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ORIGINAL PAPER

# Fabrication of carbon nanotube and dysprosium nanowire modified electrodes as a sensor for determination of curcumin

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**Abstract** Two sensitive sensors for determination of curcumin (CM) were described. CM can be detected using multiwall carbon nanotube (MWCNT)-modified electrodes and dysprosium nanowire carbon paste electrode using the technique of adsorptive stripping voltammetry (AdSV) in stationary solution and the fast Fourier transform voltammetry at the flowing solution. Both electrodes did show less passivation effect that occurs on the unmodified electrodes and displayed better stability and reproducibility. This electrode enabled selective determination of CM in the presence of interfering species. Under optimized conditions, CM could be detected over a linear range with a detection limit of $5.0 \times 10^{-9}$ mol $L^{-1}$ and $5.0 \times 10^{-10}$ mol $L^{-1}$ for the traditional square wave and fast Fourier transform square wave voltammetry (FFTSWV) with RSD between 0.2 and 0.5%. Comparison with other reported methods showed these studies are about 100 times more sensitive than previous ones. Good selectivity and high sensitivity obtained by Square wave voltammetry can open new possibilities of direct CM determination.

**Keywords** Curcumin · Dysprosium nanowire · Carbon nanotube · Square wave voltammetry

## 1 Introduction

Curcumin (CM) [Fig. 1; (1E,6E)-1,7-bis (4-hydroxy-3-methoxyphenyl)-1,6- heptadiene-3,5-dione] is known for its antitumor [1, 2], antioxidant, antiarthritic, anti-amyloid, anti-ischemic [3], and anti-inflammatory properties [4]. Anti-inflammatory properties may be due to inhibition of eicosanoid biosynthesis [5]. In addition it may be effective in treating malaria, prevention of cervical cancer, and may interfere with the replication of the HIV [6]. CM is used in many foods as coloring agent, including mustard, margarine, processed cheese, cakes, curry powder, soft drinks, and sweets. CM inhibits the growth of Helicobacter pylori, which causes gastric ulcers and has been linked with gastric cancers. CM can bind with heavy metals such as cadmium and lead, thereby reducing the toxicity of these heavy metals. This property of CM explains its protective action to the brain. CM acts as an inhibitor for cyclooxygenase, 5-lipoxygenase, and glutathione S-transferase. It fights free radical formations in blood and body tissues, effectively scavenging superoxide radical [7], the hydroxyl radical and nitrogen dioxide among other reactive oxygen species [8]. Recently the study of the mechanism of its chemiopreventive activity has attracted increasing attention [9]. Some results [10] provided a novel insight into the roles and mechanisms of CM in inhibition of colon cancer cell growth and potential therapeutic strategies for

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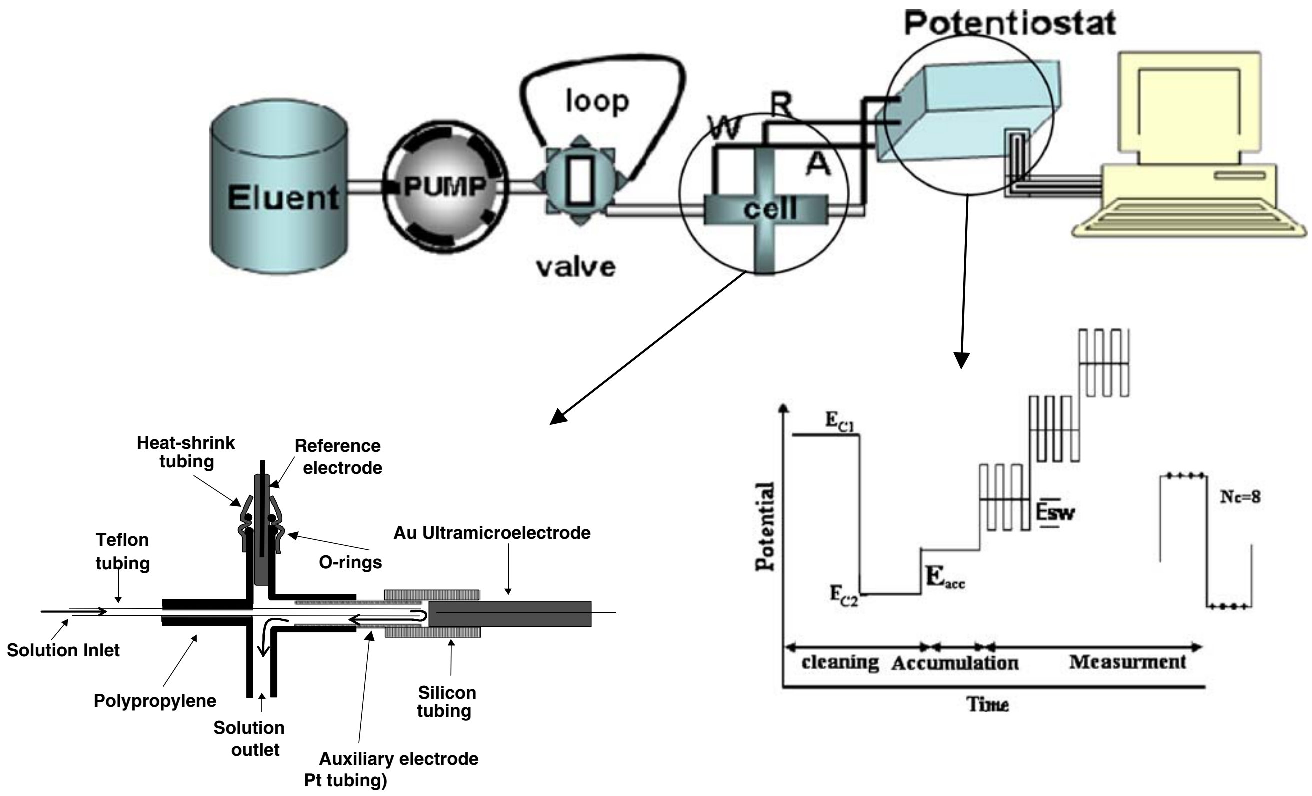

**Fig. 1** The schematic of flow injection electrochemical system by focusing on the electrochemical cell and the potential program that applied by potentiostate

treatment of colon cancer. Other findings [11] demonstrate that CM is an effective radioprotective agent, inhibiting acute and chronic effects, but not death, after irradiation. CM is well absorbed, both in vitro [12] and in vivo [13]. Toxicologically, it is relatively inert and does not appear to be very toxic to either animals [14] or humans [15]. Although electrochemical methods have been employed as a detection method, study of CM by electrochemical method has been scarce.

On the other hand, many attempts have been made to utilize nanostructures in electrochemistry. CNTs as a new material found an important class of carbon materials that prepare many applications, for example, energy conversion and storage [16], electromechanical actuators [17], and chemical sensing [18] due to their novel structural, electronic, physical and mechanical properties. Recent electrochemical studies have verified that CNTs possess very good electrochemical properties with a strong capacity against electrode fouling [19–23], suggesting their ability in the development of electrochemical methodologies for biological-oriented determinations. Furthermore, the metal nanowires get the extensive researchers attention because of their special electrical, magnetic, and optical properties and physical properties. They can also be used for highly sensitive detection of gas [24–26] chemical [27–30] or biological sample [31–34] due to the large surface-to-volume ratio. In a metal nanowire, the electrical resistivity is much higher than its bulk resistivity because of surface and grain boundary scattering effects of conduction electrons when one dimension of the nanowire is comparable to or smaller than the electron mean free path [29, 35]. In recent days, nanowires found many applications in electrochemistry because of their ability to facilitate the electron transferring and make better catalytic property [36] and making more effective surface. In this study we utilized two new sensors for detection of CM in the range of $1.0 \times 10^{-6}$–$2.0 \times 10^{-9}$ mol $L^{-1}$; a glassy carbon electrode modified by carbon nanotubes (CNT) and carbon paste electrode modified by Dysprosium nanowire which were compared by unmodified ones. The experiments are continued to know more about the optimization of the effective parameters on the determination of the component. No reports for determination of CM by the nanostructure modified electrode with the electrochemical method were found. The modified electrodes were applied in milk which is used in India as a kind of medical solution to treat a sort of skin sores which are not so deep and serious. Both electrodes give nearly the same sensitivity for determination of anticancer flavonid CM. The sensors are able to apply in blood samples or food industries.

## 2 Experimental

### 2.1 Chemicals

CM was obtained from Merck Co. (Darmstadt, Germany). A stock solution of CM ($5.0 \times 10^{-3}$ mol $L^{-1}$) was prepared just before use by dissolving CM in minimum amount of ethanol (about 1 mL), and then diluted with supporting electrolyte as the working solutions. Tris–HCl, acetate ($CH_3COONa/CH_3COOH$), and phosphate ($NaH_2PO_4/Na_2HPO_4$) buffers were investigated to choose the best supporting electrolyte. All buffers were made at 50 mM of solution for measurements by both electrodes. MWCNT (diameter 10–20 nm, length 1–2 mm, purity >95%) was purchased from Shenzhen Nanotech Port Co. Ltd. (Shenzhen, China) and used without further purification. All used chemicals were of analytical reagent grade obtained from Merck or Fluka. Doubly distilled water was used throughout. The Dysprosium oxide ($Dy_2O_3$) was purchased from Merck (Germany), CAT No.1.12151.0010. Commercial low fat milk was purchased from a local grocery and it was used for determination of spiked CM samples and used without further pretreatment; just the pH of milk was adjusted to pH 4 by adding some drops of HCl. It did not make any participation or any other change in milk.

For the determination of CM in plasma, a distinct amount of aqueous CM solutions (1.0 μmol $mL^{-1}$) were added to 2 mL of untreated plasma. The mixture was vortexed for 30 s. In order to precipitate the plasma proteins, the plasma samples were treated with 0.4 mL perchloric acid $HClO_4$ 20%. After that, the mixture was vortexed for a further 30 s and then centrifuged at 6,000 rpm for 5 min.

For the FFT method a 50 μl aliquot of the obtained supernatant was injected into the FIA system.

The sufficient volume of the rest of solution was used for the stationary electrochemical method.

#### *2.1.1 Preparation of modified electrodes*

The Carbon nanotube modified glassy carbon electrode was constructed by drop coating of the emulsion of CNT in dimethylformamide (DMF) on the surface of electrode and drying in air. An acid treatment of MWCNTs were first suspended in DMF (1 mg $mL^{-1}$) and sonicated for 10 min, after that a 10 μL aliquot of the casting suspension was placed onto the GCE surface and the solvent allowed evaporating. The surface of electrode renewed after a series of experiments (about 10 runs) by removing the CNT layer and making another modification.

The DyNW/CPE was prepared by hand-mixing 0.97 g graphite powder (particle diameter = 10 mm, from Merck). 0.03 g DyNW and 0.34 mL paraffin oil (High viscosity paraffin (density = 0.88 g $cm^{-3}$, from Fluka) adequately in agate mortar. The resulting paste was packed tightly into a PTFE sleeve and the electrode surface was polished to a smooth finish on a piece of weighing paper. The DyNW/CPE surface was renewed where necessary by removing a little part of paste and smoothing the surface and polishing the electrode.

#### *2.1.2 Instruments*

Cyclic and square wave voltammetric measurements were performed using an Autolab potentiostat PGSTAT 30 (Eco Chemie B·V., Netherlands), equipped with the GPES 4.9 software and a home-made ultravoltammetry system which introduced and described in detail at our previous articles [37–45].

The second electrochemical method was the FFT-SWV technique that was used in flow injection solution. It was modified in the potential excitation waveform and current sampling and data processing. The potential waveform consisted of three sections; (a) electrode conditioning and (b) accumulation part (c) measurement of the potential waveform contained in three additional potential steps, from $E_{c1}$ to $E_{c2}$ (for cleaning the electrode surface) and Es (for accumulation of component). The measurement part of the waveform contains multiple SW pulses (which the current sampling has been done four times per every pulse, Nc = 8) with amplitude of $E_{sw}$ and frequency of $f$, were superimposed on a staircase potential function, which was changed by a small potential step of ΔE. The values of potential pulse of SW ($E_{SW}$) and ΔE were in a range of few mV (10–50 mV). In potential ramp, the currents were sampled four times per each SW polarization cycle. After preparing the solution, the measurements were carried out in the continuous fast Fourier transform stripping square wave voltammetric mode (FFTSW). A three-electrode configuration includes a modified carbon electrode (with a diameter of 2 mm) as a working electrode, platinum wire as an auxiliary electrode, and Ag/AgCl as a reference electrode. The schematic of flow injection set up was shown in Fig. 1.

## 3 Result and discussion

### 3.1 Cyclic voltammetric behavior of CM at CNT/GCE and DyNW/CPE

Figure 2 shows SEM images of glassy carbon electrodes (a) along the surface modification by CNT and TEM image of synthesized DyNW (b). The aggregates strings

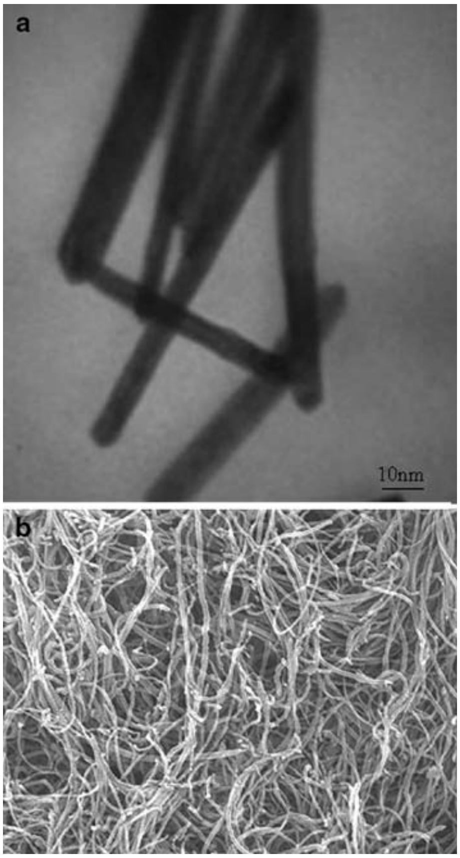

**Fig. 2** **a** TEM image of Dysprosium nanowires and **b** SEM image of CNT on the surface of glassy carbon electrode

of carbon nanotube are found in GC/CNT with diameters of 20–30 nm and the nanowires with the 30 nm diameter. The cyclic voltammetry of CM $1.0 \times 10^{-5}$ mol $L^{-1}$ dissolved in buffer 0.05 mol $L^{-1}$ phosphate pH 4 on the two unmodified (a) and modified (b) electrode surfaces was recorded. The result showed that the modified sensors showed good increase in current (about 10 times) and negative shift in oxidation potential (about 20 mV) that it is a suitable feature for sensitive determination of this compound. CM has a well defined redox peak on the surface of this electrode in the range of 0.1–0.6 V that the redox peaks are similar to the other study on the carbon paste electrode [46]. Actually, CM showed a first quasi-reversible peak at 0.46 and 0.44 V and one more irreversible anodic peak at more positive potential at 0.8 V, pH 4 in 0.05 mol $L^{-1}$ phosphate buffer and the second peak would be decreased by more reparative cycling.

The redox peak has been known as an electron transferring process of the catechol moiety to ketone group. CM probably could be oxidized in the same manner of anodic oxidation of compounds with 3-methoxy-4-hydroxyphenyl substituent. Subsequent scans show that the current decreased, which makes that the CM can be adsorbed on the surface of electrodes and make passivation of the surface. The mechanism of oxidation of CM is CEC but in this study just the first quasi-reversible peak has been mentioned and this current is used as a signal for determination.

In Fig. 3 the effeIn, the characteristic of quasi-reversible electrochemical oxidation of the hydroxyphenol unit within the CM molecule has been shown (a for the DyNW/CPE and b for CNT/GCE) in the range of 0.05–1.2 $Vs^{-1}$, the regression equations are $I_{pa} = 0.1033X - 27.963$ μA, $v$: $mVs^{-1}$, $r = 0.998$) and ($I_{pa} = 0.0952X + 0.0667$ μA, $v$: $mVs^{-1}$, $r = 0.9982$). The $I_{pa}$ was directly proportional to the scan rate $v$ over the range of 0.05–0.8 $Vs^{-1}$, which suggested a surface-controlled process on the modified electrode.

The peak potential shifts in positive direction with increasing scan rate. Furthermore, it is linear to ln$v$ in the range of 0.5–1.5 V, following the regression equation: $E_{pa} = 0.5074 + 0.0192 \ln v$ ($E_{pa}$: V, $v$: V $s^{-1}$, $r = 0.9869$) and $E_{pa} = 0.495 + 0.0596 \ln v$. According to the Eq. 1 [47]

$$\begin{aligned} E_{pa} &= E_0' + m\left[0.78 + \ln\left(D^{1/2}k_s^{-1}\right) - 0.51\ln m\right] \\ &\quad + (m/2)\ln v \\ m &= RT/[(1-\alpha)n_\alpha F] \end{aligned} \tag{1}$$

The electron transfer coefficient α is calculated and it is 0.6 ($n = 2$) on the surface of DyNW/CPE and 0.7 for the CNT/GCE.

### 3.2 Type of buffer and effect of pH on the voltammetric behavior of CM

The influence of type of supporting electrolyte on the oxidation peak of CM was studied. When the concentration of CM is $1.0 \times 10^{-5}$ mol $L^{-1}$ and the pH was kept at 5, based on the highest current developed in supporting electrolytes (Tris–HCl, acetate, citrate and phosphate buffer) the suitable buffer was selected.

For further studies this buffer was used as a fixed supporting electrode for more experiments. The effect of buffers was shown at modified electrodes and the recorded currents were 1.0, 3.2, and 4.5 μA for phosphate, Tris–HCl, and acetate buffers, respectively on the surface of CNT/GCE and 2.0, 5.0, and 6.0 μA on the surface of DyNW/CPE. The phosphate buffer prepares the best supporting electrolyte in which the current is generated from oxidation of CM.

After selection of buffer, further study was done for evaluation of pH. Therefore, a range of pHs from 2 to 9 was prepared by phosphate buffer and the oxidation current and potential of flavonoid was determined at the surface of CNT/GCE and DyNW/CPE. As can be seen in Fig. 4a, b the high current can be developed at pH 4 for both electrodes. So the phosphate buffer with a pH 4 was used as a

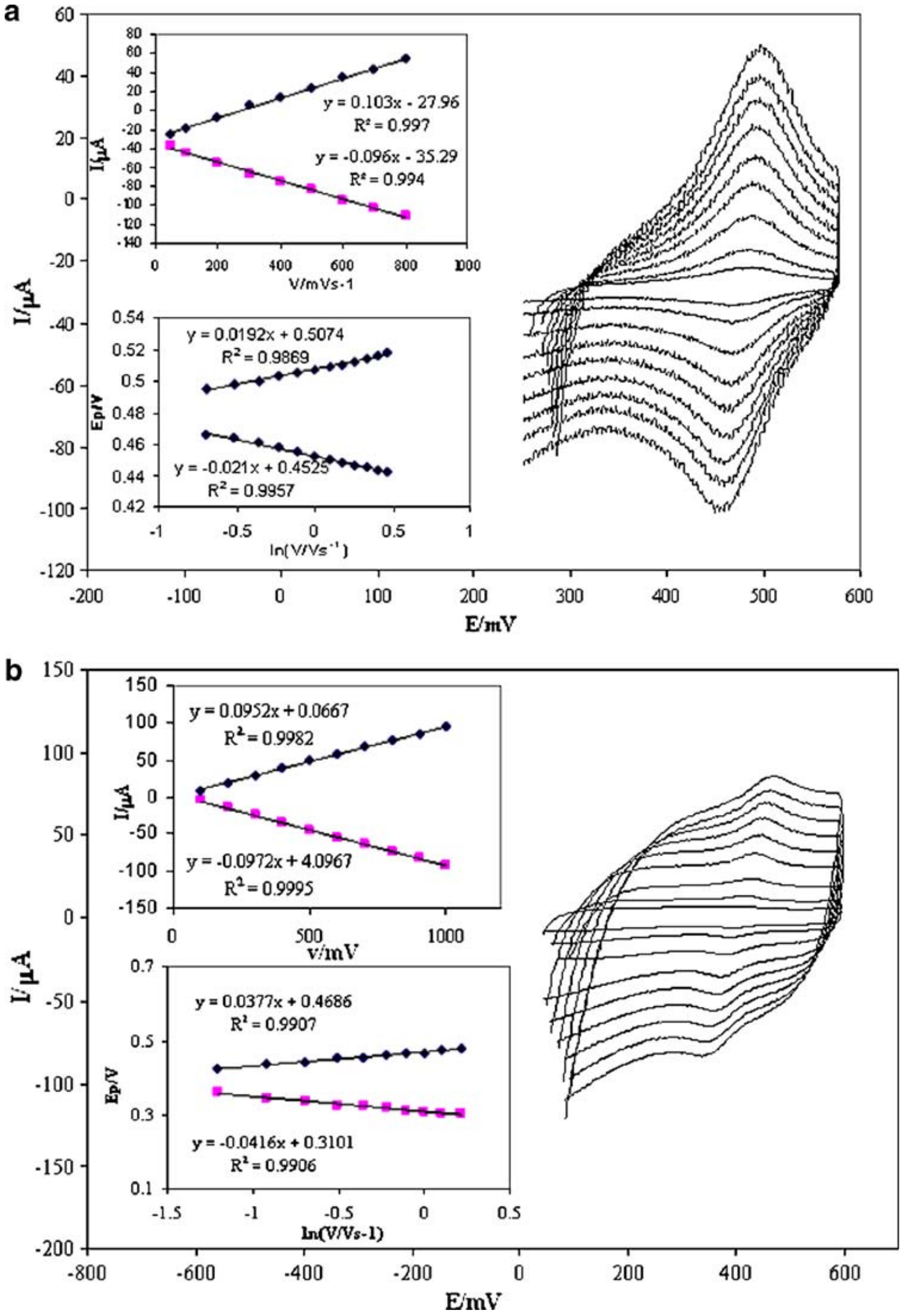

**Fig. 3** Voltammogram of $1.0 \times 10^{-5}$ mol $L^{-1}$ of CM at different sweep rate **a** on the DyNW/CPE and **b** CNT/GCE. Inset of figures; dependence of peak current (**a**) and peak potential (**b**) to scan rate. Accumulation potential −0.5 V, accumulation time 50 s

supporting electrolyte for both described voltammetry methods.

The effect of pH on the formal potential and anodic peak current was investigated by cyclic voltammetry in the solution containing $2.0 \times 10^{-5}$ mol $L^{-1}$ CM. The value of $E'_o$ which depends on the pH value of the buffer solution, shows that the redox couple of CM includes some proton transfer in the reduction and oxidation processes. According to the Nernst equation, the slope of 0.059 V $pH^{-1}$ reveals that the proportion of the electron and proton involved in the reactions is 1:1. As can be seen in Fig. 4a and b the slope of $E_{pa}$ versus pH is near to Nernst slope, so the CM oxidation is a two-electron process, the number of protons involved is also predicted to be two that are in agreement with other reports. Some preliminary experiments show us that CM can adsorb on the surface of electrodes by applying negative potential, in Fig. 5 the effect of potential applying on the surface of DyNW/VPE

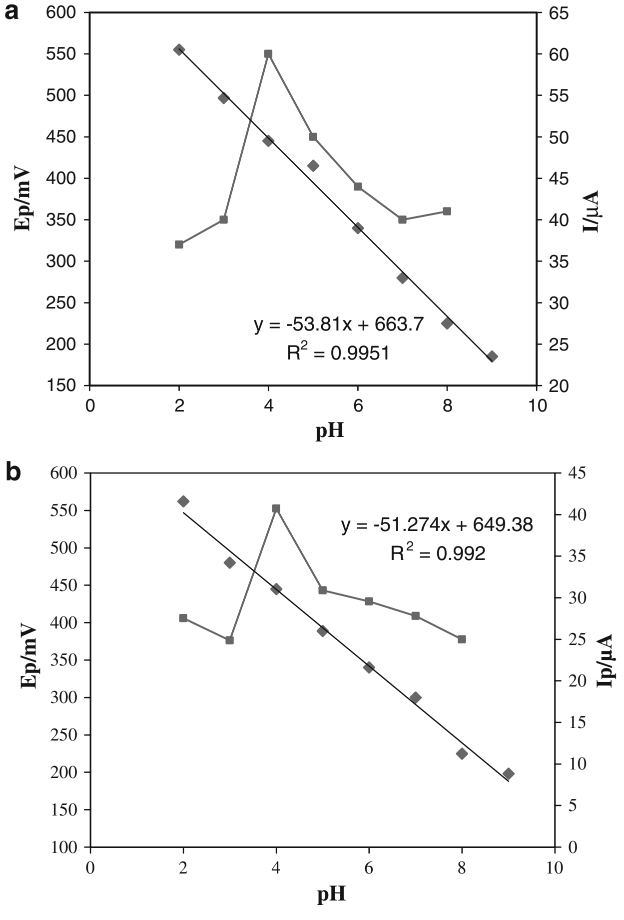

**Fig. 4** Graph of dependence of current and formal potential of $1.0 \times 10^{-5}$ mol $L^{-1}$ CM on the modified electrode, **a** DyNW/CPE and **b** CNT/GCE in different pH solutions between 2 and 9, scan rate 0.1 $Vs^{-1}$

was presented. As can be seen the stripping method make more current and is more sensitive. The effect on the surface of CNT/GCE is similar.

### 3.3 Variation of peak current with accumulation potential and time

As shown in Fig. 6a, b, when the accumulation potential is changed from −0.1 to −0.8 V, the peak current increases gradually and then it leveled off on the both modified electrodes. This means that a more negative potential is favorable to the accumulation of CM. It can be explained because the association constant of CM is about 8–10 [6]. Therefore, the molecule in this pH is protonized and has positive charge. Both nanostructures are neutral under this condition; the accumulation of CM must result from its adsorption on the electrode surfaces. Hence, it is thought that the role of accumulation potential is to neutralize the net charge on the electrode surface or tempt to adsorption of CM.

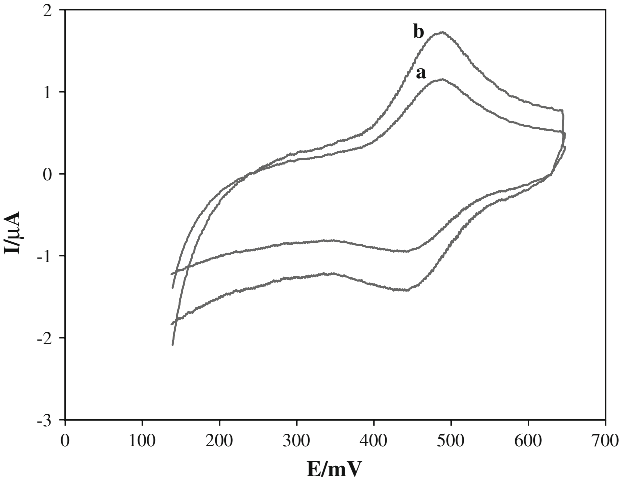

**Fig. 5** preliminary investigation of the effect of accumulation potential on the current of redox voltammogram of CM. Applying potential is -300 mV in buffer pH 8. Electrode is DyNW/CPE. (a) Before accmulation and (b) after accumulation

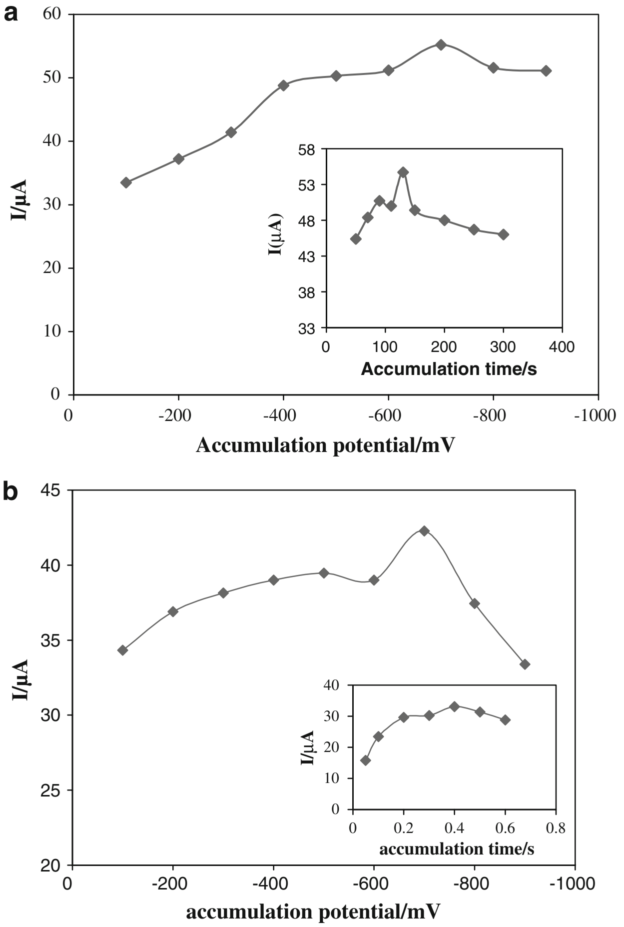

**Fig. 6** The effect of accumulation time and potential on the current signal. [CM] = $1.0 \times 10^{-5}$ mol $L^{-1}$, **a** on the surface of CNT/GCE and **b** on the surface of DyNW/CPE in 0.05 mol $L^{-1}$ phosphate buffer pH 4

The peak height grows with increasing accumulation time. For a 1.0 × $10^{-5}$ mol $L^{-1}$ CM solution, the peak current almost stops increasing after 110 s accumulation (Fig. 6a) on the surface of CNT/GCE. This indicates that the accumulation of CM at the electrode surface nearly reaches a saturation state after 110 s. In this study, −0.7 V was selected as the accumulation potential and 110 s as the accumulation time for the CNT/GCE at the traditional square wave voltammetry.

In the fast Fourier method the procedure is slightly different. At this system the flowing solution brings the component on the surface of electrode by every injection of sample. The potential program as mentioned in our previous articles [37–43] contains three sections: (1) cleaning of the surface of electrode, (2) accumulation of component and (3) the measurement part that the square wave program will apply. These parts are continuously applied on the surface of electrode, which means potential program apply in sub-second to obtain enough data (current sampling) when CM passes through the electrode surface. This makes the system slightly different because the accumulation time, here, cannot be so long. The accumulation time and potential was optimized for this method. Obviously, the accumulation potential was the same as the first method in this article and then the accumulation time was investigated between 0.05 and 0.9 s. As can be seen in the Fig. 6b the optimized accumulation time was 0.4 s at −0.7 V accumulation potential. Figure 7 shows the 3D voltammogram of the injection of CM at concentration of 1.0 × $10^{-5}$ mol $L^{-1}$ in the optimum condition on the surface of DyNW/CPE in flowing solution by using FFTSWV. The time axis shows the run time, which means the time needs for repetitive injections. The buffer flowing voltammograms are recording during whole run experiment which is about 200 s or more, and when the CM injected the component, it carry to the surface of electrode and redox of component make the anodic peak as pointed by two curser at Fig. 7. 200 s is sufficient time for some injection with the meaningful separation between the peaks.

### 3.4 Optimization of square wave parameters

Frequency is of utmost importance in SWV, since it determines the intensity of the signal and, in turn, the sensitivity of the technique. Furthermore, the pulse amplitude is another parameter that strongly influences the peak current in SWV thus determining the sensitivity of the technique. So both parameters were optimized for two electrochemical methods. The frequency and amplitude of SWV was obtained 15 Hz and 40 mV, respectively, in traditional square wave voltammetry.

In fast voltammetric analysis, the SW frequency and amplitude are important factors since analyte signal, background noise, and peak shape rely on speed of excitation signal. It should be noted that the solution resistance, electrode diameter, and stray capacitance of the system will limit the sensitivity gains obtained by raising the SW frequency. However, increasing the SW frequency will increase the SW peak current, or the sensitivity, but this will be tempered by a higher charging/faradic current ratio. Due to this fact that, the SW frequency acts similar to sweep rate in cyclic voltammetry. Therefore, using very high SW frequencies causes a shorter potential scan times, consequently, the response peak for the analysis becomes smaller and skewed, due to insufficient time for oxidation of the electrode surface. But for the redox reaction it should be optimized for electron transfer rate. While application of lower SW frequencies results to a longer potential scan times, which result to lower number of potential scan for each injected sample zone. The best obtained frequency and amplitude for this method were 500 Hz and 50 mV.

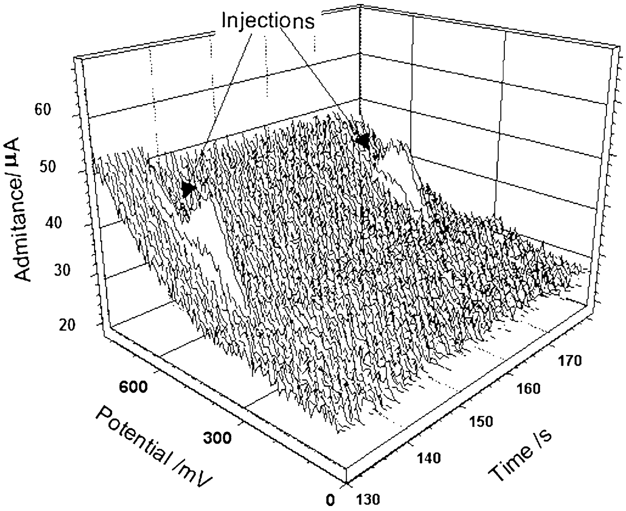

**Fig. 7** Three dimensional FFT Square Wave voltammograms at DyNW/CPE recorded during some injection experiment. The bulk solution was 0.05 mol $L^{-1}$ of phosphate buffer, and the frequency was 500 Hz. The injected amount of solution contained 1.0 × $10^{-5}$ mol $L^{-1}$ CM in buffer pH 4

### 3.5 Calibration curve at CM determination

In order to test the feasibility of this method for CM determination, the relationship between peak current and CM concentration is studied which was shown in Fig. 8. Under the selected conditions, when the concentration of CM changes from 1.0 × $10^{-8}$ mol $L^{-1}$ to 1.0 × $10^{-6}$ mol $L^{-1}$, the anodic peak current and CM concentration show linear relationship in the ranges of 2.0 × $10^{-9}$ M–1.0 × $10^{-6}$ mol $L^{-1}$ and 1.0 × $10^{-8}$ mol $L^{-1}$–1.0 × $10^{-6}$ mol $L^{-1}$ for the DyNW/CPE and CNT/GCE, respectively. The regression

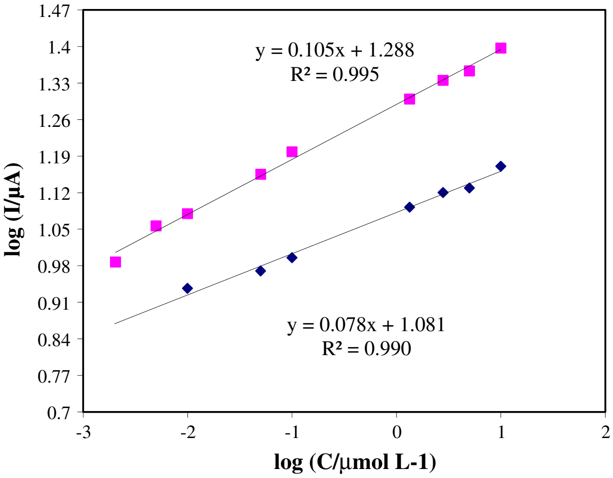

**Fig. 8** Calibration curve (a) DyNW/CPE and (b) CNT/GCE at the optimum condition in phosphate buffer 0.05 mol $L^{-1}$ pH 4

equations are: $Ip$ (μA) = 0.1053C + 1.2888 (μmol $L^{-1}$, $R^2 = 0.9955$) for the range of $2.0 \times 10^{-9}$–$1.0 \times 10^{-6}$ mol $L^{-1}$ and (Ip/μA) = 0.0788C + 1.0818 (μmol $L^{-1}$, $R^2 = 0.9904$) for the range of $1.0 \times 10^{-8}$–$1.0 \times 10^{-6}$ mol $L^{-1}$. CM could be detected over a linear range with a detection limit of $5.0 \times 10^{-9}$ M and $5.0 \times 10^{-10}$ M for the traditional square wave and FFTSWV with RSD between 0.2 and 0.5%. When the concentration of CM exceeds $7.0 \times 10^{-6}$ mol $L^{-1}$, the peak current almost keeps unchanged. On the other hand, when the concentration is lowered to $2.0 \times 10^{-9}$ mol $L^{-1}$, the peak is still discernible and measurable, which is better than that reported in literature [10]. A limit of detection using the lower linear range (based on $3\sigma$ equation) for each method based on the calibration curve was obtained as 0.5 and 5.0 nmol $L^{-1}$. By considering the linear range of modified electrodes and the detection limits and the slope of calibration curve the DyNW/CPE is slightly more sensitive than CNT/GCE but both electrodes are the most sensitive sensors in comparison of all other reported methods [10].

## 3.6 Regeneration and reproducibility of CNT/GCE and DyNW/CPE

The regeneration and reproducibility of the electrodes were investigated. Regeneration of the CNT/GCE was done by making another modified electrode and after some series (about 6–7 runs). For DyNW/CPE regeneration was done by cutting a small piece of paste and smoothing the surface of electrode after some runs (about 10–15 injections). To check the reproducibility a concentration of $1.0 \times 10^{-6}$ mol $L^{-1}$ was determined about seven times and the relative standard deviation (RSD) of the peak current was 1.7–2.2% for both electrodes, respectively.

## 3.7 Interference of foreign species

The interference of some coexistent species was examined on both electrodes that some change on current was summarized in Table 1. It was found that the influence of metal ions studied, such as $Zn^{2+}$,K + , $Cu^{2+}$, $Al^{3+}$, Na + , $Ag^{+}$, $Mg^{2+}$, and $Ca^{2+}$, was negligible for quantitative analysis under the selected experiment conditions when they are 200 times higher concentration than CM. Part of this can be ascribed to the positive potential window used, in which many metal ions do not cause redox peaks. In the presence of 100-fold glucose the peak current was only changed about 2.21% for both. When 10-fold ascorbic and some amino acids such as phenyl alanin were presented, the anodic peak of CM showed a slight change. Their interference resulted from their redox and adsorption at the electrode. The interference of other flavonoids such as trolox and rutin was also studied. As their anodic peaks have an overlap with the peak of CM, they interfere with the determination. Therefore, when they are present, separation procedure is required before determination.

## 3.8 Analytical application

The traditional stationary square wave voltammetry and FFTSWV was applied to the determination of CM in milky solution plasma samples. Prior to determination the commercial milk just adjusted to pH 4 by adding some drops of concentrated HCl. A standard addition method was adopted to evaluate the determination results. The analytical results are shown in Table 2 and 3 and in addition, the recovery of

**Table 1** Influence of potential interferences on the voltammetric response of $1.0 \times 10^{-8}$ mol $L^{-1}$ of CM

| Species | Current (μA) in presence of interferences on the surface of DyNW/CPE | Current (μA) in presence of interferences on the surface of CNT/GCE |
|---|---|---|
| $K^+$ | 8.0 | 12.0 |
| $Na^+$ | 8.1 | 11.91 |
| $Mg^{2+}$ | 8.4 | 11.96 |
| $Ag^+$ | 8.1 | 12.2 |
| $Cu^{2+}$ | 8.2 | 11.90 |
| $Zn^{2+}$ | 8.0 | 12.10 |
| $Ca^{2+}$ | 8.1 | 12.10 |
| L-Lysine | 8.3 | 11.95 |
| Phenylalanine | 8.2 | 11.97 |
| Methionin | 8.0 | 11.80 |
| Glucose | 8.0 | 11.85 |

The current of CM in the absence of interferences is 8.2 μA on the surface of DyNW/CPE and 12 μA on the surface of CNT/GCE

The currents are average of five replicate determination

**Table 2** Measurement results of CM in milk solution ($n = 5$)

| No. | Add (μmol $L^{-1}$) | Found (μmol $L^{-1}$) ± RSD% |  | Recovery (%) |  |
|---|---|---|---|---|---|
|  |  | DyNW/CPE | CNT/GCE | DyNW/CPE | CNT/GCE |
| 1 | 0.005 | 0.0052 ± 0.05 | 0.0049 ± 0.03 | 104 | 98 |
| 2 | 0.05 | 0.048 ± 0.20 | 0.051 ± 0.18 | 96 | 102 |
| 3 | 0.1 | 0.099 ± 0.230 | 0.097 ± 0.190 | 99 | 97 |
| 4 | 1.00 | 0.98 ± 0.25 | 1.03 ± 0.31 | 98 | 103 |

**Table 3** The result of recovery assay to accuracy and precision of the proposed method for human plasma samples

| Plasma samples | Spiked (μmol $L^{-1}$) | Found | Recovery (%) | R.S.D (%) |
|---|---|---|---|---|
| DyNW-CPE | 0.1000 | 0.1030 | 103.0 | 0.17 |
|  | 0.0500 | 0.0495 | 99.0 | 0.09 |
|  | 0.0100 | 0.0102 | 102.0 | 0.12 |
| CNT-GCE | 0.1000 | 0.0982 | 98.2 | 0.15 |
|  | 0.0500 | 0.0510 | 102.0 | 0.08 |
|  | 0.0100 | 0.0102 | 102.0 | 0.04 |

Average of nine determinations; *RSD* relative standard deviation

methods were estimated and the average recovery (also shown in Table 2, 3) was between 99.0–103% and 98.2–102%. The relative standard deviation of each sample for seven replicate determinations was less than 3.0%. The results demonstrated that the proposed method had good accuracy in CM measurement.

## 4 Conclusion

Two novel modified electrodes for sensitive determination of CM have been fabricated. CM can be accumulated on the surface of the DyNW/CPE and CNT/GCE at the potential of −0.7 V and at phosphate buffer pH 4. The modification causes decrease in the overpotential and makes higher current and more sensitivity. After optimization of the effective parameters a linear relation between concentration and current was obtained in the range of 1.0–0.01 and 1.0–0.002 μmol $L^{-1}$ for the DyNW/CPE and CNT/GCE, respectively. The use of MWCNTs and DyNW allow their large surface area to be exploited upon which CM adsorbed and oxidized on the surface of electrode. Both electrodes show very good accuracy and reproducibility. The electrodes were applied for determination of CM in the milk solution which was mixed by CM directly. That means these electrodes are useful for determination of this anti-cancer and anti-oxidant in urine or blood samples. It would be useful in some clinical or food industries. CM was added as a coloring agent, and in some counterfeit samples these sensors make us able to recognize these samples. Quantification of CM has been made and favorably compared with reported values and showed that these methods are about 100 times more sensitive than previous ones. Good selectivity and high sensitivity obtained by Square wave voltammetry can open new possibilities of direct CM determination.

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