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Research Article

Electrocatalytic Study of Paracetamol at a Single-Walled Carbon Nanotube/Nickel Nanocomposite Modified Glassy Carbon Electrode

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A rapid, simple, and sensitive method for the electrochemical determination of paracetamol was developed. A single-walled carbon nanotube/nickel (SWCNT/Ni) nanocomposite was prepared and immobilized on a glassy carbon electrode (GCE) surface via mechanical attachment. This paper reports the voltammetry study on the effect of paracetamol concentration, scan rate, pH, and temperature at a SWCNT/Ni-modified electrode in the determination of paracetamol. The characterization of the SWCNT/Ni/GCE was performed by cyclic voltammetry. Variable pressure scanning electron microscopy (VPSEM) and energy dispersive X-ray (EDX) spectrometer were used to examine the surface morphology and elemental profile of the modified electrode, respectively. Cyclic voltammetry showed significant enhancement in peak current for the determination of paracetamol at the SWCNT/Ni-modified electrode. A linear calibration curve was obtained for the paracetamol concentration between 0.05 and 0.50 mM. The SWCNT/Ni/GCE displayed a sensitivity of 64 mA M^{-1} and a detection limit of 1.17×10^{-7} M in paracetamol detection. The proposed electrode can be applied for the determination of paracetamol in real pharmaceutical samples with satisfactory performance. Results indicate that electrodes modified with SWCNT and nickel nanoparticles exhibit better electrocatalytic activity towards paracetamol.

1. Introduction

The demand for new sensor materials is increasing due to the growing electrochemical industry. Nanomaterials have received considerable attention recently due to their excellent physicochemical properties and potential applications in electrocatalysts, photocatalysts, supercapacitors, and field emission devices. Electrodes modified with nanomaterials exhibit excellent characteristics that are superior to conventional mediators, such as metal oxides [1], polymers [2–5], inorganic complexes [6], and DNA [7]. Research on modified electrodes with nanomaterials has been conducted with different types of nanoparticles [8, 9], carbon nanotubes (CNTs) [10–14], and composites of nanomaterials [15–24].

CNTs have unique properties, such as superior thermal and electrical conductivities, excellent physicochemical properties, and high surface area [12, 13]. The single-walled carbon nanotube (SWCNT), a one-dimensional nanostructured material, is widely used in electrode modification due to its high surface to volume ratio. SWCNTs have the advantage over multiwalled carbon nanotubes (MWCNTs) due to their unique cylindrical single graphite sheet and excellent electron transfer activity. CNT modified electrodes have been evaluated and are considered to have good sensitivity and reproducibility [12, 13, 25].

Mechanical attachment [21] is a simple and inexpensive method for the fabrication of chemically modified electrode (CME). Great attention has recently been centered on the CME via CNTs, through the determination of various substances such as metal ions [8, 26], antibiotics [27], biochemicals [28–31], chemicals [32], and drugs [33, 34]. Nanoparticles exhibit good electrocatalytic activity with some electroactive substances including paracetamol. A hybrid of SWCNT and nanoparticles could be used as

a promising electron transfer mediator. The configuration of SWCNT/nanoparticles nanocomposite attracts great interest due to its three-dimensional nanostructures with high surface areas.

Paracetamol (acetaminophen, 4-acetamidophenol, or N-acetyl-*p*-aminophenol) is a pharmaceutical product with antipyretic and analgesic properties. It is an effective drug used to relief headache, toothache, neckache, and various pains. Paracetamol is also widely prescribed for cold, flu, and fever. Chronic use or overdose of paracetamol leads to the accumulation of toxic metabolites in the liver, which may cause severe or fatal hepatotoxicity and nephrotoxicity, skin rashes, and pancreas inflammation. Quantitative determination of paracetamol is important in the quality assurance of pharmaceutical industry and vital for the healthcare industry. Therefore, the development of a simple, rapid, sensitive, and accurate analytical method for the determination of paracetamol is needed. The electrochemical determination of paracetamol using various modified electrodes constructed from CNTs has been reported [12, 14, 25, 35–38].

In this paper, a composite made of single-walled carbon nanotubes and nickel was selected as the mediator and used in the fabrication of GCEs. A sensitive electroanalytical methodology based on SWCNT and nickel-modified GCE for the determination of paracetamol was developed. Cyclic voltammetry for the characterization of the SWCNT/Ni-modified electrode will be discussed.

2. Materials and Methods

2.1. Chemicals and Reagents. Single-walled carbon nanotubes (SWCNTs) with the purity of 90% and nickel (Ni) nanoparticles (99.9%, 40–60 nm) were purchased from SkySpring Nanomaterials, Inc. Panadol (GlaxoSmithKline, GSK), a commercial product for paracetamol, was used for the recovery study. All the following chemicals were used without further purification: paracetamol (or 4′-hydroxyacetanilide, $C_8H_9NO_2$) from Merck Schuchardt OHG, Germany, and potassium dihydrogen phosphate (KH_2PO_4). Deionized water from Reverse Osmosis Water Purifier was used for all solution preparations.

2.2. Instrumentation. An electrochemical workstation CV-50W Voltammetric Analyzer, Bioanalytical Systems, Inc. (BASi), connected to an external desktop computer, was used for all voltammetric measurements. Examination of the surface morphology of the nanocomposite was carried out using a variable pressure scanning electron microscope (LEO 1455 VPSEM) attached to an energy dispersive X-ray spectrometer (Oxford Inca EDX) with an acceleration voltage of 20 kV.

2.3. Preparation of Modified Electrode. Prior to use, the surface of the GCE was polished with 0.05 μm alumina slurry and cleaned in an ultrasonic bath for 3 minutes. A SWCNT/Ni-modified electrode was prepared as follows: highly pure SWCNT nanopowder and nickel nanoparticles were mixed in a 1 : 2 ratio until a homogenous nanocomposite was obtained. The prepared SWCNT/Ni composite was deposited on the GCE surface (3 mm in diameter) via mechanical attachment [21]. Dissolved oxygen was removed from the electrolyte by bubbling pure nitrogen gas through the solution prior to electrochemical measurements.

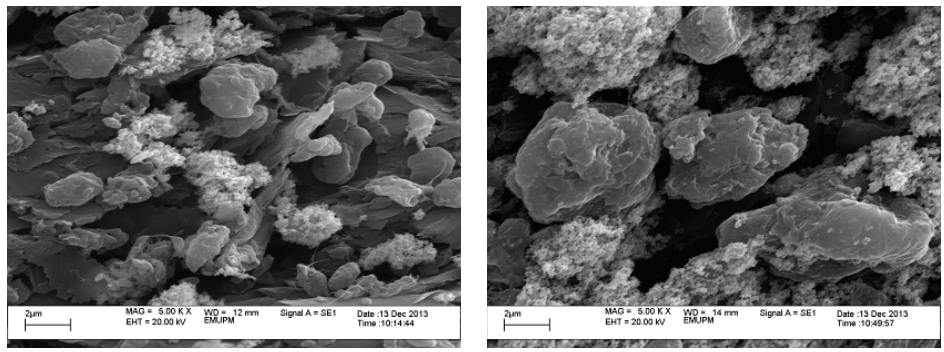
2.4. Electrochemical Characterization. An appropriate amount of paracetamol standard solution was added to an electrolytic cell containing about 10 mL of 0.1 M KH_2PO_4 electrolyte solution at pH 5.2. A three-electrode configuration was used, with the SWCNT/Ni-modified GCE employed as the working electrode. A silver/silver chloride (Ag/AgCl, 3 M KCl) electrode and a platinum wire (1 mm diameter) were used as reference electrode and auxiliary electrode, respectively. Unless otherwise indicated, all the electrochemical measurements were performed between −1.0 and 1.0 V, at a scan rate of 100 mV s^{-1} and temperature of 25 ± 2°C.

3. Results and Discussion

3.1. Electrode Morphology. The SWCNT/Ni nanofilm that was deposited on the basal plane pyrolytic graphite electrode (BPPGE) was examined using VPSEM. The micrograph of the graphite electrode surface prior to electroanalysis is shown in Figure 1(a). It is apparent from the figure that the irregularly shaped SWCNT/Ni nanocomposite was distributed on the graphite surface in bundles with diameters in the range of 1 to 4 μm. Irregular arrays of microcrystals and surface porosity were obtained. The SWCNT/Ni-modified electrode was then immersed in 0.1 M KH_2PO_4 solution containing 0.1 mM paracetamol and subjected to cyclic voltammetry. The scanning electron micrographic image of the SWCNT/Ni nanocomposite after electroanalysis was recorded as in Figure 1(b). However, it was also observed that the nanocomposites increased in size from 1–4 to 4–10 μm. The strong attraction of paracetamol to the SWCNT/Ni nanofilm may be due to the electrostatic interaction between the nanomaterials and the electroactive species.

3.2. Enhancement Study. An experiment was performed to elucidate the electrochemical behavior of SWCNT/Ni/GCE towards the redox reaction of paracetamol. Figure 2 depicts the voltammograms of 0.1 mM paracetamol in 0.1 M KH_2PO_4 at (a) bare GCE, (b) Ni-modified GCE, and (c) SWCNT/Ni-modified GCE in 0.1 M KH_2PO_4 solution. A pair of stable and well-defined curves was observed with the bare and modified electrodes. The enhancement factor of 5 in anodic peak current infers that SWCNT/Ni-modified GCE is more sensitive than the other electrodes in the determination of paracetamol and that the SWCNT/Ni nanofilm has good electrocatalytic activity with paracetamol.

The suggestive scheme for the mediator behavior of nanofilm in the electrocatalytic oxidation of paracetamol is shown in Figure 3. The enhanced peak current could be attributed to the better electron conductivity of SWCNT/Ni/GCE. The SWCNT/Ni immobilized on the GCE electrode surface provides a high surface area, which increases the conductive surface, facilitating electron transfer [12, 25], and leads to higher sensitivity when compared to



(a) (b)

Figure 1: Variable pressure scanning electron microscopy (VPSEM) images of SWCNT/Ni composites on a basal plane pyrolytic graphite electrode (BPPGE, 5 mm diameter) surface (a) before and (b) after the electroanalysis.

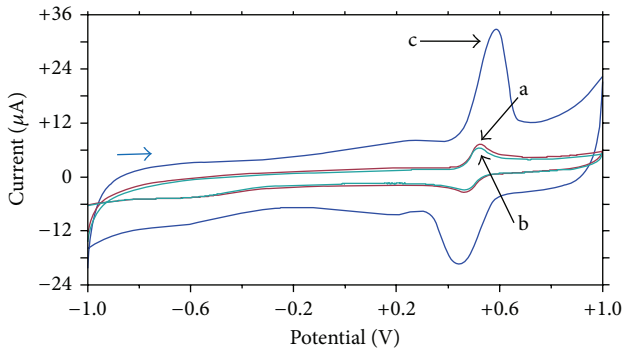


Figure 2: Cyclic voltammetry scanning of 0.1 mM paracetamol in 0.1 M KH_2PO_4 at (a) bare GCE, (b) Ni-modified GCE, and (c) SWCNT/Ni-modified GCE versus Ag/AgCl. Scan rate: 100 mV s^{-1}.

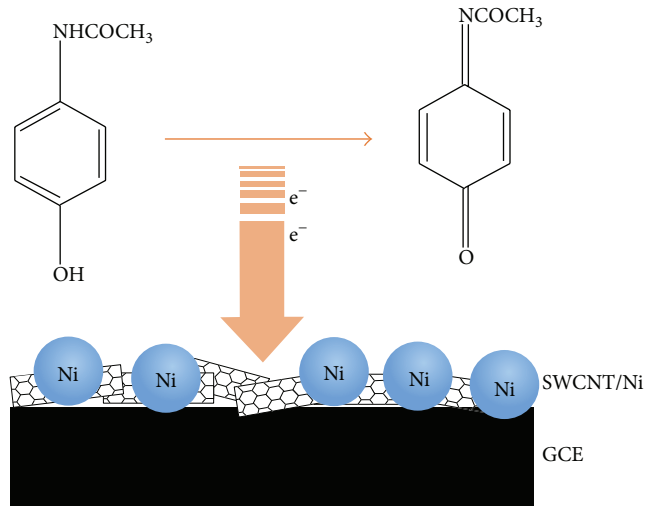


Figure 3: The suggestive scheme for the mediator behavior of SWCNT/Ni nanoparticles in electrocatalytic reaction of paracetamol.

a bare GCE. It is clear that the SWCNT/Ni nanofilm can be used as a potential electron transfer mediator for the determination of paracetamol.

3.3. Effect of Scan Rate. The effect of varying scan rate is used to determine the type of mass transport process involved and to study electrode kinetics. Cyclic voltammograms of the electrocatalytic reaction of paracetamol at a SWCNT/Ni/GCE were obtained at increasing scan rates in the range of 2–1000 mV s^{-1}. The increase in the scan rate induced an increase in the anodic peak current, which resulted in the shifting of the anodic peak current in a more positive potential direction. As shown in the plot of log anodic peak current against log scan rate (Figure 4), the peak current response increased linearly with the scan rate. The linear regression equation was $y = 0.685x + 0.319$ with a correction coefficient of 0.999. Based on the equation obtained, a slope of 0.69 reveals that the mass transport of electroactive species towards electrode surface is controlled by both diffusion and adsorption processes.

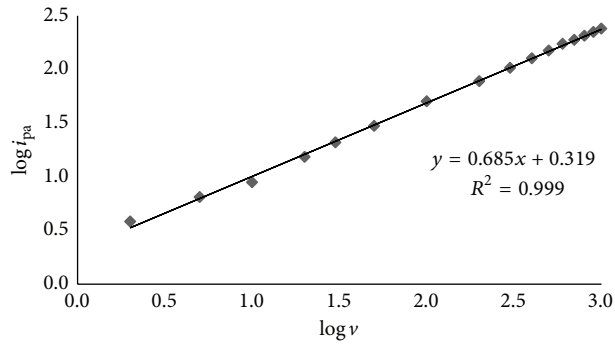


Figure 4: Plot of log i_{pa} versus log v.

3.4. Effect of Potential Cycling. The stability of the SWCNT/Ni-modified electrode was evaluated by cyclic voltammetry. The modified electrode was subjected to 5 continuous potential cycles to study the stability of the electrocatalytic reaction of paracetamol. A significant decay was observed in the peak current during the first cycle (Figure 5). This suggests that the nanocomposite was weakly bonded to the electrode surface by mechanical attachment technique.

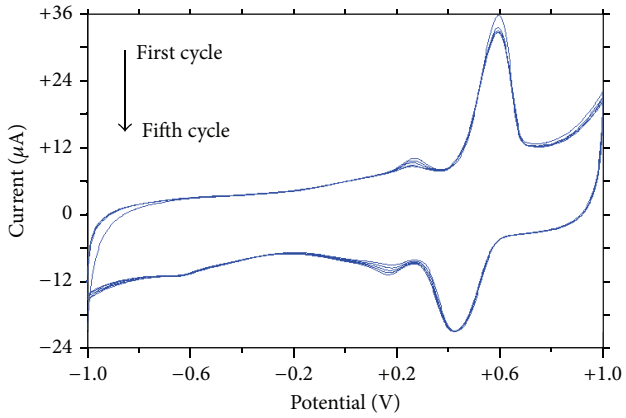


Figure 5: Multiple cycle voltammograms for 0.1 mM paracetamol in 0.1 M KH_2PO_4 at a SWCNT/Ni-modified electrode. Scan rate: 100 mV s^{-1}.

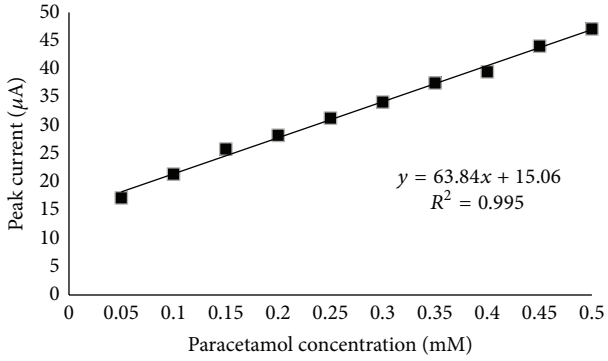


Figure 6: Standard calibration plot of paracetamol in 0.1 M KH_2PO_4 using a SWCNT/Ni-modified electrode versus Ag/AgCl.

Stability was observed in the peak currents from the second cycle onwards. Even after the fifth cycle, the anodic peak current for the oxidation of paracetamol remained high. The stability of the modified electrode could be attributed to the presence of the nanofilm, which forms a network-like nanostructure that restricts the loss of the SWCNT/Ni nanocomposite. The SWCNT/Ni/GCE was relatively stable while in 0.1 M KH_2PO_4.

3.5. Effect of Paracetamol Concentration. The effect of varying paracetamol concentration in 0.1 M KH_2PO_4 electrolyte solution was explored at the SWCNT/Ni/GCE. A series of well-defined peaks was obtained from the voltammetric responses to the additions of paracetamol over the range of 0.05–0.50 mM. A linear relationship was developed between the anodic peak current (i_{pa}) and the concentration of paracetamol (Figure 6). As described by the equation $y = 63.84x + 15.06$, a good sensitivity response towards the oxidation of paracetamol was found to be 64 mM A^{-1}. Using the plot, an excellent correlation of $R^2 = 0.995$ was determined and a low detection limit of 1.17×10^{-7} M was obtained. The electrochemical behavior of the SWCNT/Ni-modified GCE for the determination of paracetamol is comparable to some of the previously reported electrodes [12, 39].

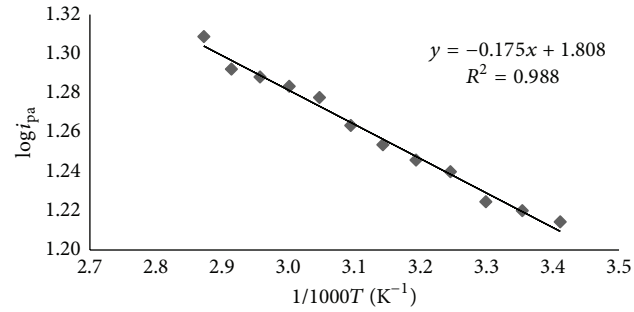


Figure 7: Plot of anodic peak current versus reciprocal of temperature for the electrolysis of 0.1 mM paracetamol at a SWCNT/Ni-modified electrode. Scan rate: 100 mV s^{-1}.

3.6. Effect of Temperature. The effect of temperature on the determination of paracetamol at the SWCNT/Ni-modified electrode was examined by cyclic voltammetry. The peak current increased gradually when temperature was increased in the range of 20–75°C. A plot of log anodic peak current against reciprocal of temperature was obtained with a slope of 0.175 (Figure 7). The plot was fairly linear and was in agreement with the thermodynamic expectation of Arrhenius equations [39].

The relationships between conductivity, diffusibility, and temperature are described by the following Arrhenius equation:

$$\sigma = \sigma^o \mathrm{Exp}\left(-\frac{E_a}{RT}\right), \qquad D = D^o \mathrm{Exp}\left(-\frac{E_a}{RT}\right), \tag{1}$$

where σ is conductivity, σ^o is standard conductivity, D is diffusibility, D^o is standard diffusibility, E_a is activation energy, R is specific gas constant (8.314 J K^{-1} mol^{-1}), and T is temperature (K). σ/D are conductivity/diffusibility and σ^o/D^o are standard conductivity/initial diffusibility.

Based on the Arrhenius plot, the activation energy of 1.45 kJ mol^{-1} was determined. The elevation of temperature was accompanied with an increase in peak current and shifting of peak potential towards a lower potential. The diffusion resistance of the electrode surface decreased with increasing temperature. This contributed to improved electron transfer rate at the electrode/electrolyte interface, which led to the higher anodic peak current. Therefore, the electrocatalytic reaction of paracetamol at the SWCNT/Ni/GCE is significantly temperature dependent.

3.7. Effect of pH. In most cases, the pH of the electrolyte solution is an important factor that influences the electrochemical reaction at an electrode surface. The study of varying solution pH is to determine the optimum pH for an electrocatalytic reaction and the number of protons involved in the reaction. The effect of pH was investigated in the range of 3–12 at the SWCNT/Ni/GCE. Figure 8 illustrates the change of anodic peak current for 0.1 mM paracetamol by varying the pH of 0.1 M KH_2PO_4 supporting electrolyte. As can be seen from

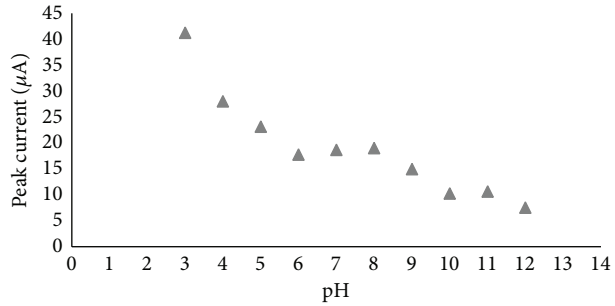


Figure 8: Effect of solution pH on the electrocatalytic activity of a SWCNT/Ni-modified GCE. Scan rate: 100 mV s^{-1}. pH: 3–12.

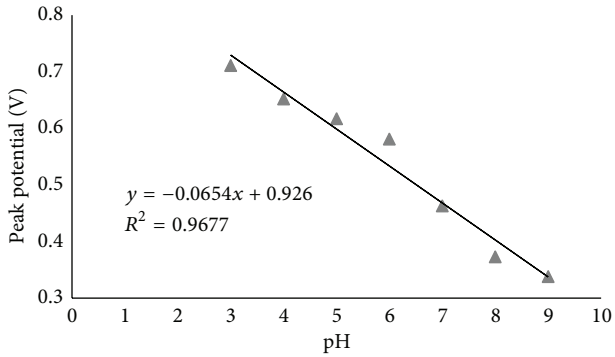


Figure 9: A plot of anodic peak potential for the electrochemical reaction of 0.1 mM paracetamol in various pH of 0.1 M KH_2PO_4 electrolyte solution at a SWCNT/Ni/GCE. Scan rate: 100 mV s^{-1}. pH: 3–9.

the plot, the peak current of paracetamol increased when pH was reduced from 5 to 3. The maximum current response was observed at pH 3. The anodic peak current increased slightly by increasing the pH from 6 to 8. Higher than pH 9, the peak current response decreased significantly, which was probably due to the deprotonation in the oxidation process that favors a higher pH. Acidic electrolytic solution promotes electron transfer and hence the oxidation of paracetamol. When pH increases, deprotonation occurs. At higher pH, the anodic peak current diminishes. The results indicate that the redox response of paracetamol is pH dependent at the SWCNT/Ni-modified GCE.

It was also found that the peak potential for paracetamol varies with pH, reducing with the increase of pH (Figure 9). This suggests that protons are involved in the electrode process. In a Nernstian reaction, E_{pa} is described as a function of solution pH where the slope is equal to $0.0592(m/n)$ V per unit pH. m and n are the number of protons and electrons which are taking part in the electrode reaction, respectively. Based on the plot, the relationship between the peak potentials and pH is linear and is described as E_{pa} = 0.926–0.065 pH, with an R^2 of 0.968. The results suggest that, in the oxidation of one unit of paracetamol molecule, two electrons and two protons are produced.

Table 1: Repeatability study for the determination of paracetamol at SWCNT/Ni-modified electrodes.

Repetition	Peak current
	μA
1	26.15
2	29.96
3	28.43
4	27.73
5	29.85
Mean	28.42
RSD (%)	5.6

Table 2: Recovery study for the electrochemical process of commercial sample (Panadol). Five replicates of 1.0 mM paracetamol determination at SWCNT/Ni-modified electrodes.

Real life sample	Recovered concentration (mM)	Recovery rate (%)	Mean recovery (%)	RSD (%)
1	1.034	103.4		
2	0.973	97.3		
3	0.956	95.6	96.9	1.9
4	0.945	94.5		
5	0.937	93.7		

3.8. Repeatability. To evaluate the repeatability of the proposed method, the SWCNT/Ni-modified electrode was subjected to a reproducibility study in which five measurements were obtained for every freshly prepared modified electrode. Table 1 shows the anodic peak current at the SWCNT/Ni/GCE for the determination of paracetamol in 0.1 M KH_2PO_4 electrolyte solution. The determination of paracetamol was performed at a newly constructed modified electrode on different days. The relative standard deviation (RSD) of the five measurements was calculated to be 5.6%, which demonstrates the repeatability of the method. The data indicate that the SWCNT/Ni/GCE adopted in the determination of paracetamol and the fabrication technique will produce highly reproducible results. Similar results have been previously reported by using graphene-modified GCEs [40].

3.9. Recovery. In order to evaluate the practical utility and validity of the SWCNT/Ni-modified electrode, the modified electrode was examined with commercial paracetamol pills using cyclic voltammetry. Table 2 shows the results obtained from the SWCNT/Ni-modified electrode for 1.0 mM paracetamol in Panadol pills (GSK). Five replicate measurements for the determination of paracetamol with a fresh electrode surface at every measurement produced a mean recovery of 96.9 ± 1.9%. From the results obtained, it can be seen that the SWCNT/Ni/GCE demonstrated good electrocatalytic activity. Good recovery indicates the suitability and reliability of the proposed method. Therefore, the SWCNT/Ni-modified electrode is reliable and thus is recommended for routine analyses.

Table 3: The elemental profile of the SWCNT/Ni nanofilm deposited on the BPPGE surface (a) before and (b) after the electroanalysis in 0.1 M KH_2PO_4 electrolyte containing 0.1 mM paracetamol. Scan rate: 100 mV s^{-1}.

(a)

Spectrum	In stats.	C	Ni	Total
Spectrum 1	Yes	67.71	32.29	100.00
Spectrum 2	Yes	94.94	5.06	100.00
Spectrum 3	Yes	93.26	6.74	100.00
Spectrum 4	Yes	94.93	5.07	100.00
Mean		87.71	12.29	100.00
Std. deviation		13.36	13.36	
Max.		94.94	32.29	
Min.		67.71	5.06	

(b)

Spectrum	In stats.	C	O	P	K	Ni	Total
Spectrum 1	Yes	20.88	13.54		0.70	64.88	100.00
Spectrum 2	Yes	68.12	21.52	1.50	1.92	6.95	100.00
Spectrum 3	Yes	78.55	5.08		0.32	16.06	100.00
Spectrum 4	Yes	68.89	20.00	1.57	2.11	7.43	100.00
Max.		78.55	21.52	1.57	2.11	64.88	
Min.		20.88	5.08	1.50	0.32	6.95	

3.10. Elemental Study. The attachment of SWCNT/Ni nanocomposite to the BPPGE surface and the elemental compositions of the nanofilm can be confirmed by using EDX. Table 3 presents the EDX data of the SWCNT/Ni nanofilm embedded on the BPPGE surface before and after the electrochemical cycles. As can be seen in the table, the EDX profiles show the presence of carbon and nickel prior to the electroanalysis. After the electroanalysis, the potassium, oxygen, and phosphorus spectra were found, which infer that the electrolyte component was incorporated into the nanostructure during the redox. The results suggest that the nanofilm underwent elemental modification.

4. Conclusions

A simple three-electrode system was employed for paracetamol determination. GCEs mechanically attached with SWCNT/Ni nanocomposite were prepared and used in the determination of paracetamol in 0.1 M KH_2PO_4 supporting electrolyte. The characterization studies indicate that the anodic peak current is affected by scan rate, paracetamol concentration, pH, and temperature. The GCE modified with SWCNT/Ni nanocomposite provided good current response in low pH. The modified electrode holds a promising prospect for the determination of paracetamol, with good repeatability and recovery. The SWCNT/Ni-modified GCE exhibited relatively stable and sensitive electrochemical behavior. Electrode preparation is quick and simple. Only small amounts of nanomaterials were used, minimizing wastage. Therefore, a chemically modified electrode fabricated with SWCNT/Ni nanocomposite via mechanical attachment technique can be used for the determination of paracetamol when coupled with cyclic voltammetric analysis.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

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