

## Electrochemical Sensor Using Glassy Carbon Electrode Modified with HPM $\alpha$ FP/Ppy/GCE Composite Film for Determination of Ofloxacin

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In this work, an electrochemical sensor HPM $\alpha$ FP / Ppy /GCE (HPM $\alpha$ FP: 1-phenyl-3-methyl-4-(2-furoyl)-5-pyrazolone, Ppy: polypyrrole, GCE: glassy carbon electrode) was prepared for the determination of ofloxacin (OFL: (+)-9-Fluoro-2,3-dihydro-3-methyl-10-(4-methyl-1-piperazinyl)-7-oxo-7H-pyrido(1,2,3-de)-1,4-benzoxazine-6-carboxylic acid). The electrochemical parameters of ofloxacin were investigated by cyclic voltammetry and differential pulse voltammetry. In pH=7.0 phosphate buffer solution, one sensitive oxidation peak of OFL with  $E_p=0.88V$  is obtained on the electrochemical sensor. The difference of peak potential( $\Delta E_p$ ) was 70mV lower than which on bare glassy carbon electrode, and the potential of ofloxacin moved negatively slightly which on Ppy modified electrode. Compared to the bare GCE and Ppy /GCE, the electrochemical sensor showed an excellent electrocatalytic effect on the oxidation of ofloxacin and displayed a shift of the oxidation potential in the negative direction with significant increase in the peak current. Under the optimized condition in voltammetric method, the concentration calibration range and detection limit are  $2 \times 10^{-6} \sim 1 \times 10^{-4}$  mol/L and  $6.5 \times 10^{-8}$  mol/L for OFL. This developed method had been applied to the direct determination of OFL in ophthalmic solution samples.

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**Keywords:** Acylpyrazolone; Polypyrrole; Ofloxacin; Modified electrode

### 1. INTRODUCTION

Ofloxacin (OFL) is a member of the fluoroquinolone derivative class of synthetic antibiotics [1]. It exhibits broad activity against both gram negative and gram positive bacteria through inhibition of their DNA gyrase [2]. It is widely used in the treatment of respiratory tract and urinary tract infections [3]. To date, various techniques have been utilized for the determination of OFL in pharmaceutical preparations or biological samples. It mainly includes potentiometric titration [4],

spectrophotometry [5, 6], spectrofluorimetry [7, 8], HPLC [9,10], capillary electrophoresis [11,12]. However, electrochemical sensor has obtained wide application in biomedical monitoring. For example, a carbon nanotubes film modified electrode[13], a nano-ZnS / poly (Styrene sulfonic acid sodium salt) modified electrode [14], a solid-phase PbO<sub>2</sub> sensor[15] have been published for the detection of OFL. It is well known that the drug analysis is an important branch of analytical chemistry, which has extensive impact on public health. Therefore, the establishment of simple, rapid, sensitive and reliable method for the determination of active ingredient is welcomed and necessary.

In this work, Polypyrrole (Ppy) was prepared which is one of the most extensively used conducting polymers [16] and has been studied because of its ease of fabrication, high conductivity, good biocompatibility and low cost [17-20]. The existence of surface positive charge on the Ppy film could provide a selective interface for the molecular interaction and the presence of amine group (–NH–) on the pyrrole ring may lead to enhancement of biomolecular sensing [21-23]. In addition, the sensitivity of a Ppy-modified electrode could be significantly improved when it is doped with suitable active materials such as peptide [24] and DNA [25]. Nowadays, this polymer becomes one of the major tools for nanobiotechnological applications [26]. Various approaches have been considered for the synthesis of Ppy, including chemical and electrochemical methods [27]. It was reported that the catalytic activity of Ppy films depends on the synthesis conditions [27,28].

1-Phenyl-3-methyl-4-(2-furoyl)-5-pyrazolone is a kind of  $\beta$ -diketo compound. They play a key role in coordination chemistry [29] and are potential antifungal agrochemicals, antiviral, antipyretic analgesic, and anti-inflammatory in medicine [30,31]. The neutral acylpyrazolones may exist with several tautomeric forms and as reported [32,33]. The enol form OH is weakly acidic, as a surfactant, which makes it suitable for electrochemical analysis [34,35]. Due to the aromaticity of HPM $\alpha$ FP, they can adsorb onto the surfaces of the Ppy through  $\pi$ - $\pi$  force and hydrogen bond to form the composite film [36]. As far as we know, there are no reports on the fabrication of the electrochemical sensor and its response on ofloxacin.

In our previous work, HPM $\alpha$ FP modified GCE (HPM $\alpha$ FP/GCE) was applied to determination of amino acid and purine [37,38]. In order to extension of the application of HPM $\alpha$ FP modified electrode in the bioelectrochemistry, we are reporting a novel electrochemical sensor using glassy carbon electrode modified with HPM $\alpha$ FP/Ppy/GCE composite film which shows the great capability of sensitive and selective determination of ofloxacin.

## 2. EXPERIMENTAL PART

### 2.1. Apparatus

All electrochemical measurements that contains cyclic voltammetric (CV) and differential pulse voltammetry (DPV) were performed in an analytical system model CHI-650A electrochemical workstation (Shanghai Chenhua instruments company, China). A conventional three-electrode system was used with a platinum wire as an auxiliary electrode and a saturated calomel electrode (SEC) as

reference electrode. The working electrode was either an unmodified GCE or a polymer film modified electrode ( $\phi 4$  mm) for the electrochemical measurements.

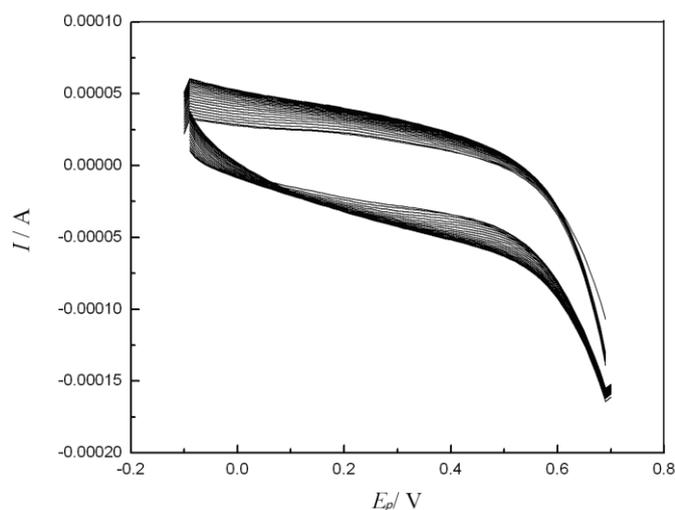
## 2.2. Materials

Ofloxacin was obtained from National Institute for the control of pharmaceutical and biological products (Shanghai, China, [www.reagent.com.cn](http://www.reagent.com.cn)). A  $1 \times 10^{-3}$  mol/L stock solution of ofloxacin was done with twice distilled water. The stock standard solution was stored in a refrigerator at approximately 277 K and remained stable for at least one month. Working standard solutions were prepared by suitable dilution of the stock standard solution. Pyrrole (analytical reagent, for short py, made in Shanghai reagent company, China.) was made as 0.1% water solutions,

HPM $\alpha$ FP was synthesized according to the method proposed Dong (1983) (yield 73%, mp 373.5-374.5 K) with further purification [39], and a standard solution (0.01 mol/L) of HPM $\alpha$ FP was prepared by anhydrous ethanol solution. Other chemicals were of analytical reagent grade and used without further purification. The phosphate buffer solution (PBS, 0.10 mol/L) of various pH values were used as supporting electrolyte. All solutions were prepared with double distilled water. The experiments were conducted at the room temperature ( $298 \pm 2$  K).

## 2.3. Preparation of the modified electrode

Prior to modification, the bare GCE was polished successively with 1.0 and 0.3 micron alumina slurry on chamois leather, respectively. Electrode was rinsed with double distilled water. The electrode was put into nitric acid (1:1), anhydrous ethanol, in order to remove adhered alumina and rinsed thoroughly with distilled water. Glass carbon electrodes after polishing and ultrasonic cleaning was put into 0.5 mol/L  $H_2SO_4$  solution, then it was polarization deal with cyclic voltammetry scanning, until a reproducible voltammogram was obtained (about 10 min).



**Figure 1.** 0.1 mol/L  $H_3PO_4$ - $NaH_2PO_4$  (pH = 6.0) + 0.1 mol/L py, the scan rate: 0.25 V/s and scanning potential range: -0.1 ~ 0.7 V

The electrode pretreated was put in pure water for standby. Putting the electrode pretreated into system: 0.1 mol/L  $\text{H}_3\text{PO}_4\text{-NaH}_2\text{PO}_4$  (pH =6.0)+0.1 mol/L py, connecting three electrodes system and connected with electrochemistry system, control the scan rate: 0.25V/s and scanning potential range: -0.1~0.7V, the blue-purple polymer film was obtained by cyclic scanning 20 times (the continuous cyclic voltammograms of polymerization process: Fig1). Capabilities of Ppy prepared in this conditions was very steady, the properties of Ppy has not evidently changes after putting in PBS (pH=6.0) after four weeks. Finally, the GCE was carefully coated with 1  $\mu\text{L}$  of HPM $\alpha$ FP solution and left for the solvent to evaporate at room temperature in the air. When the modified electrode completely dried, it can be used.

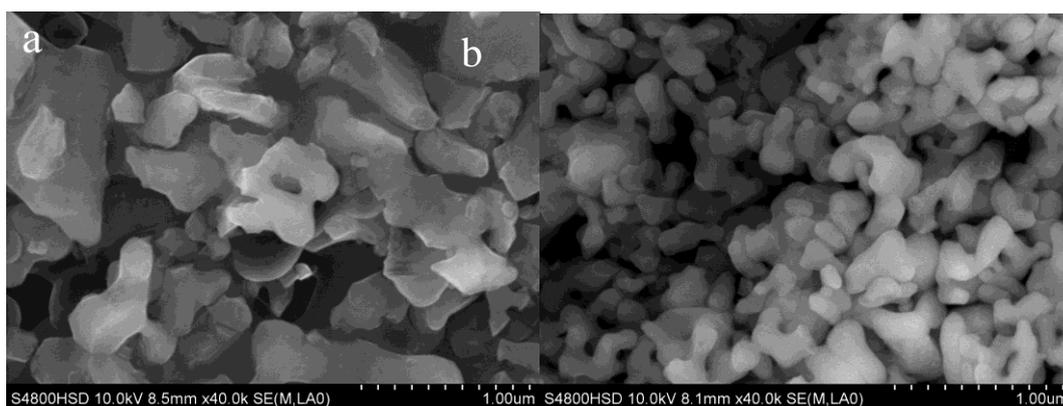
#### 2.4. Experimental procedure

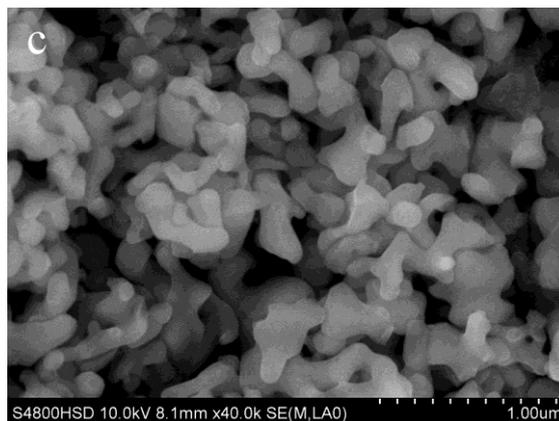
PBS 0.1 mol/L (pH=7.0) with certain amount of OFL was transferred into a cell, and the three-electrode system was installed in it. High-purity  $\text{N}_2$  was used to remove oxygen. Cyclic voltammetry and differential pulse voltammetry were recorded between 0.2V and 1.4V. All experiments were carried out at room temperature ( $298\pm 2$  K).

### 3. RESULTS AND DISCUSSION

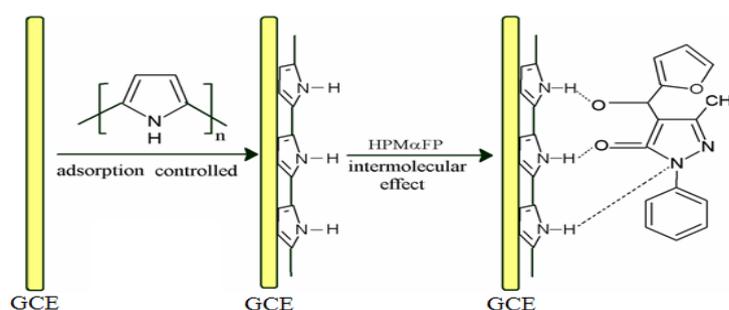
#### 3.1. Electrochemical characteristic of electrode

The microscopic structure of modified electrodes was characterized using scanning electron microscope (SEM) images. Figure 2 exhibits typical images of polypyrrole (Fig.2a), HPM $\alpha$ FP (Fig.2b), and HPM $\alpha$ FP/Ppy films coated onto GCE (Fig.2c). As it can be clearly seen, the Ppy-modified electrode surface shows a uniform formation and equally distributed flakes of polymer film. The electrode surface area is substantially increases. HPM $\alpha$ FP dispersed over the glassy carbon surface, and at the HPM $\alpha$ FP/Ppy film, HPM $\alpha$ FP adsorbed on the surface of Ppy. The reasons were concluded in the following aspects: i) at the polypyrrole and HPM $\alpha$ FP, some active functional groups maybe existed, such as -NH-, carbonyl, and hydroxy.





**Figure 2.** SEM images of the surface of (a) Ppy /GCE, (b) HPM $\alpha$ FP/GCE, (c) HPM $\alpha$ FP/ Ppy /GCE



**Scheme 1.** The interaction between polypyrrole and HPM $\alpha$ FP

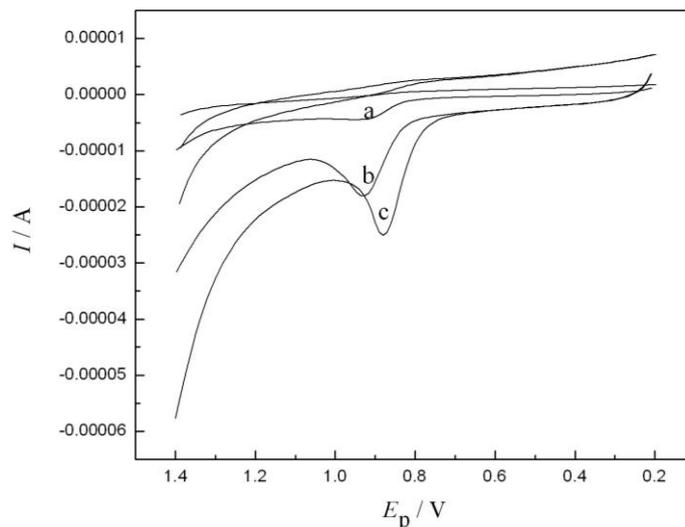
The intermolecular effect (hydrogen bond) was formed between Ppy and HPM $\alpha$ FP; ii) Some aromaticity was consist in HPM $\alpha$ FP which contains benzene, parazole, and furfuran. The  $\pi$ - $\pi$  interaction between the aromaticity of HPM $\alpha$ FP and pentagonal structure of Ppy was attributed to the easy arrival of HPM $\alpha$ FP to the surface of Ppy [36] (as shown in Scheme 1).

### 3.2. Electrochemical behavior of the modified electrode

The electrochemical behavior of OFL was studied by us. Fig. 3 described the cyclic voltammograms of  $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  OFL in pH 7.0 PBS at three different working electrodes. At the bare GCE (Fig. 3a), it can be seen that an irreversible oxidation peak appeared at about 0.95V. While the response was considerably improved at the Ppy /GCE and HPM $\alpha$ FP /Ppy /GCE.

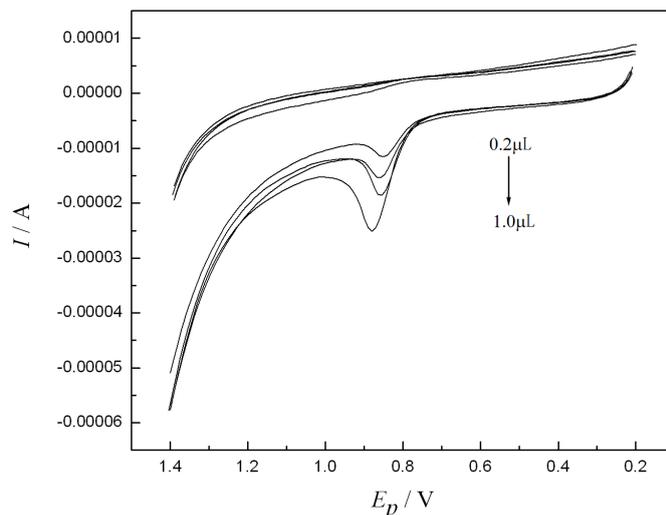
It can be observed that the oxidation peak current of OFL at Ppy /GCE modified electrode was enhanced significantly than the sum of response currents at GCE(Fig. 3b). From the comparison of the bare GCE, at the HPM $\alpha$ FP /Ppy modified GC electrode, the oxidation peak potential of OFL located at 0.88V and shifted negatively by about 70mV (Fig. 3c). The above results indicated that the composite film modified electrode exhibited the synergistic effect including high conductivity, fast electron-transfer rate, and inherent catalytic ability. This phenomenon was probably due to the hydrogen bond

between OFL and HPM $\alpha$ FP or OFL and Ppy, which can remarkably increase the accumulation amount of OFL.



**Figure 3.** Cyclic voltammograms of  $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  OFL (pH=7.0) at (a) bare GCE, (b) Ppy /GCE, (c) HPM $\alpha$ FP /Ppy /GCE. Scan rate:  $100 \text{ mV} \cdot \text{s}^{-1}$

### 3.3. Effect of Ppy-HPM $\alpha$ FP amount



**Figure 4.** Cyclic voltammograms of different HPM $\alpha$ FP amounts from  $0.2 \mu\text{L}$  to  $1.0 \mu\text{L}$  vs. the current of  $1.0 \times 10^{-5} \text{ mol/L}$  OFL in  $0.10 \text{ M PBS}$  (pH 7.0). Scan rate:  $100 \text{ mV s}^{-1}$

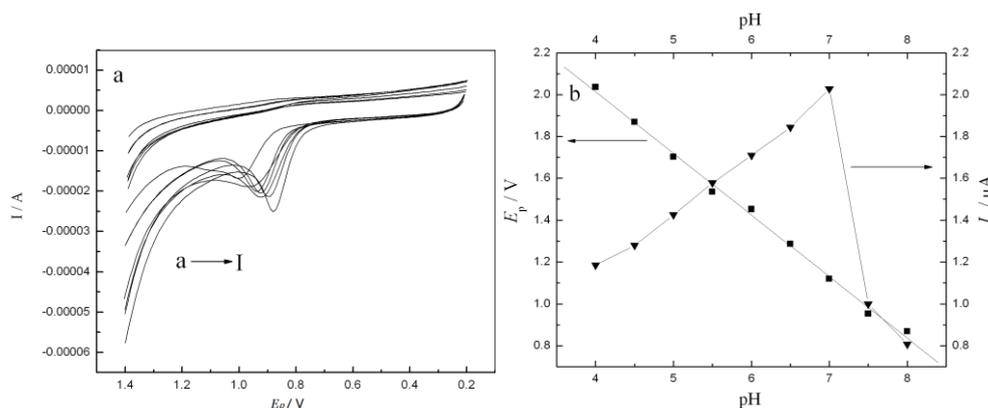
Effect of different HPM $\alpha$ FP and Ppy amount on peak current of ofloxacin was investigated. The results showed that the variation of oxidation peak current of OFL was as a function of the amount of Ppy-HPM $\alpha$ FP (Fig. 4). With further increase of the amount of polypyrrole to 20 times, the oxidation peak current increased slightly. However, too much polypyrrole may be more easily abraded from the surface of GCE. So, the polymerization scanning polypyrrole intercalative 20 times was selected. On the other hand, with the amount of HPM $\alpha$ FP increased, the reactive site of the modified electrode to

OFL also enhanced. When the HPM $\alpha$ FP was beyond 1.0  $\mu$ L, the peak current decreased. This was due to the surface of Ppy/GCE casted too thick to impede the charge exchange. To sum up, 20 times polypyrrole and 1.0  $\mu$ L HPM $\alpha$ FP was selected in the subsequent analytical experiments and the maximum electrocatalytic response on ofloxacin was achieved.

### 3.4. Effect of solution pH

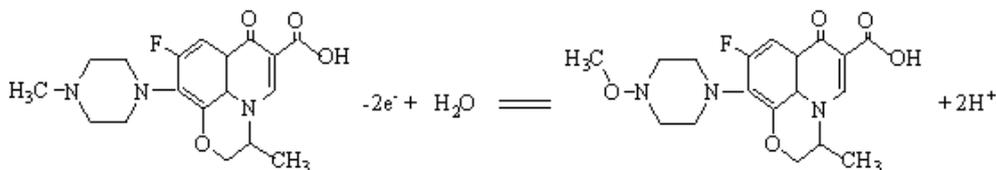
Influence of solution pH on electrochemical behavior of  $1.0 \times 10^{-5}$  mol/L OFL at HPM $\alpha$ FP /Ppy /GCE was studied in the pH range from 4.0 up to 8.0. The results were shown in Fig. 5. It was found that the oxidation peak potentials shifted negatively with increasing pH (Fig.5a). The pH values around 7.0 should provide the highest oxidation currents justified by the selection of pH 7.0 for the subsequent experiments using the HPM $\alpha$ FP/Ppy/GCE film electrode. A linear relationship could be obtained between the peak potential and solution pH, which indicated that protons are directly involved in the oxidation of OFL (Fig.5b). The pH dependence of oxidation peak potential obeyed the equation,  $E_p(\text{V})=1.1287-0.0353\text{pH}$  ( $r=0.9986$ ). It was found that  $dE_p/d\text{pH} = RTm/\alpha nF=0.035$  [40] in the pH range of 4.0-8.0. Then it can be calculated that the proton transfer number ( $m$ ) was 2. The reaction mechanism for ofloxacin was shown in scheme 2 [36].

### 3.5. Determination of ofloxacin

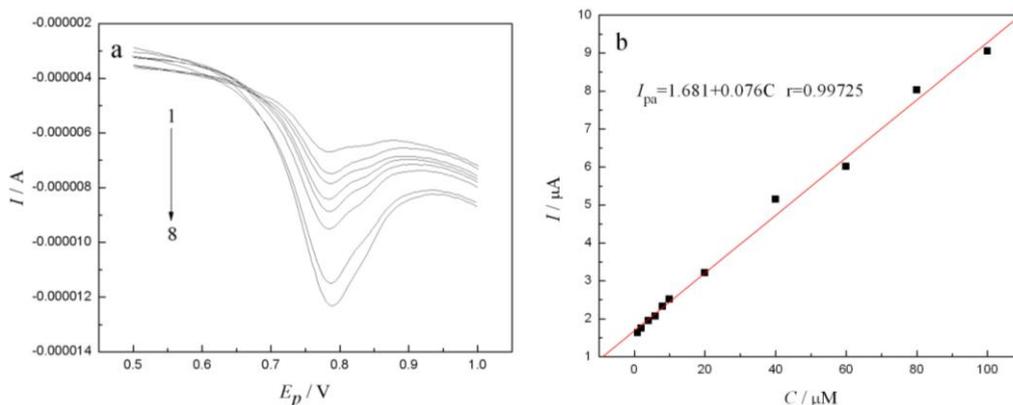


**Figure 5.** (a) Cyclic voltammograms of  $1.0 \times 10^{-5}$  mol  $L^{-1}$  OFL at different pHs(a-D):4.0,4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0. Scan rate:  $100\text{mV s}^{-1}$  (b) Influence of pH on the peak current ( $I_{pa}$ ) and peak potential ( $E_p$ ) of OFL

Differential pulse voltammetry (DPV) technique was employed to develop a voltammetric method for determination of ofloxacin. Under the optimal conditions, the oxidation peak current was proportional to OFL concentrations in the range of  $1 \times 10^{-6} \sim 1 \times 10^{-4}$  mol  $L^{-1}$  (Fig.6). The linear regression equation was  $I_{pa}(\text{A})= 1.681+ 0.076C$  ( $r=0.99725$ ). The detection limit was found to be  $4.85 \times 10^{-7}$  mol/L. This detection limit was lower, and the sensitivities were higher than those obtained by other electrochemical methods.



**Scheme 2.** The reaction mechanism for OFL



**Figure 6.** (a) DPVs of HPM $\alpha$ FP /Ppy /GCE in 0.10 M PBS (pH 7.0) containing different concentration of OFL in the range of 1 to 100  $\mu$ M, (b) Plot of the peak current vs. the concentration of OFL

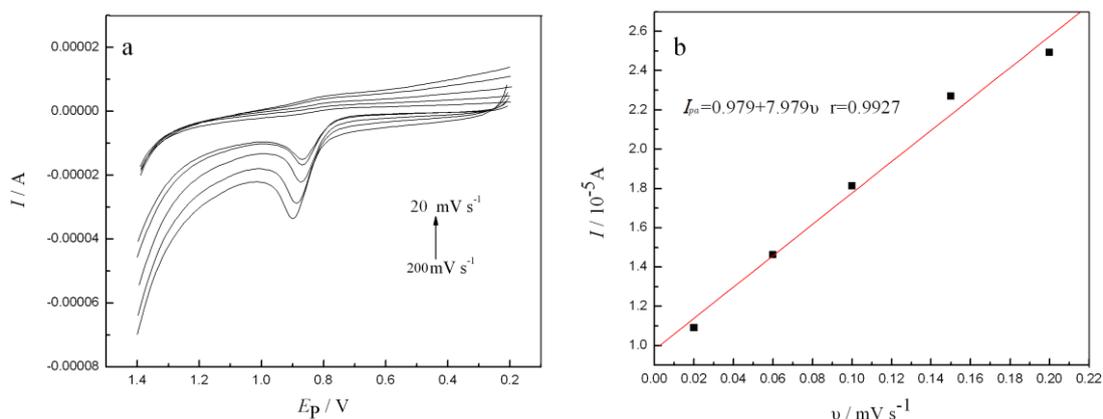
### 3.6. Effect of accumulation potential and time

Accumulation potential and time are two crucial conditions for the accumulation step. The influence of the accumulation potential on the oxidation peak current was evaluated over the potential range of 0.2 to 1.4V on a HPM $\alpha$ FP /Ppy. The results indicated that, with the decrease of potential in the range of 0 to 1.4V, the electrochemical response have no obvious change. To the accumulation time, the experimental results showed that it has obvious effects on the oxidation peak current of OFL. The peak current increased with increasing accumulation time in the range of 0-120 sec indicated that OFL was adsorbed onto the modified electrode surface. Further increment of the accumulation time, the oxidation peak current increased slightly. This phenomenon may be due to the electrode surface becomes saturated Hence, an accumulation time of 120 sec was chosen for the best conditions for the method proposed.

### 3.7. Effect of sweep rate

A concentration of  $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  OFL was chosen, and the responses of the detector to the potential sweep rate were recorded at different sweep rates ranging from 20 to 200  $\text{mV s}^{-1}$  (Fig.7a). The cyclic voltammetric results demonstrated that along with the increase of the scan rate, the oxidation peak currents of OFL increased gradually, the peak current varied linearly with the scan rate according to the equation:  $I_{\text{pa}}(\text{A}) = 0.979 + 7.979v$  ( $r = 0.9927$ ) as shown in Fig. 7b. Such behaviors

indicating that the HPMαFP/Ppy composites could efficiently accelerate the electron transfer at the GCE with a diffusion-controlled process.



**Figure 7.** (a) Cyclic voltammograms of  $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  OFL in 0.10 M PBS (pH 7.0) at various scan rates ( from inner to outer ): 20 to  $200 \text{ mV} \cdot \text{s}^{-1}$ , (b) Plot of the  $I_{pa}$  vs.  $v$

### 3.8. Interferences

The effect of interfering ions or biomolecules on the recovery of ofloxacin was investigated. The tolerance limit was defined as the maximum concentration of the interfering substance that caused an error less than  $\pm 5\%$  for determination of OFL. Under the optimum experimental conditions, the proposed method was used for the determination of ofloxacin at  $1 \times 10^{-4} \text{ mol/L}$  level, some interference experiments were carried out. The tolerable limits of interfering substance were given in Table 1. Generally, the results point out a high selectivity for OFL over many common inorganic ions and biomolecules.

**Table 1.** The tolerance limit of interfering substances on CV determination of OFL ( $1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ ) using HPMαFP /Ppy /GCE

Substance	Tolerance limit ( $\times 10^{-5} \text{ mol/L}$ )
$\text{K}^+, \text{Na}^+, \text{Mg}^{2+}, \text{Zn}^{2+}, \text{Cl}^-, \text{H}_2\text{PO}_4^-, \text{HPO}_4^{2-}, \text{PO}_4^{3-}$	200
Glucose, Uric acid, Urea, Dobutamine	100
Cytosine, L-leucine, DL-serine, Guanine, DL-phenylalanine, Adenine	50
Chlortrimeton, Benzoic acid, Oxalate, Lactic acid	10

### 3.9. Sample analysis

In order to confirm the sensitivity and generality of the proposed method, we have utilized this method for the determination of ofloxacin ophthalmic solutions ( Harbin General Pharmaceutical

Factory, China) by standard addition method. The results are listed in Table 2. The recoveries and relative standard deflection (RSD) obtained were found respectively to be 99.8-100.9% and 1.1-2.0%, which indicate that the proposed method can be used efficiently for the ofloxacin in commercial samples.

**Table 2.** Recovery test of ofloxacin in ophthalmic samples (n=5)

Sample	Added ( $\times 10^{-6}$ mol/L)	Expected ( $\times 10^{-6}$ mol/L)	Found ( $\times 10^{-6}$ mol/L)	Recovery (%)	RSD (%)
1	0.0	3.16	3.25	/	1.6
2	1.0	4.16	4.20	100.9	1.2
3	2.0	5.16	5.15	99.8	1.5
4	4.0	7.16	7.19	100.4	2.0
5	6.0	9.16	9.21	100.5	1.1

#### 4. CONCLUSIONS

In this work, a novel electrochemical sensor using glassy carbon electrode modified with HPM $\alpha$ FP/Ppy/GCE composite film was firstly performed to investigate the electrochemical behavior of ofloxacin in detail. The oxidation of OFL was found to be an irreversible two-electron and two-proton process with adsorption character. This electrochemical sensor showed excellent selectivity and high sensitivity. Also the proposed method offers important advantages such as easy fabrication, reproducibility, stability, and anti-jamming. In further experiment, improvement of the detection limit of the proposed method was required in order to determine OFL in more little sample.

#### ACKNOWLEDGEMENTS

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