when the pH is in the range of 6.0 ~ 8.0, the photocurrent response intensity increases with the increase of pH; however, when the pH is in the range of 8.0 ~ 10.0, the intensity of PEC response decreases with increasing pH. To sum up, in this experiment, in the BBS electrolyte solution with pH 8.0, FeTCPc@ZnO with a modification solution concentration of 4.0 mg/mL was used to coat 30 μL on the ITO glass conductive electrode for subsequent experiments.

3.5 Detection performance of PEC sensor for OTC

Under the optimal conditions, BBS electrolyte solution with pH 8.0 and 4 mg/mL FeTCPc@ZnO with a coating amount of 30 μL , PEC detection was performed on a series of concentrations of OTC. As the concentration of OTC increases, the photocurrent response of FeTCPc@ZnO/ITO decreases, that is, the photocurrent response of the PEC sensor detecting OTC is inversely proportional to its concentration. In the range of 0.5 nM ~ 0.25 mM, the photocurrent response of the PEC sensor detecting OTC shows a good linear relationship with the logarithm of its concentration, as shown in Fig.4 (A, B), the linear regression equation is $I(A) = -1.58 \times 10^{-7} \lg C - 2.35 \times 10^{-7}$, $r = 0.9907$, and the limit of detection (LOD) is 0.251 nM(3s/k). The PEC sensor constructed in this paper has a wide linear range, and its detection limit is low. Therefore, the PEC sensor constructed in this experiment can be used for the actual detection of OTC.

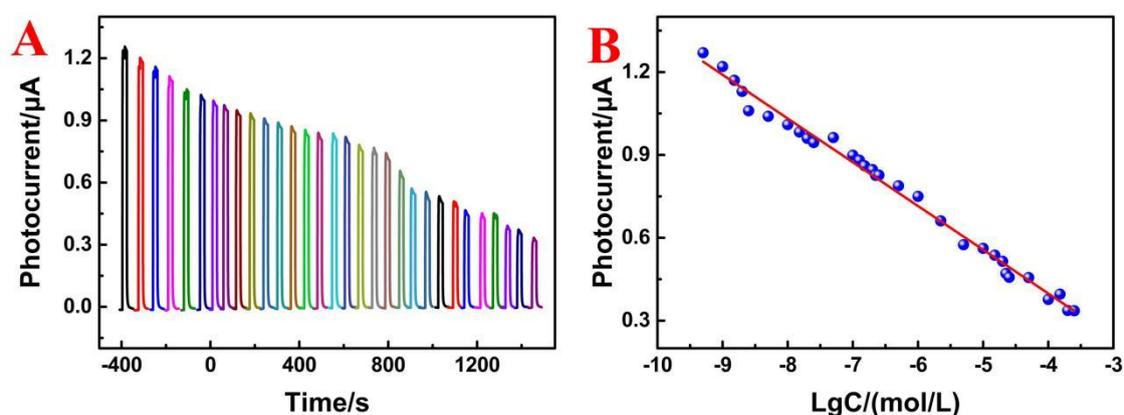


Figure 4. (A and B) PEC detection series of OTC and its linear relationship

3.6 Research on the stability, reproducibility and selectivity of electrodes

In order to study the stability of the PEC sensor, when the concentration of OTC in the electrolyte solution is 0.5 μM . Under the best conditions, the FeTCPc@ZnO/ITO glass conductive electrode is within the measurement range of 25 consecutive times within 1500 s. The results of the experiment are shown in Fig.5 (A), the relative standard deviation (RSD) of the current value is calculated to be 0.58%, the current fluctuation is not obvious, indicating that the stability of the PEC sensor is excellent in the short term. The same method was used to prepare FeTCPc@ZnO/ITO working electrode, and the concentration of 0.5 μM OTC was measured. The test was performed every

three days, continuously for 15 days, and a total of 5 tests to study the long-term stability of the PEC sensor. The result is shown in Fig.5 (B). The photocurrent signal of the prepared working electrode is stable within 15 days, and the RSD is 3.80%, indicating that the prepared FeTCPc@ZnO/ITO has long-term stability.

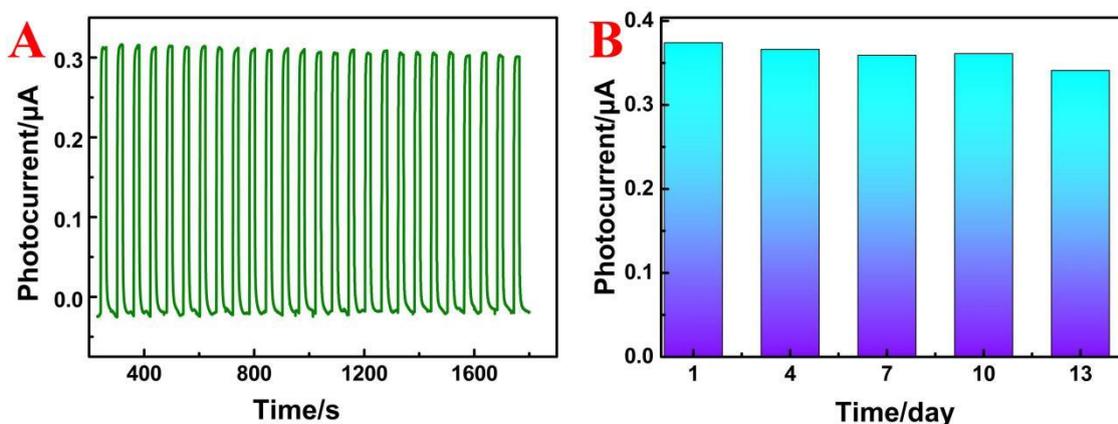


Figure 5. (A) Short-term stability test of FeTCPc@ZnO/ITO, (B) Test the photoelectric response of the same concentration of oxytetracycline hydrochloride within 15 days

In order to study the selectivity of this PEC sensor, the coexisting components of the actual sample and other common ions were selected as interference components in this experiment, under the concentration of 0.5 μM OTC. In addition, 400-fold concentration of acetate ion, L-alanine, L-leucine, Mg^{2+} , CO_3^{2-} , Zn^{2+} , Ba^{2+} ; 150-fold concentration of Ca^{2+} , Cl^- , NO_2^- , K^+ , HCO_3^- ; 100-fold concentration of NO_3^{2-} , L-threonine, L-valine do not interfere with the photocurrent of 0.5 μM OTC (photocurrent change < 5%). These results indicated that FeTCPc@ZnO/ITO has an excellent selectivity for OTC, and it might be applied to determine OTC in real samples.

3.7 Determination of OTC in medicine

Under the optimal conditions, in order to verify the feasibility of the PEC sensor in the actual sample analysis, the commercially available OTC tablets were tested.

Table 1. Determination recovery rate of OTC

Sample number	Sample content(μM)	Added (μM)	Found (μM)	Recovery (%)	RSD (%)
1	0.155	5.00	5.10	98.9	2.3
2	0.0764	2.50	2.60	100.9	
3	0.00382	1.00	0.967	96.3	

The OTC tablets were detected by the standard addition recovery method, and the results obtained are shown in Table 1. The RSD obtained from three repeated tests was 2.7%, and the spiked recovery rates of the sample were 98.9%, 96.3%, and 100.9%. It proves that the PEC sensor has high accuracy and reliability, and can be used in the actual detection of OTC.

4. CONCLUSION

A one-step hydrothermal method was used to synthesize FeTCPc@ZnO, and modify it on the ITO glass conductive electrode to construct a PEC sensor for the detection of OTC. Under the best conditions, OTC shows a good linear relationship in the concentration range of 0.5 nM ~ 0.25 mM, LOD is 0.251 nM (3s/k). The content of OTC in OTC tablets was determined, and the recovery rate of standard addition was within 96.3% ~ 100.9%. Compared with HPLC, this method has the advantages of low cost, simple operation, wide linear range, high sensitivity, and low detection limit. In the future, PEC detection devices based on FeTCPc@ZnO/ITO can be further developed for the detection of other substances in the environment or food.

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