

ประสิทธิภาพของวัสดุนาโนที่ปรับปรุงที่ผิวหน้าอิเล็กโทรด เพื่อตรวจวัดสารซูดานอนุพันธ์ที่หนึ่งโดยใช้วิธีเคมีไฟฟ้า

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บทคัดย่อ

สารซูดานอนุพันธ์ลำดับที่หนึ่งเป็นสารก่อมะเร็ง จัดเป็นสารอันตรายประเภท 3 ปัจจุบันห้ามใช้เป็นสารเติมแต่งสีในอาหาร ในการทดลองนี้ได้ทดสอบสารซูดานโดยวิธีอิเล็กโทรเคมีคัลเซนเซอร์ ร่วมกับการใช้อิเล็กโทรดคาร์บอนแบบพิมพ์สกรีน (SPCE) ที่ปรับปรุงผิวหน้าด้วยวัสดุนาโน ได้แก่ กราฟีนออกไซด์ (GO) ซิลิกอนไดออกไซด์ (SiO₂) และเหล็กออกไซด์ (Fe₃O₄) จากนั้นศึกษาสมบัติเชิงอิเล็กโทรเคมีของอิเล็กโทรดคาร์บอนแบบพิมพ์สกรีนในเชิงปฏิกิริยาออกซิเดชันแบบไม่ผันกลับของสารซูดานอนุพันธ์ลำดับที่หนึ่ง โดยหาอัตราคงที่แบบมาตรฐาน (k_s) โดยใช้เทคนิคลิเนียลสวิฟโวลแทมเมตรี พบว่าค่า k_s เท่ากับ 7.72×10^{-3} ($\pm 8 \times 10^{-4}$) เซนติเมตรต่อวินาที 9.19×10^{-3} ($\pm 1.4 \times 10^{-3}$) เซนติเมตรต่อวินาที และ 5.72×10^{-3} ($\pm 8 \times 10^{-4}$) เซนติเมตรต่อวินาที สำหรับ GO/SPCE SiO₂/SPCE และ Fe₃O₄/SPCE ตามลำดับ ส่วนพื้นที่อิเล็กโทรดที่สามารถทำปฏิกิริยาได้ (A) หาจากสมการของ Anson โดยใช้ potassium hexacyanoferrate (III) เข้มข้น 0.1 มิลลิโมลาร์ และใช้ค่าสัมประสิทธิ์การแพร่ของสารเท่ากับ 7.6×10^{-6} ตารางเซนติเมตรต่อวินาที ทั้งนี้ใช้สมการของ Anson เช่นกันในการหาปริมาณโมลของสารที่ทำปฏิกิริยาต่อพื้นที่ (Γ) โดยใช้สารซูดาน 20 ไมโครโมลาร์ และใช้ค่าสัมประสิทธิ์การแพร่ของสารเท่ากับ 3.41×10^{-5} ตารางเซนติเมตรต่อวินาที พบว่าได้ค่า A เท่ากับ 7.91×10^{-4} ($\pm 1.92 \times 10^{-4}$) ตารางเซนติเมตร 5.77×10^{-4} ($\pm 1.84 \times 10^{-4}$) ตารางเซนติเมตร และ 7.41×10^{-4} ($\pm 3.65 \times 10^{-4}$) ตารางเซนติเมตรสำหรับอิเล็กโทรดแบบ GO/SPCE SiO₂/SPCE และ Fe₃O₄/SPCE ตามลำดับ ส่วนค่า Γ ของ GO/SPCE และ SiO₂/SPCE เท่ากับ 6.47×10^{-12} ($\pm 2.90 \times 10^{-10}$) โมลต่อตารางเซนติเมตร และ 1.06×10^{-9} ($\pm 1.12 \times 10^{-9}$) โมลต่อตารางเซนติเมตร ในกรณีของอิเล็กโทรดแบบ SPCE และ Fe₃O₄/SPCE ไม่สามารถหาค่า Γ ได้จากการศึกษาการปรับปรุงผิวหน้าอิเล็กโทรดแบบต่างๆ พบว่าการปรับปรุงผิวหน้าอิเล็กโทรดด้วย SiO₂/SPCE เหมาะสำหรับการวัดซูดานอนุพันธ์ที่หนึ่งมากที่สุด

คำสำคัญ : สารซูดานอนุพันธ์ที่หนึ่ง / สารเติมแต่งในอาหาร / วัสดุนาโน / เทคนิคเคมีไฟฟ้า

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Efficiency of Nanomaterials Modified Screen-Printed Electrode for Sudan I Detection Based on Electrochemical Experiments

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Abstract

Sudan I is a category 3 carcinogen, which is now banned from being used as a food colorant. Here we examined the electrochemical sensing of Sudan I. Screen-printed electrodes (SPCE) were modified by nanoparticles: graphene oxide (GO), silicon dioxide (SiO₂), and magnetic iron oxide (Fe₃O₄). The electrochemical characteristics of the SPCE were studied for the irreversible electrochemical oxidation of Sudan I. The standard rate constants (k_s) for the reaction were determined using linear sweep voltammetry. The values of k_s were found to be 7.72×10^{-4} ($\pm 8 \times 10^{-4}$) cm/s, 9.19×10^{-3} ($\pm 1.4 \times 10^{-3}$) cm/s and 5.72×10^{-4} ($\pm 8 \times 10^{-4}$) cm/s for GO/SPCE, SiO₂/SPCE, and Fe₃O₄/SPCE, respectively. The total active area (A) was determined from the Anson equation using 0.1 mM potassium hexacyanoferrate (III), assuming a diffusion coefficient of 7.6×10^{-6} cm²/s. Surface coverages (Γ (mol/cm²)) were also determined from the Anson equation, using 20 μ M Sudan I and assuming a diffusion coefficient of 3.41×10^{-5} cm²/s. A was found to be 7.91×10^{-4} ($\pm 1.92 \times 10^{-4}$) cm², 5.77×10^{-4} ($\pm 1.84 \times 10^{-4}$) cm² and 7.41×10^{-4} ($\pm 3.65 \times 10^{-4}$) cm² for GO/SPCE, SiO₂/SPCE, and Fe₃O₄/SPCE, respectively. Γ was found to be 6.47×10^{-12} ($\pm 2.90 \times 10^{-10}$) mol/(cm²) and 1.06×10^{-9} ($\pm 1.12 \times 10^{-9}$) mol/(cm²) for GO/SPCE and SiO₂/SPCE, respectively. Nevertheless, Γ of SPCE and Fe₃O₄/SPCE could not be determined. The analytical determination by the modified SPCEs reveals that SiO₂/SPCE is suitable for Sudan I detection.

Keywords : Sudan I / Additive Food / Nanomaterials / Electrochemical Techniques

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1. Introduction

Sudan, a diazo dye, is used as a food additive in order to enhance and sustain the colour of food products over time. For example, chilli and chilli products have higher prices when sudan red I is coated onto them. Sudan has been shown to cause tumor in the mice and can cause cancer in humans [1]. Therefore, food safety guidelines have been issued for the sudan contained in food and beverages [2-3].

Conventional methods which have been used for sudan detection including spectrophotometry [4-6] high performance liquid chromatography (HPLC) [7, 8] mass spectrometry (MS) [9] and reversed-phase (RP) liquid chromatography–tandem mass spectrometry interfaced with electrospray (LC–ESI–MS/MS) [10]. These methods have problems such as high cost, long measurement times, the need for skilled users, and the use of organic solvents in the sample preparation.

Electrochemical methods can often be used with inexpensive portable equipment and can provide highly sensitive techniques. Nanomaterials such as graphene oxide (GO), silicon dioxide (SiO_2) and magnetic beads (Fe_3O_4) have different properties. GO is carbon sheet that can increase the electrode area which will increase the electrochemical signal. SiO_2 , also known as silica, has high adsorption of dyes such as sudan. The Fe_3O_4 is a powder which is non-toxic. The octahedral sites in the magnetite structure contain ferrous and ferric species. The electrons coordinated with these iron species are thermally delocalized and migrate within the magnetite structure causing high conductivity [11]. Moreover, there is a report of the treatment water by using the magnetic nanocomposites to adsorb dyes [12]. So these nanomaterials have proved beneficial [13-16]. Hence, the effects of

the nanomaterial can include increased electrode area, improved electrode kinetics and adsorption of the analyte that can enhance the electrochemical signal and increase the sensitivity of detection.

The aim of this work was to perform a preliminary investigation of nanoparticle modified SPCE for sudan detection. Cyclic voltammetry (CV), linear sweep voltammetry (LSV), chronocoulometry (CC), and differential pulse voltammetry (DPV) were used to characterize the electrode modifications.

2. Materials and Methods

2.1 Apparatus

All electrochemical measurements were performed using an Autolab PGSTAT 10 computer-controlled potentiostat (Eco Chemie) with GPES software. The working electrode was a screen printed carbon track (1.5 mm. x 3.5 mm.) and the reference/counter electrode was a screen printed Ag/AgCl track (2 mm. x 3.5 mm.). (Quasence Co. Ltd, Thailand).

2.2 Reagents

Sudan I (1-[2,4-dimethylphenyl] azo]-2-naphthalenol) was purchased from Sigma-Aldrich (U.S.A). A stock solution of 1 mM sudan I was prepared daily in absolute ethanol (Merck, U.S.A). A phosphate buffer solution (PBS) pH 6 was used without supporting electrolyte because sudan dye was found to precipitate in salt solutions. Chronocoulometric experiments used 1 mM potassium hexacyanoferrate ($\text{K}_3\text{Fe}(\text{CN})_6$) which was diluted with double distilled water. All chemicals used were the analytical grade. GO was supplied by Dr. Porramate Chumyim (GO was synthesized at Rice University, U.S.A). 99% of SiO_2 was purchased from Sigma-Aldrich (U.S.A), the diameter was about 10-20 nm and Fe_3O_4 nanoparticles powder was about 20-30 nm

in diameter which was purchased from Aldrich (U.S.A).

2.3 Modification of the nanoparticles modified electrode

The bare SPCE was rinsed with absolute ethanol and deionized water in order to remove any impurities and the surface was then dried in a N₂ stream. Each nanoparticle sample (2 mg) was suspended in 70% absolute alcohol and the mixture was sonicated for approx. 2 h. A 2 µL aliquot of each mixture was drop-dried on the carbon working electrode. The modified SPCE were stored at room temperature in a desiccator.

3. Results and Discussion

3.1 The standard rate constant

Many reports have studied the electro-oxidation of sudan I. The number of electrons transferred was found to be 2 and the pH effect suggested the number of protons transferred was also 2. As shown in Figure 1, it has been suggested the

anodic peak of sudan I is due to the oxidation of phenolic hydroxyl group to quinonyl [13, 18]. The electrochemical behavior of sudan I has also been investigated at Fe₃O₄/GC electrodes and it was found that the anodic peak current was irreversible. The standard heterogeneous rate constant (k_s) for the reaction was determined by LSV technique, using the following eq.1 [16,19].

$$k_s = 2.415 \exp(-0.02F/RT) D^{1/2} (E_p - E_{p/2})^{-1/2} \nu^{1/2} \quad (1)$$

E_p and $E_{p/2}$ refer to the peak potential and the potential at the half peak current from linear sweep voltammograms of 20 µM sudan I at a bare SPCE (a) and an SPCE modified with GO/SPCE (b) and SiO₂ GO/SPCE (c) and Fe₃O₄ GO/ SPCE (d). In figure 2, k_s was calculated using the diffusion coefficient (D) of sudan I to be 3.14 x 10⁻⁵ cm²/s [16, 20], a scan rate (ν) 100 mV/s, F is the Faraday constant, R is the gas constant and the temperature (T) was 298 K. The value of k_s was inversely proportional with

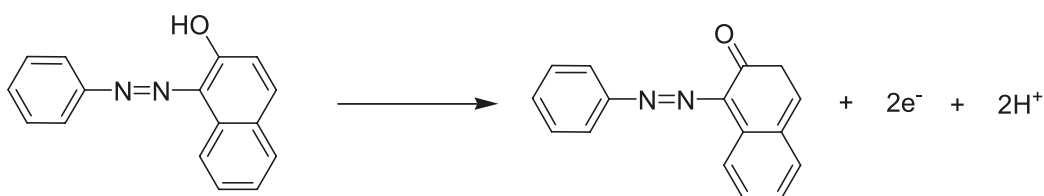


Figure 1 The possible reaction of Sudan I occurred after the applied electric potential to an electrode [18].

$E_p - E_{p/2}$ value and proportional to the rate of electron transfer at the electrode surface. k_s of the different electrode modifications is shown in Table 1. Tens replicates were performed for each modification. The heterogeneous electron transfers rate constant of sudan I was fastest at SiO₂/SPCE/ ($k_s = 9.19 \times 10^{-3}$) because the value of $E_p -$

$E_{p/2}$ which related to the electron transfer was lower than the other modified electrodes. Different values of k_s reflect the favorability of electron transfer at the nanoparticles surface. This can be affected by factors such as conductivity and adsorption onto the surface. We note that the k_s value for Fe₃O₄/GCE is higher than at Fe₃O₄/SPCE.

Table 1 The standard heterogeneous rate constant.

Electrode	$E_p-E_{p/2}$ (mV)	K_s (cm/s)	Reference
Fe ₃ O ₄ /GCE	52	7.61×10^{-3}	Yin, H., 2011 [15]
SPCE	62	7.00×10^{-3} (SD $\pm 6 \times 10^{-4}$)	This work
GO/SPCE	51	7.72×10^{-3} (SD $\pm 8 \times 10^{-4}$)	This work
SiO ₂ /SPCE	36	9.19×10^{-3} (SD $\pm 1.4 \times 10^{-3}$)	This work
Fe ₃ O ₄ /SPCE	93	5.72×10^{-3} (SD $\pm 8 \times 10^{-4}$)	This work

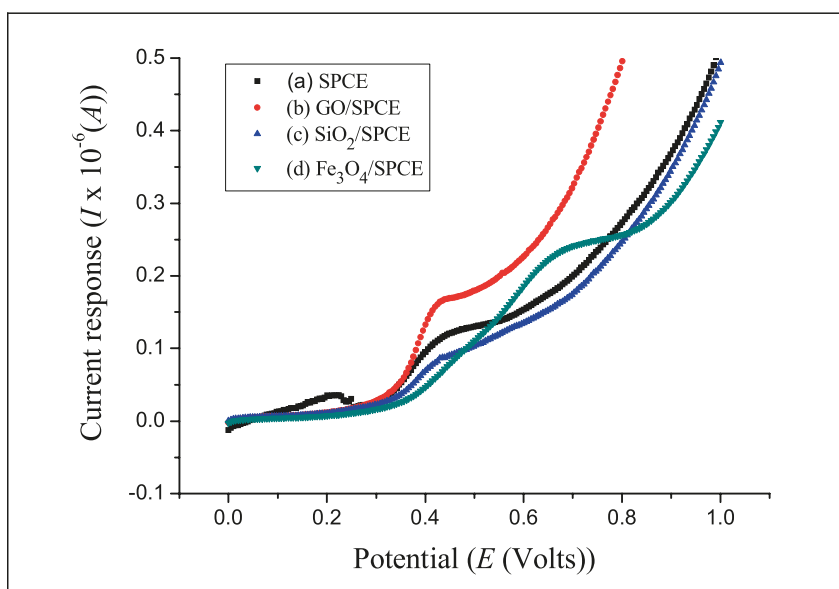


Figure 2 Linear sweep voltammogram of sudan I at the concentration is 20 μM in the mixed solution of ethanol:buffer (1:9) and the scan rate is 100 mV s^{-1} where (a) SPCE, (b) GO/SPCE, (c) SiO₂/SPCE, (d) Fe₃O₄/SPCE, respectively.

This is because reaction occurs at both the Fe_3O_4 and the underlying electrode and hence suggests the reaction is more favourable at glassy carbon than at screen printed carbon.

On the other hand, it was found that the electron is difficult to transfer at $\text{Fe}_3\text{O}_4/\text{SPCE}$ might be because of the high resistance of 4 oxygen of Fe_3O_4 on SPCE. It is effect to the high resistibility or low conductivity at the electrode modification. So $E_p - E_{p/2}$ has wide values. This lead to the slowest rate is slowest. The value of k_s for $\text{Fe}_3\text{O}_4/\text{SPCE}$ was lower than k_s for $\text{Fe}_3\text{O}_4/\text{GCE}$ because sudan I reacted at the surface of Fe_3O_4 and the surface of the electrode. The surface of GCE is bigger and high conductivity than SPCE. Therefore, the k_s of sudan I reaction at $\text{Fe}_3\text{O}_4/\text{GCE}$ is higher than $\text{Fe}_3\text{O}_4/\text{SPCE}$.

3.2 The effective surface area of modified electrode

The total active area means the total surface the analyte can react at. In this case, that surface is the surface of the electrode and the nanoparticles. The slope of a chronocoulometric plot, as shown in Figure 3 was used to determine this total active area by using the equation 2 [20].

$$Q = (2nFAcD^{1/2}t^{1/2})/\pi^{1/2} + Q_{dl} + Q_{ads} \quad (2)$$

Q represents coulombs, n represents the number of electrons transferred in the reaction, F represents the Faraday constant (96485.3 coulombs/mol), A represents the total active area (cm^2), c represents the concentration of $\text{K}_3\text{Fe}(\text{CN})_6$ (0.1 mM), D represents the diffusion coefficient of $\text{K}_3\text{Fe}(\text{CN})_6$, which we used as $7.6 \times 10^{-6} \text{ cm}^2/\text{s}$ [16-17, 21]. t represents time (s), Q_{dl} is the charge from the electrode capacitance, Q_{ads} represents

the reaction of adsorbed $\text{K}_3\text{Fe}(\text{CN})_6$. $\text{K}_3\text{Fe}(\text{CN})_6$ was used because it is a well-characterized mediator with well-known properties. The slope of this equation is equal to $2nFc$ multiplied by the square root of the diffusion coefficient divided by the square root of pi. Therefore, we can calculate the total active area.

From the same equation and the intercept of the chronocoulometric plot in Figure 3, we related Q_{dl} and Q_{ads} by using bare and modified electrodes. We assume the double layer charge, Q_{dl} , is the approximately the same in both cases because the interface is approximately the same in both cases (Because the nanoparticle coverage is low). Therefore, we can use subtraction to eliminate Q_{dl} and the remaining charge must be due to the adsorbed reactant. This will be proportional to the nanoparticle coverage (eq.3) since we do not expect strong adsorption of $\text{K}_3\text{Fe}(\text{CN})_6$ on the carbon electrode.

$$Q_{ads} = nFA\Gamma \quad (3)$$

The total active area and the surface coverage are shown in Table 2. Different quantities of nanoparticles will have been adsorbed onto the SPCE since the adsorption properties are different. Therefore, the total active surface areas are different. Note also that the experiments with the $\text{Fe}_3\text{O}_4/\text{GCE}$ used a larger electrode, and therefore the available area is larger compared to $\text{Fe}_3\text{O}_4/\text{SPCE}$. The surface coverage for different SPCE modifications reflects the favorability of sudan I adsorption onto each nanoparticle. GO/SPCE shows a higher total active area than other modifications of the SPCE electrode but is lower than $\text{Fe}_3\text{O}_4/\text{GCE}$ because of the surface of the SPCE smaller than GCE. In the case of

Table 2 The effective area of the electrode surface.

Electrode	Total active area (cm ²)	Γ (mol/cm ²)	Reference
Fe ₃ O ₄ /GCE	7.20×10^{-3}	9.74×10^{-12}	Yin, H., 2011 [16]
SPCE	3.92×10^{-4} (SD $\pm 1.17 \times 10^{-4}$)	N/A	This work
GO/SPCE	7.91×10^{-4} (SD $\pm 1.92 \times 10^{-4}$)	6.47×10^{-12} (SD $\pm 2.90 \times 10^{-10}$)	This work
Fe ₃ O ₄ /SPCE	7.41×10^{-4} (SD $\pm 3.65 \times 10^{-4}$)	N/A	This work
SiO ₂ /SPCE	5.77×10^{-4} (SD $\pm 1.84 \times 10^{-4}$)	1.06×10^{-9} (SD $\pm 1.12 \times 10^{-9}$)	This work

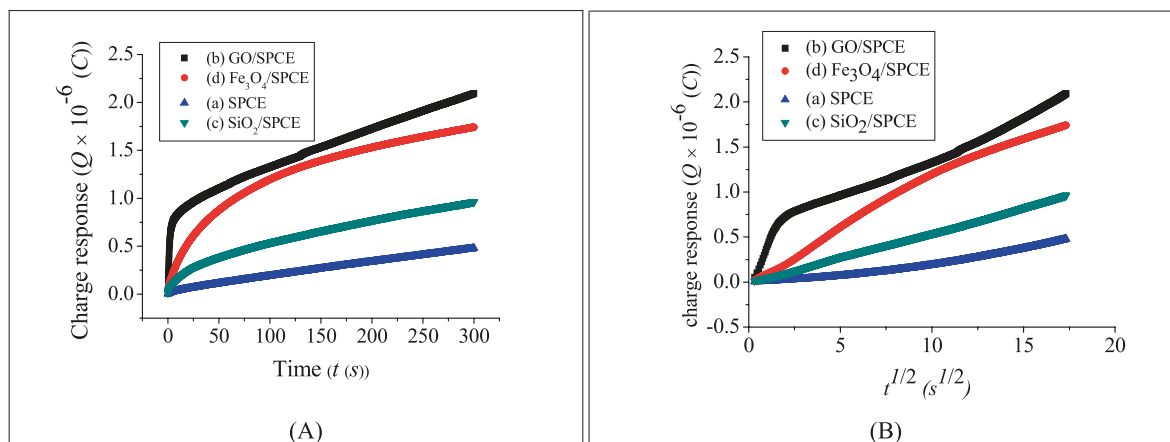


Figure 3 Chronocoulometric response to a single potential step was applied at the interval time of 0.1 s, the detection potential (E_{det}) of 0.4 volts. The corresponding plots of (A) $Q-t$ and (B) $Q-t^{1/2}$ were used for calculated the total active area (A) in the equation 2. Comparison of chronocoulometric response recorded at the bare SPCE (a) and the nanoparticles modified electrode with GO/SPCE (b), SiO₂/SPCE (c), and Fe₃O₄/SPCE (d). This modified electrode was analyzed in the presence of 0.1 mM K₃[FeCN₆].

SPCE and $\text{Fe}_3\text{O}_4/\text{SPCE}$, the surface coverage cannot be calculated from these values ($\Gamma < 0 \text{ mol/cm}^2$) because the intercept ($Q_{dl}+Q_{ads}$) is smaller than Q_{dl} ($n=10$). To investigate the kinetic results. A differential pulse voltammogram of 25 mM sudan I at the different modified electrodes is shown in Figure 4. The background current of

each electrode is not similar because of the difference in the active areas of the different coatings. The background current does not affect detection because the oxidation current was subtracted. GO/SPCE shows the highest oxidation peak, which suggests there was more sudan I adsorbed on the GO surface. This contradicts the

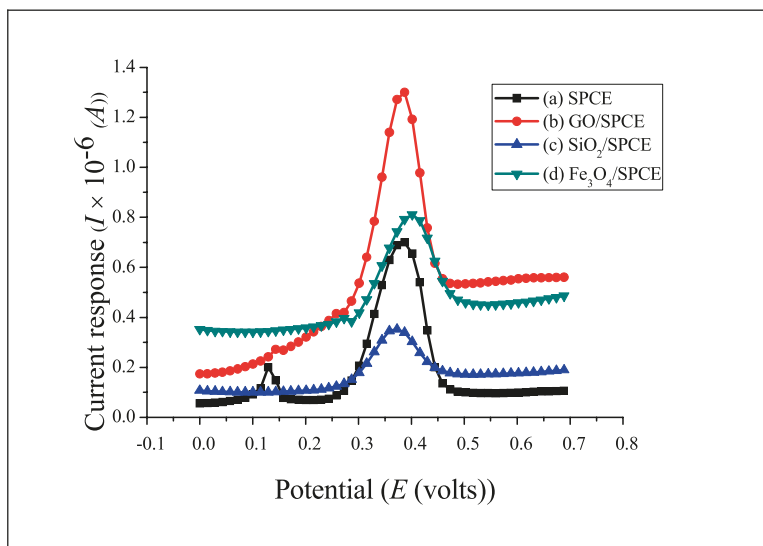


Figure 4 Differential pulse voltammetric response with the accumulation times of 300 s. 25 μM of sudan I were used to test with (a) the bare of SPCE, and the nanoparticles modified electrode of (b) GO/SPCE, (c) SiO_2/SPCE , and (d) $\text{Fe}_3\text{O}_4/\text{SPCE}$, respectively.

results of the coulometric experiments and may be because the timescale of the experiments was different, i.e. initial adsorption was higher at SiO_2 but over a longer time period (during the differential pulse measurements) the GO adsorption was higher.

In Figure 5, the graph was plotted between the oxidation current response and sudan I concentrations. These experiments used differential pulse voltammetry including the

electrode modification. It can be seen that GO/SPCE gave the highest current response, probably because of the high effective electrode area and high heterogeneous rate constant. Consideration at the low concentration; 0.2-10 μM . The oxidation currents at SPCE and GO/SPCE are similar because there are similar rate constants at these surface, but GO/SPCE has a greater dynamic range, possibly because the GO coating increases the effective surface area.

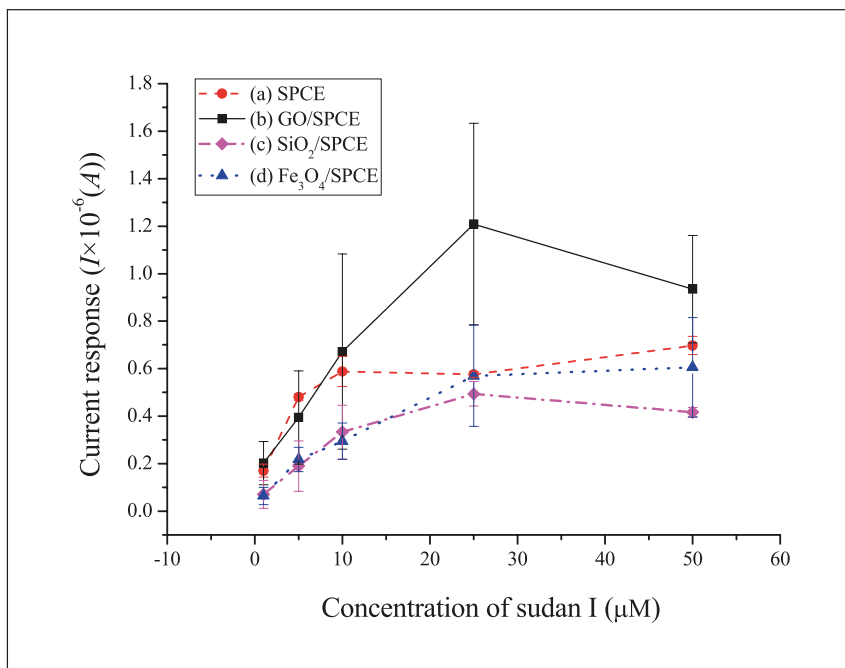


Figure 5 Differential pulse voltammetric response with the concentration of sudan I is in the range of 0.2 to 50 μM ($n=3$). The bare electrode is SPCE (a) then it was modified with GO/SPCE (b), SiO_2/SPCE (c), and $\text{Fe}_3\text{O}_4/\text{SPCE}$ (d), respectively.

4. Conclusion

A series of nanomaterial modifications were applied to screen printed electrodes for sudan I detection. The efficiency of the modified electrode can consider from the heterogeneous rate constants, the total active area, and the surface coverage. It was implied that the electron transfers of sudan I reaction occurred faster or slower rate at the different surface which related to the kinetics of electrode process and it was also demonstrated that increasing the effective electrode area could increase the sensor's dynamic range. Use of GO also produced the highest currents, possibly because of better adsorption of sudan I onto GO. Therefore, the use of GO/SPCE for sudan detection may be a useful area for future research in the development of a sudan sensor.

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