

Full Paper

Synthesis and Application of Polyaniline/Multi Walled Carbon Nanotube Nanocomposite for Electrochemical Determination of Folic acid

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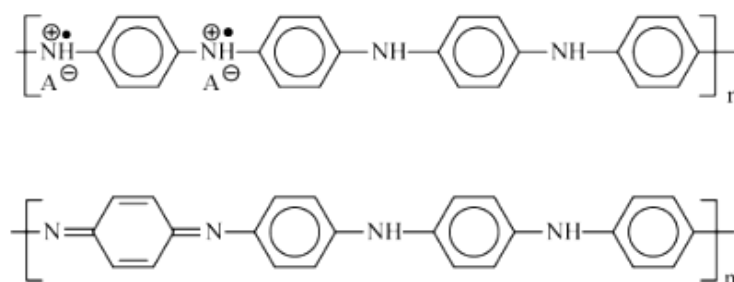
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Abstract- A composite of polyaniline with multi-wall-carbon nanotubes (PANi/MWCNTs) was synthesized by an *in situ* chemical oxidative polymerization method. The PANi were synthesized chemically using aniline as the monomer and ammonium peroxydisulfate as the oxidant. The PANi/MWCNTs were characterized physically using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). With this nano composite as the modifier, a voltammetric sensor for folic acid (FA) was constructed on a glassy carbon electrode (GCE). Folic acid undergoes a $2e^-/2H^+$ transfer electrochemical reduction process at 0.7 V with respect to Ag/AgCl reference electrode in pH 7. PANi/MWCNTs modified electrode showed good cyclic voltammetric (CV) response in wide linear range from 10^{-6} M to 10^{-4} M. This modified showed excellent sensitivity and stability for determination of folic acid. The response mechanism of folic acid at PANi-MWCNTs/GCE was discussed in detail.

Keywords- Nanocomposite, Polyaniline, Multi-Walled Carbon Nano Tubes, Electrochemical Behavior, Folic Acid

1. INTRODUCTION

Electroactive polymers have been an area of immense interest over the past 30 years since the first discovery of conducting poly acetylene in 1977 by Shirakawa et al [1]. Extensive research on several conjugated polymers including poly (*p*-phenylene), polyaniline (PANI), polypyrrole, polythiophene, polyindole, polycarbazole, polyfluorene, poly (*p*-phenylene vinylene), and their substituted derivatives have led to their applications in rechargeable batteries, microelectronics, sensors, electrochromic displays, and light-emitting and photovoltaic devices [2,3]. Among the various conjugated polymers, PANI (Scheme 1) has received special recognition owing to its good stability and interesting redox behavior. [4-9]. In the past few years, several novel methodologies have been developed for the preparation of nanostructured PANI in the form of dispersions, nanowires, nanofibers, and nanotubules [10-16].

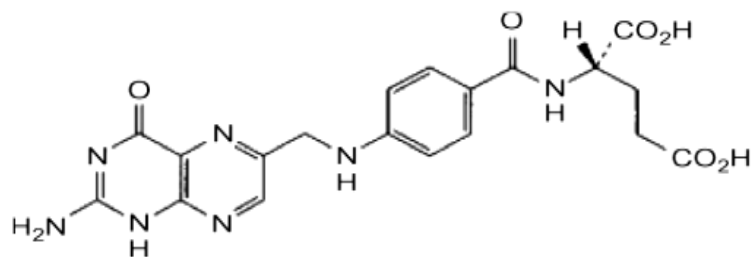


Scheme 1. ES forms of PANI

The discovery of fullerenes [17] and carbon nano tubes (CNTs) [18] has led to an explosion of research in nanoscience and nanotechnology. In fact, the focus in nanoscience has since shifted from synthesis to applications. A logical extension is to find new combinations of the existing materials as hybrid materials, blends, and nano composites for exploitation of their complementary properties. [19-22]. In this context, there has been a new surge of interest in developing conducting polymer–CNT composites as novel futuristic materials. One main reason for this is that common applications of the two components offer the possibility to observe synergetic effects. Already, various studies have proved that certain discrete properties of the components of conjugated polymer–CNT composites are enhanced, thus validating their high suitability for some technological applications. [23,24].

Folic acid, N-[*p*-{(2-amino-4-hydroxy-6-pteridiny) methyl} amino} benzoyl]-l-glutamic acid (as shown below), is chosen as the analyte for this investigation because it is an electroactive component of considerable biological importance [25]. It has long been recognized as part of the Vitamin B complex found in some enriched foods and vitamin pills. It is usually employed in the treatment or prevention of megaloblastic anaemia during

pregnancy, childhood and other clinical situations often associated with alcoholism and liver diseases. [26]. A lack of folic acid gives rise to gigantocytic anaemia, associated with leukopaenia, devolution of mentality, psychosis, etc. Simple and sensitive methods are required for its determination in pharmaceutical, clinical and food samples. Published methods for the determination of folic acid include high-performance liquid chromatography (HPLC) [27-31], spectrophotometry [31-33], flow injection chemiluminescence [34] and Fluorimetric method [35].



Folic acid

Scheme 2. Folic acid structure

Various electrochemical methods have been employed for the study of direct electrochemistry of FA and its determination [36-38]. Cakir et al. [39] studied the simultaneous determination of FA and riboflavin in pharmaceutical samples by square wave voltammetry (SWV). Kalimuthu et al. [40] used ultrathin electropolymerized film of 5-amino-2-mercapto-1, 3, 4-thiadiazole modified glassy carbon electrode for the selective determination of FA in common physiological interferents by differential pulse voltammetry (DPV) and amperometry. Methods like SWV, DPV [41,42] chronoamperometry [43,44] and differential pulse cathodic stripping voltammetry [45] were used for the FA determination studies. FA has been simultaneously determined along with norepinephrine [46], uric acid [47] and ascorbic acid [48] by DPV at modified carbon nano tube paste electrodes [49].

This work focuses mainly on the preparation, characterization, and applications of PANI-CNT nano composites. The possible interactions between PANI and CNT that may be responsible for enhancement in certain properties of the composites are highlighted. Wherever applicable, the literature on CNT composite materials with substituted derivatives of PANI is also included. A novel, simple, rapid and sensitive cyclic voltammetric method for determination of folic acid is proposed.

The PANi-MWCNT nano composite modified GCE exhibits excellent CV to FA at negative over potential with good sensitivity and linear range.

2. EXPERIMENTAL

2.1. Reagents and solutions

All reagents were of analytical reagent grade and were used as received. Aniline (99%), Ammonium peroxydisulfate (98%), hydrochloric acid (37%), ethanol (99.9%), carbon nano tube, tetrahydrofuran (THF), Folic acid (96-102%) and phosphate buffer solution (PBS) were Merck. Just before synthesis nano composite, aniline was distilled. Aniline was stored in refrigerator. Doubly distilled water obtained from a Millipore Milli-Q water purification system was used throughout the experiments.

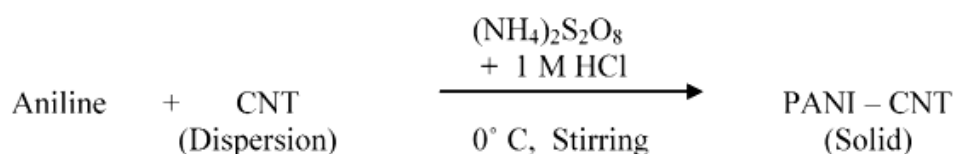
A 1×10^{-3} M folic acid standard solution was prepared by dissolving 22 mg folic acid in 10 mL of 0.1 M NaOH and completing the volume to 50 mL with doubly distilled water. This solution was kept in a refrigerator and protected from light. Working standards were daily prepared by diluting the stock solution with doubly distilled water. Inert atmosphere was set by passing N_2 over the solution during experiments. All the experiments were conducted at ambient temperature (25 ± 2 °C).

2.2. Instrumentation

Electrochemical measurements were performed with an Autolab potentiostat/galvanostat model PGSTAT 30 (Metrohm, Utrecht, Netherlands) and a system was run on a pc using GPES 4.9 software. A Glassy Carbon electrode was used as working electrode. A platinum wire was employed as counter electrode and a saturated Ag/AgCl (saturated KCl) served as the reference electrode and all potentials in the text refer to it (all electrodes obtained from Azar Electrode CO., Urmia, Iran). A model KQ 3200 ultrasonic cleaner (Kunshan Ultrasonic Industrial Factory) was used for cleaning the electrodes.

2.3. Synthesis of nano composite polyaniline-carbon nano tube

The nanocomposite of protonic acid doped polyaniline with functionalized MWCNT was synthesized using in situ chemical oxidation polymerization. This procedure entailed dissolving MWCNT and aniline monomer in 1 M HCl solution ultrasonicated to remove impurities like amorphous carbon and metal catalysts. The dark MWCNT/aniline suspension was in an ice bath and stirred. Ammonium peroxydisulfate (APS) dissolved in 1 M HCl was added to the solution, and stayed room temperature, and the resulting green suspension was then filtered and dried.



2.4. Preparation of modified electrode

To fabricate the PANI-MWCNT modified electrodes, the GCE was polished using 0.05 μm alumina slurry and Buehler polishing cloth. The GCE was washed and ultrasonicated in deionized water and ethanol for 5 min each to remove any adsorbed alumina particles on the electrode surface. 3 μl of PANI-MWCNT drop casted onto the well polished GCE surface and dried at 50 $^{\circ}\text{C}$.

3. RESULTS AND DISCUSSION

3.1. Surface morphological characterization of PANI-MWCNT nano composite using SEM

Scanning electron microscopy (SEM) is an excellent technique for investigating the morphology of PANI-MWCNT composites. In general, the SEM characterization of these composites reveals a uniform wrapping of MWCNT by PANI forming core-shell nanostructures [50-53]. The shell diameter depends on PANI content in the composites. Gupta and Miura have reported that beyond 73%wt of PANI, the wrapping gets terminated and the PANI is deposited independently around the surface of the composite [54]. Scanning tunneling microscopy (STM) [55], atomic force microscopy (AFM) [56-58], and transmission electron microscopy (TEM) techniques [59,60] have been used in morphological characterization, and the results of these studies also reveal a nice encapsulation of CNT by the polymer. (Fig. 1)

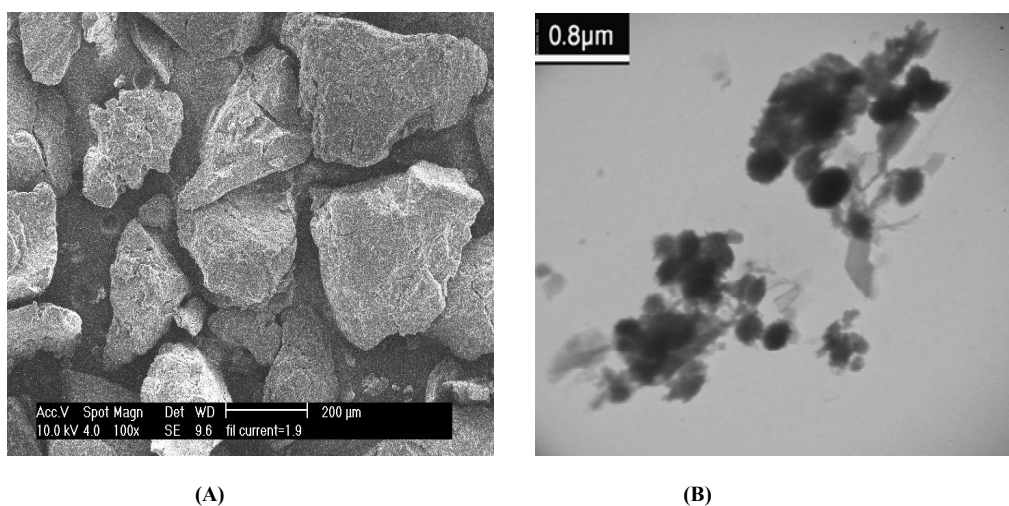


Fig. 1. (A) SEM image of PANI-MWCNT nano composite 0.25%w/w (B) TEM image of PANI-MWCNT nano composite 0.25%w/w

3.2. Electrochemical properties of the PANI-MWCNT nano composite modified GCE

The electrochemical properties of the PANI-MWCNT nano composite modified GC electrode with dipping technique were studied, using cyclic voltammetry. Fig. 2 shows typical cyclic voltammogram of the bare and PANI-MWCNT nano composite modified GC electrodes in 0.1 M KCl solutions in phosphate buffer electrolyte solution (pH=7) at scan rate 50 mV s^{-1} . It shows that the oxidation and reduction peak areas of PANI-MWCNT nano composite modified GC electrode are much larger than the bare glassy carbon electrode.

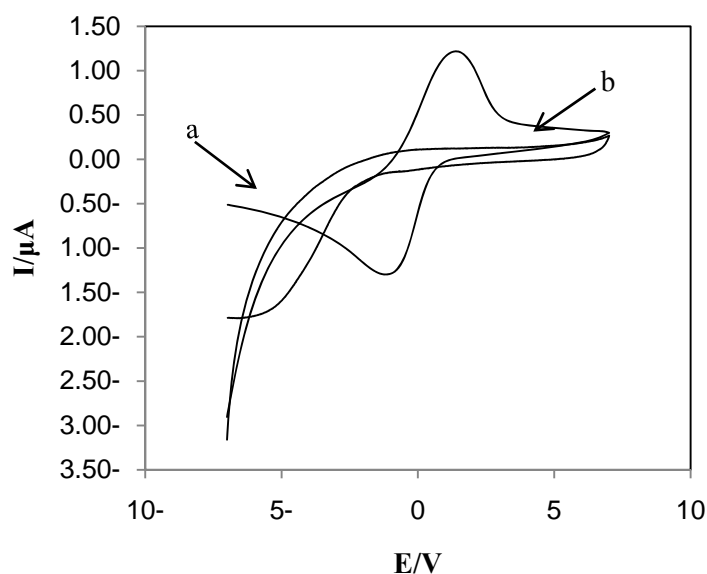


Fig. 2. Cyclic voltammograms of the (a) bare GC electrode and (b) PANI-MWCNT modified GC electrodes by dipping in 0.1 M KCl solutions in phosphate buffer electrolyte solution (pH=7) at scan rate 50 mV s^{-1}

3.3. Electrocatalytic reduction of folic acid at the PANI-MWCNT modified GC electrode

Fig. 3 shows the cyclic voltammogram of FA at two electrodes in 0.1 M PBS (pH=7). Cyclic voltammograms were recorded in the potential range of 0.8 to -0.8 V vs. Ag/AgCl reference electrode at a scan rate of 0.05 V s^{-1} . In prior to each experiment, purified N_2 was purged into PBS containing $100 \mu\text{M}$ for 10 min. FA shows a well-defined cathodic peak at PANI-MWCNTs 0.25%w/w GCE (b) at -0.1189 V. Wang, et al. [61] reported two couples of redox peaks and an irreversible reduction peak between 0.4 and -1.4 V for FA at SWCNT modified electrode in pH=5.5. Jiang et al. [62] observed a pair of oxidation and reduction peaks at MWCNT modified GCE with ΔE_p 0.061 V and with a peak current ratio of 1:1, in the potential range of -0.6 to -0.2 V in pH=6.4 PBS. Cakir et al. reported three cathodic peaks for FA at -0.4, -0.87 and -1.2 V in pH=5.89 at a static mercury drop electrode using SWV.

Their results also suggest that the peaks at -0.4 and -1.2 V are not good enough for analytical purpose but the peak at -0.87 is well developed and provide the basis for quantitative determination of FA [37]. Chen et al. [49] observed a single reduction peak at -0.7 V at MWCNT-PVS/GCE in the potential range of -0.2 to -1.2 V. However, we observed a single reduction peak at -0.14 V at PANI-MWCNTs/GCE in the potential range of 0.8 to -0.8V. This cathodic peak to the reduction of FA by $2e^-/2H^+$ reduction process in which FA is converted to 5,8-dihydro FA [39,63].

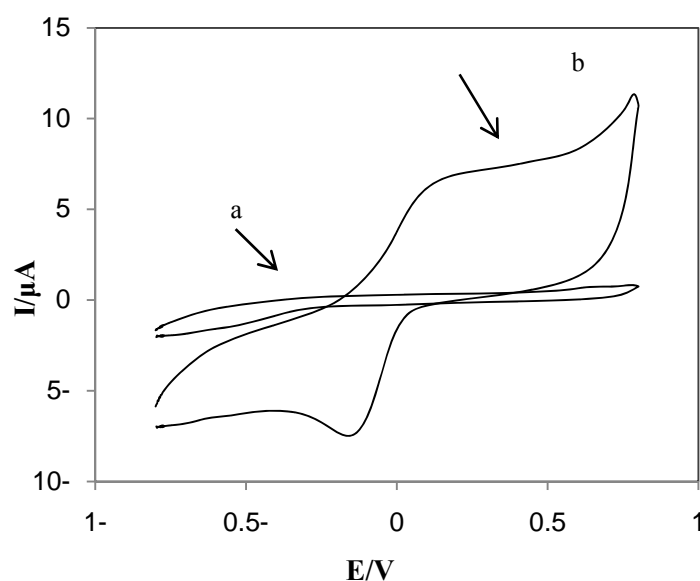


Fig. 3. Cyclic voltammograms of 100 μM Folic acid at (a) bare GC electrode and (b) PANI-MWCNT modified GC electrodes in phosphate buffer electrolyte solution (pH=7) at scan rate 50 mV s^{-1}

From Fig. 3 (a) bare GCE too shows a very less prominent reduction peak for at -0.65 V. On comparison with the bare GCE, a 510 mV shift in peak potential and the increase in peak current demonstrate the efficient electrocatalytic behavior of PANI-MWCNT composite towards the reduction of FA with good background current stability. Hence, the cathodic peak at -0.14 V is well developed and used for the quantitative and qualitative determination of FA.

The nature of the reduction process was found to be CE controlled in the buffer system studied, as evidenced from the linear plots of the peak current (i_p) vs. square root of the scan rate ($v^{1/2}$) for folic acid. Fig. 4A shows the cyclic voltammograms of PANI-MWCNT modified GC electrode in 0.1 M phosphate buffer (pH 7.0) containing 100 μM FA at scan rates: 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mV s^{-1}

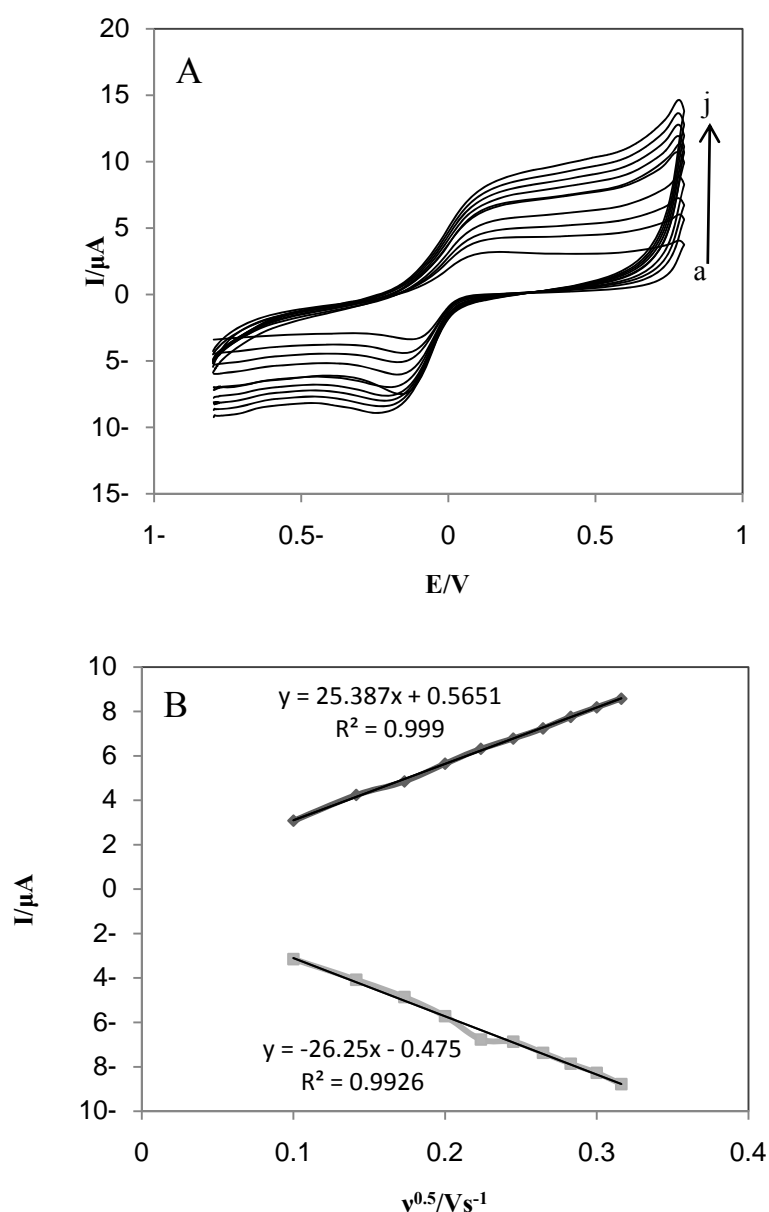


Fig. 4. (A) Cyclic voltammogram of PANI-MWCNTs GCE in phosphate buffer electrolyte solution (pH 7.0) containing 0.1 mM Folic acid at scan rates of (a) 10 (b) 20 (c) 30 (d) 40 (e) 50 (f) 60 (g) 70 (h) 80 (i) 90 and (j) 100 mV s^{-1} (B) dependence of the peak current with square root of the scan rate

It can be noted from Fig. 4B that the cathodic currents increase and the peak potential shifts as the scan rate increases. When peak current values were plotted against $v^{1/2}$ (Fig. 3B), the following linear relationship was obtained:

$$I_p = -0/475 + 26/25 v^{1/2} (\text{mV}^{1/2} \text{ s}^{1/2}), \quad R^2 = 0.992 \quad (1)$$

This behavior suggests that the reduction process is controlled by diffusion. $v^{1/2}(\text{mV s}^{-1})^{1/2}$ Thus, according to the following equation for a totally quasi-reversible diffusive process:

$$I_p = 3.01 \times 10^5 n [(1-\alpha) n_\alpha]^{1/2} A c D^{1/2} v^{1/2} \quad (2)$$

And considering $(1-\alpha)n_\alpha=0.57$ (see below), $D=1.92 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$ (see chronoamperometric studies), $A=0.49 \text{ cm}^2$, it is estimated that the total number of electrons involved in the cathodic reduction of Folic acid is $n \approx 2$ ($n=1.8$).

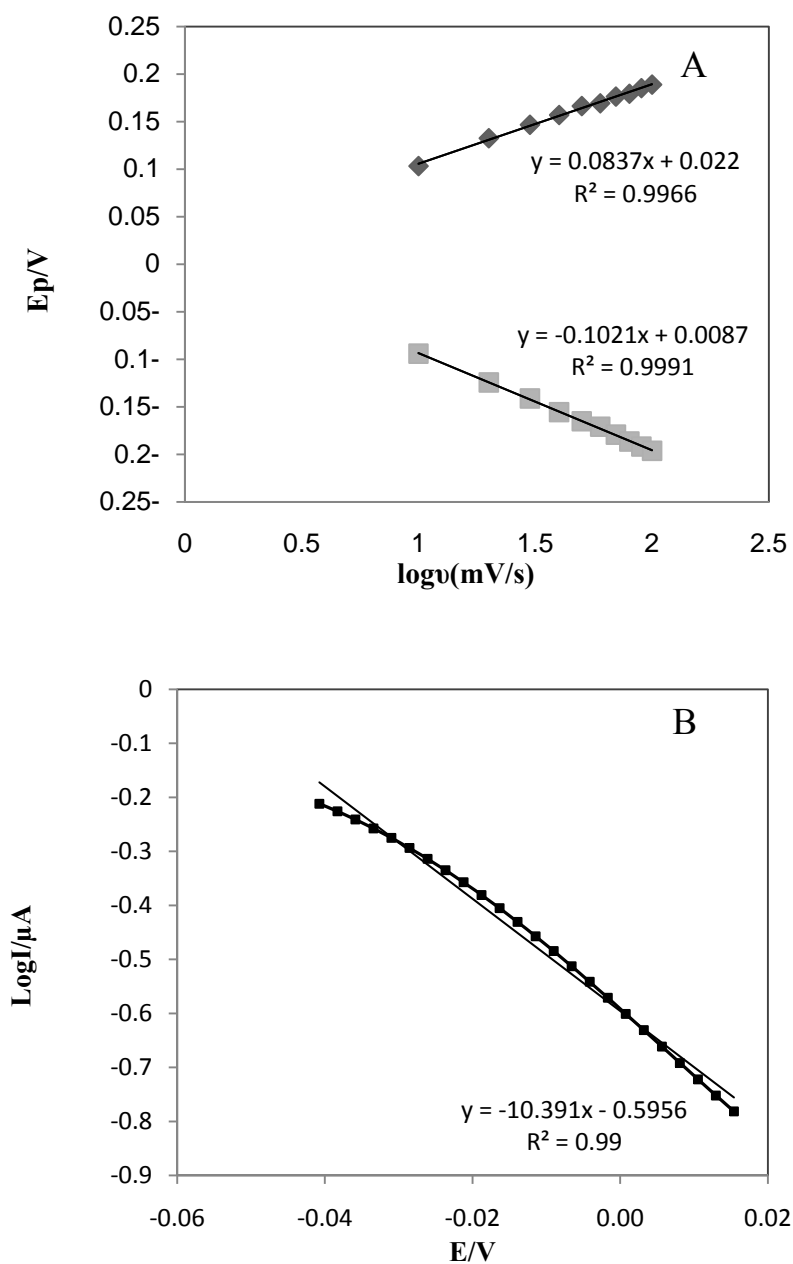


Fig. 5. (A) Plot of E_p vs. $\log v$. (B) Tafel plot Derived from data of the rising part of the current-voltage curve at a scan rate of 10 mV s^{-1}

In order to get information on the rate determining step, The peak potential, E_p , is proportional to $\log v$ as can be seen in Fig. 4A. The slope of E_{pc} vs. $\log v$ is 0.102 V. The tafel slope may be estimated according to the equation for the totally quasi- reversible diffusion-controlled process:

$$E_p = (b \log v) + \text{constant} \quad (3)$$

So, $b = 0.102$ V. this result is close to that obtained from polarization measurement [64].

This slope indicates a one electron transfer to be rate limiting assuming a transfer coefficient of $\alpha = 0.57$

The tafel slope, b , can be obtained by another method a tafel plot was drawn (Fig. 5B). Derived from data of the rising part of the current-voltage curve at a scan rate of 10 mV s^{-1} , A slope of 10.39 V^{-1} is obtained which indicates that the rate limiting step is one electron transfer (assuming a transfer coefficient of $\alpha = 0.5$) using the following equation:

$$\text{Slope} = (1-\alpha)n_e F / 2.3RT \quad (4)$$

Table 1. Comparison of linear range for determination of FA at various electrodes

Modified electrodes	Electrochemical methods	Linear range of detection	Ref
Gold electrode	Oxidative adsorptive stripping voltammetry	8.0×10^{-9} to 1.0×10^{-6} M	[36]
MWCNTs	Stripping voltammetry	3.0×10^{-7} to 8×10^{-5} M	[37]
Calixarene modified carbon paste electrode	Differential adsorptive stripping voltammetry	8.79×10^{-12} to 1.93×10^{-3} M	[38]
MWCNT-PVS/GCE	Amperometric	5.3×10^{-5} to 1.7×10^{-3} M	[41]
(PMO ₁₂) doped polypyrrole (PPy) film	DPV	1.0×10^{-8} to 1.0×10^{-7}	[42]
Pencil graphite electrode	Differential pulse cathodic stripping voltammetry	0.007 to $0.156 \mu\text{g mL}^{-1}$	[45]
Mercury electrode	AC adsorptive stripping voltammetry	1×10^{-8} to 1×10^{-11} M	[66]
Carbon paste electrode	Differential pulse cathodic stripping voltammetry	6×10^{-9} to 6×10^{-4} M	[67]
SWCNT-ILPE	DPV	2.0×10^{-9} to 4.0×10^{-6} M	[68]
MWCNT-PANI/GCE	CV	1.0×10^{-6} to 100.0×10^{-6} M	This work

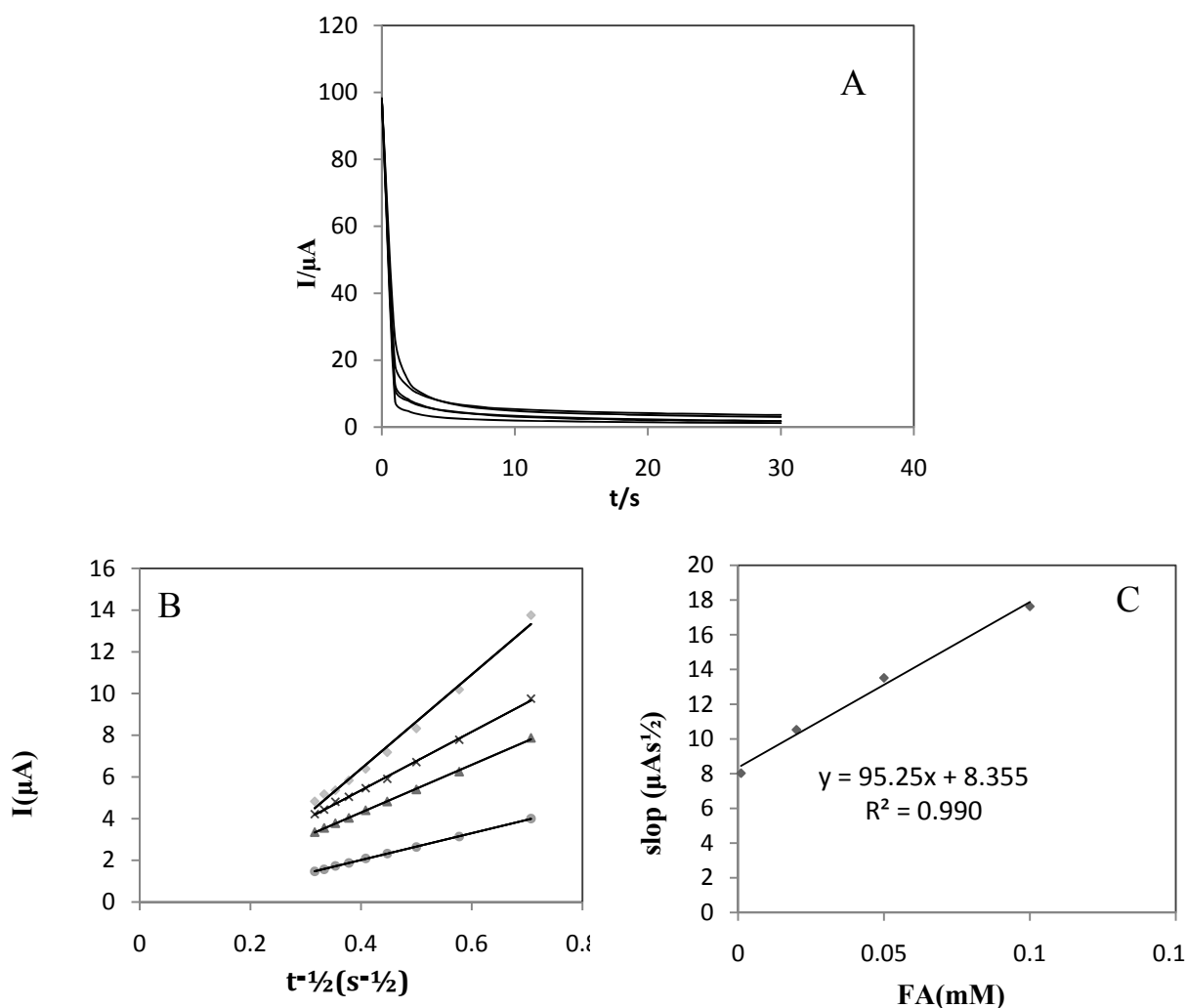


Fig. 6. (A) Chronoamperometric response of PANI-MWCNTs GCE a in 0.1 M phosphate buffer solution (pH 7.0) containing different concentrations of Folic acid for a potential step of 400 mV vs. SCE In the range of 1, 25, 50 and 100 μM . (B) Plot of plot of I vs. $t^{-1/2}$ obtained from chronoamperometric experiments. (C) Inset shows the relationship between the slope of the linear segments and the FA concentration

The relationship between current and time can be described by the Cottrell equation [65]:

$$I = n F A D^{1/2} c / \pi^{1/2} t^{1/2} \quad (5)$$

Where D is the diffusion coefficient (cm^2s^{-1}) and c is the bulk concentration (mol cm^{-3}). The plot of I vs. $t^{-1/2}$ will be linear, and from the slope, the value of D can be obtained. Fig. 6B shows the experimental plots of the resulting straight line were then plotted vs. the concentration of folic acid (Fig. 6B, inset), from which we calculated a diffusion coefficient of $1.92 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$ for folic acid.

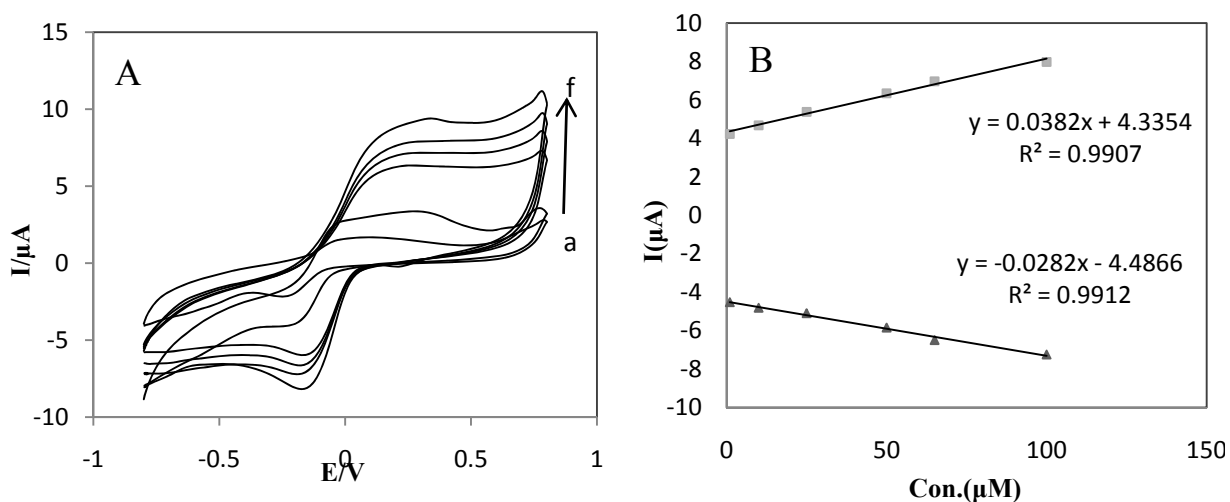


Fig.7. (A) Cyclic voltammogram for increasing concentrations of folic acid from 1 to 100 (a to f) μM in buffer solution (pH 7.0) containing 0.1 M PBS on PANI-MWCNTs modified electrode. Scan rate was 50 mV s^{-1} . (B) Calibration plot for concentrations of Folic acid from cyclic voltammogram

The cyclic voltammogram at different concentrations of FA are shown in Fig. 7A. A plot of the peak current values as a function of the concentration was drawn. The plot was linear in the concentration range of 1-100 μM FA. A comparison of linear range of FA determination at various electrodes from previous reports is given in Table 1.

4. CONCLUSION

In this present study the preparation of PANi-MWCNTs and their employment for the measurement of FA have been described. The PANi-MWCNTs were prepared using an *in situ* chemical polymerization reaction between MWCNTs and PANi monomer. The presence of functionalized MWCNT composites caused an increase in the FA reduction current. The morphology of the PANi-MWCNTs was studied by the SEM technique and TEM.

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