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Highly Selective, Sensitive and Fast Determination of Folic Acid in Food Samples Using New Electrodeposited Gold Nanoparticles by Differential Pulse Voltammetry

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A novel method was initially developed for the activation of a gold electrode modified with gold nanoparticles by applying a high potential in the presence of sodium hydroxide. In a second stage, the selective oxidation of folic acid was investigated on the gold electrode described above. The effects of chemical and instrumental parameters such as NaOH concentration, scan rate, activation potential, and the duration of high potential application were investigated and the parameters were optimized. The results showed that 1.0 mol L^{-1} NaOH solution at a scan rate of 100 mV s^{-1} and with an applied potential of 4.50 V for 60 s produced the best results. The optimized sensor was then used to measure folic acid by differential pulse voltammetry. A good linear correlation was found between the peak current of folic acid and its concentration in the range of 1.0×10^{-8} to 1.0×10^{-6} mol L^{-1} with a detection limit of 7.50×10^{-9} mol L^{-1}. The effects of potential interfering compounds on the determination of folic acid were studied. The proposed method is highly selective and sensitive to folic acid. Finally, the new sensor was used to measure folic acid in real samples such as folic acid tablets, wheat flour, fortified wheat flour, and spinach.

Keywords: Gold nanoparticles; Electrodeposition; Folic acid determination; Voltammetry.

1. INTRODUCTION

Folate includes folic acid and derivatives that occur in nature and that are required in the single-carbon metabolism such as amino acid [1] and nucleic acid biosynthesis [2] as well as in cell division and growth. This vitamin is essential for rapid cell growth like blood production, especially during pregnancy [1]. Folic acid is commonly measured using such methods as HPLC–MS,

spectroscopy, ELISA and microbial methods. However, most of these methods are cost-intensive and time-consuming [3] due to their long extraction and purification process times [4]. These shortcomings warrant the development of a new, rapid, sensitive and selective method for folic acid determination.

Electrochemical sensors have found wide applications in critical care, safety issues, and industrial hygiene as well as in process and quality control. The principle of electrochemical sensors is based on the fact the current generated by the oxidation or reduction of an electroactive analyte on the working electrode surface is measured by the electrochemical detector within a specified fixed or varying potential [5]. The instruments used for electrochemical detection are simple to construct, cheap, and miniturizable [6].

The combination of nanoparticles and electrochemistry lead to more reliable and powerful methods. Nanotechnology has recently become one of the most exciting ongoing fields in sensor fabrication [7]. Many types of nanomaterials of different sizes, shapes, compositions, and properties have been made available and their use in sensors has led to a variety of new signal transduction technologies [8].

Nanoparticles of noble metals, especially gold nanoparticles, have attractive electronic, optical, thermal, and catalytic properties; hence, their potential applications in physics, chemistry, biology, medicine, materials science, and interdisciplinary fields [9]. Two important factors that influence the catalytic behavior of gold nanoparticles are their size and crystallographic orientations that are influenced by the method and conditions of their synthesis and deposition [10]. Gold nanoparticle–modified electrodes can be prepared using such different methods as gold colloid deposition and electrodeposition. The two commonly used techniques for gold colloid deposition are electrostatic and covalent bonding. Electrostatic interactions occur between the colloidal gold nanoparticles, which are stabilized with citrate before being negatively charged, and the electrode surface. Covalent bonds are created between gold and surface functional groups (–SH, $–NH_2$, –CN); this method is called 'self–assembling monolayer' (SAM). Sometimes SAMs are more disordered and less crystalline than those formed on smooth surfaces. This is because the presence of more defects in the structure of SAM, redox processes is blocked [11]. Electrodeposition of gold may be affected by the different conditions created due to the medium, pH level, gold solution concentration, and the particular technique used). Amongst the different preparation methods, electrochemical deposition is a fast, easy, and convenient method for the preparation of gold nanoparticles [10].

The bulk gold electrode is known to be inactive or poorly active towards many electrochemical reactions. Recently, surface–modified Au–electrodes have been suggested for many electrocatalytic and electroanalytical applications because of their higher activity compared to the bulk Au electrode. Therefore, electrodeposition of a highly dispersed Au–nanoparticle on an inert base is remarkable due to its extraordinarily high catalytic activity in many reactions [12].

Electrochemical methods have also been used to detect folic acid and to investigate its redox properties. The dropping mercury electrode [13], the hanging mercury electrode [14-19], the glassy carbon electrode modified with phosphomolybdic-polypyrrole film [20], the carbon paste electrode modified with *p*-tert-butyl-calix[6]arene (CME–6) [21], and the glassy carbon electrode coated with single-walled carbon nanotubes (SWNTs) paste [22] have so far been used for the electrochemical determination of folic acid. In addition Xiao et al. (2008) used 2-mercaptobenzothiazole self–

assembled gold electrode (MBT/SAM/Au) for the voltammetric FA determination with a detection limit of 4.0×10^{-9} mol L^{-1} [23]. In another research, the gold electrode modified with carbon nanotubes was used by Wei et al. (2006) to measure folic acid using cyclic voltammetry, chronoamperometry, and chronocoulometry with a detection limit of 1.0×10^{-8} mol L^{-1} [24]. These solid electrodes have shown good sensitivity to folic acid but are often associated with complicated construction and preparation, high costs (e.g., calix[n]arenes, and SWNTs), and relatively low surface stability and reproducibility.

The aim of the present study is to investigate the effect of electrodeposition of Au–nanoparticles on a polycrystalline Au–electrode signal in the NaOH solution and its application as a selective sensor for folic acid analysis. The Au–electrode with newly deposited Au–nanoparticles is used for folic acid determination using an electrochemical method. The present study introduces for first time a new method for gold nanoparticles activation that is not only simple, fast, and inexpensive but also enhances the sensitivity and the reproducibility of the sensor for folic acid detection.

2. EXPERIMENTAL

2.1. Chemicals

All solutions were prepared using reagent grade chemicals. Doubly distilled water was used throughout. Reagent grade folic acid, NaOH, and KNO_3 were purchased from Aldrich chemicals (Milwaukee, USA).

Stock solutions of folic acid (1.0 mmol L^{-1}) were prepared by dissolving accurately weighed amounts of folic acid in NaOH (0.10 mol L^{-1}). The solution was kept in the dark at 4 °C.

Folic acid working solutions for voltammetric investigations were prepared by dilution of the stock solution with NaOH (0.10 mol L^{-1}).

2.2. Apparatus

PalmSens (The Netherlands) electrochemical instrument was used for the electrochemical measurements. The three–electrode system composed of a gold electrode (with 3 mm in diameter) as the working electrode, an Ag/AgCl (3 mol L^{-1} KCl) as the reference electrode, and a platinum wire as an auxiliary electrode was used.

The morphology and size of gold nanoparticles were determined by SEM (Philips XL30, Netherlands) before and after activation.

2.3. Methods

2.3-1- Electrode cleaning

The gold electrode used was polished with 1.0, 0.3, and 0.05 mm alumina powder on a sandy paper for 3 min and washed ultrasonically in 50% ethanol/water solution. In a second step, it was

electrochemically cleaned in 0.5 mol L^{-1} H_2SO_4 solution by cyclic voltammetric scanning between 0.30 and 1.50 V until a standard cyclic voltammogram was obtained. Finally, the gold electrode was rinsed with doubly distilled water and absolute ethanol.

2.3.2. Gold nanoparticles electrodeposition

The clean gold electrode was put in a solution containing 6.0 mmol L^{-1} $HAuCl_4$ and 0.1 mol L^{-1} KNO_3 and the electrochemical potential was applied at −400 mV for 300 s. Then, the modified gold electrode was washed in deionized distilled water and absolute ethanol before drying [25].

2.3.3. Differential pulse voltammetry

The gold electrode modified with gold nanoparticles (Au/NPs) was immersed in 10 mL NaOH (1.0 mol L^{-1}) and the differential pulse voltammetry was conducted between –1.30 to +1.00 V vs. Ag/AgCl reference electrode (E_{pulse} and t_{pulse} were 0.025 V and 0.07 s, respectively).

2.3.4. Activation of the Au/NPs–modified gold electrode

The modified electrode was immersed in NaOH and the different potential (1.50 to 5.50 V) was applied in solution using a power supply. Differential pulse voltammetry was conducted between –1.30 to +1.00 V vs. Ag/AgCl reference electrode (E_{pulse} and t_{pulse} were 0.025 V and 0.07 s, respectively) on the Au/NPs modified gold electrode in 10 mL NaOH (1.0 mol L^{-1}). The voltammograms were compared before and after activation. The effects of NaOH concentration, scan rate, potential of activation, and activation duration on the modified gold electrode signal were optimized. During the optimization, the height of the current signal was monitored as a probe signal.

2.3.5. Scanning electron microscopy

The procedures of gold nanoparticles electrodeposition and activation were performed on a 1.0 × 1.0 cm^2 gold plate, and SEM scanned the surface of the modified gold plate before and after activation.

2.3.6. EIS analysis of the electrodes

Impedance measurements were obtained using a standard three–electrode electrochemical cell that included: a bare gold electrode, an Au/NPs electrodeposited gold electrode, and an activated modified gold electrode, all as working electrodes, as well as a platinum counter–electrode and an Ag/AgCl reference electrode in 0.1 mol L^{-1} KCl solution containing 5.0 mmol L^{-1} $[Fe(CN)_6]^{3-/4-}$. All impedance experiments were conducted with Autolab PGSTAT. Electrochemical impedance spectra

(EIS) were performed in 0.1 mol L^{-1} KCl solution containing 5.0 mmol L^{-1} $[Fe(CN)_6]^{3-/4-}$. The frequency ranged from 0.1 to 100 kHz at a formal potential of 0.18 V, and the amplitude of the alternate voltage was 5 mV [26].

2.3.7. Folic acid determination

A new Au/NPs–modified gold electrode was dipped in 10 mL of 1.0 mol L^{-1} NaOH containing different concentrations of folic acid. Then, differential pulse voltammograms were recorded in the potential range of 0 to +1.00 V *vs.* Ag/AgCl reference electrode at a scan rate of 100 mV s^{-1}. Folic acid interacted with the gold and decreased the oxidation signal of the Au/NPs–modified gold electrode.

2.3.8. Real sample preparation

One tablet (1.0 mg) of folic acid was ground and dissolved in 0.10 mol L^{-1} NaOH in a 100–mL standard flask. The mixture was filtered after stirring for 15 min. A suitable aliquot of the clear filtrate was diluted with 0.1 mol L^{-1} NaOH to prepare appropriate sample solution [27]. Wheat flour or fortified (fortified with 1.5 ppm folic acid) wheat flour extract was prepared by dispersing in an appropriate amount of 0.10 mol L^{-1} NaOH solution and stirred. The solution was then centrifuged at 12000 rpm for 10 min before the mixture was filtered using a 0.45 μm micropore membrane [23]. Finally, 100 g of chopped dry spinach (dried at room temperature) was mixed with 0.10 mol L^{-1} NaOH, homogenized for 10 min, and centrifuged at 12000 rpm for 10 min. The supernatant was filtered using a 0.45 μm micropore membrane.

3. RESULTS AND DISCUSSION

3.1. Au/NPs electrodeposition and activation

As shown in Fig. 1, the peak potential of gold oxidation in NaOH solution was about 0.80 V that negatively shifted after Au/NPs deposition at about 0.30 V. The shifts of the oxidation potentials of nanoparticles localized on a solid electrode could occurred in two opposite directions: when the substrate is inert to the nanoparticles, the potential shifts negatively, and when metal nanoparticles interact with the substrate, it shifts positively. On the other hand, the magnitude of the electrooxidation potential shift of nanoparticles depends on the magnitude of the surface Gibbs free energy of nanoparticles itself and Gibbs free energy of interaction of metal–substrate interaction. The latter is influenced by the likely formation of alloys and/or intermetallic compounds in the metal-substrate system, meaning the difference in work functions ($\Delta\Phi$) between metal nanoparticles and the substrate [28]. Thus, if $\Delta G° > 0$, the metal does not interact with the substrate material, and the maximum current potential of nanoparticles oxidation is reduced compared to the corresponding value for bulk metal. The magnitude of the negative potential shift is affected by particle size. These data are consistent with the reported elsewhere [29].

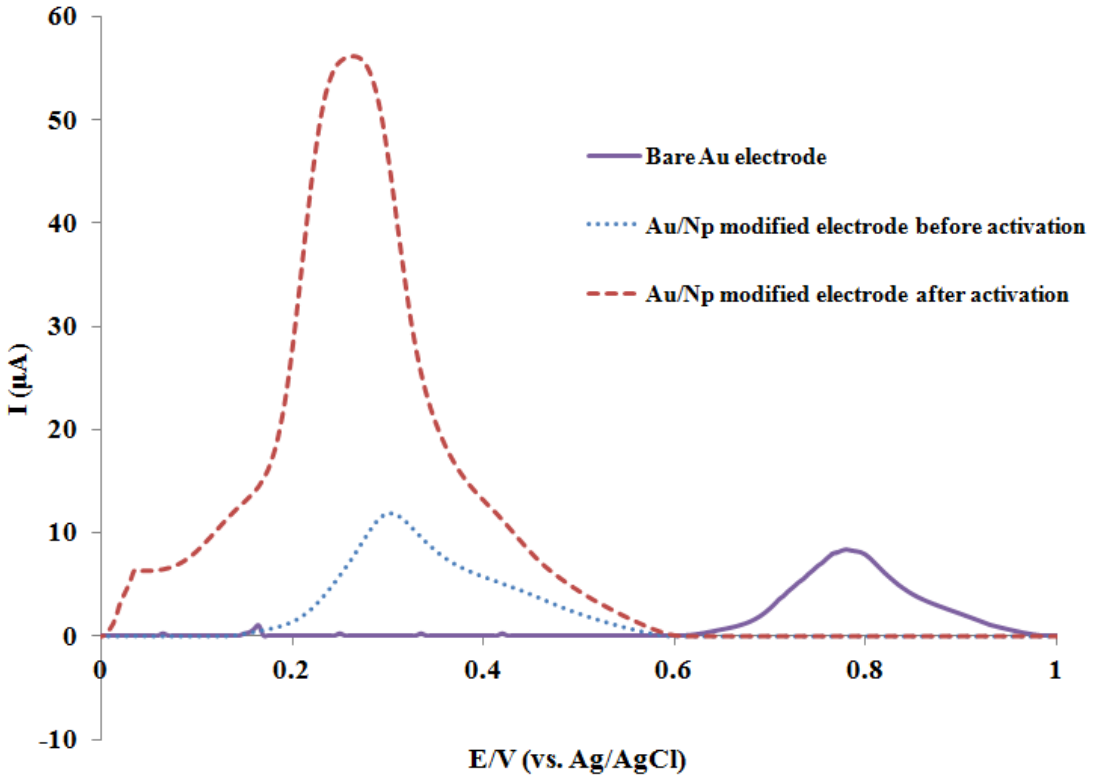

Figure 1. Effect of modification of gold electrode with gold nanoparticle and performing activation potential.

After activation of the modified gold electrode at a high potential of about 4.0 V (that is the optimized value here), the electrooxidation signal of the electrode intensely increased. This considerable increase could be due to such different causes as reduced size, increased porosity, or new material formation. To obtain further evidence, SEMs of the Au/NPs were taken before and after activation for evaluation (Fig. 2). Fig. 2 depicts the gold electrode modified with gold nanoparticles before and after activation at a high potential. It has been shown that the Au/NPs are agglomerated after deposition. On the other hand, the size of Au/NPs reduced and made a more uniform structure when a high potential was applied. As mentioned above, this reduced size could be the cause of the enhanced oxidation signal.

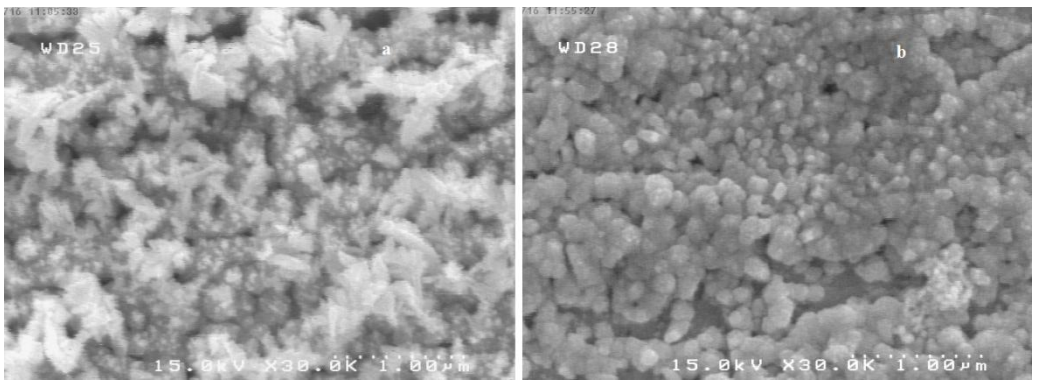

Figure 2. SEM micrograph of electrodeposited gold nanoparticle before and after activation.

3.2. EIS analysis of electrodes

Electrochemical impedance spectroscopy (EIS) is a powerful technique for convenient determination of both kinetic and mass-transport parameters as well as the charge transfer coefficient using minor electrochemical perturbation. The impedance spectra include a semicircle portion and a linear portion. The semicircle portion at higher frequencies corresponds to the electron transfer limited process and the electron transfer resistance (R_{et}) equals the semicircle diameters. The linear portion at lower frequencies shows a controlled diffusion process. Fig. 3 shows the EIS of the bare, the modified, and the activated gold electrodes. The diameter of semicircle was decreased after gold nanoparticle activation, that due to decrease in electron transfer resistance after the gold nanoparticle size reduction.

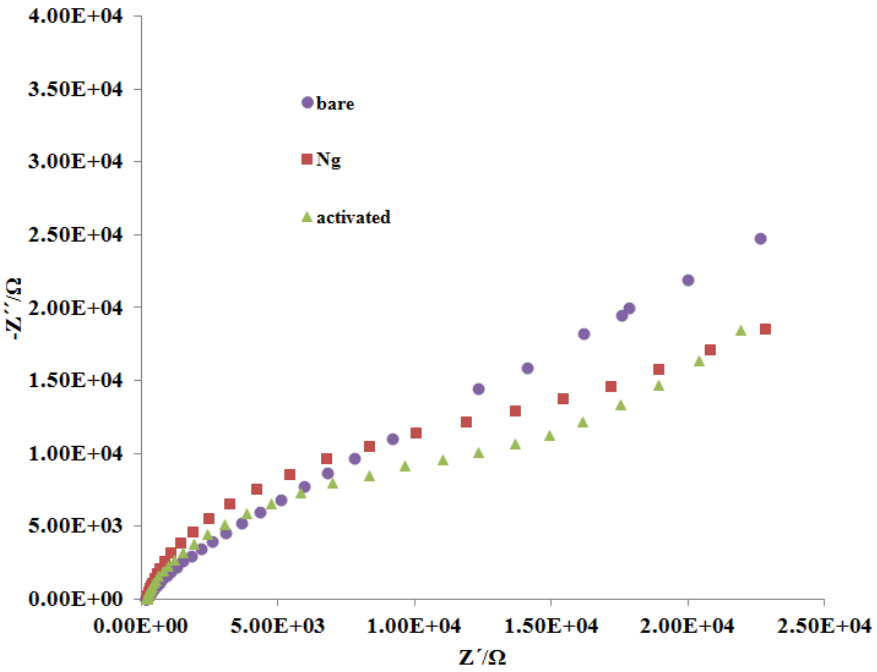

Figure 3. Nyquist plots obtained with the bare (●), the modified (■) and the activated (▲) gold electrode.

3.3. Optimization of variables

The influence of NaOH concentration on the oxidation signal of the Au/NPs–modified gold electrode was studied in the range of 0.1 to 2.0 mol L^{-1} (Fig. 4). The results showed that the oxidation peak of folic acid increased with increasing NaOH concentration up to 1.0 mol L^{-1}, beyond which it would start to decline. This could be due to the reduced soluble oxygen concentration in the electrolyte that is essential for the oxidation of surfaces, thus decreasing the rate of oxygen transfer to the electrode surface. In addition, in alkaline solution, folic acid was converted to folate with negative charge. Therefore, it is better statistically adsorbed at the surface of the electrode at positive potential. Therefore, 1.0 mol L^{-1} NaOH solution was used to activate the Au/NPs–modified gold electrode.

The effect of scan rate on the oxidation peak current at the Au/NPs–modified gold electrode was investigated in the range of 10 – 150 mV s^{-1} by differential pulse voltammetry (Fig. 5). It was found that the oxidation peak current was directly and linearly dependent on the scan rate from 10 to 100 mV s^{-1}. This confirms that the system is adsorptive-controlled current.

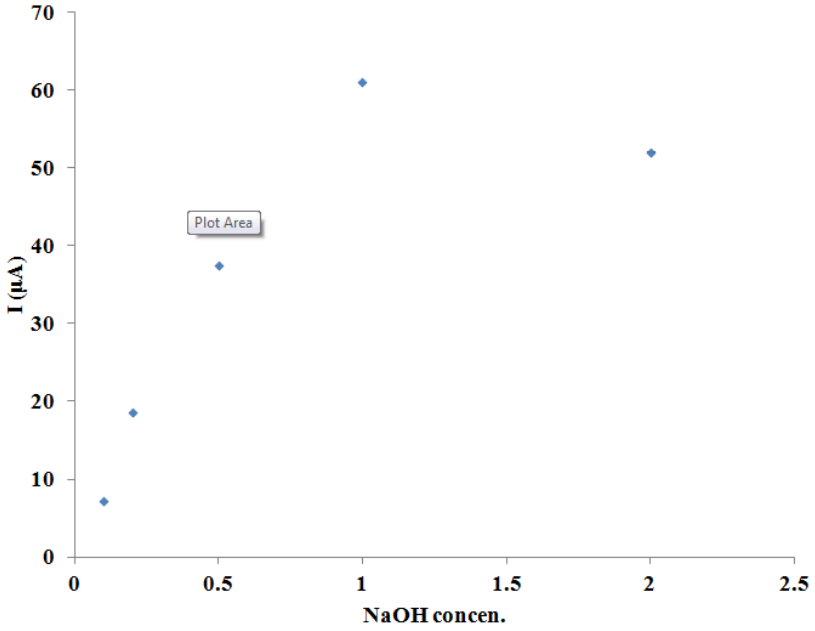

Figure 4. Optimization effect of NaOH concentration on current signal of modified gold electrode in NaOH solution.

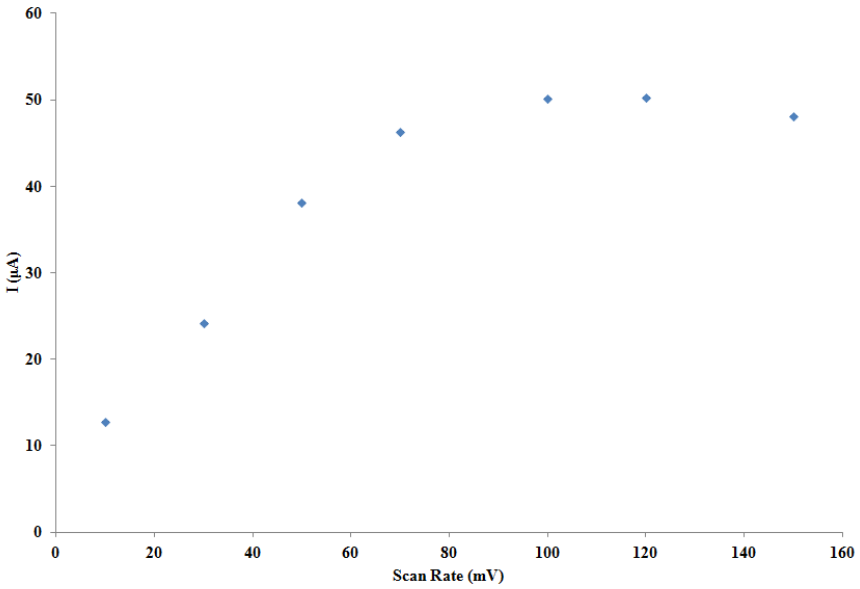

Figure 5. Effect of scan rate on current signal of modified gold electrode in NaOH solution.

The electrical double layer is the array of charged particles and/or oriented dipoles existing at every material interface. The inner layer, known as the inner Helmholz plane (IHP), contains solvent

molecules and specifically adsorbed ions. The outer Helmholz plane (OHP), shows the imaginary plane passing through the center of solvated ions at their closest approach to the surface. The solvated ions are nonspecifically adsorbed and are attracted to the surface by long-range coulombic forces. Both Helmholz layers create the compact layer that its charge is strongly held by the electrode and can survive even when the electrode is pulled out of the solution. The electrical double layer resembles a (parallel-plate) capacitor.

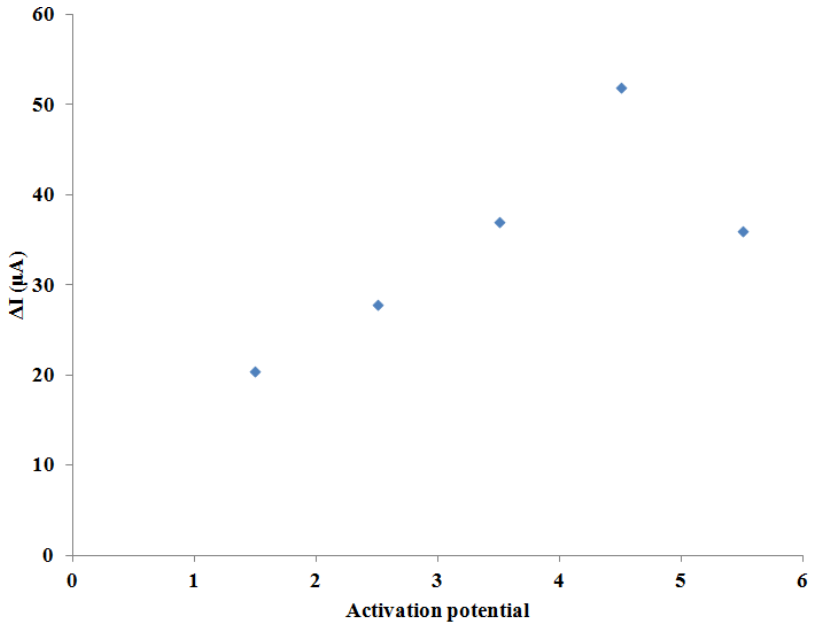

Figure 6. Effect of activation potential on current signal of modified gold electrode in NaOH solution.

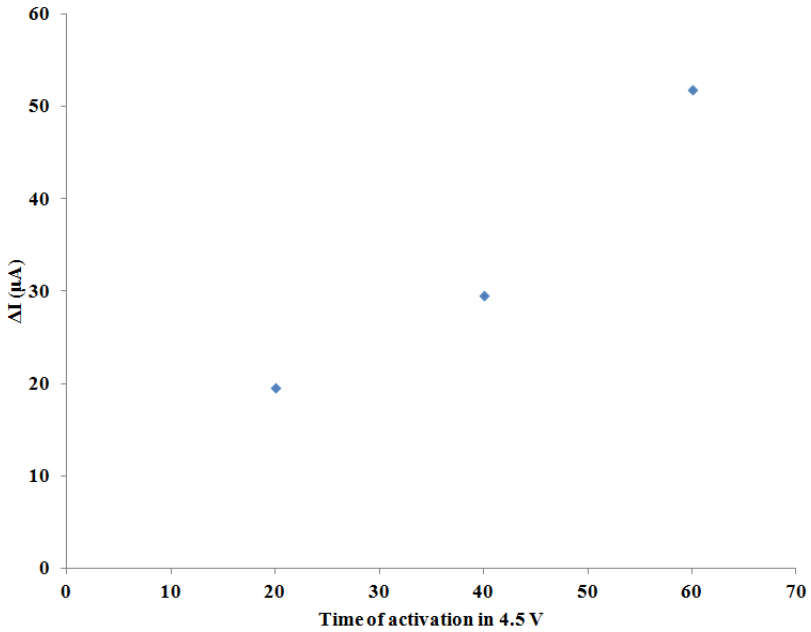

Figure 7. Effect of the time of activation potential on current signal of modified gold electrode in NaOH.

The experimental work showed dependence of the double-layer capacitance on the applied potential and electrolyte concentration. The capacitance was increased with decreasing in electrolyte concentration. In addition increasing in scan rate could cause to increase in rate of transfer of ion and material to double layer capacitor, that could decreased the oxidation current, after scan rate of 100 mV s^{-1} [30].Another factor that had to be optimized was the potential of Au–electrode activation. The activation potential was enhanced when it increased from 1.50 V to 4.50 V (Fig. 6). This is due to the increasing oxidation signal peak of folic acid as affected by the reduced size of the nanoparticles; using potentials greater than 4.50 V. However, it caused the oxidation peak of the Au/Np modified gold electrode in NaOH to decrease, which could be due to surface damages.

Duration of high potential application for activation is another important factor that needed to be optimized (Fig. 7). Our study showed that enhancement in the duration up to 60 s induced increments in the oxidation current, but longer durations caused damages to the surface that could be seen as a deep hollow area in the signal.

3.4. Interaction of folic acid with the Au/NPs–modified gold electrode

As presented in Fig. 8, adsorption of folic acid onto the surface of the activated electrode caused the peak current of the Au/NPs–modified gold electrode to reduce. Increasing folic acid concentration induced further reduction in the peak current. This phenomenon was due to the presence of amine (–NH) group on one ring in the folic acid structure that could be adsorbed onto the gold surface [31]. These findings indicate that the Au/NPs–modified gold electrode is a suitable probe for the detection of folic acid at trace levels.

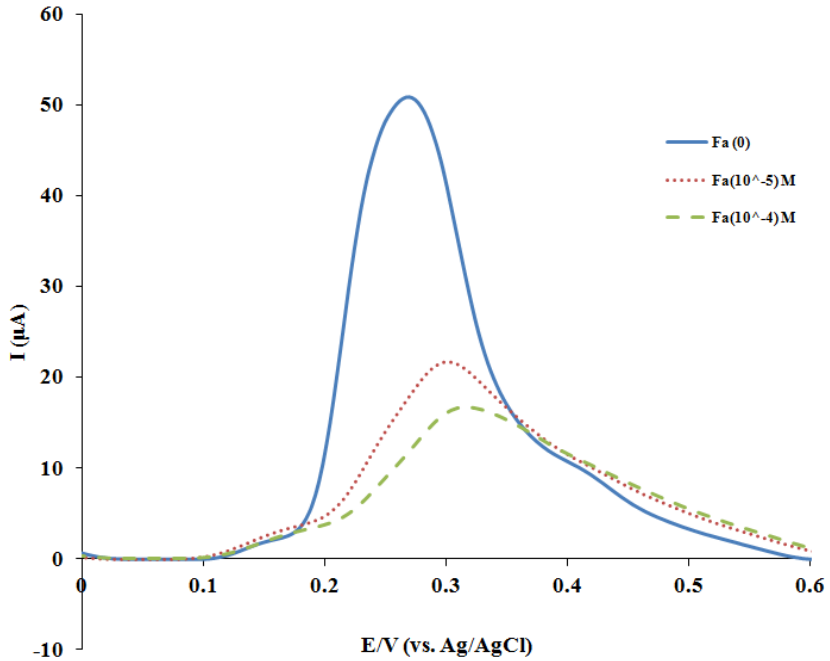

Figure 8. Effect of folic acid addition on the current signal of activated modified gold electrode.

4. CALIBRATION CURVE

The dependence of the peak current of the Au/NPs–modified gold electrode on folic acid was evaluated under optimized conditions. The calibration curve for the determination of folic acid was drawn using differential pulse voltammetry. The differential pulse voltammograms of various concentrations of folic acid are illustrated in Fig. 9. The oxidation peak current was linear over the range from 1.0×10^{-8} to 1.0×10^{-6} mol L^{-1} with a regression equation of Ip (μA) = $4.0 \times 10^{6} C_{FA}$ + 2.81 (R^2 = 0.9861, n = 5) where C_{FA} is the folic acid concentration in μmol L^{-1}.

The detection limit for the determination of folic acid at this modified electrode was 7.5×10^{-9} mol L^{-1}. Ten replicate experiments were carried out with 1.0×10^{-6} mol L^{-1} folic acid solution. The relative standard deviation was 3.2%. The results indicated that the modified gold electrode exhibits excellent reproducibility.

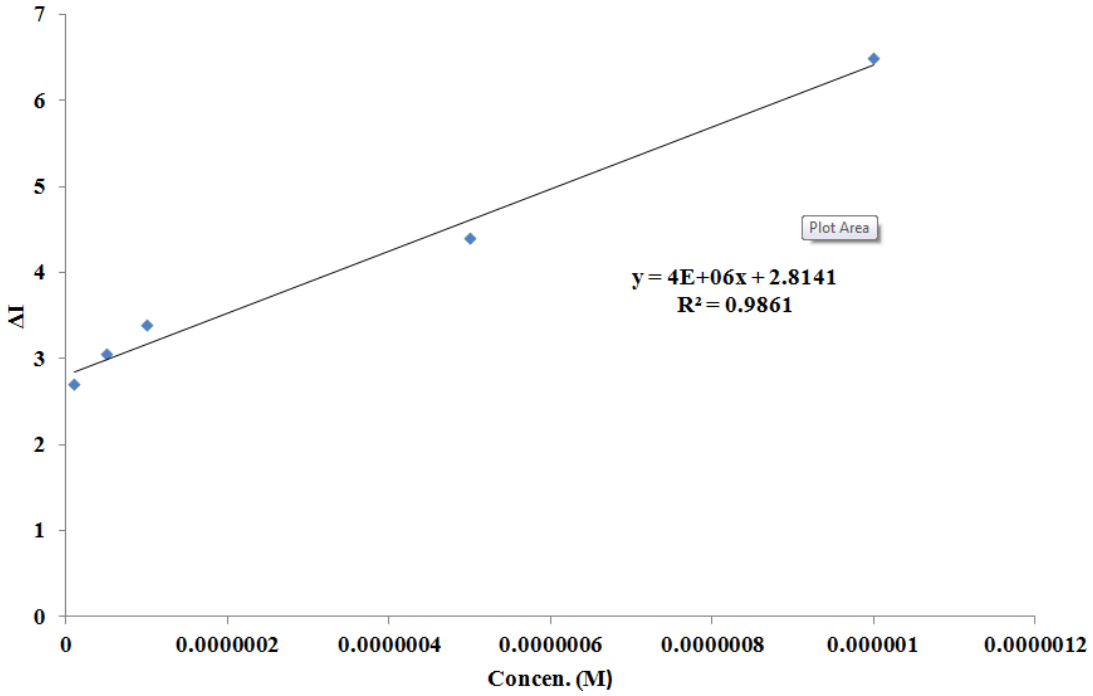

Figure 9. The relationship between peak current and concentration of FA on activated modified gold electrode in NaOH solution.

5. INTERFERENCE STUDY

To evaluate the effect of potential interfering compounds on the determination of folic acid at 1.0×10^{-6} mol L^{-1} level, experiments were conducted with different concentrations of the potential interfering materials. It was found that 500–fold of vitamins B_1, B_2 and B_6 and 1000–fold of vitamin C, histidine, tryptophan, and cystein concentrations did not interfere significantly with the current response, which indicates that the modified gold electrode has a good selectivity for the determination of folic acid.

6. REAL SAMPLE ANALYSIS

Table 1. Determination of folic acid in real sample with standard addition method (n=3)

Sample	Number	Added (µmol)	Found (µmol)	Recovery%
Tablet	1	0	0.23±0.005	–
	2	0.6	0.85±0.010	102.40
	3	1	1.28±0.011	104.06
Wheat flour	1	0	0.05±0.010	–
	2	0.6	0.63±0.005	96.92
	3	1	1.06±0.005	100.95
Fortified wheat flour	1	0	0.38±0.010	–
	2	0.6	0.95±0.015	96.93
	3	1	1.35±0.011	97.82
Spinach	1	0	0.27±0.005	–
	2	0.6	0.85±0.010	97.70
	3	1	1.25±0.005	98.42

Folic acid tablet, wheat flour, fortified wheat flour, and spinach were selected for real sample analyses using the standard addition method. Folic acid quantities in these samples were determined after alkali extraction (Table 1). The results show that this nanosensor is suitable for folic acid determination.

7. CONCLUSION

In the present work, a new simple and reproducible method was developed for the preparation of Au–nanoparticles. The results showed that in the new procedure, the size of Au/NPs reduced to make them more uniform. The nanoparticles thus obtained were then used for folic acid determination based on the reduced Au/NPs–modified gold electrode oxidation current signal. Au/NPs were deposited on a gold electrode using a simple and fast electrochemical method and a high potential was applied to create a high increment in the oxidation current signal of the Au/Np modified gold electrode in NaOH. The reduced oxidation signal of the Au/NPs after folic acid addition was found to be due to the absorption of folic acid onto the gold preventing or reducing gold oxidation, which made the electrode highly reproducible.

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