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Three-dimensional Nitrogen-Doped Graphene Aerogel as an Excellent Electrode Material for Highly Sensitive Determination of Midecamycin

Yu Xie, Xue Ma, Yunhui Yu, Peng Zhou, Limin Lu^{*}, Guoying Peng, Xigen Huang, Guangbin Liu^{*}, Wenmin Wang, Haohua He

Key Laboratory of Crop Physiology, Ecology and Genetic Breeding, Ministry of Education, Institute of biotechnology and physical agriculture engineering, College of Science, Jiangxi Agricultural University, Nanchang 330045, PR China *E-mail: <u>lulimin816@hotmail.com</u>

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Abuse of midecamycin (MD) has posed a series of side effects to human health. Therefore, the detection of MD is critical to optimal treatment and avoidance of toxic concentrations. Till now, several carbon materials such as multi-walled carbon nanotube (MWCNT) and graphene modified electrodes were developed for MD determination. However, in relative with these one or two-dimensional (1D or 2D) carbon materials, 3D structural materials display more excellent characteristics, such as higher specific surface, better electrical conductivity and more desirable electrocatalytic activity. Inspired by this, in this study, a novel electrochemical MD sensing platform has been proposed based on 3D N-doped graphene aerogels (NGAs) material. Electrochemical results indicate that NGAs modified electrode exhibited prominent sensing performances toward MD, which is mainly ascribed to the fact that the 3D porous structure provides multiple electron path and unhindered substance diffusion. Besides, the large specific surface area ensures rich active sites for the catalytic reaction of MD. Furthermore, N doping can effectively adjust their bandgap and electron density. Under the optimized conditions, the as-prepared sensor could detect MD concentrations down to 0.01 μ M (S/N= 3) with the linear range of 0.03–21 μ M. The sensor exhibited good performances with high sensitivity, selectivity, and long-term stability.

Keywords: Electrochemical sensor; N-doped graphene aerogels; Detection; Midecamycin

1. INTRODUCTION

Midecamycin (MD) (Scheme 1), a kind of macrolide antibiotics has strong antibacterial activity against Gram positive and negative bacteria via inhibiting bacterial protein synthesis [1]. MD is widely used in skin infection and respiratory tract infection, and can also be used for mycoplasma pneumonia

[2]. However, excessive use of MD may cause toxic concentrations. Therefore, the detection of MD is of great significance for optimizing the treatment process and toxicity assessment. In comparison with some traditional methods, such as gas chromatography, spectrophotometry and mass spectrometry [3], electrochemical methods are highly desirable for MD detection because they are more simple, sensitive, response rapidly, and cost-effective. In most case, electrochemical sensors usually require the use of modified electrodes. Till now, different functional electrodes were reported for the electrochemical determination of MD, like reduced graphene oxide [4], multi-walled carbon nanotube (MWCNT) [5] and carbon fiber [6]. However, these carbon nanomaterials exist some disadvantages, such as intrinsically low surface area and relatively poor conductivity, which decline the detection sensitivity [2].



Scheme 1. Chemical structure of MD.

Graphene aerogels (GAs), a macrostructure integrated by using a single graphene (GR) sheet as a nano-sized building block, aroused widespread concerns due to their unique 3D mesoporous structure, prominent conductivity, high specific surface and abundant pore volume [7]. Owing to their exceptional physicochemical properties, the application of GAs as novel electrode materials in electrochemical sensors attracted increasing attention. For instance, GAs were used as electrochemical sensing interface by Li et al., which was capable of detecting dopamine with high sensitivity and stability [8]. Sun et al. proposed the utilization of GAs modified electrode for the determination of quercetin [9]. Although GAs yields a significant signal enhancement in these analytical methods, it should be also worth noting that GAs is a highly defect-free hydrophobic material, which limits its further application [8]. Therefore, the surface derivative of GAs is important for the further improvement on electrochemical performance of GAs-based sensors.

Heteroatom doping has been widely applied to modify carbon materials because it can manipulate surface chemical, cause lattice defects, adjust the band structure and tailor electronic properties [10]. Among them, nitrogen (N) is deemed as an ideal chemical doping element since it has a suitable atomic size and possesses pentavalent electrons and can form strong valence bonds with carbon atoms [11]. Incorporating N into GR lattice not only greatly enhances the conductivity owing to the extra electron density provided by the doped N atoms, but also increases the surface chemical activity and electron transfer rate [12]. Therefore, N doping has been recognized as a useful method to

improve the electrochemical performance of GAs [13]. For instance, Song et al. established an electrochemical sensor based on NGAs for sensitively detecting uric acid, ascorbic acid and dopamine. The electrochemical result indicated NGAs/GCE showed better electrocatalytic ability than GAs/GCE [14]. Chen et al. used free-standing 3D NGAs electrode as sensing interface for fabricating sensitive DNA sensor to detect ssDNA [15]. Based on the excellent properties of NGAs mentioned above, it is believed that NGAs will be a promising electrode material for MD detection.

Herein, NGAs were prepared via a simple one-pot hydrothermal method using graphene oxide (GO) as carbon source and dopamine as nitrogen source. And then, a new electrochemical sensor for MD detection was designed using NGAs modified electrode. With the synergic effects of well-defined 3D porous architecture, large specific surface and highly electrical conductivity of GAs, as well as excellent electrocatalytic ability induced by nitrogen doping, the sensor displayed excellent performance for determination of MD with low detection limit, exceptional sensitivity, and satisfactory stability.

2. EXPERIMENTAL

2.1 Reagents

MD (99%) was supplied by Toronto Research Chemicals Co., Ltd. (Toronto, Canada). Na₂HPO₄, NaH₂PO₄ and methanol were produced by XiLong Scientific Co., Ltd. (Shenzhen, China). GO was from XFNANO Co., Ltd. (Nanjing, China). Graphite powder (99.85%), N, N-dimethylformamide (DMF) (98%) and dopamine (DA, 98.5%) were received from Aladdin chemistry Company (Shanghai, China). MD solution (5 mM) was prepared using methanol. 0.1 M phosphate buffer solution (PBS) with different pH value was prepared by mixing Na₂HPO₄ and NaH₂PO₄ in certain proportions. Redistilled water was used throughout.

2.2 Apparatus

Morphological image of NGAs was captured from S3400N scanning electron microscope (SEM, Hitachi, Japan). The analysis result of transmission electron microscopy (TEM) was examed with a Tecnai G20 (FEI, USA). ESCALAB 250Xi spectrometer (Thermo Fisher Scientific, USA) was used to investigate the X-ray photoelectron spectroscopy (XPS). Raman analysis was tested by DXR Raman spectrometer (Thermo Fisher Scientific, USA). All experiments were implemented on a three-electrode system of CHI 760E electrochemical workstation (Shanghai, China), consisting of saturated calomel electrode, a platinum wire ($\Phi = 1 \text{ mm}$) and GCE ($\Phi = 3 \text{ mm}$).

2.3 Preparation of NGAs

NGAs were synthesized by a facile hydrothermal method [13]: 15 mg DA was mixed with 15 mL GO aqueous dispersion (1 mg mL⁻¹) and sonicated about 40 min. The mixture was transferred into

Teflon lined autoclave with following heating for 12 h at 180 °C to generate N-doped graphene hydrogels (NGHs). After cooling down, NGHs were washed with ethanol and redistilled water. The NGHs were freeze-dried to obtain NGAs. Meanwhile, GAs were synthesized by the same procedure without adding DA as the source of N.

2.4 Fabrication of the electrochemical sensor

1 mg of GR, GAs, and NGAs were suspended in 1 mL DMF, respectively. Before modification, GCEs were polished thoroughly to obtain a clean surface, and then cleaned thoroughly ultrasonically with redistilled water. 5 μ L of the above materials were dropped onto GCEs, respectively. These modified GCEs were dried under an infrared lamp to form GR/GCE, GAs/GCE and NGAs/GCE.

2.5 Detection procedure

Electrochemical detections were measured in 5 mL of 0.1 M PBS (pH 7.0) containing desired concentration of MD. CV was measured within $0.3 \sim 0.9$ V at 50 mV s⁻¹ with accumulation of 120 s at 0 V. LSV was recorded between 0.4 ~ 0.8 V at 50 mV s⁻¹ with accumulation of 120 s at 0 V. Electrochemical impedance spectra (EIS) was recorded at 0.25 V with frequency between 0.1 and 10000 Hz and amplitude of 5 mV. The fabrication procedure of NGAs/GCE and the detection process of MD were shown in Scheme 2.





3. RESULTS AND DISCUSSION

3.1 Characterization of NGAs

The morphological characterization of NGAs was studied through SEM and TEM. From Fig. 1A, internal porous 3D interconnected frameworks could clearly be observed for NGAs, indicating

NGAs were formed by randomly cross-linking of wrinkled nanosheets. Furthermore, a lamellar structure with a typical corrugated thin layer was observed from TEM (Fig. 1B). Such a 3D structure of NGAs provides high surface area and generates plenty of active sites, which are favourable for the increase of the catalytic activity and sensing sensitivity.

XPS spectra were applied to discover the structure and chemical composition of the NGAs. From the XPS spectra of NGAs (Fig. 1C), we can see that three main peaks were at 284.8 eV (C 1s), 400.55 eV (N 1s) and 532.82 eV (O 1s), respectively. Moreover, the deconvoluted N 1s XPS spectrum suggests the presence of three different peaks: pyridinic-N (400.2 eV), pyrrolic-N (401.5 eV) and quaternary-N (402.3 eV) (Fig. 1D). These three different surface electronic states of N atoms revealed the successful incorporation of N atoms into the carbon–carbon bonds [16, 17].



Figure 1. (A) SEM and (B) TEM image of NGAs; (C) XPS spectra of NGAs and (D) the corresponding high-resolution N1s peak.

In addition, the quality and structure of NGAs were further characterized via Raman spectra (Fig. 1C). Two peaks at 1330 and 1580 cm⁻¹ were observed in the Raman results of the GO (a), GAs (b) and NGAs (c), which represent D and G bands, respectively. The D band proves the presence of some defects among the disordered GR sheet, while the G band represents the graphitic hexagon-pinch mode [17]. The intensity ratio of D and G band (I_D/I_G) reflects the disorder degree of the sp² domains. As show the I_D/I_G of GAs (1.092) increases in relatively to that of GO (0.964), owing to the decrease of the sp² domain after reduction of GO [18, 19]. Furthermore, the NGAs show higher intensity ratio

of I_D/I_G (1.174) than that of GAs (1.092), which is probably attributed to structural distortions and vacancies in the GR lattice because of N atom doping [20, 21].

EIS was an effective technique to study the changes in electron transfer resistance on electrode surface. In Nyquist plots of EIS, diameter of the semicircle represents the charge transfer resistance (Rct), whereas the linear portion refers to the diffusion process [22, 23]. Fig. 2B shows the EIS of various modified electrodes. As shown, the Rct of GR/GCE (b) was smaller than that of bare GCE (a) ascribing to the excellent electron transfer capability of GR. Moreover, the Rct of GAs/GCE dramatically decreased compared with GR/GCE, which was attributed to the fast charge transport through the mesoporous structure of GAs. After N was incorporated into GAs, the Rct further decreased. This is because the porous, flexible, 3D-networked structure of NGAs could generate more channels for interface electron transfer, as well as the additional electron density provided by the N atom further enhanced the conductivity of NGAs [12].



Figure 2. (A) Raman spectra of the GO (a), GAs (b) and NGAs (c); (B) EIS plots of bare GCE (a), GR/GCE (b), GAs/GCE (c) and NGAs/GCE (d) in 0.1 M KCl containing 5 mM $[Fe(CN)_6]^{3-/4-}$.

3.2 Electrochemical behaviors of MD

Fig. 3 displays the cyclic voltammograms (CVs) for the electrochemical oxidation of MD at different modified electrodes. As shown, there was no peak at bare GCE (a) as a result of the slow electronic transfer of bare GCE. GR/GCE (b) exhibited a faint peak owing to the good conductivity of GR. In contrast, a distinct oxidation peak was observed at the GAs/GCE, which could be ascribed to the exceptional conductivity and large active surface area of GAs. For NGAs/GCE, anodic peak current was increased significantly in comparison with that at GAs/GCE. This is because that N doping could open lattice gap and create more defects leading to good electron transfer ability and higher catalytic activity [24]. These excellent electrocatalytic properties of NGAs/GCE revealed NGAs is an appropriate electro-catalyst for quantitative analysis of MD.



Figure 3. CVs of 20 μM MD on the bare GCE (a), GR/GCE (b), GAs/GCE (c) and NGAs/GCE (d) in 0.1 M PBS (pH 7.0).

3.3 Optimization of the detection condition

To get high detection performance for MD, the conditions including the volume of NGAs, accumulation potential, accumulation time and solution pH were optimized in the presence of 14 μ M MD by LSV and CV.

3.3.1 Influence of the volume of NGAs

From Fig. 4A, we can see that the current response of MD elevated significantly as the volume of NGAs increased from 1 to 5 μ L, which is probably because an increase in the volume of NGAs led to an elevation in catalytically active sites, thereby promoting the electron transfer rate. However, the peak current decreases when further increase of the NGAs volume, which was due to the fact that too much NGAs on the electrode surface blocked hampered the electrical conductivity [4]. Thus, 5 μ L was optimal volume to detect MD.

3.3.2 Effect of accumulation potential

It was clearly seen in Fig. 4B that the peak current enhances with increment of accumulation potential within $-0.4 \sim 0$ V. While the peak currents decreased as the potential was more positive than 0 V. This phenomenon might be attributed to the fact that a partial of MD oxidized on the surface of NGAs/GCE at high potential [25]. Therefore, 0 V was adopted for further measurement.

3.3.3 Effect of accumulation time

By prolonging the accumulation time, the adsorption amount of MD on the electrode surface can be increased and then the detection sensitivity can be improved. As shown from Fig. 4C, the peak

current grew significantly with time increasing from 0 s to 120 s. After that, the value of current density approximately reached a plateau when enrichment time further increases, which is due to the saturation adsorption at the surface of NGAs/GCE. Accordingly, 120 s was fixed as the optimal accumulation time.



Figure 4. Variation of the peak current of 14 μM MD in 0.1 M PBS (pH 7.0) with different (A) NGAs valume, (B) accumulation potential and (C) accumulation time.

3.3.4 Effect of pH values

The influence of solution pH to the electrooxidation of MD was studied by CV. In Fig 5A, the peak potential (E_{pa}) shifted negatively as pH increased from 5.0 to 9.0, demonstrating the participation of protons in electrode reactions [26, 27]. The linear relationship of E_{pa} and pH value was expressed as $E_{pa} = 1.028 - 0.051$ pH ($R^2 = 0.994$) (Fig. 5B). The slop value was -51 mV pH⁻¹, which is nearly to the theoretical value (-59 mV pH⁻¹), showing the equal numbers of electrons and protons participating in the electrode reaction of MD [28, 29]. Meanwhile, it also can be noticed that the peak current (I_{pa}) reached the maximum at pH of 7.0, which might be due to the fact that the NGAs showed higher electrocatalytic activity in pH 7 than other pH. Thereby, 7.0 was recommended as the optimal pH for further experiments.

3.3.5 Scan rates and electrochemical reaction kinetics

To study the kinetics mechanism of MD oxidation on NGAs/GCE surface, CV within 14 μ M MD was recorded at different scan rate (Fig. 5C). It shows that the anodic peak currents (I_{pa}) increased

continuously with increasing scan rates. The equation was fitted as I_{pa} (μA) = -0.006 + 0.100 v (R^2 = 0.999) (inset of Fig. 5C), suggesting the oxidation of MD at the NGAs/GCE was adsorption controlled process [30]. Meanwhile, it is clearly that the E_{pa} of MD shifts positively as the scan rate increases. As can be seen in Fig. 5D, E_{pa} exhibited a good linear relationship with ln v and the equation was obtained to be E_{pa} = 0.468 + 0.048 ln v (R^2 = 0.999). For a totally irreversible adsorption controlled-process, E_{pa} is defined as [29]:

 $E_{pa} = [RT/2(1 - \alpha) nF] \ln v + constant$

where T and R are the absolute temperature and the gas constant, respectively. n, α , F and v are the number of transferred electrons, the transfer coefficient, the Faraday constant and the scan rate, respectively. The slope of the line between E_{pa} and $\ln v$ is equivalent to $RT/2(1-\alpha) nF$, thus, the obtained value of $(1-\alpha)n$ was 0.53. The value of α is usually estimated as 0.5 in a completely irreversible electrode process [31, 32], so the value of n is calculated as 1. The oxidation of MD at the NGAs/GCE was a one-electron and one-proton transfer process based on the above calculations.



Figure 5. (A) CVs of NGAs/GCE in PBS with different pH containing 14 μM MD. (B) Effect of pH value on the E_{pa} and I_{pa}; (C) CVs of 14 μM MD in 0.1 M PBS (pH 7.0) on NGAs/GCE at different scan rates (v) from 10 to 400 mV s⁻¹. Inset: the relationship of I_{pa} and v; (D) The relationship of Ep and ln v.

3.4 Determination of MD at NGAs/GCE

Under the optimum experimental parameters, the proposed electrochemical sensor was used to detect different concentration of MD by LSV. In Fig. 7, the LSV response elevates as the concentration of MD increases. The LSV response was linear positive correlation to the concentration of MD ranging

from 0.03 to 21 μ M. The equation was fitted as I (μ A) = 0.427 + 0.318 c (μ M) (R² = 0.998) (inset of Fig. 7) and the detection limit reached 0.01 μ M (S/N= 3). Furthermore, the comparison of detection performance between the NGAs/GCE and previously reported modified electrodes was summarized in Table 1. As shown, the NGAs/GCE based sensor was more sensitive with lower detection limit. The satisfactory result was attributed to the unique structure of the three-dimensional aerogel as well as the extra electron density donated by N atoms.



Figure 6. LSV of 0.03, 0.2, 0.6, 0.8, 1, 2, 4, 7, 9, 12, 14, 16, 18 and 21µM MD on NGAs/GCE in 0.1 M PBS (pH 7.0) as well as liner calibration curve (inset).

 Table 1. Performances of different electrode for MD detection

Modified electrodes	Liner range	Detection limit (LOD)	Reference
^a 3DGR/ ^b βCDA/GCE	0.07–250 μM	0.04 µM	[2]
^c RGO/GCE	0.3–80 µM	0.1 µM	[4]
MWCNTs/GCE	0.5–20 µM	0.5 μM	[6]
NGAs/GCE	0.03–21µM	0.01 µM	This work

^aThree-dimensional graphene.

^bβ-cyclodextrin aggregates.

^creduced graphene oxide.

3.5 Reproducibility, stability and interference study

To further explore the reproducibility, eight NGAs/GCEs were used to detect 10 μ M MD. The relative standard deviations (RSD) of these measured LSV response was about 2.8%, revealing that the proposed electrode had desirable reproducibility. The storage stability was evaluated via detecting 10

 μ M MD once a day for three weeks. The LSV responses remained approximately 96.2% of the original current value, reflecting the good stability.

The selectivity of NGAs/GCE was examined with the addition of different foreign interferences into 10 μ M MD and the LSV response was detected. The result indicated that 100-fold concentration of Na⁺, Ag⁺, Zn²⁺, Cu²⁺, Ca²⁺, Pb²⁺, Fe³⁺, Cl⁻, NO₃⁻, PO₄³⁻ or SO₄²⁻, 35-fold concentration of guanine, adenine, dopamine, glucose, uric acid, saccharose, carboxymethylcellulose, azithromycin and chloramphenicol have negligible response to MD sensing (the peak current changes below 5.0%), which confirmed that the prepared sensor showed good selectivity for MD detection.

3.6 Application on real samples

The practicality of the as-synthesized NGAs sensor was examed by determining MD in urine samples. The samples taken from volunteers in Jiangxi Agricultural University Hospital were diluted 40 times and then centrifuged for removing suspended particles. The contents of MD were obtained with standard addition method. From Table 2, the recoveries of MD were about 97.5–102.6% and RSDs are below 5%, suggesting the NGAs sensor could be successfully employed for MD detection.

Sample	Added (µM)	Found (µM)	Recovery (%)	RSD (%)
1	0.08	0.078	97.5	3.11
2	0.36	0.354	98.3	4.53
3	1.70	1.712	100.7	1.24
4	5.42	5.565	102.6	2.83
5	8.51	8.421	98.9	3.27

Table 2. Recoveries of MD from the urine samples (n = 5).

4. CONCLUSIONS

This work presents a facile and effective strategy for voltammetric detection of MD at NGAs modified GCE for the first time. The morphological and structural features of NGAs were characterized systematically by various technologies and the experimental conditions were checked and optimized. The electrooxidation of MD was verified to be an adsorption controlled process. Owing to the outstanding electrocatalytic activity, superior charge transfer and high specific surface area of NGAs, the electrochemical response of the modified electrode toward MD was significantly enhanced. Moreover, the application potential of this sensor is further confirmed by determination of MD in urine samples and obtained satisfactory results. Such good sensing performance demonstrated that NGAs can be promising electrode materials for practical applications.

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