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Sensitive Detection of Methyl Parathion in Human Urine Using Carboxyl-Group Functionalized Carbon Nanotubes/Carbon Paper-Based Electrochemical Sensor

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The excessive use of methyl parathion (MP) has a serious negative impact on human health and ecological environment. In order to monitor the MP residual, a highly sensitive electrochemical sensor was fabricated with the carboxyl-group functionalized carbon nanotubes modified carbon paper electrode (COOH-CNT/CPE) for the determination of MP. The carboxyl-group functionalized carbon nanotubes (COOH-CNT) possessed high electrical conductivity, large specific surface area, and good electrochemical catalytic performance. The existence of carboxyl groups contributed to the uniform dispersion of carbon nanotubes in liquid solution. Moreover, carbon paper electrode (CPE) presented low cost and easy operation. Research results showed good synergistic interaction of the fabricated COOH-CNT/CPE sensor. Under the optimal conditions, the fabricated COOH-CNT/CPE sensor exhibited good determination performance of MP with a low detection limit of 27 nM in a great linear MP concentration of 0.06-4 μM and 4-30 μM. Moreover, the COOH-CNT/CPE sensor could show good practicability for the determination of MP in human urine. This work is meaningful to the development of the simple, low-cost, and sensitive MP sensor.

Keywords: COOH-CNT/CPE sensor; Synergetic interaction; Electrochemical determination; Methyl parathion; Human Urine

1. INTRODUCTION

As a type of insecticide, methyl parathion (MP) plays a profound role in the field of agricultural production. However, the excessive use of methyl parathion (MP) has a serious negative impact on human health and ecological environment because of the high toxicity. It has severe repercussions for the nerve signals transmission by inhibiting the denaturation of acetylcholine esterase [1-3]. Thus, the

detection and analysis works are becoming increasingly important to ensure food security and protect human health and ecological environment. At present, the determination of MP is carried out by some traditional analysis technology such as high-performance liquid chromatography, liquid chromatography-mass spectrometer, and gas chromatography, etc [4-6] Although these methods have good accuracy, their large-scale application is seriously limited by the high cost, complex professional operation and large analysis equipment.

Recently, electrochemical sensors have been used to perform the determination of MP because of the advantages of low cost, simple fabrication, and high detection efficiency [7, 8]. It is important to note that the fabrication of high-performance electrochemical sensors has much to do with the modification materials [9]. According to the existing literatures [9-13], the determination performance of MP can be enhanced by introducing the modification materials such as carbon materials, metal nanoparticles, transition metal oxides, and its composites. Among them, carbon materials (carbon nanoparticles, carbon nanotubes, graphene sheet, mesoporous carbon) play a major role in the development of high-performance MP sensor due to the high electrical conductivity, large specific surface area, and special microstructural morphology [14-16]. Especially, carbon nanotubes have high electrical conductivity, large specific surface area, and one-dimensional nanotube morphology, which can improve the charge transfer efficiency and surface adsorption performance [3]. Yue et al. [17] reported the carbon nanotubes modified carbon paper electrode as electrochemical sensor. The obtained catechol sensor showed good determination performance with a limit of detection of 0.029 μM in the range of 1-100 μM. Ma et al. [18] fabricated an Au nanoparticle modified carbon nanotube electrode for the determination of MP, which achieved the rapid and sensitive determination of MP with a detection limit of 50 μg mL^{-1} in the linear concentration ranging from 0.50-16 mg mL^{-1}. Such high performance has much to do with the important function of carbon nanotube. These results indicate that carbon nanotube can effectively improve the sensing performance of electrochemical sensors.

In this work, a highly sensitivity electrochemical sensor was fabricated by using the carboxyl-group functionalized carbon nanotubes modified carbon paper electrode (COOH-CNT/CPE) for the determination of MP. The carboxyl-group functionalized carbon nanotubes possessed high electrical conductivity, large specific surface area, and good electrochemical catalytic performance. The existence of carboxyl groups contributed to the uniform dispersion of carbon nanotubes in liquid solution. Moreover, carbon paper electrode (CPE) presented low cost and easy operation, which efficiently promoted the large-scale commercial application and avoided some tedious pretreatment process such as polishing and ultrasonic cleaning. More delightfully, the fabricated COOH-CNT/CPE sensor exhibited good performance in determining MP.

2. EXPERIMENTAL

The COOH-CNT/CPE sensor was successfully fabricated by drop-coating technology. First of all, a certain amount of COOH-CNT (Shanghai Aladdin Bio-Chem Technology Co., LTD) was weighed and put in dimethylformamide (DMF, Shanghai Aladdin Bio-Chem Technology Co., LTD). After ultrasonic dispersion for 60 mins, the uniform suspension could be obtained. And then, the carbon paper

(CP, Hefei Kejing Materials Technology Co., LTD) in certain size (0.5×3.0 cm^2) was tailored as electrode for the surface modification of COOH-CNT. Subsequently, the black COOH-CNT-DMF suspension (50 μL) was drop-coated on the surface of CP. After drying for 15 mins by using the infrared lamp, the COOH-CNT/CPE sensor was successfully fabricated to analyze the MP residual.

To confirm the phase structure, surface morphology and particle size distribution, COOH-CNT were studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The determination performance of MP at the fabricated COOH-CNT/CPE sensor was performed by means of CHI660E electrochemical workstation. The working electrode, counter electrode, and reference electrode were COOH-CNT/CPE electrode, platinum wire, saturated calomel electrode (SCE), respectively. The phosphate buffer solution (0.1 M, PBS) was prepared by using a certain amount of NaH_2PO_4 and Na_2HPO_4 solution.

3. RESULTS AND DISCUSSION

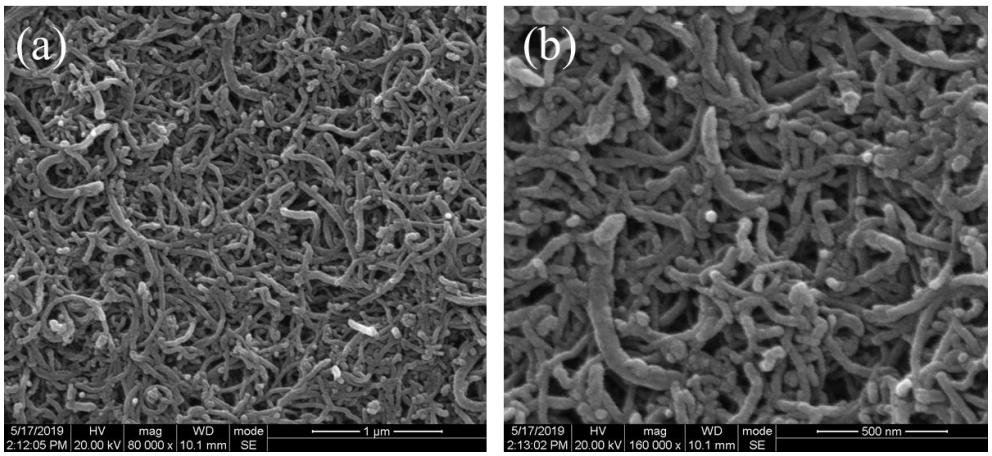

Figure 1. SEM images of COOH-CNT at different magnification.

Figure 1 shows the SEM images of COOH-CNT obtained from Shanghai Aladdin Bio-Chem Technology Co., LTD. It can be seen that COOH-CNT presents obvious nanometer size with an average diameter of about 40 nm. Moreover, this nano-structured carbon material presents one-dimensional nanotube morphology. These results indicate that COOH-CNT possess high electrical conductivity and good surface affinity because of one-dimensional nanotube structure, evenly distributed conductive network, and large specific surface area, which suggest the good sensing performance of the fabricated COOH-CNT/CPE sensor [19].

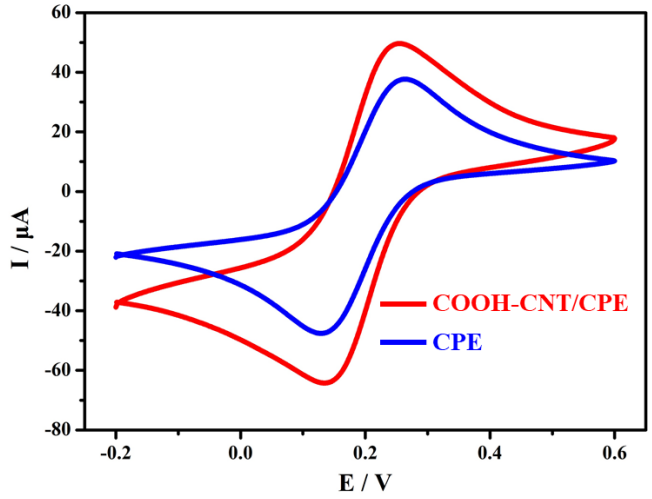

Figure 2. CV curves of the CPE and COOH-CNT/CPE sensors in 5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ solution containing 0.1 M KCl at a scan rate of 50 mV s^{-1}.

The electrochemical performance of the unmodified CPE and COOH-CNT/CPE sensors were investigated by cyclic voltammetry (CV) method. Figure 2 shows the corresponding CV curves of these two sensors. As shown here, there is no obvious redox peaks in the CV curve of the unmodified CPE sensor, which suggests the unsatisfactory performance of the unmodified CP sensor. By contrast, the fabricated COOH-CNT/CPE sensor shows obvious redox peaks in the CV curve with significant peak current response, which has much to do with the high electric conductivity of COOH-CNT [18]. Especially, the one-dimensional nanotube morphology and uniform distribution of COOH-CNT can be conducive to the formation of evenly distributed conductive network, which can promote the charge transport in the interface between the COOH-CNT/CPE electrode and electrolyte [3].

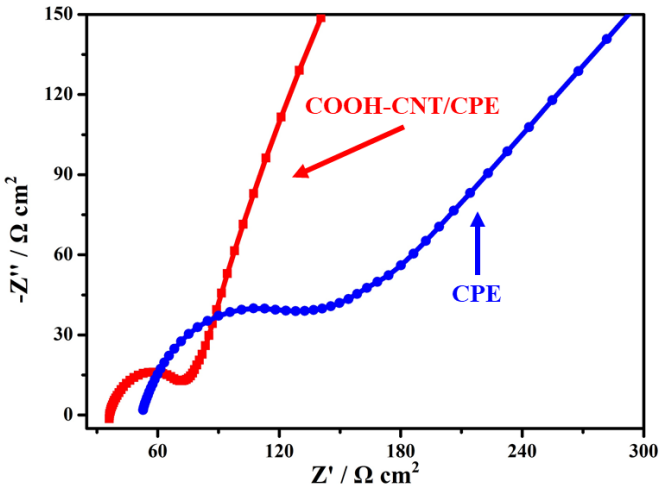

Figure 3. Nyquist plots of the CPE and COOH-CNT/CPE sensors in 5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ solution containing 0.1 M KCl.

In order to further study the electrochemical performance, the Nyquist plots of the unmodified CPE and COOH-CNT/CPE sensors were investigated to confirm the important function of COOH-CNT. Figure 3 shows the corresponding EIS results of these two sensors. As shown here, that the Nyquist plots are consisted of a semicircle in the range from high to medium frequency region and a slope in the low frequency region. According to the reported works, the semicircle corresponds to the charge transfer resistance (R_{ct}), which is closely related to the electrochemical performance [1, 7]. As shown in Figure 3, the unmodified CPE sensor presents a relatively large R_{ct} value, which suggests an undesirable electrochemical performance. By contrast, the COOH-CNT/CPE sensor shows a lower R_{ct} value than that of the unmodified CP sensor, which has strong connections with the surface modification of COOH-CNT. On one hand, COOH-CNT has high electric conductivity, which can enhance the charge transport efficiency. On the other hand, the one-dimensional nanotube morphology and uniform distribution of COOH-CNT can provide an evenly distributed conductive network, which can optimize the charge transport path [3, 18]. As a result, the electrochemical performance of the COOH-CNT/CPE sensor was significantly improved by means of the modification function of COOH-CNT.

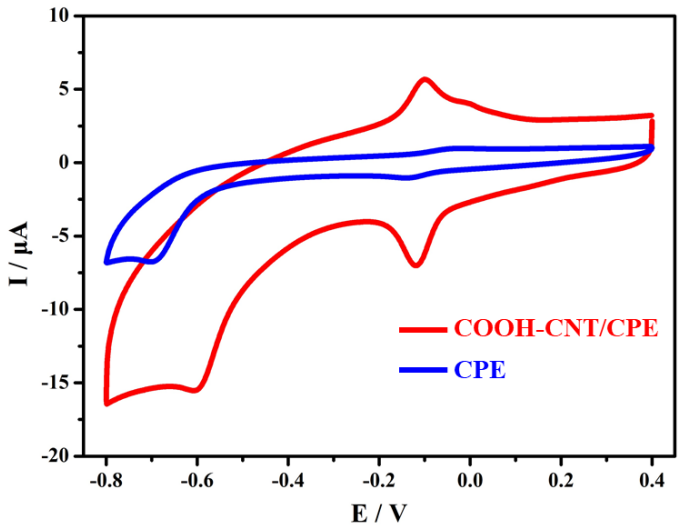

Figure 4. CV curves of the CP and COOH-CNT/CPE sensors in 0.1 M PBS containing 30 μM MP.

The determination performance of MP at the fabricated COOH-CNT/CPE sensor was investigated by CV method. Figure 4 presents the corresponding CV results of the unmodified CPE and COOH-CNT/CPE sensors in 0.1 M PBS containing 30 μM MP. The pH value is controlled around 7.0, and the scanning rate is controlled at a scan rate of 50 mV s^{-1}. It can be found that the unmodified CPE sensor presents not very obvious CV curve. The corresponding redox peaks only present relatively low peak current response, which indicates that the unmodified CP sensor is difficult to achieve the highly sensitivity determination of MP. By contrast, the fabricated COOH-CNT/CPE sensor shows a completely different result. The CV curve of the fabricated COOH-CNT/CPE sensor presents an obvious irreversible reduction peak and a pair of obvious reversible redox peaks. According to the reported works, the irreversible reduction peak has much to do with the irreversible reduction from nitro group

to hydroxylamine group, and the redox peaks have much to do with the reversible redox reaction of hydroxylamine group [1, 3]. Compared with the unmodified CP sensor, the COOH-CNT/CPE sensor presents much high peak current response, which suggests that the introduction of COOH-CNT can significantly improve the electrochemical sensing performance for the determination of MP.

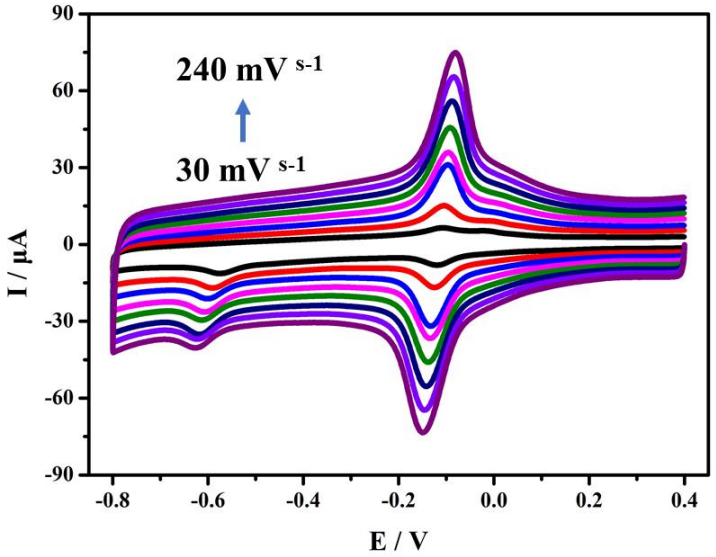

Figure 5. CV curves of the COOH-CNT/CPE sensor in 0.1 M PBS containing 30 μM MP at a scan rate of 30-240 mV s^{-1} and (b) plot of peak current vs. scan rate.

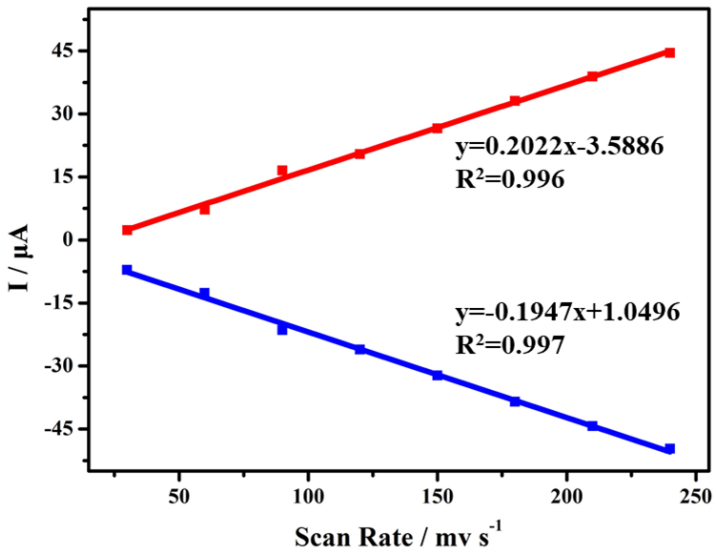

Figure 6. Relation of peak current vs. scan rate at the COOH-CNT/CPE sensor in 0.1 M PBS containing 30 μM MP.

Figure 5 presents the influence of scan rate on the CV curves of the COOH-CNT/CPE sensor. The corresponding scan rate is 30, 60, 90, 120, 150, 180, 210, and 240 mV s^{-1}, respectively. As shown here, as the scan rate increases, both the irreversible reduction peak and a pair of reversible redox peaks

show the gradually increased peak current responses. These results suggest that the determination performance of MP at the fabricated COOH-CNT/CPE sensor has much to do with the scan rate. Figure 6 presents the relationship of peak current with scan rate. It can be found that the peak current responses depend linearly on the scan rate with regression equations of $I_O(\mu A)=0.2022v-3.5886$ ($R^2=0.996$) and $I_R(\mu A)=-0.1947v+1.0496$ ($R^2=0.997$), respectively. The above analysis suggests that the electrochemical reaction of MP at the fabricated COOH-CNT/CPE sensor belongs to the adsorption-controlled process [15, 17].

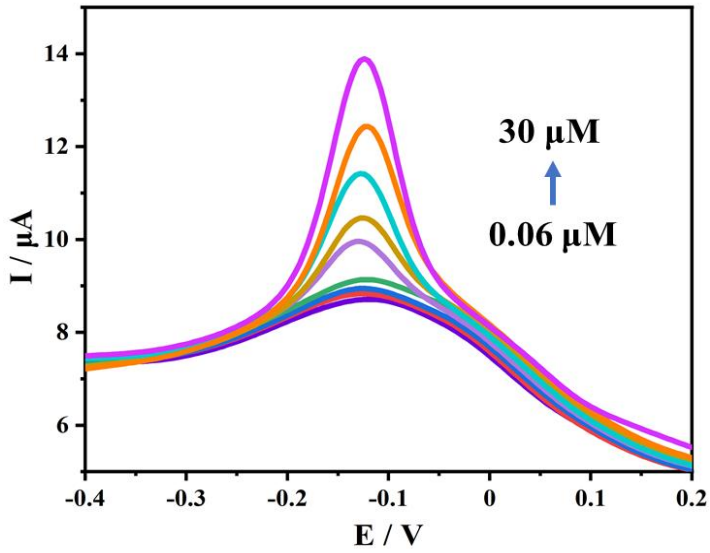

Figure 7. DPVs for the COOH-CNT/CPE sensor in 0.1 M PBS containing different MP concentrations ranging from 0.06 to 30 μM.

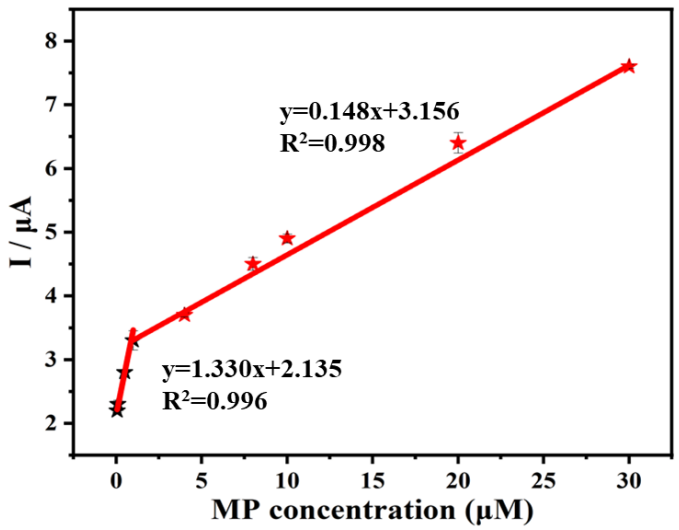

Figure 8. Relationship between oxidation current and MP concentration at the COOH-CNT/CPE sensor in 0.1 M PBS containing different MP concentrations ranging from 0.06 to 30 μM.

DPV method is an important technology for the determination of MP. Figure 7 presents the DPV result of the COOH-CNT/CPE sensor, which was tested at the MP concentration ranging from 0.06 to 30 μM in 0.1M PBS. It can be obviously found that the peak current response demonstrates a significantly increasing tendency with the increasing of the concentration of MP. As shown in Figure 8, the peak current response increases linearly with the MP concentration ranging from 0.04-4 μM and 4-30 μM. The corresponding regression equation is I(μA)=3.156+0.148C (R^2=0.998, Low concentration: 0.04-4 μM) and I(μA)=2.135+1.330C (R^2=0.996, High concentration: 4-30 μM). The two linear ranges in the calibration curves can be attributed to the fact that the MP molecules are moved very fast to the electrode surface when the addition of lower concentrations and the movement of MP molecules were quite slow when the addition of higher concentrations. According to the analysis results, the COOH-CNT/CPE sensor shows a low detection of limit of 27 nM (S/N=3). Table 1 lists the MP determination of other reported works and this work. Compared with other reported works, the fabricated COOH-CNT/CPE sensor shows relatively good MP determination performance, which has much to do with the high electrical conductivity, large specific surface area, and good electrochemical catalytic performance of the carboxyl-group functionalized carbon nanotubes. Moreover, in consideration of the low cost of CP and simple fabrication of COOH-CNT/CPE sensor, this work provides an important reference for the practical application of the fabricated COOH-CNT/CPE sensor.

Table 1. Comparison of the performance the existing reports and this wo

Electrode	Analytical method	Detection limit (nM)	Linear range (μM)	Reference
AuNPs/Nafion/GCE	SWV	100	0.5-120	[13]
Pd/MWCNTs	DPV	190.04	0.38-53.19	[20]
BCL@MOF/nanofibers/chitosan/GCE	DPV	67	0.1-38	[21]
COOH-CNT/CPE	DPV	27	0.06-30	This work

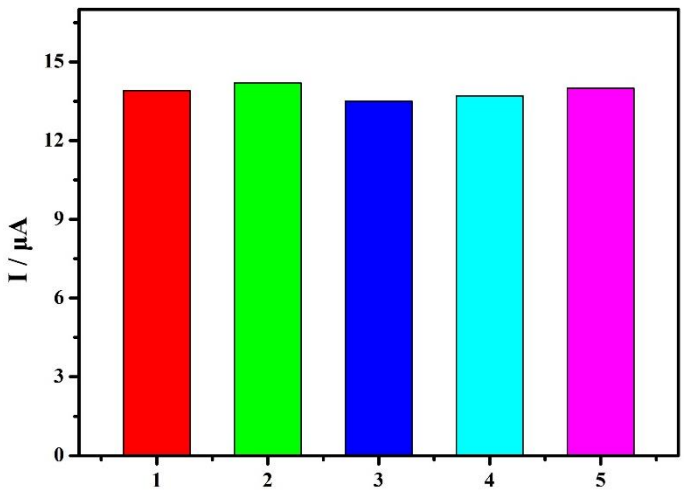

Figure 9. Selectivity of the COOH-CNT/CPE sensor for MP (1: methyl parathion; 2: methyl-paraoxon; 3: p-nitrophenol; 4: carbaryl; 5: dichlorvos).

The interference study was investigated based on the DPV measurement. Figure 9 shows the selectivity of the COOH-CNT/CPE sensor for MP in the mixed solution containing other organic substances (methyl-paraoxon, p-nitrophenol, carbaryl, dichlorvos) at the same concentration. As shown here, it is obvious that the presence of interferences does not have much influence on the MP determination performance. This suggests that the fabricated COOH-CNT/CPE sensor has good selectivity for the determination of MP.

Table 2 lists the MP determination performance of the COOH-CNT/CPE sensor in real samples such as water and human urine. In order to more accurately reflect the MP determination performance, these two samples were divided into three parts. To study the precision of MP determination, the corresponding relative standard deviation (RSD) and recovery were analyzed. According to the measurement results, the COOH-CNT/CPE sensor presented quite satisfactory RSD values and recoveries of MP, which suggest the good practical feasibility of the COOH-CNT/CPE sensor.

Table 2 Determination of MP in real samples using the fabricated sensor.

Sample	MP spiked (μM)	MP found (μM)	Recovery (%)	RSD (%)
Water	10	10.03	100.3	2.31
	20	19.87	99.4	3.04
Human urine	10	9.98	99.8	3.17
	20	20.04	100.2	1.98

4. CONCLUSIONS

We fabricated a highly sensitivity electrochemical sensor based on the COOH-CNT/CPE electrode, which was employed to achieve the determination of MP. Compared with the traditional glassy carbon electrode and carbon paste electrode, the CPE presented the advantages of low cost and easy operation, which efficiently promoted the large-scale commercial application and avoided some tedious pretreatment process such as polishing and ultrasonic cleaning. Under the optimal conditions, the fabricated COOH-CNT/CPE sensor exhibited good determination performance of MP with a low detection limit of 27 nM in a great linear MP concentration of 0.06-4 μM and 4-30 μM. Such high performance was mainly benefited from the high electrical conductivity, large specific surface area, and good electrochemical catalytic performance of the carboxyl-group functionalized carbon nanotubes.

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