

Fabrication of Graphene Oxide-MWCNTs Nanocomposite Modified Glassy Carbon Electrode for the Sensitive Determination of Amitrole

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We have demonstrated a highly sensitive amperometric amitrole (3-Amino-1,2,4-triazole) sensor constructed with graphene oxide (GO) and multi walled carbon nanotubes (MWCNTs) through electrochemical potentiostatic approach. The characterization studies of GO-MWCNTs composite were performed using field emission scanning electron microscopy (FESEM), cyclic voltammetry (CV) and amperometric i-t techniques. The high performance of GO-MWCNTs modified electrode towards amitrole was confirmed from the resulting low over potential and well defined sharp peak currents. The high sensitivity ($4300 \mu\text{A}/\text{mM cm}^{-2}$) and low limit of detection ($0.450 \mu\text{M}$) were attained by our fabricated electrode in a wide working potential range from 5 to $3545 \mu\text{M}$ (linear range). GO-MWCNTs film coated glassy carbon electrode (GCE) also offers considerable stability along with good repeatability and reproducibility. The demonstration of practicability for our fabricated modified electrode was achieved in lake and tap water samples.

Keywords: Graphene oxide, MWCNTs, cyclic voltammetry, amperometry, Amitrole.

1. INTRODUCTION

Pesticides are introduced in agriculture with the aim of controlling pests and increasing productivity. Conversely, pesticides used in excess may lead to health problems in human beings as well as environmental safety issues[1]. When the concentration of several pesticides exceeds the toxic level fixed by Environmental Protection Agency (EPA), it makes the environment unfriendly for living beings [2]. Amitrole (3-Amino-1,2,4-triazole), a highly soluble, polar and low volatile herbicide used along with some active agents as weeds control in agriculture fields, industries and roads is a

human carcinogen [3]. The higher limit of amitrole in drinking water enacted by the European Economic Commission (EEC) was 0.1 $\mu\text{g/L}$ [4]. Thus, the sensitive detection of amitrole has become extremely significant with the aim of getting harmless water. A number of diagnostic methods namely, capillary electrophoresis [5], high performance liquid chromatography [6] and gas chromatography [7] have been evolved for the determination of amitrole. But, these methods suffer from some of the critical properties of amitrole including tough extraction method, poor solubility in organic solvents, less volatile nature and high polarity leading to its high solubility in water medium. Additionally, high cost, complicated protocols and time consumption of the above mentioned methods turned the current researchers to focus on the electrochemical methods [8]. This electrochemical method of detection provides simple operating procedure, quick response, better repeatability and reproducibility as well as high sensitivity and selectivity towards the chosen analyte [9].

On the other hand, the unmodified (bare) electrodes utilized in electrochemical methods possess certain drawbacks namely high over potential and fouling of electrode surface. In order to overcome these shortcomings, the chemically modified electrodes were used in the electrochemical methods¹⁰. The electrochemical amperometric method of detection has gained more attention because of certain advantages: high performance of the sensor can be attained by modifying the applied potential and interference of other molecules can be reduced. Recently, nickel [11] and gold [9] nanoparticles have been utilized for the determination of amitrole. Similarly, multi-walled carbon nanotubes (MWCNTs) [8, 10–12] and single-walled carbon nanotubes (SWCNTs) [13] based metal phthalocyanines have also been used as electrocatalyst for the determination of amitrole.

Since, MWCNTs show a good electro catalytic activity for the determination of amitrole, we have prepared graphene oxide functionalized MWCNTs nanocomposite for the application of electrochemical amitrole sensor. The main reasons for the introduction of GO into MWCNTs are high surface area and hydrophilicity of various functional groups (hydroxyl (-OH), carboxyl (-COOH), and epoxide groups) and easy functionalization [14–15]. Recently, GO-dispersed MWCNTs have been showed as attractive electrode materials in various applications such as sensors [16–17], biosensors [18] and super capacitors [19] because of its ability to form a three-dimensionally arranged hierarchical structure which can offer the highest edge density per unit normal area [20]. In our work, the fabricated GO-MWCNTs electrode exhibited an enhanced catalytic activity towards the electro-oxidation of amitrole compared to only MWCNTs and GO modified electrodes. Moreover, our modified electrode achieved good sensitivity, wide linear range and low limits of detection.

2. EXPERIMENTAL

2.1 Materials and Reagents

Graphite powder (<20 μm), Sodium dihydrogen phosphate (NaH_2PO_4), Sodium phosphate dibasic (Na_2HPO_4), Multiwalled carbon nanotubes (MWCNTs), Amitrole and all the other chemicals were purchased from Sigma-Aldrich at an analytical grade (<http://www.sigmaaldrich.com/taiwan.html>). The supporting electrolyte used throughout the electrochemical studies was 0.05 M (PB) Phosphate Buffer (pH 7) solution, prepared from sodium phosphate dibasic and sodium dihydrogen phosphate (Na_2HPO_4 and NaH_2PO_4). Prior to each

experiment, all the solutions were deoxygenated with pre-purified N₂ gas for 15 min unless otherwise specified. Double distilled water (conductivity ≥ 18 M Ω cm) was used for all the experiments.

2.2 Apparatus

Electrochemical measurements were performed with the modified GCE (area 0.071 cm²) as working electrode, saturated Ag|AgCl (saturated KCl) as reference electrode and Pt wire as counter electrode in a conventional three electrode system using CHI 6171D work station (cyclic voltammetry). Analytical rotator AFMSRX (PINE instruments, USA) with a rotating disc glassy carbon electrode (RDE, area 0.21 cm²) was utilized to carry out the amperometric (i-t) measurements. Field emission scanning electron microscopy (FESEM) studies was done with Hitachi S4700.

2.3 Fabrication of GO/MWCNTs modified GCE

Graphite oxide was prepared through the earlier reported modified Hummer's method in the literatures. The first step is the addition of powdered graphite in to a beaker which contains concentrated H₂SO₄ [21]. Secondly, KMnO₄ was gradually added by simultaneously stirring and cooling, in order to retain the temperature of the above mixture below 20 °C. After a time period of 60 min, 2.8 L deionized water with 30 % H₂O₂ was utilized to terminate the reaction. The resulting suspension was stirred at 35 °C for 2 h to get a bright yellow color. The removal of metal ions was done by washing the suspension with 1:10 HCl. Later, the separated sticky stuff was dried at 60 °C to attain agglomeration. The suspension was washed several times using a large measure of deionized water till its pH value is approximately 7. Finally, 1 mg/ml of the as prepared graphite oxide suspended in double distilled water was ultra-sonicated for 2 h. The resulting yellowish brown colored graphene oxide (GO) solution was used for the preparation of GO-MWCNTs. 2 mg MWCNTs was added in to an aqueous solution of 10 ml GO (1 mg/ml) and it was sonicated for 2 hours to get a homogeneous GO-MWCNTs mixture. The obtained GO-MWCNTs was washed with double distilled water for several times to remove excess of MWCNTs. Finally, the GO-MWCNTs mixture was centrifuged at 1400 rpm to eliminate the unreacted GO.

The glassy carbon electrode surface was polished with a Buehler polishing kit using 0.05 μ m alumina slurry and washed with double distilled water. It was dried at room temperature. Then 10 μ l of GO-MWCNTs composite was drop cast onto the pre-cleaned GCE and dried at ambient conditions. Further, it was used for the electrochemical experiments. For control, individual GO and MWCNTs modified GCEs were also fabricated.

3. RESULT AND DISCUSSION

3.1 Characterization of GO and GO-MWCNTs

FESEM technique was employed to study the surface morphology of GO and GO-MWCNTs composite. Figure 1A displays the crumpled thin sheet image of only GO. Also, the incorporation of

cylindrical MWCNTs with the GO surface can be obviously seen from the FESEM image of GO–MWCNTs composite (Figure 1B).

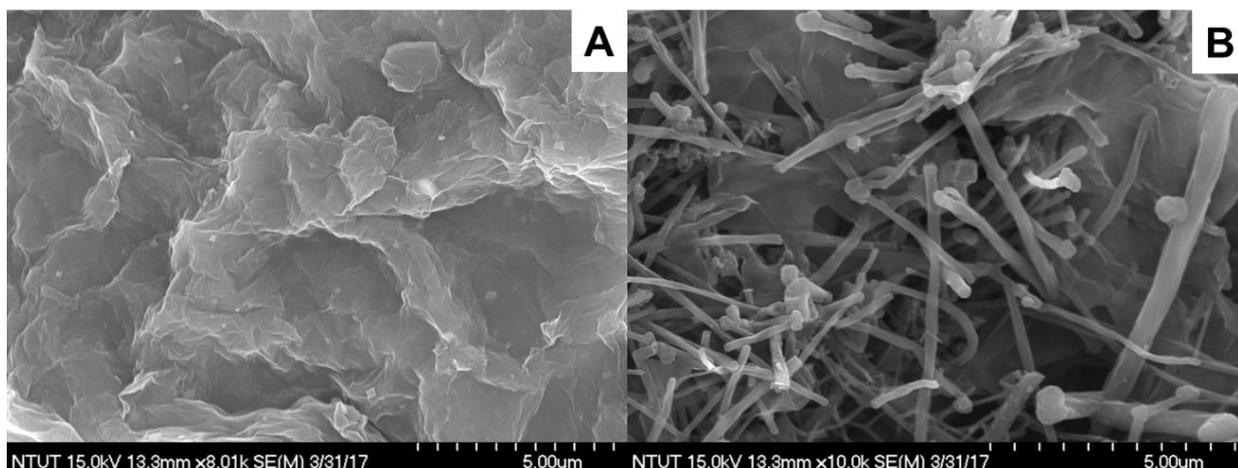


Figure 1. SEM images of GO (A) and GO–MWCNTs (B).

3.2 Determination of amitrole: CV

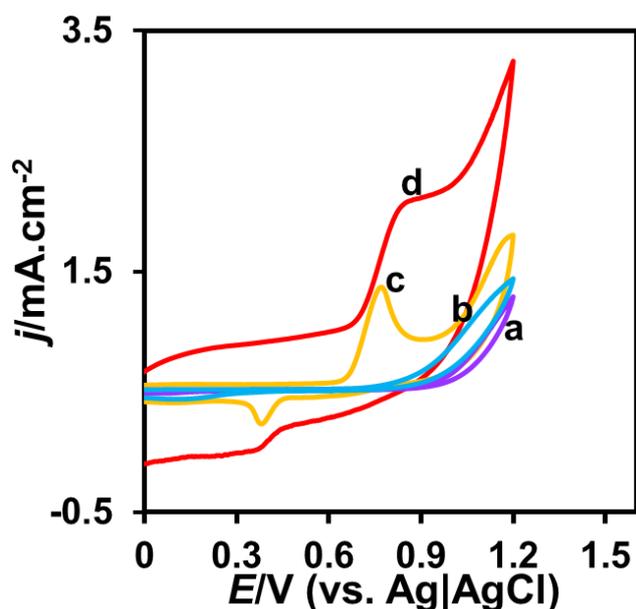


Figure 2. Cyclic voltammograms obtained at unmodified GCE (a) and GO (b), MWCNTs (c) and GO–MWCNTs (d) modified GCEs in 0.05 M PB (pH 7) solution containing 1 mM amitrole at the scan rate of 50 mV s^{-1}

The performance of different film such as unmodified (bare) GCE (a), GO (b), MWCNTs (c) and GO-MWCNTs (d) modified GCEs in 0.05 M PB (pH 7) solution containing 1 mM amitrole at the scan rate of 50 mV/s was studied by cyclic voltammetry and their cyclic voltammograms are presented in Figure 2. At bare GCE (a), there was no significant anodic peak current (current density (j)=1.02

mAcm^{-2}) was observed. After modified by GO (b), a little enhanced anodic peak (current density (j)= $1.10 \text{ mA}\cdot\text{cm}^{-2}$) towards the electro-oxidation of amitrole was observed than that of bare GCE. A sharp anodic oxidation peak (current density (j)= $1.32 \text{ mA}\cdot\text{cm}^{-2}$) with higher negative potential (0.761 V (vs. Ag|AgCl) shift was observed for MWCNTs/GCE which indicates the good catalytic activity of MWCNTs. Notably, a large capacitive as well as anodic peak current was obtained for GO-MWCNTs compared to bare GCE (a), GO (b) and MWCNTs (c) modified GCE. The obtained anodic peak current (j)= $2.07 \text{ mA}\cdot\text{cm}^{-2}$) at GO-MWCNTs was one and half times higher compared to MWCNTs and nearly three times higher than that of bare GCE and GO modified GCE. The enhanced peak current of GO-MWCNTs towards amitrole is mainly because of synergistic effect between MWCNTs (catalytic activity) and GO (high surface area) of the composite electrode.

3.3 Effect of scan rate

The influence of varying scan rate (0.1 to 1 V/s) on the electro-oxidation of amitrole at GO-MWCNTs film modified GCE for 1 mM amitrole in 0.05 M PB (pH 7) solution was studied (Figure 3). When the scan rate was increased from 0.1 to 1 V/s, the respective oxidation peak current also increases. In addition, a shift in the anodic peak potential towards the positive direction and the linear calibration plot drawn between I_p and $v^{1/2}$ (Inset to Figure 3) validate that, the oxidation of amitrole at GO-MWCNTs coated GCE is a diffusion controlled process [22].

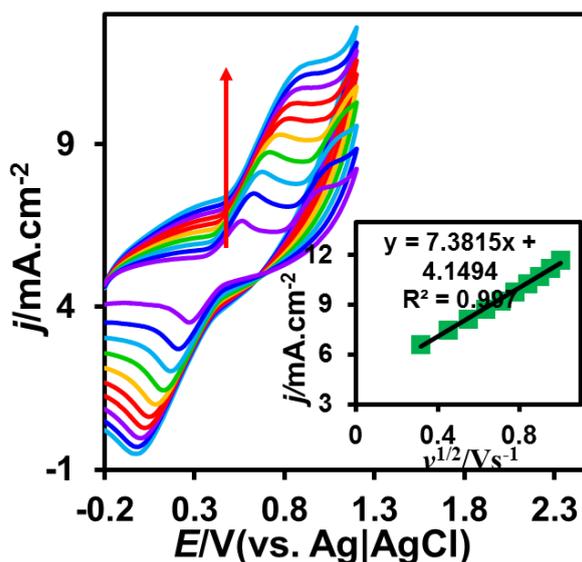


Figure 3. Cyclic voltammograms of GO-MWCNTs/GCE at different scan rates (from 0.1 to 1 V/s) for 1 mM amitrole in 0.05 M PB (pH 7) solution

3.4 Determination of diffusion coefficient (D_0)

The diffusion coefficient (D_0) for the electro-oxidation of amitrole at GO-MWCNTs/GCE was evaluated by using the hydrodynamic rotating disc electrode technique. The CVs for the

electrochemical behaviour of GO–MWCNTs modified GCE towards 1 mM amitrole in 0.05 M PB (pH 7) solution was presented in Figure 4. The rotation rate was varied from 200 to 2000 rpm (a–g). The linear dependency of I_p with $\omega^{1/2}$ was evident from the equivalent Levich plot. It indicates that amitrole oxidation at GO–MWCNTs/GCE is only mass transport limited. The value of D_0 for the modified electrode was calculated by the following Levich equation [23].

$$I_L = I_{LEV} = 0.620 nFAD_0^{2/3} \gamma^{-1/6} \omega^{1/2} C_0$$

Here, D_0 –diffusion coefficient; γ –kinematic viscosity; ω –rotation speed; C_0 –bulk concentration of electrolytic solution (amitrole) and other parameters of the equation with their own meanings. From the above equation the D_0 value was estimated to be $1.58 \times 10^{-5} \text{ cm}^2/\text{s}$.

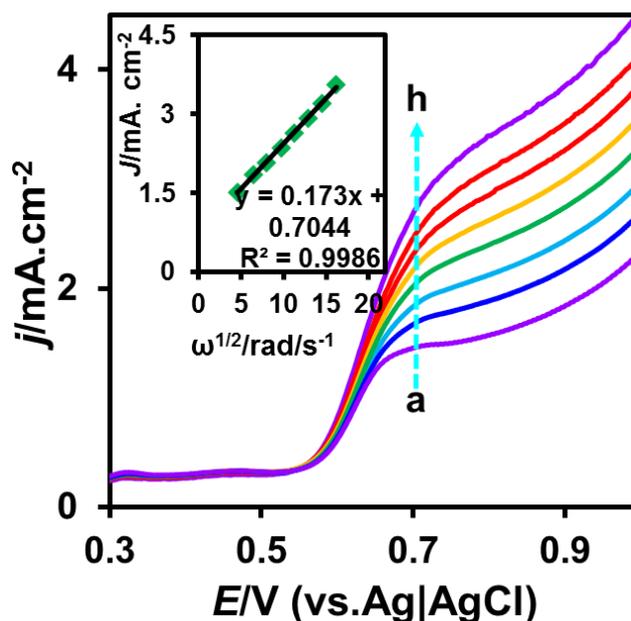


Figure 4. RDE voltammograms at GO–MWCNTs/GCE in 0.05 M PB (pH 7) solution containing 1 mM amitrole at different rotation rates (a) 200, (b) 400, (c) 600, (d) 900, (e) 1200, (f) 1600 and (g) 2000 RPM.

3.5 Amperometric *i-t* measurement

The amperometric *i-t* response of GO-MWCNTs/GCE towards the determination of amitrole was displayed in Figure 5. The amperometric sensitive detection of amitrole using GO-MWCNT film modified rotating disc electrode in 0.05 M PB (pH 7) solution was performed at the conditions: applied potential 0.7 V, rotation speed 1500 rpm and concentrations of amitrole 5 μM , 50 μM and 500 μM . GO-MWCNTs/GCE exhibited a fast and steady amperometric response for each addition of amitrole with varying concentration. The attainment of 95.8 % steady state response current within 4 s supports the superior electrocatalytic behavior of GO-MWCNTs coated GCE. The inset calibration plot shows the linear dependency of [amitrole] with I_p . The electroanalytical parameters such as linear range (5 to 3545 μM), LOD (0.450 μM) and sensitivity (4300 $\mu\text{A}/\text{mM cm}^{-2}$) were also evaluated from the above expression. The equation $\text{LOD} = 3 s_b/S$, was used to calculate the limit of detection, where s_b –standard

deviation of blank signal and S =sensitivity [24]. The valued electroanalytical parameters (linear range, LOD and sensitivity) of our fabricated electrode are better than the formerly reported metal–metal oxide (NiNPs, lead and ruthenium oxide) and carbon based amitrole sensors of the literatures [11, 12 & 26]. Relative to the metal phthalocyanines based modified electrodes [10,13, 25, 27 & 28], our proposed sensor possess comparable sensitivity and a wide linear range (Table 1).

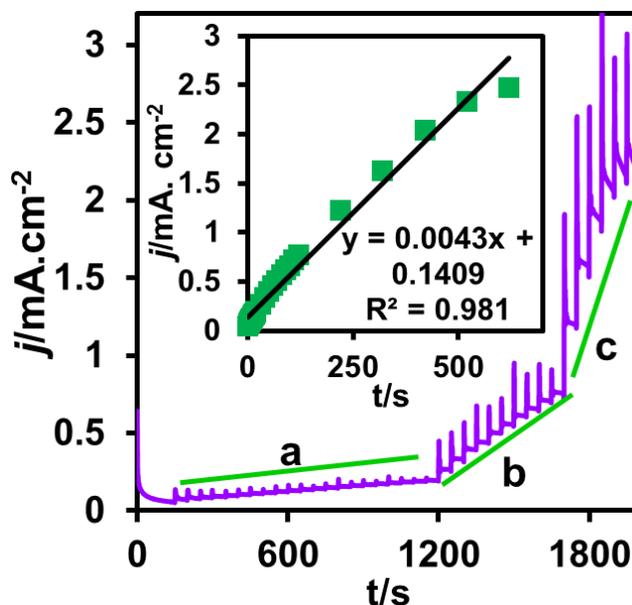


Figure 5. Amperograms obtained at GO–MWCNT modified rotating disk GCE upon successive addition of 5 μM , 50 and 500 μM of amitrole into 0.05 M PB (pH 7) solution. Rotation speed = 1500 rpm; $E_{\text{app}} = + 0.70$ V. Inset: plot of j_p (mA) versus [amitrole] (μM)

Table 1. Comparison of analytical parameters for the determination of amitrole at GO-MWCNTs/GCE with other films modified electrodes.

Modified Electrode	Linear range(μM)	Sensitivity	LOD (μM)	Ref.
FeTAPc ^a /BPPGE ^b -MWCNT	–	8.80 $\mu\text{A nM}^{-1}$	0.0005	[10]
Nickel nanoparticles	25.8–1110	–	–	[11]
Carbon nanotubes paste	0.8 to 7.0	–	0.6	[12]
CoTOBPc ^c –SWCNT	1–30	1.130 $\text{A M}^{-1}\text{cm}^{-2}$	–	[13]
CoTCPc ^d –EA ^e –SWCNT	10–160	0.76 $\text{A M}^{-1}\text{cm}^{-2}$	0.1	[25]
Nafion/lead–ruthenium oxide	30–250	0.73 $\mu\text{A } \mu\text{M}^{-1}$	0.38	[26]
FePc ^f	0.001–0.012	3.44 $\mu\text{A nM}^{-1}$	0.0036	[27]
FeTAPc ^a -SWCNT dendrimer	63–100	0.6603 $\mu\text{A } \mu\text{M}^{-1}$	0.215	[28]
GO-MWCNTs	5 to 3545	4300 $\mu\text{A mM}^{-1}\text{cm}^{-2}$	0.45	This work

^aFeTAPc– iron (II) tetraaminophthalocyanine, ^bBPPGE– basal planepyrolytic graphite electrode, ^cCoTOBPc–2,(3)-tetra-(4-oxo-benzamide)phthalocyaninato cobalt(II), ^dCoTCPc– cobalt (II) tetracarboxyl-phthalocyanines, ^eEA– ethylene amine, ^fFePc–iron phthalocyanine,

3.6 Real sample analysis

The demonstration of practical feasibility for GO-MWCNTs modified GCE was done in lake and tap water samples. Whatman filter paper was utilized to eliminate the impurities and dust particles in the water samples. The spiked concentrations of amitrole (50 μM and 100 μM) in both water samples were determined by the amperometric i-t technique (Table 2). The recovery results provided by GO-MWCNTs/GCE were satisfactory. This reveals the better practicability of our proposed sensor.

Table 2. Determination of amitrole in lake and tap water samples at GO-MWCNTs/GCE.

Samples	Added (μM)	Found (μM)	Recovery (%)	RSD* (%)
Lake water	50	49.21	98.42	2.6
	100	99.03	99.03	2.43
Tap water	50	48.95	97.9	2.79
	100	98.97	98.97	2.51

3.7 Selectivity studies

The selectivity of GO-MWCNTs coated GCE towards amitrole was carried out using amperometric i-t method. 100 folds excess concentration of several interfering anions and cations namely, Na^+ , K^+ , Ca^{2+} , Ba^{2+} , Mg^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , F^- , Cl^- , I^- and $(\text{COO})_2^{2-}$ were taken along with amitrole for this study. A noticeable amperometric response was shown for a very low concentration of amitrole (10 μM). On the other hand, no visible response was observed for the addition of the above mentioned interferents. Thus, even in the presence of other biomolecules, GO-MWCNTs film modified GCE can perform the selective determination of amitrole.

3.8 Stability, Repeatability and Reproducibility

The stability of GO-MWCNTs/GCE was examined by storing it in 0.05 M PB (pH 7) solution (4 $^\circ\text{C}$) after every day experiment. A good electrocatalytic response towards every addition of 10 μM amitrole was exhibited by our GO-MWCNTs film coated GCE. During the period of storage, no shift in the peak potential was observed at GO-MWCNTs/GCE towards the electro-oxidation of 10 μM amitrole. The retained value of 95.6% initial response current displays the considerable storage stability of GO-MWCNTs modified GCE.

Repeatability and reproducibility studies of GO-MWCNTs coated GCE were also performed in 0.05 M PB (pH 7) solution at the fixed scan rate of 50 mV/s using 10 μM amitrole. For six continuous

measurements, an acceptable repeatability with 2.8% of relative standard deviation (RSD) was attained by single fabricated electrode. An appreciable reproducibility with the RSD of 3.1 % was achieved using six individual modified electrodes for six independent measurements.

4. CONCLUSIONS

To conclude, an amperometric sensor for the sensitive determination of amitrole was fabricated through electrochemical method. FESEM and CV techniques were utilized for the characterization of GO-MWCNTs film. The outstanding electrocatalytic activity of GO-MWCNTs coated GCE was confirmed in terms of valued electrochemical parameters namely, a wide linear range (5 to 3545 μ M), low limit of detection (0.450 μ M) and high sensitivity (4300 μ A/mM cm^{-2}). Additionally, an appreciable repeatability, reproducibility and stability were delivered by our modified electrode. The better practicability of GO-MWCNTs/GCE was successfully demonstrated in various water samples. Simple fabrication procedure, less time consumption, good stability as well as the excellent electrocatalytic activity takes our GO-MWCNTs film modified GCE in to the near future sensing and bio sensing applications.

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