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Electrochemical Determination of Catechol Using Functionalized Multiwalled Carbon Nanotubes modified Screen Printed Carbon Electrode

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In this work, a simple, disposable electrochemical sensor based on functionalized Multiwalled carbon nanotubes (f-MWCNT) modified screen printed carbon electrode (SPCE) was developed, which was used for the determination of catechol (CT). Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy was used to characterize the f-MWCNT. In addition, the f-MWCNT/SPCE displayed excellent electrocatalytic activity towards the electrochemical determination of CT. Under the optimized conditions, the sensing platform showed wide linear responses for CC from 0.08 to 725 μM with detection limits (S/N=3) of 30 nM. Furthermore, f-MWCNT modified electrode was also applied to detect practical samples with satisfactory results.

Keywords: Catechol (CT), electrochemical sensor, screen printed carbon electrode (SPCE), functionalized Multiwalled carbon nanotubes (f-MWCNT)

1. INTRODUCTION

Catechol (CT) is an isomer of dihydroxybenzene, has been extensively used for diverse applications, for example manufacture of pesticides, originator to perfumes and medicines [1]. The US Environmental Protection Agency (EPA) and the European Union (EU) have categorized CT as an environmental pollutant owing to its high poisonousness and low degradability in the ecological environment [2]. Although, the International Agency for Research on Cancer (IARC) has categorized

CT as a Group 2B, thinkable human carcinogen [3]. The high exposure of CT can cause downheartedness of the central nervous system (CNS) and a lengthy rise in blood pressure in animals [4]. Hereafter, a consistent and precise finding of CT in ecological samples are more significant. Lately, electrochemical methods are extensively used for the detection of numerous analytes with CT, owing to its low price, rapid response, transportability along with high sensitivity paralleled to presented traditional analytical methods [7,8].

To date, diverse micro and nanomaterials have been effectively used for selective and synchronized determination of CT [9,10]. Especially, the nanomaterials have punctually used for sensitive detection of CT owing to its high surface area and high catalytic activity. For example, carbon nanomaterials, metal oxides, metal and metal alloy nanoparticles have been broadly engaged for electrochemical sensing of CT [11–14]. Amongst the carbon materials, the MWCNT achieves extra attention from present scientists because of their exceptional and physical properties for example electrochemically accessible area, huge surface area, robust adsorption ability, good chemical constancy, substantial mechanical strength and high electrical conductivity [15]. Though the pristine CNTs are unsolvable in water (aqueous) it would be uneasiness for the significant applications such as electrode fabrication. Fascinatingly, the functionalization method has become extra good-looking in current years due to the elimination of impurities from CNT and also improves the solubility as well as electrochemical properties. Utmost meaningfully, functionalization process generates the anchoring sites on CNT which would be more accessible to electrode fabrication. A number of applications have been established based on f-MWCNT such as an electrochemical sensor, photovoltaic, biomedical, catalysis and membranes, electronics and nanocomposites [16-19]. It unlocks the new way to make the nature-mimicking material and device at nano-scale which moving onward their applications in pharmaceuticals and industries.

The present work, authors proposed a simple, sensitive and selective method for the detection of CT based on f-MWCNT/SPCE. As prepared f-MWCNT was studied by several spectrometric methods. It was determined the CT with the limit of detection (LOD) is 30 nM. The selectivity, storage stability and reproducibility of the sensor has been studied and discussed. We also demonstrated the practical applicability of real sample analysis in CT tap water samples based on f-MWCNT modified SPCE and obtained acceptable recoveries

2. EXPERIMENTAL SECTION

2.1. Materials and methods

Pristine carbon nanotube (multi-walled O.D×L 6– 9 nm× 5 µM, >95%) and Dopamine, ascorbic acid, hydroquinone, epinephrine, norepinephrine, Nitric acid (HNO_3), sulphuric acid (H_2SO_4), and catechol were purchased from Sigma- Aldrich. The supporting electrolyte utilized for all experiments was prepared by using 0.05 M Na_2HPO_4 and NaH_2PO_4 solutions in doubly distilled water and the pH of the solution was adjusted by using 0.1 M NaOH and H_2SO_4. All other chemicals were of analytical grade and the required solutions were prepared with double-distilled (DD) water.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were carried out by CHI 750a electrochemical work station from CH Instruments. Transmission electron microscopy (TEM) was performed on a TECNAI G2 under an accelerating voltage of 200 kV. FT-IR spectra were recorded by using the model Jasco FT/IR-6600 spectrophotometer. Raman spectrum were recorded using a Raman spectrometer (Dong Woo 500i, Korea) equipped with a charge-coupled detector and Thermo SCIENTIFIC Nicolet iS10 instruments. Electrochemical studies were implemented in a conventional three electrode cell system using SPCE as a working electrode (working area = 0.072 cm^2), platinum wire as a counter electrode and saturated Ag/AgCl (saturated KCl) as a reference electrode. All the electrochemical measurements have been executed at room temperature.

2.2 Synthesis of f-MWCNT and preparation modified electrode

f-MWCNT were synthesized by previously reported method [20].The purchased pristine MWCNT was dispersed in a mixture of nitric acid and sulphuric acid with a volume ratio of (1:3) subsequently the mixture solution was refluxed at 80 °C for 24 h. Afterward, the oxidized (Carboxylic acid functionalized MWCNT (MWCNT-COOH)) MWCNT solution was diluted by a huge amount of DD water. Then f-MWCNT was filtered by using No. 1 Whatman filter paper and the product was washed many times with DD water until the concentration of acid-free when the pH of f-MWCNT is near 7. Later, the obtained f-MWCNT were dried in a vacuum oven at 80 °C for 24 h.

The final product of f-MWCNT (1 mg mL^{-1}) was re-dispersed in DD water and ultrasonicated for 5 h to get the homogeneous f-MWCNT solution. Then, about 6 μL of f-MWCNT solution was drop coated on the SPCE surface and the modified SPCE was allowed to dry at room temperature. After that, the dried SPCE was smoothly washed with DD water to remove the inaccurately committed f-MWCNT on the surface of SPCE. The obtained f-MWCNT modified SPCE was used for further electrochemical experiments.

3. RESULTS AND DISCUSSION

3.1. Characterization of f-MWCNT

The structure and morphology of the f-MWCNTs were examined by TEM and shown in Fig. 1A & B. As shown in Fig. 1A, a uniform morphology of f-MWCNT was observed with a relatively smooth surface. As shown in Fig. 1B, the HRTEM image of f-MWCNT was revealed the high purity and crystalline nature of f-MWCNT. The functional groups of the as-synthesized f-MWCNT were characterized by FT-IR study. Fig. 1C displays the FT-IR spectrum of f-MWCNT. The FT-IR spectra of f-MWCNT exhibits the four obvious bands at 3400, 1720, 1632 and 1429 cm^{-1}, which is corresponding to the vibrations of O–H stretching, –C=O stretching of –COOH, bending vibration of adsorbed water and deformation of C–O, respectively [7,21]. Raman spectroscopy is a most powerful tool to analyze the defects and disorders of the carbon materials. Fig. 1D shows the Raman spectra of f-MWCNT, the obtained peaks at 1560 cm^{-1} for the G band (E2g symmetry) of sp^2 hybridized graphitic structure and another peak at 1328 cm^{-1} for D band of sp^3 disordered carbon, respectively [22]. The band intensity ratio of as-prepared f-MWCNT is consistent with earlier reports [20].

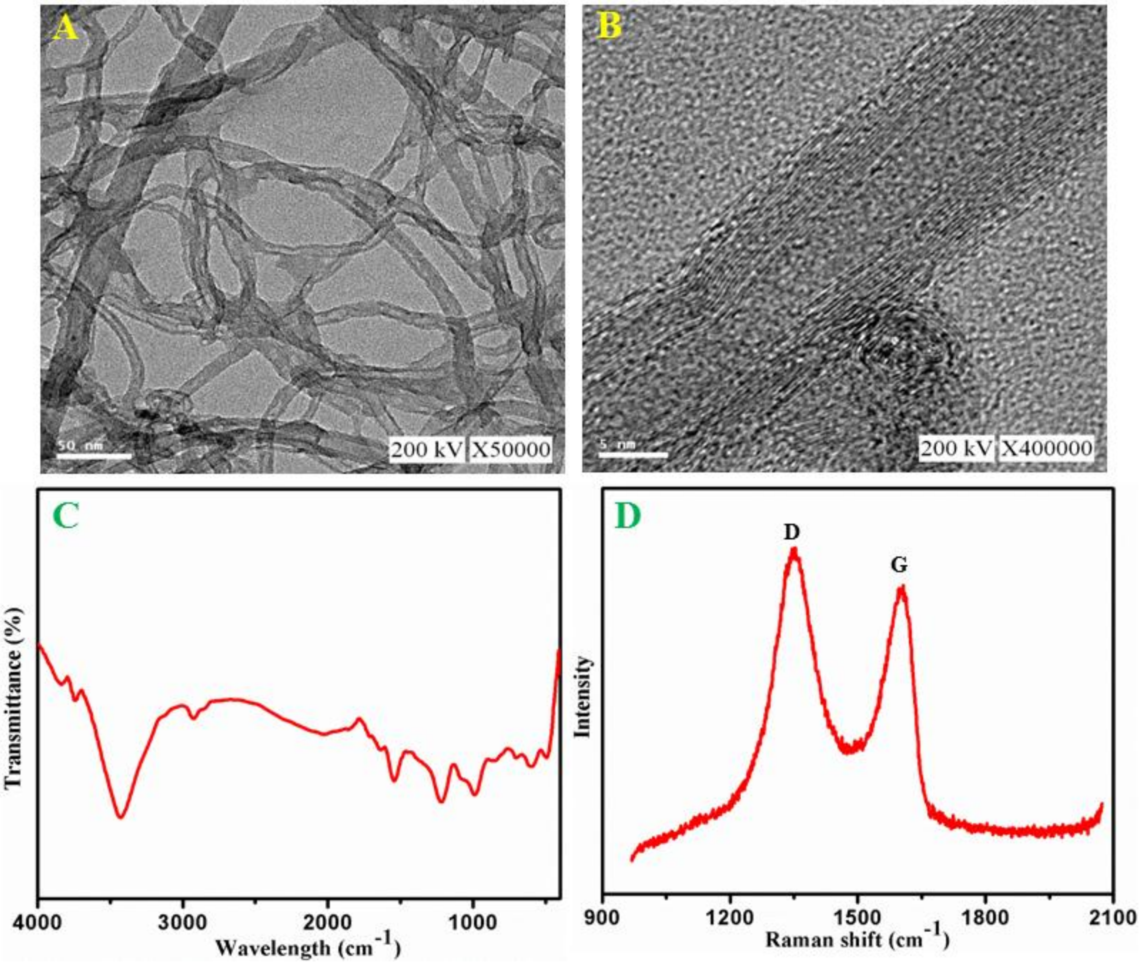

Figure 1. TEM images (A&B), FT-IR spectrum (C), Raman spectrum (D) of f-MWCNT.

3.2. Electrochemical detection of CT at f-MWCNT modified SPCE

The electrochemical behavior of CT was investigated on different modified electrodes using CV. Fig. 1A shows the CV response of bare SPCE (a) and f-MWCNT modified SPCE (b) in the presence of 500 µM CT containing N_2 saturated PBS at scan rate of 50 mV/s. The bare SPCE revealed a quasi-reversible redox characteristic peaks with weak oxidation and reduction of CT at 0.281 and 0.131 V, respectively. The peak to peak separation (Ep) of CT was observed at 0.15V for bare SPCE. On the other hand, f-MWCNT modified SPCE shows a well-defined redox behavior for CT and the anodic and cathodic peaks are observed at 0.18 and 0.15 V. The peak to peak separation (Ep) of CT was observed at f-MWCNT/SPCE as 0.03 V, which is lower than bare SPCE, indicates that the high reversibility and fast electron-transfer kinetics of f-MWCNT modified SPCE. In addition, the oxidation peak current response of CT is about 3 folds higher than that of those observed at bare SPCE. The results demonstrated that f-MWCNT modified SPCE has high electrocatalytic activity towards CT than that of unmodified SPCE.

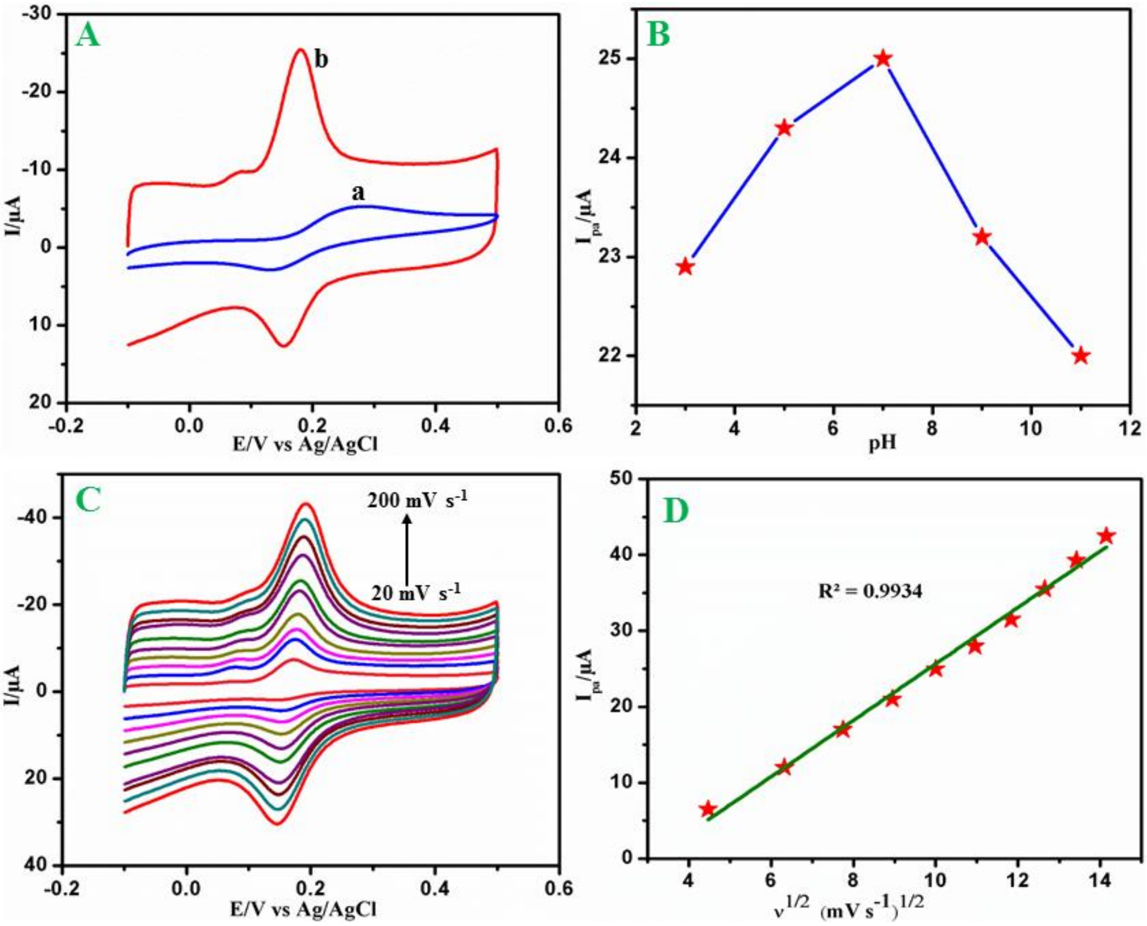

Figure 2. (A) CV of bare SPCE (a) and f-MWCNT/SPCE (b) in the presence of 500 µM CT in 0.05 M PB solution (pH 7.0) at ~~a~~ scan rate 50 mVs^{-1}. (B) Plot of oxidation peak current of CT vs. pH. (C) CV responses of f-MWCNT/SPCE at different scan rate from 20 to 200 mV/s in the presence of 500 µM CT in 0.05 M PB solution (pH 7.0). (D) Corresponding calibration plot of current vs. square root of scan rate.

3.3 Effect of pH and scan rate

The effect of solution pH on f-MWCNT/SPCE containing CV investigated with 500 µM of CT and the results are shown in Fig. 2B. Furthermore, the maximum sensitivity of CT was observed at pH 7.0 that of other Hence, pH 7.0 was chosen as an optimum for subsequent experiments. The effect of scan rate on the electrochemical behavior of CT at f-MWCNT/SPCE was investigated by CV. Fig. 2C shows the CV response of f-MWCNT/SPCE in 500 µM CT containing N_2 saturated PBS at different scan rate from 20 to 200 mV/s. The redox peak currents of CT were increases with increasing the scan rates and the peak potential was shifted towards more negative and positive direction upon increasing the scan rates from 20 to 200 mV/s. In addition, the redox peak current of CT had a linear dependence with the square root of scan rates from 20 to 200 mV/s with the correlation coefficient of 0.9934 and 0.999 (Fig. 2D). The result demonstrates that the redox behavior of CT at f-MWNCT/SPCE is controlled by a typical diffusion controlled electrochemical process [23].

3.4 Amperometric determination of CT

We also evaluated the response efficiency and sensitivity of the as-prepared electrode toward CT detection by using the highly sensitive, precise and reliable amperometric i-t method. Fig. 3A shows the amperometric current-time response of f-MWCNT modified electrode with regular injections of various CT concentrations at uniform time intervals into a constantly stirred (1400 rpm) 0.05 M PB solution (pH 7) under a preselected applied potential of +0.18 V. This can be displayed to the oxidation current increasing rapidly and reaching 97% of the steady state current within 6 s, which indicates the high electron conductivity and excellent electrocatalytic activity of CT on the f-MWCNT modified SPCE. The electrocatalytic oxidation current is directly proportional to the concentration of CT. In addition, the corresponding calibration plot of CT concentration versus amperometric current responses is shown in Fig. 3B. It displays an excellent linear response to the CT concentration in the range from 0.08 to 725 μM with a limit of detection of 30 nM. The obtained electrocatalytic performance of the f-MWCNT modified electrode toward CT detection was compared with previously reported CT sensors, and the results are summarized in Table 1.

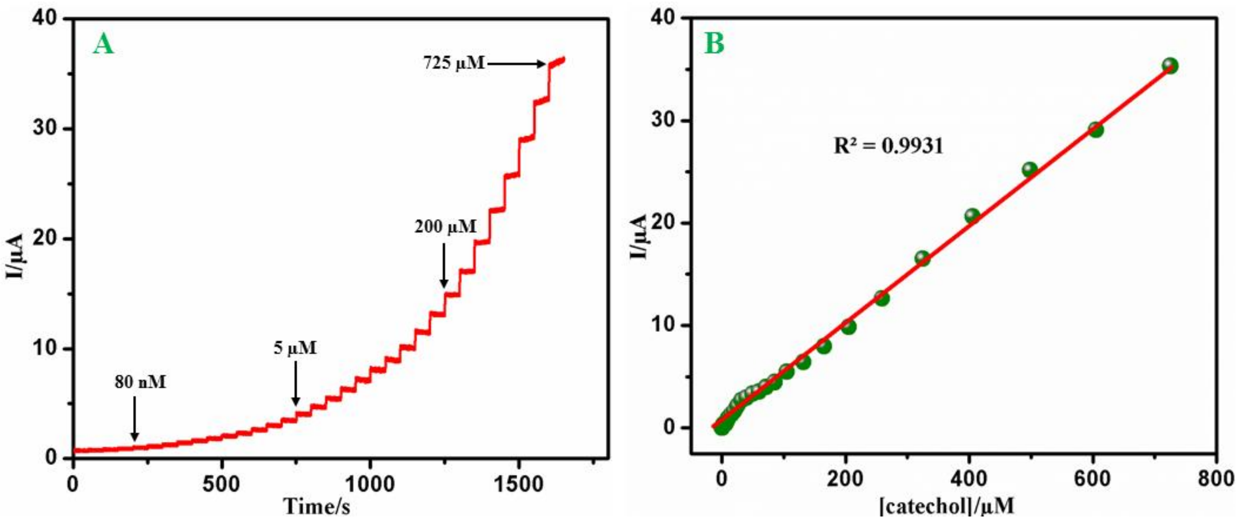

Figure 3. (A) Amperometric current response of different amount of CT at f-MWCNT modified electrode, (B) calibration plot of I_{pa} vs [catechol].

Table 1. Comparison of analytical parameters with previously reported CT sensors with various modified electrodes

Electrode	Linear range (μM)	LOD (nM)	ref
poly-SA/MWCNTs/CPE	3 – 240	160	24
AuNPs/CS@N,S co-doped MWCNTS	1 – 1000	200	25
AuNPs@CNCs	1.0 – 300	98.6	26
S/MWCNTs/PDA/AuNPs/GCE	1.0 – 10	47	27
ER(GO–TT–CNT)	0.5 – 200	11	28
CNNS-CNT	1 – 200	90	29
f-MWCNT/SPCE	0.08 – 725	30	This work

3.5. Selectivity, reproducibility, stability and Practicality of the sensor

The selectivity of the CT sensor is more important especially in the presence of high concentration of hydroquinone (HQ), since it could easily interfere with the oxidation signal of CT due to the similar structural features and chemical activity. In addition, the selectivity of the sensor is more important in the presence of the compounds which are oxidized at close oxidation potential of CT. Hence, we have investigated the selectivity of the sensor in the presence of potentially active compounds such as ascorbic acid (AA), uric acid (UA), epinephrine (EP) and norepinephrine (NEP). The selectivity of the f-MWCNT modified electrode towards CT was evaluated by DPV. The obtained results clear that 100 fold additions of AA, EP, NEP and 50 μM addition of HQ did not affect the response current and peak potential of CT. The results indicate the high selectivity of the fabricated electrode towards the detection of CT.

The reproducibility of the sensor was evaluated for the detection of 500 μM CT by CV and the experimental conditions are similar as of in Fig. 2A. The relative standard deviation of CT by five different electrodes was calculated as 2.92 %, which indicates the appropriate reproducibility of the f-MWCNT modified electrode. The storage stability of the fabricated f-MWCNT modified electrode was examined periodically up to 20 days. Prior to the analysis, the modified electrode was stored pH 7 at room temperature, and the oxidation peak current response of 500 μM CT was monitored by CV. The f-MWCNT modified electrode retains 95.6 and 92.9 % of initial current response to CT after 10 and 20 days storage in pH 7. The result indicates the appropriate stability of the modified electrode, which is due to the high chemical stability of the f-MWCNT.

The fabricated f-MWCNT modified electrode was further used for the determination of CT in tap water samples using the standard addition method. The obtained recovery results of CT in tap water samples are listed in Table 2. The recovery of CT in tap water samples was found in the ranging from 99.0 to 100.8 %, which authenticates that the appropriate practicality of the developed sensor towards the determination of CT.

Table 2. Determination of CT in water samples using f-MWCNT modified SPCE.

Water samples	Added (μM)	Found (μM)	RR (%)
1	10	9.96	99.6
2	50	49.5	99.0
3	100	100.8	100.8

4. CONCLUSIONS

In summary, we have reported a simple, highly sensitive and selective CT sensor using a screen printed carbon electrode modified with f-MWCNT. Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy was used to characterize the f-MWCNT. The f-MWCNT modified electrode displayed excellent analytical features towards the detection of CT, such as low LOD, high sensitivity, selectivity along with appropriate storage stability. Furthermore, the f-MWCNT showed good practicality for the detection of CT in tap water samples, which authenticates that the fabricated sensor could be used for sensitive and reliable determination of CT in environmental samples.

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