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THE ROLE OF COPPER DECORATING POLY(1,8-DIAMINONAPHTHALENE)/GRAPHENE ELECTRODES AS A CATALYST IN THE DETERMINATION OF NITRITE

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Abstract. Electroactive poly(1,8-diaminonaphthalene) is known to have a high affinity for metal ions thanks to amine and imine groups in the polymer chain. However, electrochemical sensors based on pristine P(1,8-DAN) have a major drawback concerning its poor electrical conductivity. To solve this problem, recently P(1,8-DAN) has been modified with some advanced nanomaterials such as carbonaceous materials or different metallic elements. In this research, we reported the synthesis and electrochemical characterization of a poly(1,8-diaminonaphthalene)/graphene composite film capable of adsorbing Cu^{2+} ions towards the application of nitrite sensing. P(1,8-DAN) was directly electropolymerized on graphene-coated glassy carbon electrode by a potential cycling between –0.15 and +0.95 V (*vs.* SCE) at a scan rate of 0.05 V/s, in aqueous solution containing 1.0 M $HClO_4$ and 1.0 mM monomer 1,8-DAN,. The adsorption of Cu^{2+} ions onto the P(1,8-DAN) thin film was caried out in 0.1 M $Cu(NO_3)_2$ solution at 80 ^oC, followed by electrochemically redution to metal Cu^0 by applying –0.4 V. The obtained copper decorating poly(1,8-diaminonaphthalene)/graphene (Gr/P(1,8-DAN)-Cu) electrodes acted as a catalyst in the enhancement of electrochemical signal for the determination of nitrite. The linear voltammetric response to the nitrite concentration was observed by a square wave voltammetric technique in the range of 0.69 to 1.12 mM with a detection limit of 0.13 mM. The results open up the path for designing other nitrite sensing based on our novel approach.

Keywords: poly(1,8-diaminonaphthalene)/graphene, nitrite, sensor, copper, catalyst.

Classification numbers: 2.4.2, 2.4.2, 2.5.3, 2.9.4.

1. INTRODUCTION

Poly(1,8-diaminonaphthalene), abbreviated as P(1,8-DAN), is known to be an electroactive polymer with strong complex adsorption capacity for some metal ions, such as Cr^{6+}, Hg^{2+}, VO^{2+},

Ag^{+}, Cu^{2+}, thanks to amine and imine groups in the polymer chain [1 - 4]. The interaction between metal ions with P(1,8-DAN) has been investigated and applied for different interesting purposes such as environmental treatment [5 - 7], separation-enrichment [8, 9], catalysis [10, 11], and sensing materials [12]. However, electrochemical sensors based on pristine P(1,8-DAN) have a major drawback concerning its poor electrical conductivity. To solve this problem, recently P(1,8-DAN) has been modified with some advanced nanomaterials such as carbon nanotubes [4, 13] and graphene [14]. Research reports have shown that graphene (Gr) has brought outstanding advantages such as improved mechanical properties, large specific surface, high adsorption capacity, high electrical conductivity and electrochemical activity. Therefore, Gr/P(1,8-DAN) composite material has been considered an ideal substrate for the development of electrochemically measured sensor electrodes.

Functionalization of sensor electrode surface by one or more metallic elements has been reported as a promising approach for enhancing sensitivity and selectivity of the sensor. These doped metals can either act as a redox catalyst that improves the electrochemical signal, or react with undesired impurities producing an electrochemical signal close to the target, thereby increasing the selectivity of the measurement. Some transition metals such as Au [15, 16], Pt [17], Pd [18], Mn [19], Ni [20], and Cu [21] have been reported as potential electrochemical catalysts, especially when they are nanostructured. To create these metal nanostructures, the synthesis via wet chemical and direct electrochemical routes is most commonly applied. It is reported that the homogenous distribution of synthesized metal nanoparticles (NPs) on the electrode surface is a very important factor affecting the stability of the sensor. Among a wide variety of available electrocatalysts, Cu has attracted attention in electrochemical sensors because of its cost-effectiveness and good electrical conductivity. The electrocatalytic properties of Cu have been reported in the determination of vitamin B6 [22], dopamine [23, 24], nitrate [25, 26], nitrite [26, 27], etc. The accurate detection of nitrite is one of the current concerns because it is widely used in the food industry (it can inhibit the growth of bacteria, keep the colors and enhance the flavors) [25 - 27]. However, when present in high concentrations, nitrite is harmful to human health. According to the World Health Organization (WHO), the nitrite content should not exceed 5 mg per kilogram of body weight for adults because of its very high risk of poisoning [28]. There are several methods for detection of nitrite including chemiluminescence [29], chromatography [30, 31], spectrophotometry [32], and electrochemical techniques [16, 25, 27, 33]. Electrochemical techniques are highly sensitive, cost–effective, easy to use and thus have attracted great attention in the detection of nitrite [16, 27, 33, 34]. However, the overpotential of direct oxidation of nitrite at conventional electrodes is extremely high [34]. To address this issue, conductive polymers based on modified electrodes have been developed with the use of poly(3,4-ethylenedioxythiophene) [35], poly(3,4-ethylenedioxythiophene) with gold nanoparticles [16], poly(3,4-ethylenedioxythiophene) with carbon nanotubes and Fe_3O_4 [36], poly(toluidine blue) with multiwalled carbon nanotubes [37], polypyrrole/chitosan nanocomposite with graphene [38], polyaniline doped graphene oxide [39], etc. As can be seen, graphene is an ideal material for electrochemical sensors combined with the remarkable catalytic activity of Cu towards potential nitrite sensing.

In this work Cu NPs have been deposited on the Gr/P(1,8-DAN) surface in two steps: (i) adsorption of Cu^{2+} ion on the composite film thanks to the good affinity of P(1,8-DAN) for this ion; (ii) electrochemical reduction of Cu^{2+} to Cu^{0}. By that way the Cu NPs would be incorporated into amine and imine groups on the polymer backbone chain, resulting in the formation of a monolayer of Cu NPs which acts as an effective catalyst for electrochemical

reaction on the electrode surface. The as-prepared Gr/P(1,8-DAN)-Cu composite film was characterized and evaluated for its sensing properties towards nitrite ions (NO_2^-).

2. MATERIALS AND METHODS

2.1. Materials

All chemicals used were of analytical grade. Monomer 1,8-diaminonapthalene (1,8-DAN), $HClO_4$, $LiClO_4$, and $NaNO_2$ were purchased from Sigma-Aldrich. Phosphate buffer solution (PBS, pH 7.4), was prepared from 0.1 M Na_2HPO_4 and 0.1 M KH_2PO_4 (Sigma-Aldrich). Single layer graphene powder was obtained from ACS Material (diameter 0.4-5.0 μm, thickness 0.6 - 1.2 nm, BET surface area ~1000 m^2/g, resistance < 0.3 Ω.cm). Nitrite solutions were prepared from $NaNO_2$ salt just before each measurement. All electrochemical measurements were carried out on a potentiostat-galvanostat Metrohm Autolab PGSTAT302N controlled by Nova 2.1 software. The electrochemical cell used in the investigation was a conventional three-electrode cell: a glassy carbon (GC) working electrode (diameter of 3 mm), a platinum grid serving as the counter electrode, and saturated calomel electrode (SCE) used as a reference. The microstructure of the samples was examined using a scanning electron microscope (SEM) S-4800 (Hitachi).

2.2. Preparation of GC/Gr/P(1,8-DAN)-Cu electrode

The glassy carbon electrode was polished before use on a cloth pad soaked with a slurry of 0.3 μm Al_2O_3 powder in water, then rinsed thoroughly with distilled water and properly dried. 5 μL of graphene suspension (0.05 mg/mL) were drop-coated onto cleaned GC working electrodes and air dried. P(1,8-DAN) was directly electropolymerized on GC/Gr using cyclic voltammetric (CV) technique in 1.0 M $HClO_4$ (in distilled water) containing 1.0 mM monomer 1,8-DAN. The P(1,8-DAN) was performed on the electrode surface after 5 cycles between –0.15 and +0.95 V (*vs.* SCE) at a scan rate of 0.05 V/s. The GC/Gr/P(1,8-DAN) modified electrode obtained was throughly rinsed with water and dried in the air. The adsorption of Cu^{2+} ions onto the polymer thin film was performed by immersing the GC/Gr/P(1,8-DAN) electrode in 0.1M $Cu(NO_3)_2$ solution at 80 ^oC for 30 min, followed by rinsing with alcohol then water for complete removal of uncomplexed Cu^{2+} ions. Finally, adsorbed Cu^{2+} ions were electrochemically reduced to metal Cu^0 by applying –0.4 V for 30 s, so we obtained the GC/Gr/P(1,8-DAN)-Cu composite electrodes.

2.3. Electrochemical determination of nitrite ions

The as-prepared GC/Gr/P(1,8-DAN)-Cu electrode was used for nitrite detection using CV and square wave voltammetry (SWV) in PBS solution. CV experiments were performed between 0 V and +1.0 V at a scan rate of 50 mV/s, while SWV was conducted in the range from +0.4 to +0.8 V at a scan rate of 10 mV/s and a frequency of 5.0 Hz.

3. RESULTS AND DISCUSSION

3.1. Preparation and characterication of GC/Gr/P(1,8-DAN)-Cu electrode

Figure 1 shows the cyclic voltamograms (CVs) recorded on the GC/Gr electrode in 0.1 M $HClO_4$ solution containing 1.0 mM 1,8-DAN monomer. At the first scan, the anodic current

started to rise rapidly from +0.31 V (*vs.* SCE), followed by a peak appearing at *ca.* +0.44 V due to the oxidation of monomer 1,8-DAN, corresponding to the oxidation of $-NH_2$ groups to the radicals. Compared with the case without Gr [40], or the case using carbon nanotubes [4], the oxidation of 1,8-DAN on the GC/Gr surface took place at a more negative potential (~ 150 mV). It's probably because of the high electronic mobility of Gr that promoted the electrochemical processes on the electrode surface. At the successive scans, the oxidation peak current of monomer decreased, a typical redox system of P(1,8-DAN) appeared from the second cycle (at +0.28/+0.15 V) with the current peaks continuously increased indicating the growth of the electroactive polymer film on the GC/Gr electrode.

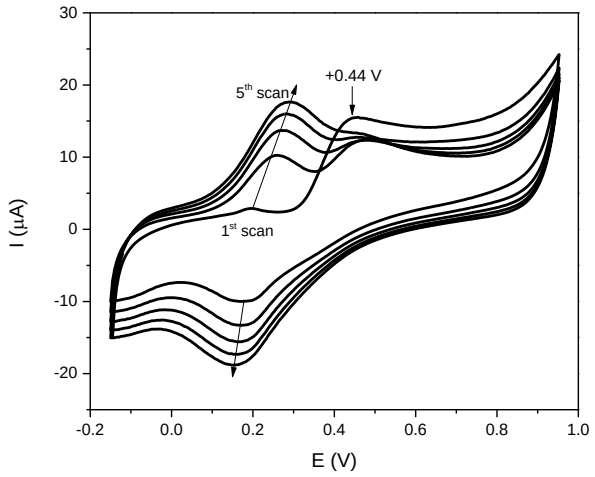

Figure 1. Cyclic voltammograms of the electro-polymerization of P(1,8-DAN) on Gr/GC electrodes in 0.1 M $HClO_4$ solution containing 1.0 mM 1,8-DAN.

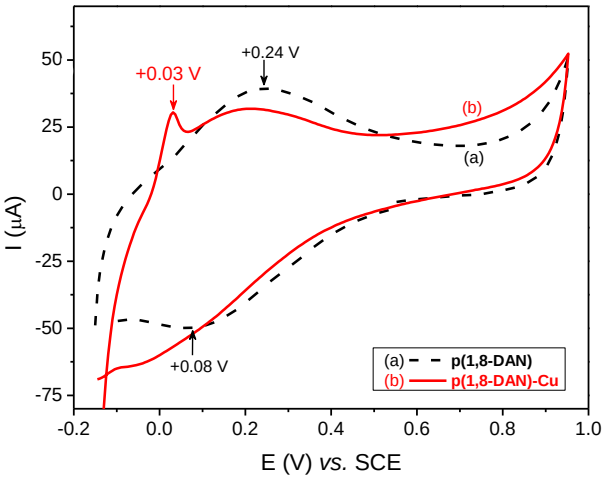

Figure 2. Voltammograme of GC/Gr/P(1,8-DAN) (curve a) and GC/Gr/P(1,8-DAN)-Cu (curve b) electrodes recorded in 0.1 M $HClO_4$ solution.

The as-prepared GC/Gr/P(1,8-DAN) electrode was further incorporated with Cu NPs according to the procedure described in Section 2.2. The electroactivity of this electrode before and after modification with Cu NPs was investigated using CV method in 0.1 M $HClO_4$ solution and is presented in Fig. 2. The obtained CV curve of Gr/P(1,8-DAN) electrode (curve 2a)

demonstrated a well-defined redox couple of P(1,8-DAN) at +0.24/+0.08 V [14, 40]. Meanwhile, on the recorded voltammograme of the Cu incorporated electrode (curve 2b) there was a novel anode peak appearing at +0.03 V, concerning the electrooxidation of Cu into Cu^{2+}. This indicated that Cu^{2+} ions were adsorbed/complexed onto the P(1,8-DAN) film via amine groups of the polymer chain to form a modified electrode GC/Gr/P(1,8-DAN)-Cu.

Figure 3A shows the SEM of the Gr/P(1,8-DAN)-Cu material indicating the presence of both Gr and amorphous structure of P(1,8-DAN) in the obtained nanocomposite. The presence of Cu NPs on the Gr/P(1,8-DAN) film was also confirmed by the EDX analysis (on an X-max 150 system from Oxford Instruments). As can be seen from Fig. 3B, the Cu content in the Gr/P(1,8-DAN)-Cu film was about 9.7 wt.%.

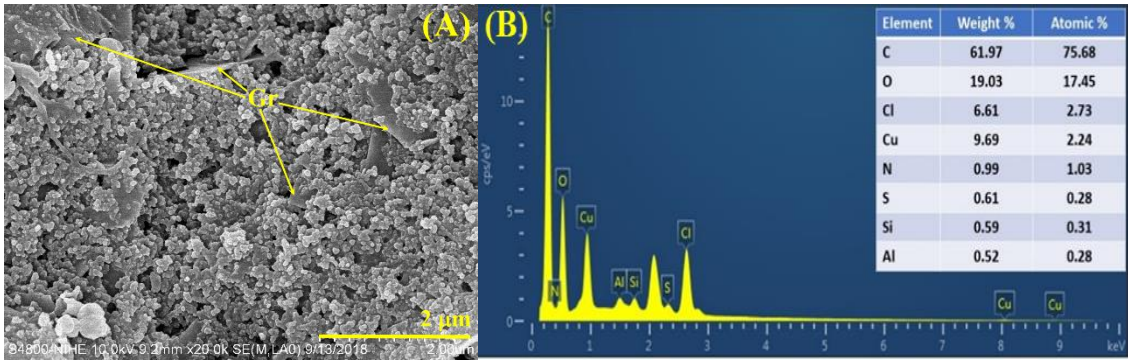

Figure3. (A) SEM image and (B) EDX spectrum of Gr/P(1,8-DAN)-Cu film.

3.2. Electrochemical sensitivity towards nitrite ions

The electrochemical response of Gr/P(1,8-DAN) and GC/Gr/P(1,8-DAN)-Cu electrodes towards nitrite ions has been investigated in PBS solution containing 1.5 mM NO_2^-, using CV technique between 0.0 and +1.0 V (*vs.* SCE). The obtained voltammogrames in Fig. 4 evidently indicate the role of Cu NPs acting as an electrochemical catalyst for nitrite oxidation reaction. The CV curve recorded on the GC/Gr/P(1,8-DAN)-Cu electrode presents an oxidation peak at +0.77 V which is much stronger than the case without Cu.

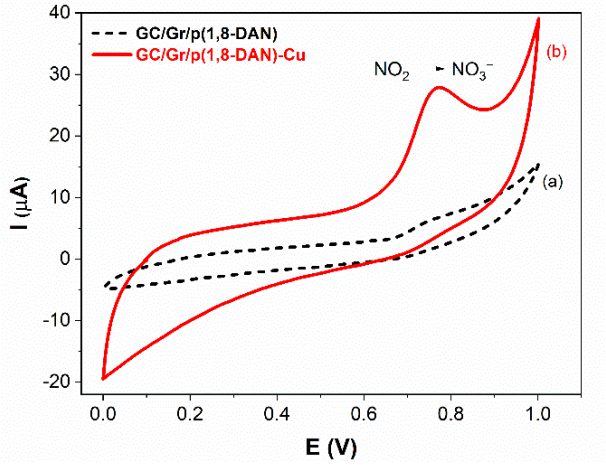

Figure 4. Voltammogrames recorded on GC/Gr/P(1,8-DAN) (curve a) and GC/Gr/P(1,8-DAN)-Cu (curve b) in PBS solution containing 1.5 mM nitrite.

The influence of some parameters of electrode preparation process on the peak current has been investigated (such as graphene content, Cu^{2+} concentration, and temperature for the Cu^{2+} adsorption). The results are shown in Fig. 5. It is found that the CV curves peak at a Gr content of 0.05 mg/mL, a Cu^{2+} concentration of 0.1 M and a temperature for the Cu^{2+} adsorption of 80 ^{o}C. Because of the quick evaporation of water, which causes considerable fluctuations in Cu^{2+} content, the temperature should not be raised over 80 ^{o}C in this experiment.

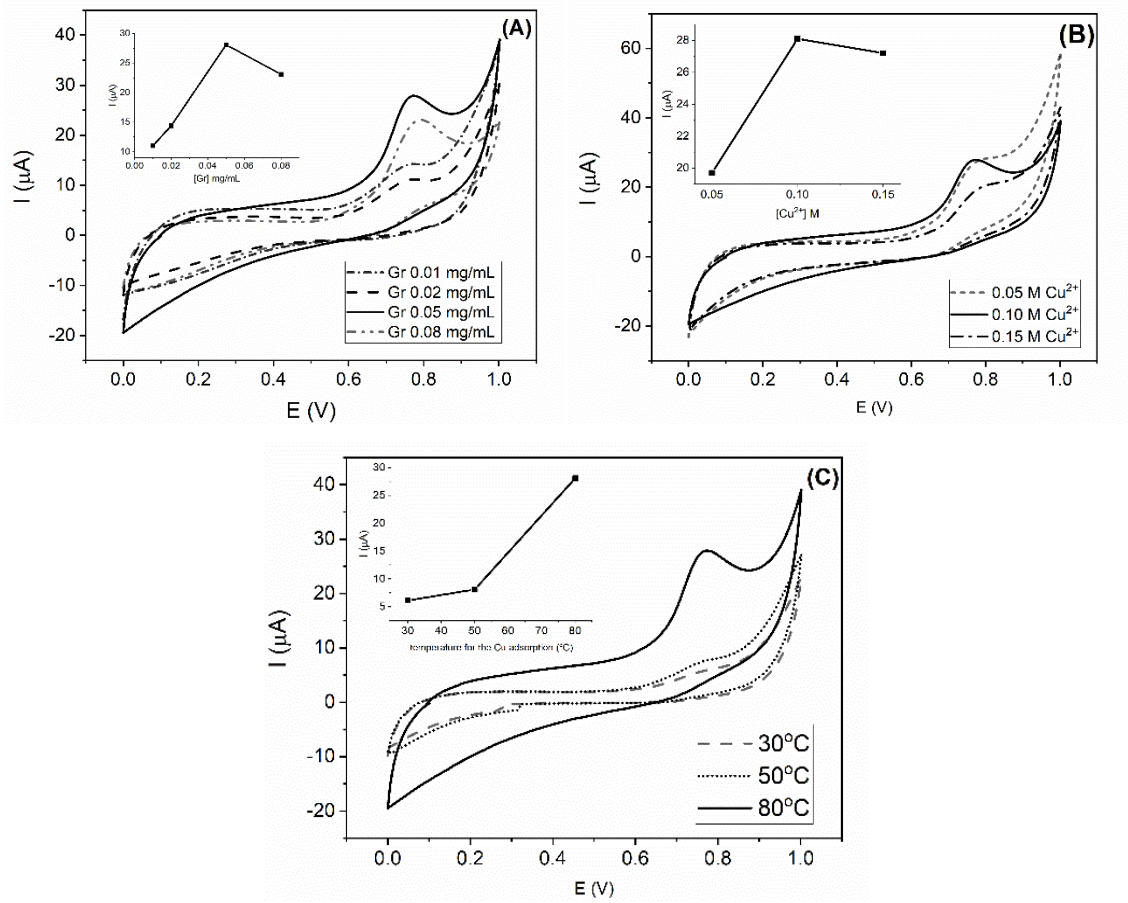

Figure 5. CVs of GC/Gr/P(1,8-DAN)-Cu electrodes were recorded on PBS containing 1.5 mM nitrite under different electrode preparation conditions: (A) various contents of graphene suspension (0.01, 0.02, 0.05, and 0.08 mg/mL); (B) various concentrations of $CuSO_4$ (0.05, 0.10, and 0.15 M); and (C) various temperatures (30, 50, and 80 ^{o}C) for the Cu^{2+} adsorption onto electrode surface. *Inset*: The plots of CV peak current at +0.77 V corresponding to changes in electrode preparation conditions.

3.3. Calibration curve for nitrite determination

The correlation between the measured electrochemical signal and the concentration of the target is an important factor of an electrode material from the point of view of applications for electrochemical sensors. In this work, square wave voltammetric (SWV) technique was used for nitrite determination because of its high sensitivity and reproducibility with short response time. Fig. 6 demonstrates the SWV curves recorded on the GC/Gr/P(1,8-DAN)-Cu electrode in PBS solutions containing nitrite with different concentrations.

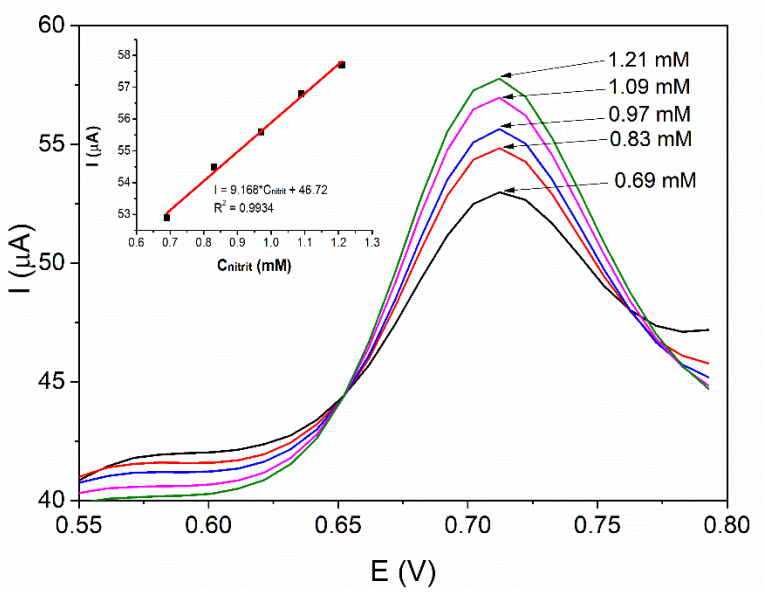

Figure6. SWV curves recorded on GC/Gr/P(1,8-DAN)-Cu electrode in PBS solutions with nitrite concentrations ranging from 0.69 to 1.21 mM. *Inset*: the corresponding calibration curve.

As shown in Fig. 6, the peak current (I_p) was linear to the nitrite concentration with R^2 = 0.9934 over a concentration range of 0.69 to 1.21 mM. The linear regression equation is I (μA) = 9.168*$C_{nitrite}$ (mM) + 46.72. So Gr/P(1,8-DAN)-Cu nanocomposite film can be used as a sensitive layer for nitrite electrochemical sensors. The limit of detection (LOD) of 0.13 mM was calculated using the formula: LOD = 3.3 × standard deviation of response/slope of the calibration curve.

4. CONCLUSIONS

This work described the preparation of Gr/P(1,8-DAN)-Cu nanocomposite film using electrochemical technique combined with adsorption. Graphene has prominent electronic properties, large specific surface area and excellent stability. P(1,8-DAN) is rich in amino groups and exhibits good copper ions adsorption. Adsorbing copper ions resulted in the formation of monolayer and uniform Cu NPs on the surface of the Gr/P(1,8-DAN) film. Electrochemical measurements indicated the role of Cu NPs as a catalyst for the electrooxidation of nitrite, so it can clearly enhance the signal peak current which is used for nitrite determination. The obtained square wave voltammetric curves on the GC/Gr/P(1,8-DAN)-Cu modified electrode showed the linear correlation between peak current and nitrite concentration in the range of 0.69 to 1.21 mM with the limit of detection of 0.13 mM. These primary results indicate that Gr/P(1,8-DAN)-Cu nanocomposite film can be developed for nitrite detection and determination in aqueous medium.

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CRediT authorship contribution statement. Bui Thi Hong Van and Do Thi Thuy carried out the experiments. Nguyen Le Huy planned the experiments and analyzed the data. Nguyen Thi Tuyet Mai

wrote the manuscript. Tran Dai Lam and Nguyen Tuan Dung supervised the project. All authors contributed to the result discussion and interpretation.

Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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