

Electrochemical Determination of Ascorbic Acid, Dopamine and Uric Acid at Polyaniline-Graphene Nanocomposites Modified Electrode

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In this work, we proposed a novel liquid-liquid interface polymerization method for preparing of PANI/GN nanocomposites. The interface polymerization method can effectively suppress secondary growth. This method was benefit for growing PANI onto GN surface uniformly. Then an electrochemical sensor for the determination of DA, AA, and UA was fabricated on glassy carbon electrode (GCE) modified with the obtained PANI/GN nanocomposites. Cyclic voltammetry (CV) and amperometric i-t curve were performed to investigate the electrochemical behaviour of DA, AA, and UA. The results indicated the PANI/GN-modified electrode had a good electrochemical response toward AA, AD, and UA in the concentrations range between 0.167 μM to 600 μM , 0.0557 μM to 530 μM , 1.500 μM to 890 μM , respectively. And the corresponding detection limit for AA, DA, and UA were 0.053 μM , 0.019 μM , and 0.57 μM , respectively. Good detection limit of 0.053 μM , 0.019 μM , and 0.57 μM were achieved for determination of AA, AD, and UA, respectively.

Keywords: graphene; polyaniline; electrochemical sensor; ascorbic acid; dopamine; uric acid

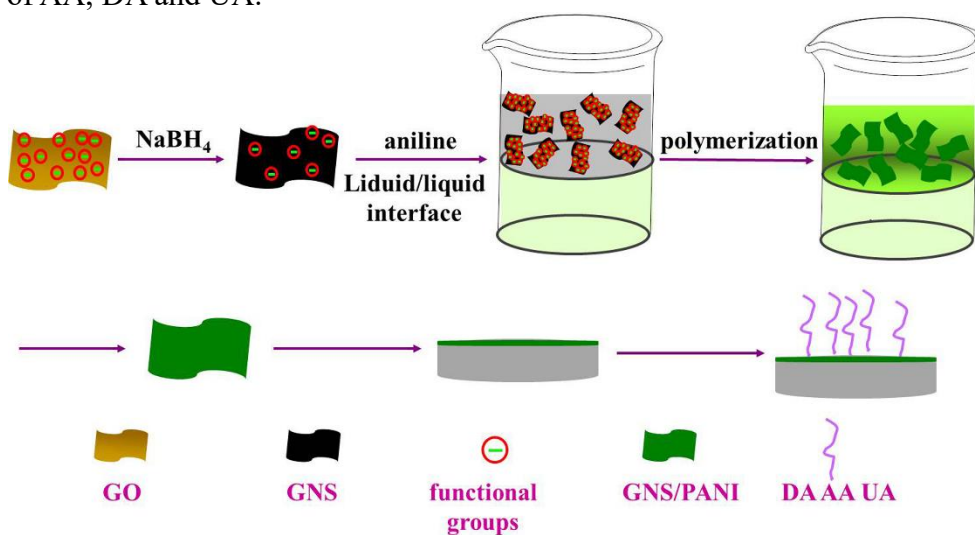
1. INTRODUCTION

Dopamine (DA), an important neurotransmitter, plays a significant role for brain's emotions, feelings, and messages of excitement and pleasure [1, 2]. The lack of dopamine will lead to Parkinson's disease, schizophrenia, Alzheimer's disease and other psychiatric diseases [3]. Uric acid (UA) is an important analyte of clinical interest. The UA produced by the oxidation of various purines and then is excreted in the urine. But if the body produces too much too late to discharge or UA excretion mechanism of degradation, it will lead a large amount of uric acid remains in the body. It will lead cardiovascular disease, obesity, diabetes, high cholesterol, hypertension, kidney disease, heart disease, leukemia and pneumonia [4-6]. Ascorbic acid (AA) is commonly used in large scale as an antioxidant in food, animal feed, pharmaceutical formulations, and cosmetic applications. The lack of AA will

cause scurvy, bleeding gums, tooth loss, and bad breath [7, 8]. Thus, the analysis of AA, DA and UA is of great significance not only in the neurophysiological research but also in the diagnosis of disease. The electrochemical method has been widely used to detect small biological molecules due to its simple operation, low cost, fast analysis, high sensitivity [9, 10].

Graphene (GN) is a two-dimensional carbon atom with a single atom thickness. Graphene has received great research interest in electrochemical fields due to its excellent electron transfer ability, high specific surface area, good mechanical properties et al [11, 12]. Polyaniline (PANI) is an important conducting polymer, due to its electrochemical stability, adjustable conductivity, high stability of the environment, and electrochemical stability. The combination of GN and PANI are an excellent material for electrochemical sensing platform simultaneously possessing the unique properties of PANI and GN. It will expand application areas of composites.

In this research, a simple nanocomposite was obtained by novel interfacial polymerization method. The PANI was grown uniformly onto the surface of GN. The obtained nanocomposites were used to fabricate electrochemical sensor toward of AA, DA and UA. The synthetic method was shown in Scheme 1. The results showed that the proposed sensor revealed excellent electrochemical activity for detection of AA, DA and UA.



Scheme 1. The schematic of preparing of PANI/GN composites and fabricating electrochemical sensor toward AA, DA, and UA.

2. EXPERIMENTAL

2.1 Materials

Graphite (99.95%, 8000 mesh) powder was purchased from Alfa Aesar. The dopamine hydrochloride (98%), uric Acid (>99 %), ascorbic acid (>99 %) and aniline were obtained from Sinopharm reagent co., LTD. The obtained aniline was redistilled before using. All other chemicals were analytical reagent grade. The 0.2 M phosphate buffer solutions (PBS) (pH=7.4) were used as the supporting electrolyte.

2.2 Preparation of PANI/GN nanocomposites

Graphite oxide (GO) was obtained from graphite flake by a modified Hummers' method [13-15]. Then the obtained GO was reduced to graphene [16-18]. The details were as follows, 30 mL (1 mg mL^{-1}) of GO dispersion solution was stirred 30 min. Then 150 mg of NaBH_4 was added into above solution. The obtained mixtures were stirred 6 h under 80°C bath. The obtained composites were collected by centrifuging and washed with ultra-pure water. Finally, the obtained composites were re-dispersed in 20 mL of ultra-pure water by ultrasonic for 20 min. The PANI/GN composites were prepared *via* a liquid-liquid interface polymerization method according to our previous report [19]. 3.0 mg of GN and 100 mg of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dispersed in 100 mL of HCl (1.0 M) aqueous solution, the mixtures were sonicated for 1 h, and the obtained solution was marked as solution A. 100 mg of aniline was dissolved in 100 mL CH_2Cl_2 in beaker. Then the solution A was gently added into the above beaker. The interfacial system was established based the organic phase used as under layer and the water phase used as upper layer. The reaction was carried out for 48 h at room temperature. As reaction time was prolonged, the dark green products were observed at the interface. The product at the aqueous layer was carefully collected, centrifuged and washed several times with ultra-pure water. The obtained PANI/GN nanocomposites were redissolved in double-distilled water.

2.3 Characterization

The scanning electron microscope (SEM) images were obtained with FEI Quanta 250 (USA). Electrochemical measurements were carried with CHI660E electrochemical analyzer (CHI, Shanghai). Glassy carbon electrode (3 mm diameter) acted as the working electrode, and an Ag/AgCl as the reference electrode, platinum wire as the counter electrode, respectively.

3. RESULT AND DISCUSSION

3.1 Characterization

The SEM was used to characteriaed the morphology of obtained PANI/GN nanocomposites. The PANI/GN showed a large wrinkle structure, the PANI grew uniformly onto the surface of GN. The PANI/GN had no apparent agglomerate. The results revealed that interfacial polymerization method was a quite effective method to grow PANI film onto the surface of GN. It was due to the PANI nucleated and polymerized onto the surface of GN at the liquid-liquid interface. The GN/PANI was hydrophilic and can move away from interface and diffuse into the water layer. This technology can suppress effectively secondary growth [20, 21].

3.2 Cyclic voltammetric detection of AA, DA, and UA

Figure 2 showed the CVs of the mixture solution of AA, DA, and UA recorded at the GN and PANI/GN modified GCE. At the GN/GCE, two peaks were observed at the potentials of 0.32 V and

0.55 V (curve a). The backer was broad which should be the overlapped signal of DA and UA. Therefore, the oxidation peak potentials of AA, DA, and UA were indistinguishable, and it was impossible to determine the individual concentration of these compounds from the overlapped oxidation peak at GN/GCE. When using the electrode made from the PANI/GN, it exhibited three well-defined oxidation peaks at 0.37 V, 0.54 V, and 0.74 V, respectively. The results showed that the proposed sensor can detect simultaneously AA, DA, and UA. That maybe due to the prepared PANI/GN nanocomposites had excellent electrochemical activity and benefit for determination of AA, DA, and UA [22, 23].

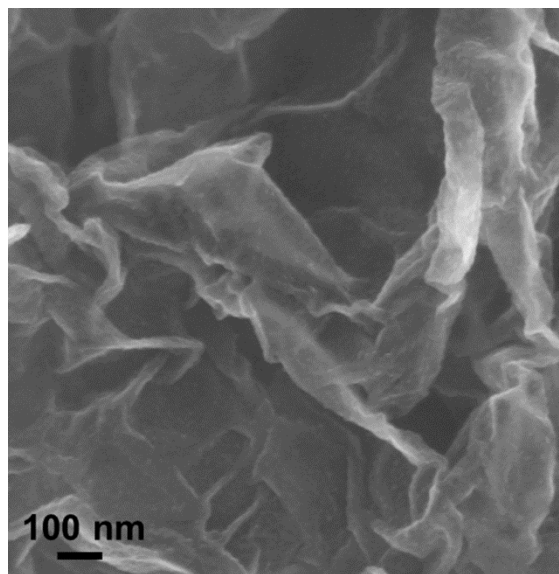


Figure 1. SEM image of PANI/GN nanocomposites.

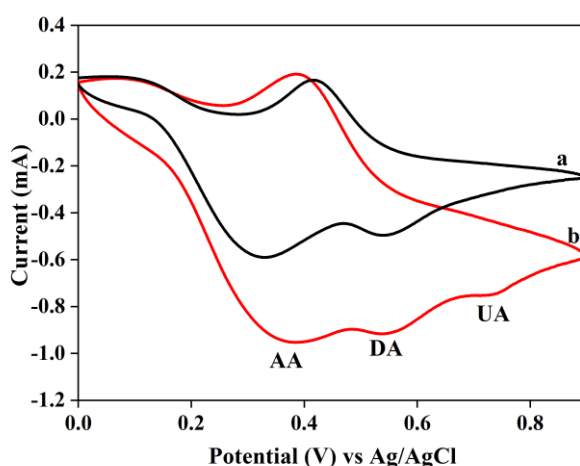


Figure 2. (A) CVs of the GN/GCE (curve a) and PANI/GN/GCE (curve b) in 0.2 M PBS (pH 7.4) containing 0.4 mM AA, 0.5 mM DA and 0.89 mM UA. Scan rate was 50 mV/s.

3.3 The effect of scan rate

The effect of scan rate on the electrochemical signal of PANI/GN/GCE was studied. The results were shown in Figure 3, it can be observed that the oxidation peak currents of AA, DA and UA were increased linearly with increasing scan rate. The linear equations of AA, DA and UA can be described as: $I_{AA} = -0.12v - 0.11$ ($R^2 = 0.9896$); $I_{DA} = -8.4v - 0.18$ ($R^2 = 0.9915$); $I_{UA} = -0.5.89v - 0.27$ ($R^2 = 0.9867$), respectively. The results showed that the electrochemical oxidation of AA, DA and UA on PANI/GN/GCE were surface-controlled processes [24, 25].

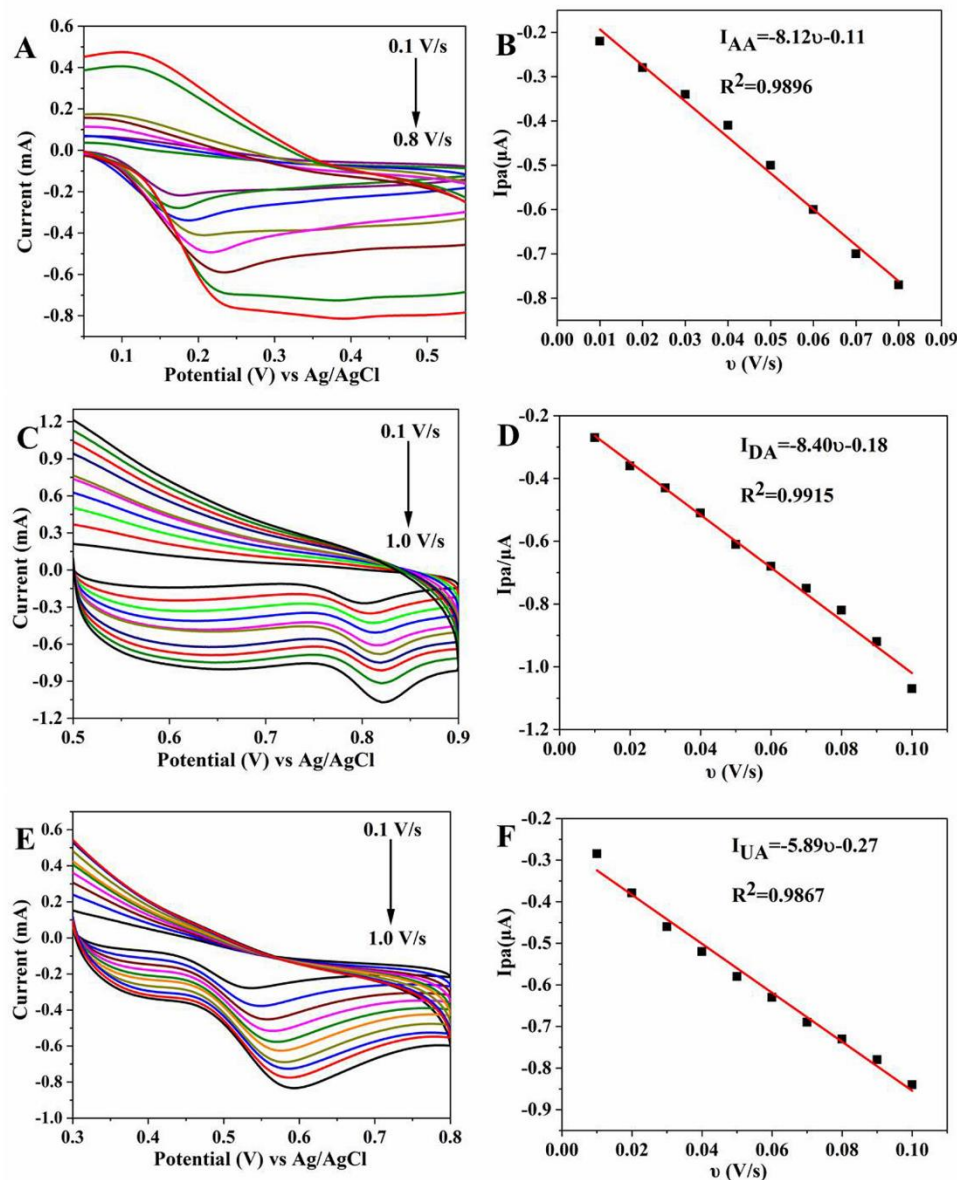


Figure 3. Effect of the scan rate on the cyclic voltammetric response of 0.4 mM AA (A), 0.5 mM DA (C) and 0.89 mM UA (E). (B), (D) and (F) corresponding plots of the anodic peak currents vs. scan rate for AA, DA and UA.

3.4 Determination of AA, DA, and UA

The amperometric *i*-*t* curve was used to detect AA, DA and UA. The amperometric responses of modified electrode to the successive addition of different concentration of AA, DA, and UA were shown in Figure 4. Figure 4A showed that the amperometric responses of PANI/GN/GCE toward AA, an excellent linear relationship between current and AA concentration from 0.167 μM to 600 μM was obtained. The linear regression equation was $y = -0.24 - 11.68x$ ($R^2 = 0.9955$). The detection limit was 0.0530 μM ($S/N = 3$). Figure 4B showed that the amperometric responses of PANI/GN/GCE toward DA, an excellent linear relationship between current and DA concentration from 0.0557 μM to 530 μM was obtained. The linear regression equation was $y = -0.07 - 13.69x$ ($R^2 = 0.9983$). The detection limit was 0.0190 μM ($S/N = 3$). Figure 4C showed that the amperometric responses of PANI/GN/GCE toward UA, an excellent linear relationship between current and UA concentration from 1.500 μM to 890 μM was obtained. The linear regression equation was $y = -0.20 - 9.48x$ ($R^2 = 0.9947$). The detection limit was 0.57 μM ($S/N = 3$). These results revealed that the proposed sensor had excellent electrochemical activity toward determination of AA, DA, and UA. The results for determination of AA, DA, and UA by different modified electrodes and different analytical parameters were compared. The results were shown in Table 1. The sensor fabricated with MWCNTs@PFFP, FeC@NGCSs, Pd@NCF, RGO/AuNPs, and AuNPs-CD-Gra for determination of AA, DA, UA were showed highest detection limit compared with the PANI/GN modified GCE. By comparison, PANI/GN modified electrode revealed a better detection limit and linearity range of AA, DA, and UA.

Table 1. Comparison of the results for determination of AA, DA, UA using different electrodes.

Electrode materials	Detection method	Linear range/ μM	Detection limit/ μM	Reference
MWCNTs@PFFP	DPV	AA: 200.000~400.000 DA: 2.000~16.000 UA: 2.000~16.000	AA: 40.000 DA: 1.100 UA: 7.300	[26]
FeC@NGCSs	DPV	AA: 1.200~120.800 UA: 4.800~263.000	AA: 0.340 UA: 1.400	[27]
Pd@NCF	DPV	DA: 0.500~230.000 UA: 0.500~100.000	DA: 0.107 UA: 0.076	[28]
RGO/AuNPs	I-T	DA: 0.140~100.000	AA: 9.500 DA: 0.140 UA: 25.000	[29]
AuNPs-CD-Gra	SWV	AA: 30.000~2000.000 DA: 0.500~150.000 UA: 0.5000~60.000	AA: 10.000 DA: 0.150 UA: 0.210	[30]
PANI/GN	I-T	AA: 0.167 ~ 600 DA: 0.0557 ~ 530 UA: 1.500 ~ 890	AA: 0.0530 DA: 0.0190 UA: 0.570	This work

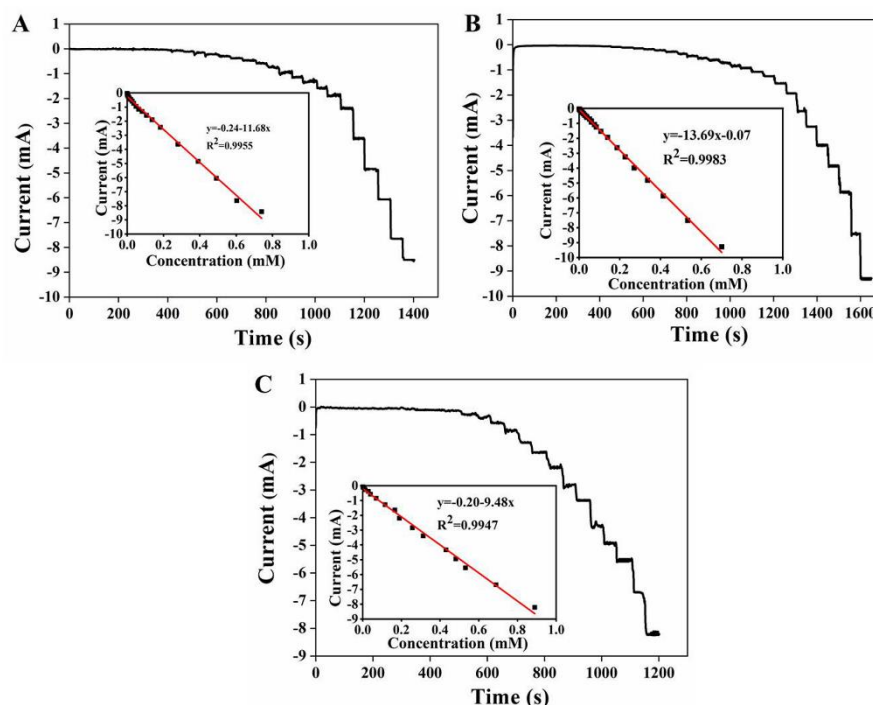


Figure 4. Amperometric responses of the PANI/GN/GCE after the subsequent addition of (A) AA, (B) DA, and (C) UA solution in a 0.2 M PBS solution. The Inset: The corresponding calibration curve of the currents vs. concentration.

3.6. Reproducibility and stability

In order to evaluate the reproducibility of PANI/GN/GCE, five PANI/GN/GCEs fabricated using the same method was used to detect 0.4 mM AA, 0.5 mM DA and 0.89 mM UA by CVs measurements. The RSD value was 4.7%, 3.8%, and 4.5%, demonstrating the fabricated sensor possessed good reproducibility. The stability of proposed sensor was also evaluated by detecting 0.4 mM AA, 0.5 mM DA and 0.89 mM UA by CVs measurements at different times with same sensor. The responses were monitored every 3 days. It was noted that the current response of PANI/GN/GCE maintained 90.3% of the initial response. These results revealed that the fabricated PANI/GN/GCE sensor had excellent stability and reproducibility.

3.7. Real samples

Human urine samples were analyzed directly after being diluted by 10 times with 0.2 M PBS (pH 7.4). The contents of AA, DA, and UA were determined using the standard addition method. To ascertain the correctness of the results, the diluted samples mentioned above were spiked with certain amounts of AA, DA, and UA and then detected. The recovery of the spiked samples ranged between 98.0% and 102.0% (Table 2), indicating that the successful applicability of the fabricated electrochemical sensors to determination of AA, DA and UA in the real biological samples.

Table 2. Determination of AA, DA, and UA levels in urine samples using the PANI/GN/GCE in 0.2 M PBS (pH 7.4). (each result was average of three determinations).

Sample	Analyte	Added/ μ M	Found/ μ M	Recovery/%	RSD/%
sample 1	AA	50	50.1	100.2	1.4
	DA	10	9.8	98.0	1.2
	UA	20	19.6	98.0	2.2
sample 2	AA	50	49.7	99.4	3.1
	DA	10	10.2	102.0	1.5
	UA	20	19.7	98.5	2.3
sample 3	AA	50	50.2	100.4	2.5
	DA	10	10.1	101.0	2.1
	UA	20	20.3	101.5	3.2

4. CONCLUSION

In this work, we proposed a novel interface polymerization technical route for preparing of PANI/GN nanocomposites. The interface polymerization method can effectively suppress secondary growth. This method was benefit for growing PANI onto GN surface uniformly. The obtained

nanocomposites were used to fabricate sensor for determination of DA, AA, and UA. The results indicated that the PANI/GN/GCE had excellent electrocatalytic activity to the oxidation of DA, AA, and UA. Moreover, the obtained sensor had excellent reproducibility and stability.

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