The Preparation of Au NPs/RGO-MoO₂ Composite Modified Electrode and Simultaneous Detection of Acetaminophen and Dopamine

Jiang-dong Gu

Shaanxi University of Science and Technology

Qiu-feng An (✉ anqf@sust.edu.cn)

Shaanxi University of Science and Technology

Wu Yang

Northwest Normal University

Ling-yan Pang

Shaanxi University of Science and Technology

Ya-fei He

Shaanxi University of Science and Technology

Research Article

Keywords: Acetaminophen, Dopamine, Au NPs, RGO-MoO₂, Electrochemical Sensor

Posted Date: September 13th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-861280/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

The Preparation of Au NPs/RGO-MoO₂ Composite Modified Electrode and Simultaneous Detection of Acetaminophen and Dopamine

GU Jiang-dong¹, An Qiu-feng¹, Yang Wu², Pang Ling-yan¹, He Ya-fei³

(1. College of Chemistry & Chemical Engineering, Shanxi University of Science & Technology, Xi'an 710021, China; 2. College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070; 3. Department of Foundation Courses, Tianjin College, Beijing University of Science and Technology, Tianjin 301830, China)

Abstract: Dopamine (DA) exists in human body fluids and is the most basic metabolite of the human body, and it is an important neurotransmitter in the central nervous system of animals. Acetaminophen (AMP) is commonly used as cold medicine to treat fever and relieve pain. The safe dosage is very important to human health. Therefore, it is very important to construct an accurate, efficient and fast detection method for detecting AMP and DA. In this paper, Au NPs/RGO-MoO₂ composite modified electrode was prepared for the detection of AMP and DA, We can see that the synergy between RGO-MoO₂ nanomaterials and Au NPs and can promote the electrochemical reaction of AMP and DA, and the oxidation peak potential difference is greater than 180 mV. The linear range of the sensor for detecting AMP is 0.05~320 μmol/L while the linear range of DA is 0.6~260 μmol/L, and the detection limits are 7.2 nmol/L and 13 nmol/L (S/N=3) respectively. The Au NPs/RGO-MoO₂/GCE sensor can be used for the detection of AMP and DA in actual samples because of its excellent characteristics such as wide linear range, lower detection limit, excellent reproducibility, stability, and high selectivity

Keywords: Acetaminophen, Dopamine, Au NPs, RGO-MoO₂, Electrochemical Sensor

Acetaminophen(also called Tylenol and Paracetamol) is used as a medicine to treat colds and also has a good effect on postoperative discomfort(such as pain, skin itching, backache, and fever)of the patients, It can effectively fight bacteria and viruses and is safe for human baby when you take it in a certain dose according to the instructions^[1-2],but it will cause harm to human health when the prescribed dose is exceeded, it may cause liver damage, acute liver failure, coma and even death ^[3]. As an important neurotransmitter of hormones and phenolamines, Dopamine (DA) is widely in the body fluid and brain tissue of mammals and plays an important role in the nervous system and have various physiological functions^[4,5]. The content of DA in normal humans is within 0.01-10μM. The abnormal concentration changes of DA usually cause a variety of diseases, for example, very low concentrations of DA will cause Epilepsy, Parkinson, and Dementia^[6,7]while the content of Dopamineat high level will affect sympathy Nerves and then increases heart rate and blood pressure ^[8]. Therefore, the rapid, sensitive and accurate detection of AMP and DA plays a decisive role in the diagnosis and clinical treatment of related diseases. Currently, there are many methods used for the detection of AMP and DA, among which the electrochemical method has

attracted people's attention because of its simple production, rapid response, high sensitivity and low cost. Therefore, it is very important to research and develop new electrochemical sensors with sensitive response and stable performance for the determination of AMP and DA.

The materials that used in the preparation of electrochemical sensors are particularly important. Appropriate modified materials can effectively improve the sensitivity and selectivity of the sensors. The materials we often use are gold nanoparticles, metal compound materials and carbon materials. Among them, it is the gold nanoparticles (AuNPs) that most widely used in electrochemical sensors for its unique physical and chemical properties (non-toxicity, high conductivity, high catalytic activity, large specific surface area, excellent Biocompatibility and long-term stability)^[9,10]. Metal oxide nanoparticles have good optical properties, mechanical properties and excellent catalytic activity^[11]. The nanoparticles have obvious catalytic effects because of the small size and large specific surface area. MoO₂ nanoparticles can be used for electrochemical sensing for its good metallic and conductive properties, high electron transfer rate. In addition, the pore structure in the crystal lattice facilitates the inflow and outflow of charged particles^[12]. Graphene has hydrogen storage characteristics, field effect characteristics, high strength characteristics, extraordinary specific surface area, high electrical conductivity and fast electron transfer ability^[13,14], which are known as the best material at room temperature at present, the speed of electron movement in it far superior to that of that ordinary conductors^[15]. In addition, Graphene also shows very good adsorption performance of aromatic organic matter^[16], which effectively enrich the analyte to improve the sensitivity of the sensor. But nanoparticles are easy to agglomerate so that their properties are affected. So we used Graphene as an ideal substrate for supporting MoO₂ electrode active materials, MoO₂ nanoparticles were dispersed on Grapheme. The result shows better dispersibility, smaller particle size and higher catalytic activity.

Based on the above analysis, the Au NPS /RGO-MoO₂/GCE electrochemical sensor was prepared by using the drip coating method and electrodeposition method. The sensor can realize the simultaneous detection of acetaminophen and dopamine, and it has high electrocatalytic capacity and good electrical conductivity to separate the two well. The method is sensitive and reliable and also has practical value.

1 Experimental part

1.1 Experimental reagents and experimental instruments

Uric acid (Shanghai Chemical Reagent Company); Dopamine (Shanghai Zhong qin Chemical Reagent Co., Ltd.); Ammonium Molybdate (Hubei Jusheng Technology Co., Ltd.); Sodium Dihydrogen Phosphate (Jiangsu Caiwei Biological Technology Co., Ltd.); Disodium hydrogen phosphate (Jiangsu Caiwei Biological Technology Co., Ltd.); concentrated sulfuric acid (Tianjin Damao Chemical Reagent Factory); Potassium ferricyanide (China Xuzhou Reagent Factory); hydrazine hydrate (Shanghai Science and Technology Co., Ltd.); potassium ferrocyanide (Xuzhou Reagent, China) General Plant); Graphite Powder (Tianjin Fuchen Chemical Reagent Factory); Chloroauric acid, analytical reagent, product of Shanghai Aladdin Biochemical Technology Co., Ltd.

Muffle furnace (Hefei Kejing Material Technology Co., Ltd.); Drying box (Shanghai Heng Scientific Instrument Co., Ltd.); Ultrasonic instrument (Kunshan Ultrasonic Instrument Co., Ltd.); pH meter (OHRUS) Koster Electrochemical Workstation (Deshang Technology Company); Three-electrode system (Pt electrode is the counter electrode, saturated calomel electrode is the reference electrode, and the glassy carbon electrode modified with MoO₂/RGO is the working electrode)

1.2 Molybdenum dioxide nanoparticles-Graphene preparation process

We heated 1.5 g of (NH₄)₆Mo₇O₂₄ up to 500°C in an argon atmosphere and control the gas flow rate to 0 sccm, the temperature was increased at a rate of 10°C/min. After keeping it for 2 hours, it was naturally cooled and washed with water, and dried at 60°C for 12 hours and then we got MoO₂ [17]. Graphene oxide was obtained according to the literature [18], We added 1.0 g MoO₂ and a certain amount of GO powder to 50mL ultrapure water and stirred continuously then wash it with ultrapure water, and place the sediment in a vacuum drying oven at 60°C. Then we put the composite material into a tube furnace under nitrogen atmosphere to control its flow rate and heated at 5°C/min to 500°C for 2h to obtain a black powder sample.

1.3 Pretreatment of glassy carbon electrode and preparation of Au NPs / RGO-MoO₂ / GCE modified electrode

The pretreatment of the glassy carbon electrode: Polish the glassy carbon electrode with Al₂O₃ suspension into a mirror surface, wash it ultrasonically with ethanol and water, and dry it with nitrogen for use. Then we pipetted 5.0 uL of RGO-MoO₂ and then dispersed it onto the surface of the glassy carbon electrode and dried it naturally to obtain RGO-MoO₂/GCE modified electrode. The modified electrode was placed in a 0.1g/L HAuCl₄ solution and deposited for 80s at a constant potential of -0.2V to obtain AuNPs/RGO-MoO₂/GCE.

2 Results and discussion

2.1 Characterization of electrode materials

It can be seen from Figure 1(A) that MoO₂ presents an irregular aggregated granular structure. We can see from figure (B) that Graphene has a sheet-layer fold-like structure, which makes graphene have a large specific surface area, and MoO₂ particles are well scattered on Graphene without obvious accumulation. From the scanning electron micrograph of Figure 1 (C) We can see that AuNPs showing a dispersed spherical structure and the distribution of gold nanoparticles is also well-distributed. It can be clearly seen from the EDS diagram shown in Figure 1(D) that the composite material is composed of four elements: C, O, Mo and Au, indicating that the gold nanoparticles were successfully electrodeposited on the RGO-MoO₂/GCE modification. On the electrode, AuNPs/RGO-MoO₂ composite material was successfully synthesized.

Figure 1 Scanning electron micrograph

It can be observed from the Raman spectrum in Figure 2 that the vibration peak at $230\ 364\ 454\ 494\ 737\ \text{cm}^{-1}$ is the peak of molybdenum dioxide monoclinic crystal. At the same time, it is the two characteristics of graphene D band and G band at 1349cm^{-1} and 1591cm^{-1} Peak, when the Graphene oxide was restored and then the D peak in the Raman spectrum was enhanced. The result shows that the two materials are successfully combined.

Fig 2. Raman spectra of RGO-MoO₂

Figure 3 shows the XPS full spectrum of RGO-MoO₂(A) high-resolution scans of Mo 3d and C 1s (Figure B and C), and Figure (A) shows that Mo appears in the composite material at the corresponding electronic binding energy. The obvious characteristic peaks of 3d, C 1s, Mo 3p and O 1s indicates that the existence of three elements. Figure (B) shows the C element at 1s high-resolution spectrum. The fitting peaks at 284.4, 284.6, 286.4, 288.7eV correspond to four different functional groups of carbon atoms: C-C/C=C, C-O, C=O, O-C=O. The Mo 3d photoelectron peak in Figure (C) shows that the four components belong to Mo⁴⁺3d_{5/2}, Mo⁴⁺3d_{3/2}, Mo⁶⁺3d_{5/2}, Mo⁶⁺3d_{3/2}, indicating that Mo⁴⁺ was oxidized in the air. Figure (D) shows the XRD of the diffraction peaks on the curve correspond to the monoclinic molybdenum dioxide

(110) (020) (111) (112) (220) (222) (031) (-231) crystal planes. The characteristic peak intensity on the curve is higher, which proves that it has better crystallinity. The strong molybdenum dioxide (110) diffraction peak masks the graphene diffraction peak (002) at the same angle, so there is no obvious graphene characteristic peak on the XRD curve of the RGO-MoO₂ composite material. At the same time, (111) (200) and (220) crystal planes of gold nanoparticles appeared on Au NPs/RGO-MoO₂ composites. The above results indicate that the composite material was successfully synthesized.

Figure 3 XPS full spectrum of RGO-MoO₂ (A), high-resolution element scanning images (B, C) of C 1s and Mo 3d, and XRD images (D) of Au NPs/RGO-MoO₂

2.2 Electrochemical properties of Au NPs/RGO-MoO₂/GCE

Figure 4(A) shows that the cyclic voltammetry (CV) graph of different modified electrodes in 0.1mmol/L potassium ferricyanide solution. It can be seen from the graph that a pair of broad redox peaks appear on bare GCE(a) and the current is also small. The redox peak was significantly narrowed and the peak current increased significantly when different nanomaterials were modified on the bare GCE. The modified electrode Au NPs/RGO-MoO₂/GCE(d) had the largest peak current, it was 3 times than that of the bare electrode. This may be due to the higher conductivity of RGO-MoO₂ composites and the excellent catalytic activity of AuNPs, which accelerates the electron transfer rate on the electrode surface.

AC impedance (EIS) spectrum in Figure 4 (B) shows that the semicircle diameter of bare GCE(a) is the largest in the high frequency region, indicating the largest resistance. The smallest semicircle diameter of AuNPs/RGO-MoO₂/GCE(d) is approximately straight line, which indicates the modified electrode has t

he best conductivity, this is consistent with the conclusion drawn from the CV diagram.

Fig. 4 CV(A) and EIS(B) of bare GCE(a), MoO₂/GCE (b), RGO-MoO₂/GCE (c) and AuNPs /RGO-MoO₂/GCE (d) in 0.1 mmol/L K₃[Fe(CN)₆] containing 0.1 mol/L KCl

2.3 Electrochemical behavior of AMP and DA on different modified electrodes

The cyclic voltammetry (CV) method was used to investigate the electrochemical behavior of AMP, DA and their mixtures on different electrodes. Figure 5(A) is the CV diagram of different modified electrodes in the PBS solution containing 1mmol/L AMP. An irreversible weak oxidation peak appears on bare GCE(a). The oxidation peak current of modified MoO₂ is higher than that of the bare electrode, but the peak is still very weak. When the RGO is continuously modified, the oxidation peak is significantly enhanced, indicating that the RGO-MoO₂ composite has good conductivity and can make the current response more sensitive. After AuNPs were deposited on RGO-MoO₂/GCE electrode, a pair of reversible redox peaks appeared. At the same time, the peak current is greatly enhanced. This might be due to the excellent conductivity and electrocatalytic properties of Au NPs, which can accelerate the electron transfer rate on the electrode surface. Figure 5(B) is the electrochemical response of 1mmol/L DA on different modified electrodes. DA has a reversible redox peak on each modified electrode. The peak currents on GCE and MoO₂/GCE electrodes were the weakest while the reversible peak current of DA on Au NPs/RGO-MoO₂/GCE increases and it is significantly higher than that of RGO-MoO₂/GCE. The reduction peak potential is also significantly positive and the oxidation peak is negative, indicating that Au NPs/RGO-MoO₂/GCE composite material has strong electrocatalytic activity. Figure 5(C) is the CV response of AMP and DA mixed solution on each electrode. It can be seen from the figure that on GCE, MoO₂/GCE and RGO-MoO₂/GCE, DA has a pair of redox peaks while AMP has only one anode peak. It can also be seen that with the further modification of the electrode material, the current response signals of AMP and DA increase in turn, and the redox peaks of the two are clearly separated, indicating that AuNPs/RGO-MoO₂/GCE has a catalytic effect on both AMP and DA. It can be used for simultaneous determination of AMP and DA.

Fig.5 CVs of 1mmol/L AMP(A), 1 mmol/L DA(B) and the mixture solution of 1mmol/L AMP and 1 mmol/L DA(C) in (pH=6.0, PBS) solution on GCE(a), MoO₂/GCE (b), RGO-MoO₂/GCE (c) and AuNPs/RGO-MoO₂/GCE (d), respectively

2.4 The influence of buffer solution pH

In order to improve the electrochemical sensing performance of the modified electrode, the influence of pH value (5.0, 5.5, 6.0, 6.5, 7.0) on the electrochemical behavior of AMP and DA on AuNPs/RGO-MoO₂/GCE electrode was studied by DPV method. As shown in Figure 6 (A), the anode peak current values of AMP and DA increase with the increase of pH value. When the pH value is 6.0, the peak currents of AMP and DA both reach the maximum. When the pH value is increased continuously, then the peak current of AMP and DA decreases, so we choose pH=6.0 as the best value. Figure 6(B) shows that the oxidation peak potentials of AMP and DA move to a lower potential with the increase of pH, indicating that protons participated in the electrochemical oxidation process of AMP and DA, and their peak potentials have a linear relationship with pH. The linear regression equation is AMP: $E_{pa}(V) = -0.0338pH + 0.5961$ ($R^2 = 0.9938$), DA: $E_{pa}(V) = -0.0459pH + 0.4556$ ($R^2 = 0.9949$). The absolute value of the slope is close to the theoretical value of 59mV/pH, indicating that the number of protons and electrons involved in the electrochemical reaction of AMP and DA are equal ^[20].

Fig. 6 (A) Effects of the pH on the oxidation peak current(A) and potential(B) of AMP and AP

2.5 Influence of scan rate

In order to explore the kinetics of the oxidation process of AMP and DA on the AuNPs/RGO-MoO₂/GCE electrode surface, the influence of the scan rate on the peak current was further studied by CV method. Figure 7 (A,B) shows that in the PBS solution containing 0.1mmol AMP and 0.2mmol DA respectively, the redox peak currents of AMP and DA increase with the increase of scanning speed, and the oxidation peak potential is more positive, and the reduction peak potential is more negative, indicating that the redox process of AMP and DA on the electrode is reversible. In addition, the linear relationship between peak current and sweep speed is shown in the inset figure. The linear regression equations of AMP and DA are: $I_{pa}(\mu A) = -16.1632 - 0.2146v$ (mV/s) ($R^2 = 0.9978$), $I_{pc}(\mu A) = 6.2517 + 0.1427v$ (mV/s) ($R^2 = 0.9957$) and $I_{pa}(\mu A) = -26.1992 - 0.8779v$ (mV/s) ($R^2 = 0.9962$), $I_{pc}(\mu A) = 13.5146 + 0.8397v$ (mV/s) ($R^2 = 0.9950$), indicating that the redox reaction of AMP and DA on AuNPs/RGO-MoO₂/GCE is an adsorption control process.

Fig. 7 Cyclic voltammograms of AMP(A) and DA(B) on AuNPs/RGO-MoO₂/GCE at the different scan rates in 0.1 mol/L PBS (pH = 7.0), Inset: Plot of peak current vs.

The relationship between peak potential and sweep speed is shown in Figure 8 (A, B). It can be seen that the peak potential of AMP and DA has a linear relationship with the natural logarithm ($\ln v$) of the sweep speed. The linear regression equation of AMP is $E_{pa}(V) = 0.3447 + 0.02475 \ln v$ (mV/s) ($R^2 = 0.9967$); $E_{pc}(V) = 0.4592 - 0.0255 \ln v$ (mV/s) ($R^2 = 0.9973$); the linear regression equation of DA is $E_{pa}(V) = 0.1800 + 0.0199 \ln v$ (mV/s) ($R^2 = 0.9967$); $E_{pc}(V) = 0.3004 - 0.0296 \ln v$ (mV/s) ($R^2 = 0.9973$). According to Laviron theory^[21], the electron transfer numbers of AMP and DA were

calculated to be 1.79 and 2.34 respectively.

Fig. 8 Relationships between the peak potentials and natural logarithm of the potential scanning rates for AMP(A) and DA(B)

According to the results that obtained, the reaction of AMP and DA on the modified electrode is a 2-proton process, and the possible reaction mechanism is speculated as shown in the figure below.

Fig. 9 Response mechanism of AMP and DA on the modified electrodes

2.6 Simultaneous determination of AMP and DA

The relationship between the electrochemical response current of AMP and DA on AuNPs/RGO-MoO₂/GCE and their concentration in PBS (pH=6.0) solution were studied by DPV method. As shown in Figure 10(A), when the fixed concentration of DA is 30 μmol/L and the concentration of AMP varied in the range of 0.05~320 μmol/L, the oxidation peak current has a good linear relationship with the concentration. The linear regression equation is $I_p (\mu A) = -0.0706c (\mu mol/L) - 6.5156 (R^2=0.9957)$, the detection limit is 7.2 nmol/L (S/N=3). Figure 10(B) shows that when the fixed concentration of AMP is 30 μmol/L and the concentration of DA changes within the range of 0.6~260 μmol/L, the oxidation peak current has a good linear relationship with the concentration. The linear regression equation is $I_p (\mu A) = -0.1387c (\mu mol/L) - 11.6271 (R^2=0.9974)$, the detection limit is 13 nmol/L (S/N=3). It shows that the modified electrode has high sensitivity.

Fig. 10 DPVs of different concentrations of AMP solutions containing 30.0 $\mu\text{mol/L}$ DA (A) and different concentrations of DA solutions containing 30.0 $\mu\text{mol/L}$ AMP(B) on AuNPs/RGO-MoO₂/GCE modified electrode.

Inset: Calibration plots of the anodic peak current versus concentrations of AMP and DA

In order to further verify the ability of AuNPs/RGO-MoO₂/GCE to simultaneously detect AMP and DA, the concentrations of AMP and DA were changed together to test the DPV response of the mixed solution. The results are shown in Figure 11(A). As the concentrations of AMP and DA increase, the oxidation peak currents of the two increase correspondingly at the same time. The peak current and concentration are in a linear relationship, and the peak shapes are completely separated and not interfered with each other. The corresponding linear equations are $I_p (\mu\text{A}) = -0.0598c(\mu\text{mol/L}) - 9.2232$ ($R^2=0.9985$) and $I_p (\mu\text{A}) = -0.0765 c(\mu\text{mol/L}) - 10.7175$ ($R^2=0.9949$). The concentration ranges of AMP and DA are 0.09~250 $\mu\text{mol/L}$ and 0.4~250 $\mu\text{mol/L}$, respectively. Compared with the reported sensors, AuNPs/RGO-MoO₂/GCE has a lower detection limit and a wider linear range, which can be applied in the Simultaneous detection of AMP and DA (Table 1).

Fig. 11 DPVs of different concentrations of AMP(0.09, 20, 60, 110, 180, 250 $\mu\text{mol/L}$) and DA(0.4, 20, 65, 115, 195, 250 $\mu\text{mol/L}$) on AuNPs/RGO-MoO₂/GCE modified electrode in 0.1 mol/L PBS (pH = 7.0) (A) and calibration plots of the anodic peak current versus concentration of AMP and AP(B)

Table 1 Comparison of the analytical performance of the different modified electrodes for determining AMP and DA

Electrode	Linear range($\mu\text{mol/L}$)		Detection limit($\mu\text{mol/L}$)		Refs.
	AMP	DA	AMP	DA	
NiO-CuO/GR/GCE	4-400	0.5-20	1.33	0.17	22

TCPP-Sa/CPE	1-90	0.4-10.3	0.2	0.1	23
AG-NAmmodified/GCE	0.1-8	1-26	0.031	0.33	24
3D-MoS ₂ /rGO/Au/GCE	-	0.3-198.3	-	0.15	25
RGO-MoO ₂ /AuNPs/GCE	0.05-320	0.6-260	0.0072	0.013	This work

2.7 Anti-interference ability, repeatability and stability of AMP and DA sensors

The anti-interference ability of AuNPs/RGO-MoO₂/GCE electrode was tested by adding some coexisting substances in the PBS solution of AMP and DA. As shown in Figure 12, amount to 100 times the concentration of inorganic ions such as Ca²⁺, Cu²⁺, Na⁺, Cl⁻, NO₂⁻ and amount to 50 times the concentration of glucose, caffeine, salicylic acid, etc, they all have no significant interference in the determination of AMP and DA. The relative error of DA is less than 5% and the relative error of AMP is less than 10%, indicating that the modified electrode has good selectivity for AMP and DA.

We prepared four AuNPs/RGO-MoO₂/GCE electrodes independently with the same method and tested the PBS (pH=6) solution containing 0.2 mmol/L AMP and 0.2 mmol/L DA to obtain the relative standard deviation (RSD) of AMP and DA are 2.48% and 2.76% respectively, it indicates that the modified electrode preparation process has good repeatability. After 50 consecutive cycles of cyclic voltammetry, the oxidation peak response currents of AMP and DA were 90.10% and 91.80% of their initial value respectively, this indicates that the modified electrode has good stability.

Fig.11 Effects of some organic molecules and inorganic ions on electrochemical determination of AMP and DA

2.8 Analysis of actual samples

In order to evaluate the practicality of AuNPs/RGO-MoO₂/GCE, We used the sensor to measure commercially available acetaminophen tablets and human urine samples. After pretreatment of the sample (pills were crushed and dissolved, filtered and diluted, and the urine was centrifuged and then the supernatant was diluted), it is measured by the standard addition method. The results show that the recoveries of the

two are 95.84%~100.60% and 98.73%~103.10% respectively. The standard deviations of the three parallel determinations were all less than 5%, indicating that the modified electrode can be used for the detection of actual samples (Table 2).

Table 2 Determination of acetaminophen and dopamine in actual samples (n=3)

Sample	Detected ($\mu\text{mol/L}$)		Add ($\mu\text{mol/L}$)		Found ($\mu\text{mol/L}$)		Recovery (%)		RSD(%)	
	AMP	DA	AMP	DA	AMP	DA	AMP	DA	AMP	DA
尿液 1	-	-	30	30	30.19	29.98	100.6	99.93	2.24	2.56
尿液 2	-	-	40	60	38.95	59.25	97.38	98.75	4.12	1.78
尿液 3	-	-	60	80	59.45	78.98	99.08	98.73	3.68	2.45
药片 1	20	-	30	30	48.83	30.03	96.10	100.10	2.75	1.26
药片 2	20	-	50	40	67.92	41.23	95.84	103.10	4.34	4.14
药片 3	20	-	60	80	79.91	80.69	99.85	100.90	1.98	3.28

3 Summary

A new type of AuNPs/RGO-MoO₂/GCE electrochemical sensor was successfully constructed by using Graphene with large specific surface area, the good conductivity of molybdenum dioxide and the high catalytic activity of Au NPs through simple and rapid drop coating and electrodeposition methods. This sensor has good conductivity and high electrocatalytic ability for AMP and DA, which can realize the simultaneous determination of AMP and DA targets without interfering with each other. The method is sensitive, fast, accurate, and selective. This sensor has good performance with wide linear range and good practical application value.

References

- [1] Kung C W, Lin C Y, Vittal R, et al. Synthesis of cobalt oxide thin films in the presence of various anions and their application for the detection of acetaminophen[J]. *Sens. Actuators B*, 2013, 182: 429-438
- [2] Adhikari B R, Govindhan M, Chen A. Sensitive detection of acetaminophen with graphene-based electrochemical sensor[J]. *Electrochim. Acta*, 2015, 162: 198-204
- [3] Anuar N S, Basirun W J, Ladan M, et al. Fabrication of platinum nitrogen-doped graphene nanocomposite modified electrode for the electrochemical detection of acetaminophen[J]. *Sens. Actuators B*, 2018, 266:373-383
- [4] He Y S, Pan C G, Cao H X, et al. Highly sensitive and selective dual-emission ratiometric fluorescence detection of dopamine based on carbon dots-gold nanoclusters hybrid[J]. *Sens. Actuators B*, 2018, 265:371-377
- [5] Zhang C, Ren J J, Zhou J X, et al. Facile fabrication of a 3,4,9,10-perylene tetracarboxylic acid functionalized graphene-multiwalled carbon nanotube-gold nanoparticle nanocomposite for highly sensitive and selective electrochemical detection of dopamine[J]. *Analyst*, 2018, 143:3075-3084
- [6] Gaskill P J, Miller D R, Gamble-George J, et al. HIV, Tat and dopamine transmission[J]. *Neurobiol. Dis.*,

2017, 105: 105 51-73

[7] Surmeier D J. Determinants of dopaminergic neuron loss in Parkinson's disease[J]. FEBS, 2018, 285: 3657-3668

[8] Fukuda S M, Shirakawa K, Jiko H, Gotoh M. Carbon nanotube multi-electrode array chips for noninvasive real-time measurement of dopamine, action potentials, and postsynaptic potentials[J]. Biosens. Bioelectron., 2013, 49: 49 270-275

[9] Zhao L Y, Li J G, Chen X L, et al. Highly sensitive electrochemical detection of hydrogen peroxide based on polyethyleneimine-Au nanoparticles-zinc protoporphyrin[J]. J. Electrochem. Soc., 2019, 166: B631–B636

[10] Liu X, Fang C, Yan J L, et al. A sensitive electrochemiluminescent biosensor based on AuNP-functionalized ITO for a label-free immunoassay of Cpeptide[J]. Bioelectrochemistry, 2018, 123: 211–218

[11] Liu H, Yu X L, Chen H F, Liu Y H. Preparation of porous carbon-manganese dioxide nanocomposite for sensitive determination of cadmium ion[J]. Int. J. Electrochem. Sci., 2017, 12: 9736-9746

[12] Zhou J, Xu N S, Deng S Z, et al Large-area nanowire arrays of molybdenum and molybdenum oxides:synthesis and field emission properties[J]. Adv. Mater, 2003, 15: 1835.

[13] Li Jialin, Xie Jiale, Gao Lixia, et al. Au nanoparticles-3D graphene hydrogel nanocomposite to boost synergistically in situ detection sensitivity toward cell-released nitric oxide, [J]. ACS Appl. Mater. Interfaces, 2015, 7(4): 2726–2734.

[14] Novikov S, Lebedeva N, Satrapinski A, et al. A. Lebedevd, Graphene based sensor for environmental monitoring of NO₂[J]. Sens Actuators B Chemical, 2016, 236(29): 1054–1060.

[15] Zhao Yuan, Huang Weijiu. Research Progress on Preparation and Performance of Graphene and Its Composite[J]. Journal of Chongqing University of Technology(Natural Science), 2011, 25(7):64-70

赵远, 黄伟九, 石墨烯及其复合材料的制备及性能研究进展[J]. 重庆理工大学学报(自然科学), 2011, 25(7): 64-70

[16] Xie Huanling, Huang Xiaoxue. Overview of photocatalytic Degradation of VOCs by TiO₂ Nanocomposites[J]. Journal Of ShanXi University Of Science & Echnology, 2019, 33(4): 88-92.

谢焕玲, 黄小雪. TiO₂ 纳米复合材料光催化降解 VOCs 的研究进展[J]. 重庆理工大学学报(自然科学), 2019, 33(4): 88-92.

[17] Xu Zhanwei, Wang Tian, Liu Xinyue, et al. Effect of Different Atmosphere on Decomposition Products of Ammonium Heptamolybdate[J]. Journal Of ShanXi University Of Science & Echnology, 2017, 35(03):53-58.

许占位, 王天, 刘鑫悦, 等. 气氛对钼酸铵分解的影响及产物的电化学性能[J]. 陕西科技大学学报, 2017, 35(03): 53-58.

[18] Yang Jinghui, Feng Chenxia, Dai Jian, et al. Compatibilization of immiscible nylon 6/poly(vinylidene fluoride) blends using graphene oxides [J]. Polymer international, 2013, 62(7): 1085-1093.

[19] Kumari L, Ma Y R, Tsai C C, et al. X-ray diffraction and Raman scattering studies on large-area array and nanobranched structure of 1D MoO₂ nanorods[J]. Nanotechnology, 2007, 18(11): 1-7.

[20] Liu Z M, Wang Z L, Cao Y Y, Jing Y F, Liu Y L. High sensitive simultaneous determination of hydroquinone and catechol based on graphene/BMIMPF₆ nanocomposite modified electrode [J]. Sens. Actuators B, 2011, 157: 540-546

[21] Laviron E. Adsorption, autoinhibition and autocatalysis in polarography and in linear potential sweep voltammetry [J]. J. Electroanal. Chem. Interfacial Electrochem., 2004, 60: 669-676

[22] Liu B, Ouyang X, Ding Y, et al. Electrochemical preparation of nickel and copper oxides-decorated graphene composite for simultaneous determination of dopamine acetaminophen and tryptophan[J]. Talanta, 2016, 146:141-121

[23] Kemmegne-Mbougouen J C, Ngameni E. Simultaneous quantification of dopamine, acetaminophen and

tyrosine at carbon paste electrode modified with porphyrin and clay[J]. Anal. Methods, 2017, 9: 4157-4166.

[24] Kim D, Lee S, Piao Y. Electrochemical determination of dopamine and acetaminophen using activated graphene-Nafion modified glassy carbon electrode[J]. J. Electroanal. Chem., 2017, 794: 221-228.

[25] Zhao Y, Zhou J, Jia Z, et al. In-situ growth of gold nanoparticles on a 3D-network consisting of a MoS₂/rGO nanocomposite for simultaneous voltammetric determination of ascorbic acid, dopamine and uric acid[J]. Microchim. Acta, 2019, 186: 92