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Electrochemical Sensor Based on MWCNTs/AuNPs/GCE for Sensitive Determination of Sudan I Content in Food Samples

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In this work, the electrochemical properties of MWCNTs/AuNPs/GCE were studied for the determination of Sudan I. The GCE surface was modified through electrodeposited AuNPs and spray pyrolysis synthesized MWCNTs. The morphology and structure of synthesized AuNPs and MWCNTs were studied by FESEM and XRD analyses. The cycle voltammetry and amperometry techniques were applied to study the electrochemical properties of MWCNTs/AuNPs/GCE. Results showed the high density and porous structure of MWCNTs and AuNPs were modified GCE surfaces. The electrochemical studies displayed that MWCNTs/AuNPs/GCE had high stability and sensitivity (6.8028 µA/mM), wide linear range (10–260 µM) and low detection limit (4 nM) for the determination of Sudan I. Comparison of MWCNTs/AuNPs/GCE with the other reported electrochemical sensors showed that the modification of sensor with MWCNTs and AuNPs were meaningfully promote the sensitivity, detection limit and linear range of electrode for the determination of Sudan I. Study of the selectivity and interference response of modified sensor in the presence of Ca^{2+}, Mg^{2+}, Al^{3+}, Na^{+}, Fe^{3+}, Zn^{2+}, beta-carotene, lycopene, lutein, cryptoxanthin and capsanthin as natural pigments displayed that the modified electrode did not show any significant response for the injections of these analytes. Response of modified electrode for the determination of Sudan I in real samples was evaluated.

Keywords: Electrochemical sensor; Sudan I; MWCNTs; Au nanoparticles; Cycle voltammetry; Amperometry

1. INTRODUCTION

Sudan I (1-(Phenyldiazenyl) naphthalen-2-ol, $C_{16}H_{12}N_2O$) as lipophilic azo dye is belonging to Sudan days family (I-IV) which use as a rich red, red-orange or yellow-orange color sources in leather, fabrics, waxes, fats, oils, polystyrene, cellulose and lacquers industrials. Evidence shows Sudan days are also used illicitly in the food industry especially in chili powder, paprika and curry pastes to promote color quality and preservative properties because of its low cost and easy production process. Application of these days' family in food productions lead to formation of mutation-inducing DNA adducts, and consequently prevalence allergenic, genotoxic and carcinogenic activities [1]. Several studies confirmed formation of tumor and cancer due to use of Sudan days in food industries [2, 3].

Therefore, Sudan I is considered as health hazardous composition by the European Union regulation. Thus, many researches are focused on development of methods for the determination of the Sudan dyes in food products [4, 5]. Liquid Chromatography-UV [6] ultra-performance liquid chromatography [7], liquid chromatography–mass spectrometry [8], UV–vis [9], electrochemical [10, 11], capillary electrophoresis [12], immunoanalysis [13], chemiluminescence flow injection analysis [14] and plasmon resonance light scattering [15] are useful techniques for the determination of Sudan days family in food samples. Most of these techniques are expensive, time-consuming and require a higher level of expertise for method development and sample preparation.

Among these methods, electrochemical techniques such as voltammetry and amperometry are low-cost, simple and easy handling analytical techniques [16-18]. Moreover, the electrochemical sensors and techniques are developed significantly because of the possibilities of modification and miniaturization of sensor tools. Application of different morphologies in micro and nano scales in the surface of sensors and change in electrode compounds are the great interest for promoting the sensors performance [19-21]. For example, CNTs, graphene and metallic nanoparticles such as Ag, Au, Pt, and Cu are studied to enhance the sensitivity, stability and selectivity of sensors [22-29]. These results show that simultaneous use of nanoparticles and MWCNTs to surface architecture of electrodes can significantly improve the Sudan I electrochemical sensors efficiency.

Therefore, this work reveals the electrochemical properties of MWCNTs/AuNPs/GCE. For this purpose, AuNPs are electrodeposited on GCE. MWCNTs are synthesized through the spray pyrolysis method and incorporated on electrodeposited AuNPs. The structure, morphology, electrochemical properties of prepared electrodes are investigated as Sudan I sensors.

2. EXPERIMENTAL

Before modification of the bare GCE (Bioanalytical Systems Inc., West Lafayette, IN, USA, d = 3 mm), the GCE surface was polished successively by silicon carbide grinding paper (grit 1200) for 10 seconds, and with Al_2O_3 powder (0.3 µm, Buehler, USA) for 5 minutes on micro-cloth pads wet with double distilled water (Struers ApS, Ballerup, Denmark), respectively. Between each polishing step, the surfaces were rinsed thoroughly with double distilled water. Then, the polished electrode was sonicated in HNO_3 solution (1: 1, *V*/*V*) for 3 minutes, 98% ethanol bath for 20 minutes, and double distilled water for 2 minutes, respectively.

In order to modification of GCE, the GCE was electrodeposited in electrochemical cell containing 0.5 M H_2SO_4 and 1mM $HAuCl_4 \cdot 3H_2O$ solution [30, 31]. The electrodeposition was performed through cyclic voltammetry technique by potential scan from -0.1 to 1.5 V vs $Ag/AgCl/KCl_{sat}$ at a scan rate of 50 mV s^{-1} in N_2-saturated for 15 minutes. Finally, the well-defined cyclic voltammogram of AuNPs/GCE was obtained.

The spray pyrolysis method was used to synthesis the MWCNTs [32, 33]. A clean quartz tube with internal diameter of 1 cm and a length of 50 cm was used. 1g $Fe(C_5H_5)_2$ (Sigma-Aldrich, 98%) as the catalyst precursor was dissolved in a 50 ml C_7H_8 (Sigma-Aldrich, 99.8%) and placed in the quartz tube. The quartz tube was heated by an electrical cylindrical furnace (Thermo scientific) at 850°C for 30 minutes and the solution paralyzed. Ar gas (Ningbo DSW International Co., Ltd., china, 99.99%) was used as the carrier gas and the gas flow rate was adjusted at 17 cm^3/s using UNIT mass flow controllers. After cooling the furnace, the synthesized MWCNTs were collected.

In order to generation carboxylate gropes on MWCNTs surface and elimination metallic and carbonaceous impurities [34], MWCNTs were sonicated in H_2SO_4/HNO_3 solution (3∶ 1, *V/V*) for 120 minutes. The carboxylated MWCNTs were filtered and rinsed repeatedly with double distilled water.

For preparation of MWCNTs/ GCE and MWCNTs/AuNPs/ GCE, 2 mg carboxylated MWCNTs were dispersed in 2ml *N*,*N*-dimethylformamide (Sigma Aldrich, 99.8 %). The GCE and AuNPs/ GCE were immersed in the carboxylated MWCNTs dispersion for 40 minutes. Finally, the modified electrodes were dried under infrared lamps and stored at 5 ℃ in a refrigerator until further use.

The real sample was prepared according to [22, 35]. A 2.00 g of chili sauce sample was mixed with 50 ml ethanol and sonicated for 60 minutes. The mixture was filtered through a 0.22 µm syringe filter (Sartorius, Goettingen, Germany) and gathered into a 50 ml volumetric flask and then diluted to the 50 ml with ethanol. The sample solutions were prepared using pH 7.

The morphology of synthesized AuNPs and MWCNTs was analyzed by scanning electron microscopy (FESEM; Hitachi S-4700, JEOL, Japan). Crystal structure of AuNPs and MWCNTs were analyzed with Xpert Pro X-ray diffractometer (XRD, PANalytical's X'Pert PRO MRD, USA) with 1.5404 Å (Cu Kα) in wavelength and 40KV/30 mA in power. Electrochemical studies were carried out in the three-electrode cell which containing Ag/AgCl/(sat KCl) as reference electrode, a Pt wire as the counter electrode bare and modified GCE (MWCNTs/ GCE, AuNPs/ GCE and MWCNTs/AuNPs/ GCE) as the working electrodes. Voltammetry on the working electrode was performed in buffers with and without Sudan I (Merck, Overijse, Belgium) solution. Autolab modular electrochemical system (Eco Chemie Ultecht) was employed for electrochemical studies. The 0.1 M phosphate buffer solutions (PBS) were prepared from H_3PO_4 and NaH_2PO_4. The pH of PBS was adjusted at pH 7.0 with HCl and NaOH solution.

3. RESULTS AND DISCUSSION

The FESEM image of Au NPs on GCE in Figure 1a shows the uniform deposition and well-distributed of round-shape nanoparticles in size of 70 nm on the surface of the GCE. As seen, the high porosity surface was prepared for AuNPs modified GCE. The FESEM image of MWCNTs/AuNPs/ GCE in Figure 1b illustrates stable incorporation of MWCNTs on AuNPs. Therefore, the high porosity and high effective surface area was prepared for both AuNPs/ GCE and MWCNTs/AuNPs/ GCE which can enhance the sensitivity of electrodes to detection of analytes.

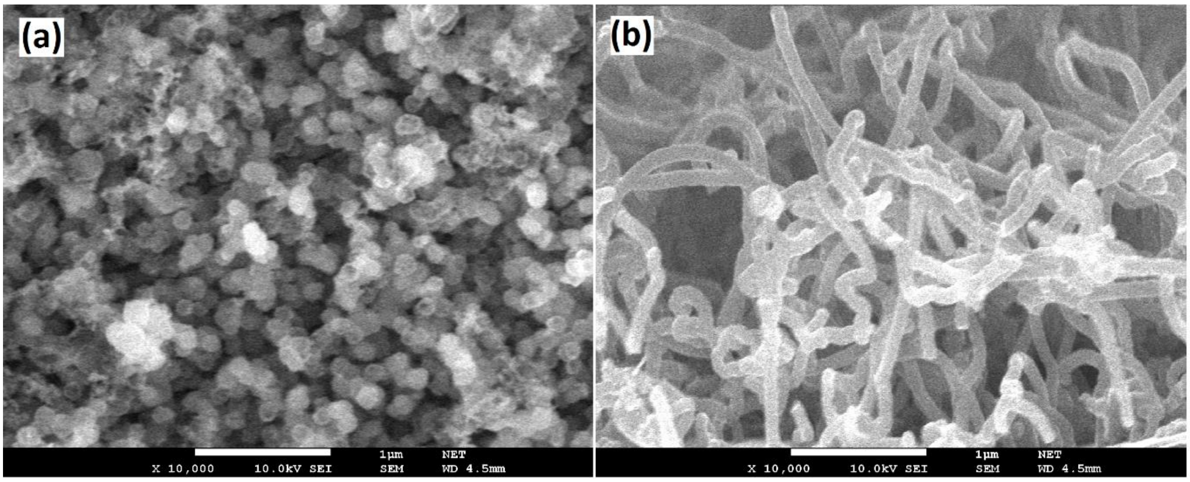

Figure 1. FESEM images of (a) AuNPs/GCE and (b) MWCNTs/AuNPs/GCE, respectively.

X-ray diffraction analysis can provide more structural information of the prepared electrodes. Figure 2 shows the XRD pattern of bare GCE, MWCNTs, MWCNTs/GCE, AuNPs/GCE and MWCNTs/AuNPs/GCE. There is only a sharp peak at 2θ = 26.1°, 26.0° and 25.9° for the bare GCE, MWCNTs and MWCNTs/ GCE, respectively, which corresponding to a basic (002) reflection of amorphous carbon accordance with standard JCPDS data reference (No. 58-1638) [36, 37].

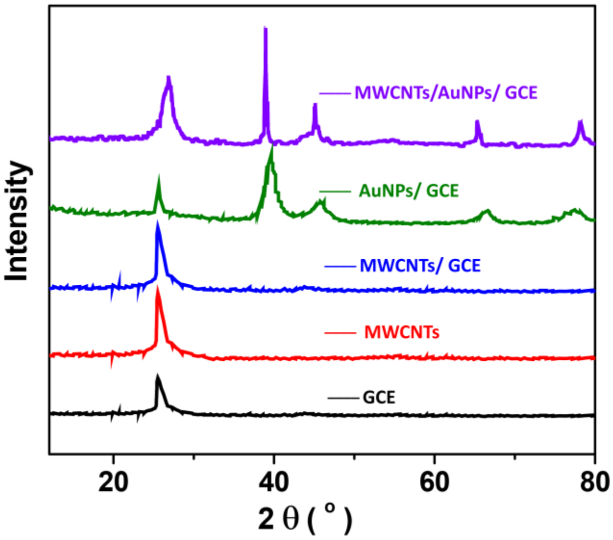

Figure 2. XRD patterns of bare GCE, MWCNTs, MWCNTs/GCE, AuNPs/GCE and MWCNTs/AuNPs/ GCE.

While after deposition of AuNPs on GCE surface, the XRD pattern of the AuNPs/ GCE displays the four intense diffraction peaks at 2θ = 38.29° , 44.38° , 64.81° , and 77.77°, corresponding to the (111), (200), (220) and (311) planes of a face centered cubic (fcc) lattice of Au nanoparticles (JCPDS 01– 1172), respectively. As shown, the XRD results for the MWCNTs/AuNPs/ GCE displays a similar pattern to AuNPs/ GCE. It can see the intensity of (002) peak was increased by incorporation of MWCNTs on AuNPs. These results indicate that MWCNTs and metallic Au nanoparticles have been incorporated on GCE. These results are similar to the report of Maluta et al. [38] for GCE modified using MWCNTs decorated with spherical Au nanoparticles.

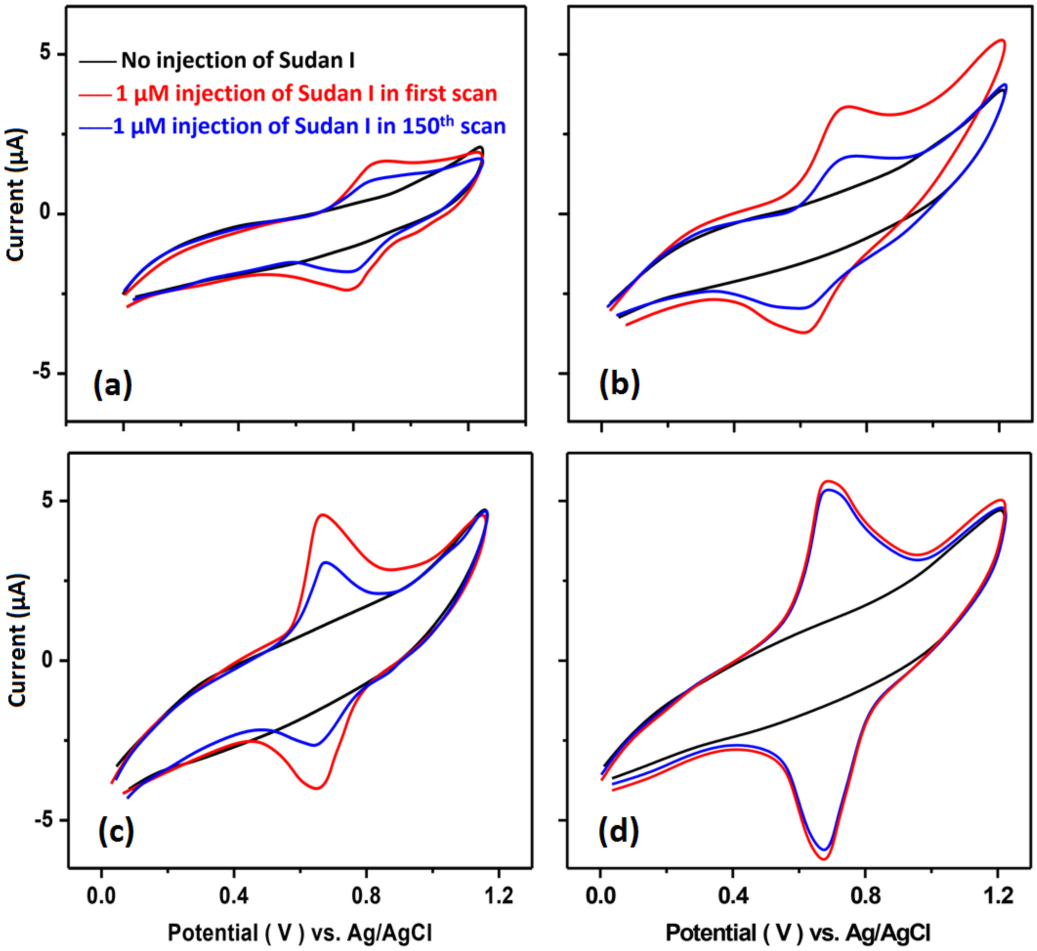

Figure 3. Recorded CVs of (a) GCE, (b) MWCNTs/ GCE, (c) AuNPs/ GCE and (d) MWCNTs/AuNPs/ GCE, respectively, in 0.1 M PBS pH 7.0 at a scan rate of 20 mV s^{-1} in absent and present of 1 µM Sudan I solution in electrochemical cell (First and 150th Recorded CVs)

The electrochemical study of bare GCE, MWCNTs/ GCE, AuNPs/ GCE and MWCNTs/AuNPs/ GCE was carried out using cyclic voltammetry (CV) technique. Figure 3 shows recorded CVs of modified and unmodified GCE in 0.1 M PBS pH 7.0 at a scan rate of 20 mV s^{-1} in the potential range of 0 to 1.2 V. As observed, there are no oxidation or reduction peaks for the all electrodes in absent of Sudan I in the electrochemical cell solution. After injection 1 µM of Sudan I solution in electrolyte, the first recorded CVs display a pair of redox peaks with reduction currents -2.47, -3.77, -4.04 and -6.20 µA and oxidation currents 1.71, 3.40, 4.57 and 5.55 µA for GCE, MWCNTs/ GCE, AuNPs/ GCE and MWCNTs/AuNPs/ GCE, respectively. The maximum redox currents were recorded MWCNTs/AuNPs/ GCE that indicate more sensitivity for the determination of Sudan I. It should be noted that MWCNTs have many advantages such as large specific surface area, fast electron transfer rate, high strength, and good adsorptive properties . Therefore, MWCNTs are often employed to construct the electrochemical sensors [39-41]. However, due to the inertness of carbon atoms and the lack of specific catalytic sites, the electrocatalytic efficiency of carbon nanostructures is very weak [42]. For improving the electrocatalytic ability, these structures must be combined or decorated with other materials [39-41]. Furthermore, the combination of the two nanostructures can create a synergistic effect, which leads to better electrocatalytic activity than any single material. According to Zhu et al. [43] and Tonelli et al. [44] studies, the porous noble metal nanostructures display higher electrochemical sensing because of their higher specific surface areas and larger pore volumes which facilitate both electron and mass transfer. Moreover, there are many corner atoms and corners in noble metals nanostructures which significantly improved their electrocatalytic ability [45, 46]. Therefore, increasing in peak current for MWCNTs/AuNPs/ GCE can be related to more porous nanostructured surfaces of MWCNTs/AuNPs/ GCE and more catalytic sites on both nanotubes and nanoparticles structures.

More study for characterization of response stability for the Sudan I determination of all prepared electrodes, the successive CVs in 0.1 M PBS pH 7.0 at a scan rate of 20 mV s^{-1} were recorded. Figure 3 displays the first and 150th recorded successive CVs after injection 1µM of Sudan I solution in an electrochemical cell. As observed, the changes of Sudan I oxidation current in 0.57 V for GCE, MWCNTs/ GCE, AuNPs/ GCE and MWCNTs/AuNPs/ GCE are about ~ 39%, 45%, 38% and 5%, respectively.

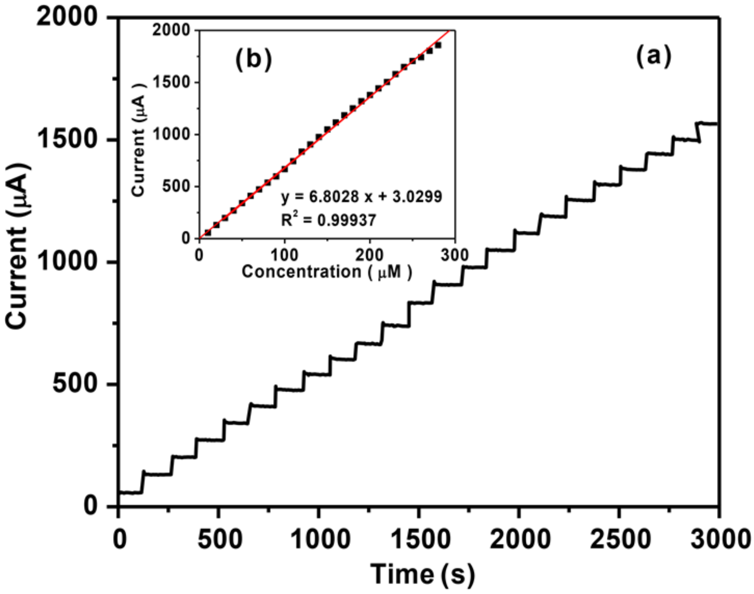

Figure 4. (a) The recorded amperometric response of MWCNTs/AuNPs/GCE in 0.1 M PBS pH 7.0 at 0.65 V in successive injections of 10 µM Sudan I solution; (b) the plots of calibration graphs.

Therefore, most unstable and stable responses are related to MWCNTs/GCE and MWCNTs/AuNPs/ GCE, respectively. It can be concluded that deposition AuNPs on GCE surface and carboxylation process of MWCNTs led to more strong covalent bonds between MWCNTs and

AuNPs/GCE. Treatment MWCNTs with H_2SO_4 lead to creation of covalent surface functionalization with carboxylic acid groups that have been used to attach MWCNTs onto the surface of metal nanoparticles [47-49]. Because of the high sensitivity and stable response of MWCNTs/AuNPs/ GCE, this electrode was selected for more electrochemical study of Sudan I determination.

To investigate the sensing properties of MWCNTs/AuNPs/ GCE such as linear range, detection limit, sensitivity, and selectivity, the amperometric responses with successive injections of Sudan I solution in 0.1 M PBS pH 7.0 at 0.65 V was recorded. First, for the determination of the linear range of electrodes, the amperometric response with successive injections of 10 µM Sudan I solution was recorded. As observed in Figure 4a, there are fast response and favorable electrocatalytic activity of MWCNTs/AuNPs/GCE for the determination of Sudan I. Moreover, with the addition of Sudan I concentration in each step, the response current was increased. For high concentration of Sudan I, response current reaches a saturation state because of reduction of active sites on MWCNTs/AuNPs/GCE surface. Figure 4b displays the calibration graphs response current vs. Sudan I concentration as equation current (µA) = 6.8028 [concentration of Sudan I (µM)] (µA/ µM) + 3.0299 (µA) (R^2 = 0.99937), which obviously exhibits high sensitivity of 6.8028 µA/mM and the linear dependence of response current on the Sudan I concentration over a wide linear range of 10–260 µM.

In order to determine the detection limit of the sensor, the amperometric response with successive injections of 1 µM Sudan I solution was recorded (Figure 5a). Figure 5b shows the calibration graphs as equation current (µA) = 6.6029 [concentration of Sudan I (µM)] (µA/ µM) – 0.99882(µA) (R^2 = 0.99982). Therefore, the detection limit of the sensor is evaluated of 4 nM.

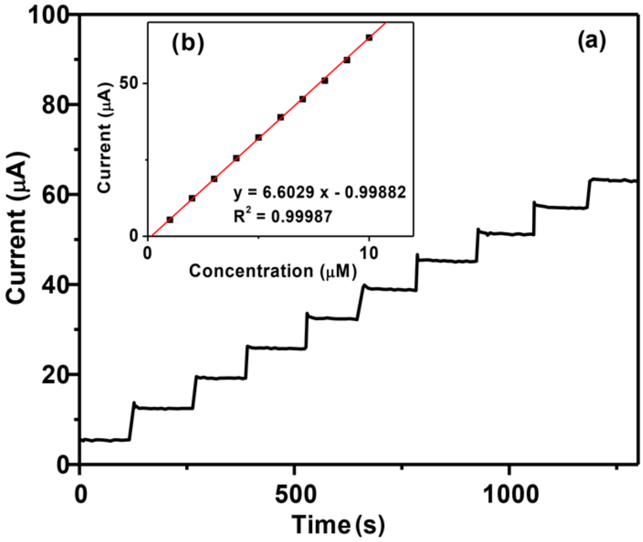

Figure 5. (a) The recorded amperometric response of MWCNTs/AuNPs/ GCE in 0.1 M PBS pH 7.0 at 0.65 V in successive injections of 1 µM Sudan I solution; (b) the plots of calibration graphs.

The sensing properties of MWCNTs/AuNPs/ GCE for Sudan I determination are compared to the other reported Sudan I electrochemical sensors. Results in Table 1 shows the high sensitivity of MWCNTs/AuNPs/GCE. Moreover, its wide linear range and low detection limit make it a good sensor for the determination of Sudan I. These results further confirm that modification of sensor with

MWCNTs and AuNPs were significantly efficient to generate high specific surface area, consequently lead to promote the electrode sensitivity.

Table 1. Comparison of MWCNTs/AuNPs/ GCE sensor performance with other Sudan I sensors.

Electrodes	**Technique**	**detection limit (nM)**	**Linear range (μM)**	**Sensitivity (μA/μM)**	**Ref.**
MWCNTs/AuNPs/ GCE	Amperometry	4	10–260	6.8028	This work
MWCNT/GCE	Amperometry	34.6	1.01–1.22	0.00215	[50]
Ag–Cu/rGO/GCE	Amperometry	0.4	0.001 – 10	0.0818	[51]
graphene/GCE	Cyclic voltammetry	0.04	0.075–7.50	3.64	[52]
Pt/CNTs/ionic liquid GCE	Cyclic voltammetry	3	0.008–600	8.2551 and 0.1478	[25]
Zno-CuO Nanoplates	Voltammetry	180	0.6–600	0.048	[53]
Reducing graphene oxide/GCE	Linear sweep voltammetry	10	0.04–8.0	3.6798	[54]
AuNp/GCE	Squarewave voltammetry	10	1000-40 and 0.7-20	0.000129 and 0.0002521	[24]
Bi_2WO_6 Nanosheets/GCE	Differential pulse voltammetry	2	0.02-114.6	3.0563	[55]

In order to study the selectivity response of MWCNTs/AuNPs/GCE as Sudan I sensor, the amperometric studies was performed in the presence of Ca^{2+}, Mg^{2+}, Al^{3+}, Na^{+}, Fe^{3+} and Zn^{2+} as metallic ion in food samples and beta-carotene, lycopene, lutein, cryptoxanthin and capsanthin as natural pigments. Figure 6 shows the recorded amperometric response of MWCNTs/AuNPs/GCE in 0.1 M PBS pH 7.0 at 0.65 V in successive injections of analytes. The results showed that the MWCNTs/AuNPs/GCE showed a clear response to all injections of Sudan I solution and did not show any remarkable response for the injections of other analytes. These results are according to other reports of Sudan I sensors [25, 56-59]. It must be considered that the similar molecular structure of Sudan I, Sudan II, Sudan III and Sudan IV may lead to the similar electrochemical responses. On the other hand, different types of Sudan would interfere with each other and lead to the overlapping in electrochemical responses. Therefore, it is suggested that four types of Sudan dyes in the typical food samples might be detected quantitatively by the electrochemical methods. For example, Ming et al. [60] showed that all Sudan dyes exhibited similar electrochemical properties, and distinct reductive peaks appeared at different potentials by voltammetry technique.

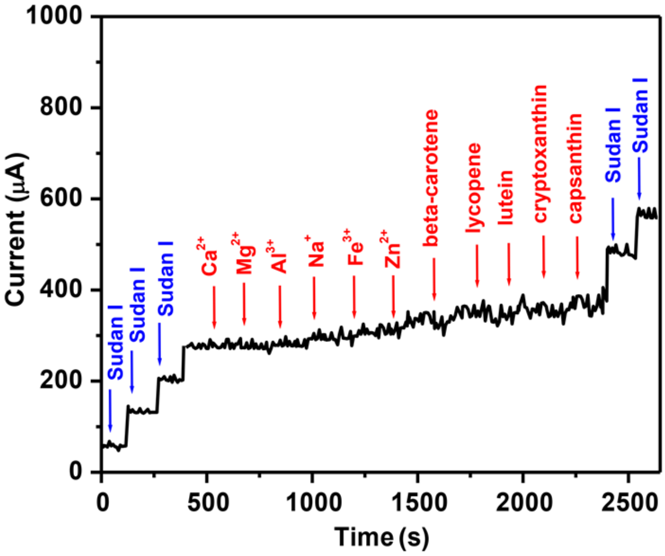

Figure 6. The recorded amperometric response of MWCNTs/AuNPs/ GCE in 0.1 M PBS pH 7.0 at 0.65 V in successive injections of 10 µM Sudan I solution and in successive injections of 15 µM Ca^{2+}, Mg^{2+}, Al^{3+}, Na^{+}, Fe^{3+}, Zn^{2+}, beta-carotene, lycopene, lutein, cryptoxanthin and capsanthin solutions.

The MWCNTs/AuNPs/ GCE was further used for the determination of Sudan I in chili sauce samples. The known concentration of Sudan I was measured in a prepared sample of chili sauce. The standard addition of Sudan I was used to determine Sudan I in the sample and the final content of Sudan I was evaluated to calculate the recovery. From the results listed in Table 2, it can be seen that the RSD is below 4.4% and the recoveries in range of 93.7-102.2 %. It illustrated that this method is reliable, excellent precision, and feasible for Sudan I determination.

Table 2. Recovery determination of Sudan I in real chili sauce samples

Injection (µM)	Measured (µM)	Recovery (%)	RSD (%)
200	205	102.2	4.4
300	301	100.0	3.8
400	375	93.7	3.7

For the determination of Sudan I in real samples, this study was repeated in chili sauce samples through amperometry technique and applied the standard addition of 0.1 µM Sudan I in electrochemical cells. The prepared electrolyte contained 1 ml of prepared real sample with 1 ml of 0.1 M PBS of pH 7.0 at 0.65V. Figure 7 shows the recorded amperometric response of MWCNTs/AuNPs/ GCE and its calibration plots. As observed, the obtained Sudan I in electrochemical cell and real samples are 0.0155µM and 0.0077 µM, respectively.

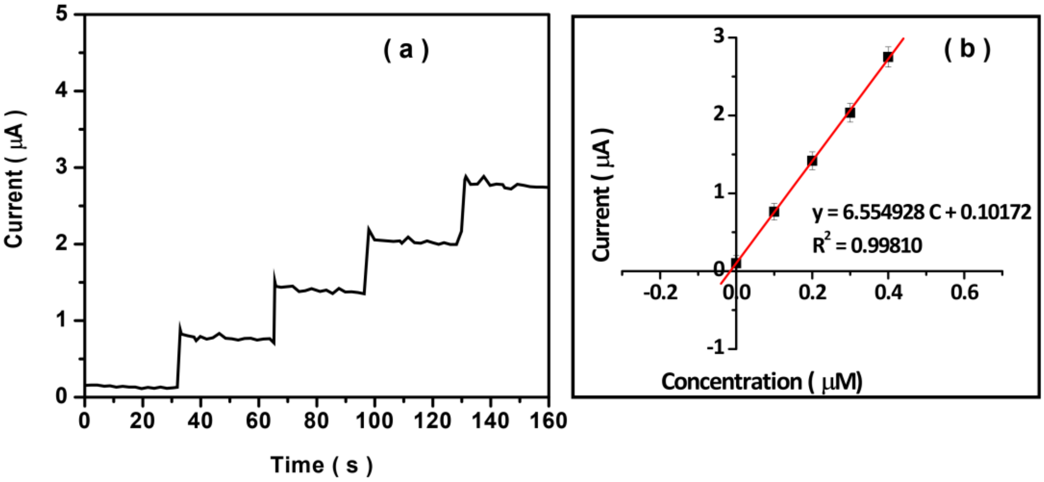

Figure 7. (a) The recorded amperometric response of MWCNTs/AuNPs/ GCE in prepared real sample with 0.1 M PBS pH 7.0 at 0.65 V in successive injections of 0.1 µM Sudan I solution; (b) the plots of calibration graphs.

4. CONCLUSIONS

In this work electrochemical properties of Sudan I sensor based on MWCNTs/AuNPs/GCE were investigated through cycle voltammetry and amperometry techniques. For fabrication the modified GCE, first, the spray pyrolysis method was employed to synthesize MWCNTs. Then, AuNPs electrodeposited on GCE surface and modified by carboxylated MWCNTs. The FESEM and XRD analysis were used to study the structure of synthesized AuNPs and MWCNTs. Results showed the high density, high aspect ratio and porous structure of MWCNTs and AuNPs were synthesized and modified GCE. The results of electrochemical studies showed that MWCNTs/AuNPs/GCE exhibited high stability and sensitivity for the determination of Sudan I because of more porous nanostructured surface of MWCNTs/AuNPs/GCE and more catalytic sites on both of nanotubes and nanoparticles structures. Moreover, carboxylation of MWCNTs lead to creation of covalent surface functionalization with carboxylic acid groups and strong attachment of MWCNTs onto the surface of AuNPs. Results also showed that the linear range, detection limit and sensitivity of MWCNTs/AuNPs/GCE were evaluated of 10–260 µM, 4 nM and 6.8028 µA/mM for Sudan I determination. Comparing the sensing properties of MWCNTs/AuNPs/GCE with the other reported Sudan I electrochemical sensors showed that the modification of sensors with MWCNTs and AuNPs were significantly efficient to promote the sensitivity, detection limit and linear range of electrodes. Study of selectivity and interference response of MWCNTs/AuNPs/ GCE as Sudan I sensor in the presence of Ca^{2+}, Mg^{2+}, Al^{3+}, Na^{+}, Fe^{3+}, Zn^{2+}, beta-carotene, lycopene, lutein, cryptoxanthin and capsanthin as natural pigments displayed that the modified electrode did not show any significant response for the injections of other analytes. Studying the Sudan I in chili sauce samples showed the MWCNTs/AuNPs/GCE was reliable, excellent precision, and feasible for Sudan I determination.

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