Electrochemical Detection of Quinoline Yellow in Soft Drinks Based on Layer-by-layer Fabricated Multi-Walled Carbon Nanotube

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A novel modified electrode based on multi-walled carbon nanotubes was fabricated by alternatively depositing poly (diallyldimethylammonium chloride) functionalized MWCNT (PDDA-MWCNT) and poly(sodium 4-styrenesulfonate) functionalized MWCNT (PSS-MWCNT) via a solution based layer-by-layer (LbL) self-assembly method followed by calcination, and applied for the electrochemical detection of quinoline yellow. The electrode modification process was monitored by UV-vis spectroscopy which showed the linear growth of the film with the bilayer number. The electrocatalytic activity of MWCNT modified electrode towards oxidation of quinoline yellow was evaluated using cyclic voltammetry and amperometric method. Under the optimal conditions, the oxidation peak current was proportional to quinoline yellow concentration in a wide range between 0.02 and 10 μM, and the detection limit was 0.004 μM (S/N = 3). In addition, the fabricated electrode also displayed excellent reproducibility and stability, and employed to determinate quinoline yellow in soft drinks.

1. INTRODUCTION

Bright, colorful and stable synthetic dyes have been extensively used in foods as food colorants for making foods more attractive and appealing. However, some of these colorants pose a potential risk to human health, especially if they are consumed in excess [1]. Quinoline yellow is one of those synthetic colorants which is widely used in beverage industry [2]. Some reports showed that the quinoline yellow may cause asthma, rashes and hyperactivity [3-5]. Macioszek and Kononowicz also

reported that quinoline yellow may have clastogenic and/or aneugenic and DNA-damaging properties [6]. Therefore, it is necessary to develop a simple and fast method to determine quinoline yellow for food quality control. At present, some methods have been established for detection of quinoline yellow, such as high-performance liquid chromatogramphy (HPLC) [7-10], spectrophotometric method [11, 12], UV-vis detector [13] and spectrofluorometry [14]. However, HPLC requires expensive and complicated instruments, time-consuming pretreatment steps and skilled operators; spectrophotometric method easily suffers from the interference species. In order to avoid these problems, electrochemical method has attracted more attentions due to its sensitivity, accuracy, lower cost and simplicity [15-20]. However, at the present stage, only several papers reported the electrochemically determination of quinoline yellow. Therefore, development of a selective, sensitive and rapid electrochemical sensor for quinoline yellow detection still remains a challenge.

Multi-walled carbon nanotubes (MWCNT) are a new type of nanomaterial offer unique advantages including enhanced electronic properties, a large edge plane/basal plane ratio, and rapid electrode kinetics [21, 22]. Therefore, MWCNT consider as an excellent candidate for electrode surface modification for specific target molecule detection [23-27]. However, the MWCNT tend to aggregation easily which results in poor dispersibility. In order to make it operable in water system, acid treatment and conducting polymers are commonly used for MWCNT surface treatment [28, 29].

In the present work, we report the preparation of MWCNT modified indium tin oxide (ITO) using the layer-by-layer technique and investigate the electrocatalytic performance towards detection of quinoline yellow. The MWCNT/ITO is generated by alternately depositing PDDA-MWCNT and PSS-MWCNT followed by calcination. The electrode modification process is monitored by UV-vis spectroscopy. The result MWCNT/ITO is used for determining quinoline yellow. Several factors affecting the electrocatalytic performances of the proposed quinoline yellow sensor are optimized.

2. EXPERIMENTS

2.1 Chemicals and materials

Poly(diallyl dimethyl ammonium chloride) (PDDA), polyethylenimine (PEI), poly(sodium 4-styrenesulfonate) (PSS), thiourea, urea, cysteine, lysine and quinoline yellow were obtained from Sigma-Aldrich. Multi-walled carbon nanotubes (MWCNT) were purchased from Jiangsu JF Advanced Technologies, Inc. The water used in all experiments was deionized by a Millipore Milli-Q system (resistivity = 18.2 MΩ) and all other chemicals were of analytical grade.

2.2 Synthesis of MWCNT Water Dispersion

20 mg MWCNT was first oxidized in a 40 mL mixture of concentrated nitric acid and sulphuric acid (1:3, v/v) under sonication for 1 h. The resulting solution was centrifuged to remove the acids and washed three times with water. PDDA-MWCNT was prepared by dispersing 10 mg acidulated MWCNT into a 10 mL PDDA solution (10 mg/mL). After sonication for 1 h, the extra PDDA was

removed by centrifugation and wash process. PSS-MWCNT was prepared using a similar procedure except using PSS instead of PDDA.

2.3 Preparation of the modified electrodes

The MWCNT/ITO was fabricated on ITO via the LbL self-assembly technique [30]. First, one precursor bilayer of PEI/PSS was firstly deposited on the ITO to enhance the surface charge density. PEI was adsorbed by immersing ITO into PEI solution (1 mg/mL) for 5 min followed by water washing. Afterwards, the ITO was inserted in a negatively charged PSS solution (1 mg/mL). Then, alternate layers of PDDA-MWCNT and PSS-MWCNT were assembled by immersing the ITO in PDDA-MWCNT dispersion and PSS-MWCNT solution (0.5 mg/mL) for 5 min until the desired number of bilayers was deposited. The multilayer modified ITO was defined as $MWCNT_n$/ITO. The prepared electrode then calcinated in a furnace under 300^oC for 1 h to remove polymers.

2.4 Characterizations

The morphology of as-synthesized electrode was observed using a ZEISS, SUPRA 55 field emission scanning electron microscopy (FESEM) measurements. The UV-vis spectra of the films were obtained by UV-vis spectrophotometer (Perkin Elmer Lambda 950) in the wavelength range from 190 to 800 nm.

2.5 Electrochemical measurement

Electrochemical measurements were performed on a CHI660D electrochemical workstation (USA), using a three electrode system. A MWCNT modified ITO was used as working electrode. A platinum wire was used as the auxiliary electrode and an Ag/AgCl (3M KCl) as the reference electrode. For real sample investigation, the soft drinks were firstly ultrasonicated for 15 min to remove the dissolved gas and filtered to remove solid impurities. The standard addition method was then applied, by adding successive concentrations of quinoline yellow.

3. RESULTS AND DISCUSSION

Figure 1A-C shows the top-view SEM images of $MWCNT_1$/ITO, $MWCNT_2$/ITO and $MWCNT_3$/ITO. It can be observed that the surface coverage increase along with the bilayers of MWCNT. After 6 cycles of LBL self-assembly deposition, the surface of ITO was fully covered with MWCNT. The self-assembly process was monitored by UV-vis spectroscopy after each round of PDDA-MWCNT/PSS-MWCNT bilayer deposition. . Figure 1D displays the spectra of the 6-bilayer MWCNT during its build up on a quartz slide. The absorbance shows a regular increase along with the number of PDDA-MWCNT/PSS-MWCNT bilayer, which confirmed the stepwise deposition process.

Moreover, the two characteristic absorption peaks at 226 and 263 nm are assigned to the absorption of PDDA and PSS on MWCNT, respectively.
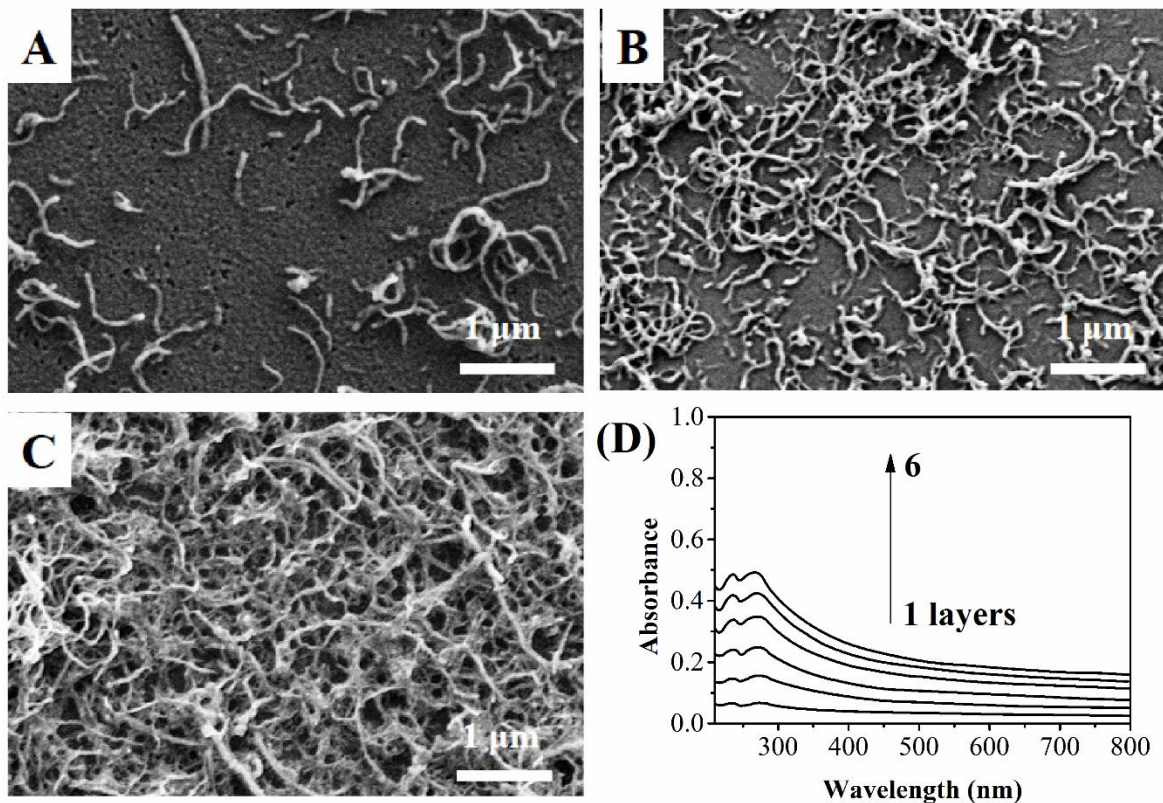

Figure 1. SEM images of (A) MWCNT$_1$/ITO, (B) MWCNT$_2$/ITO and (C) MWCNT$_3$/ITO. (D) UV-vis spectra of MWCNT$_n$/ITO (n=1-6).
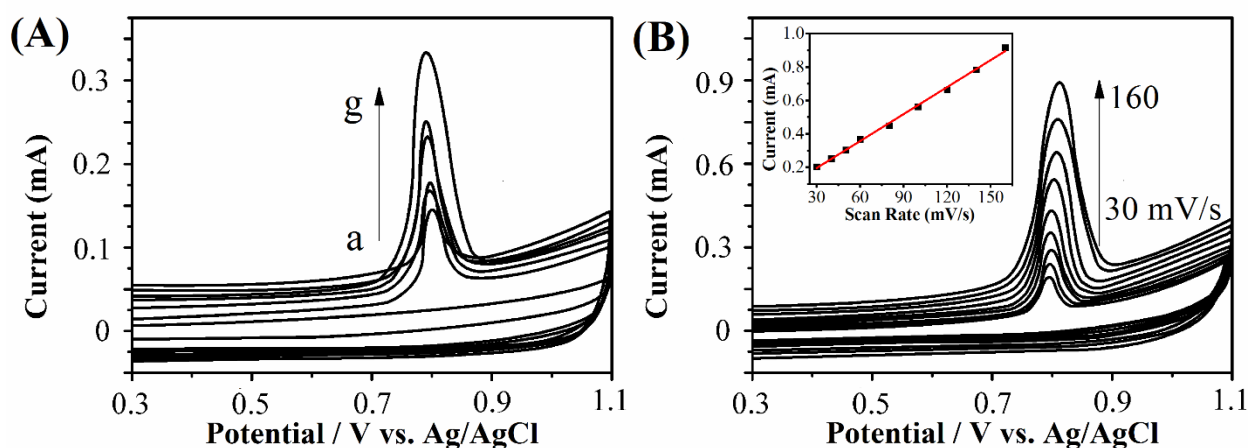

Figure 2. (A) CVs of bare different electrodes in 0.1 M PBS (pH 7.5) containing 10 μM quinoline yellow. (a to g: bare ITO, MWCNT$_1$/ITO MWCNT$_2$/ITO, MWCNT$_6$/ITO, MWCNT$_3$/ITO, MWCNT$_5$/ITO and MWCNT$_4$/ITO). (B) CVs of MWCNT$_4$/ITO in 10 μM quinoline yellow at different scan rates (30, 40, 50, 60, 80, 100, 120, 140 and 160 mV/s). Inset: the plot for the dependence of peak current on scan rate.

The electrochemical behaviours of quinoline yellow on the different electrode were studied using cyclic voltammetry (CV). Figure 2A shows the CVs of bare ITO and different bilayers of MWCNT modified ITOs towards detection of 10 μM quinoline yellow in PBS (pH 7.5) at scan rate of 50 mV/s in the potential range of 0.3−1.1 V. As shown in the figure, the bare ITO represents no distinct current response of quinoline yellow in the investigated potential scanning range (curve a). In contrast, MWCNT modified ITO all show distinct peaks at 0.79 V, corresponding to the electro-oxidation of quinoline yellow and these indicate the MWCNT modification can electrocatalytic oxidation of quinoline yellow and also enhance the electrochemical reaction rate on the electrode surface. By comparing the CV profiles of different number of bilayers of MWCNT modified ITOs, the oxidation peak current increases obviously with increasing bilayer number and reach to the maximum at 4 bilayers. These current increasing is due to the increase of electro-active surface area by increasing amount of MWCNT. Further increasing bilayers to 6 decreases the current response. The possible reason for the current decreasing is due to the adsorption effect. The thicker MWCNT layer on the ITO surface could lead to a longer time for electron transfer [31, 32]. Therefore, MWCNT$_4$/ITO has been chosen for determining quinoline yellow.

The CVs of the quinoline yellow on MWCNT$_4$/ITO at different scan rates are shown in Figure 2B. It is found that the oxidation peak current increases linearly along with the increasing scan rate in the ranged from 30 to 160 mV/s and the linear regression equation can be expressed as I (mA) = 0.03313 + 40.00539v (mV/s), R=0.997, suggesting the oxidation process of quinoline yellow at MWCNT$_4$/ITO is controlled by adsorption. This is in agreement with reported work of others [16, 17, 33].
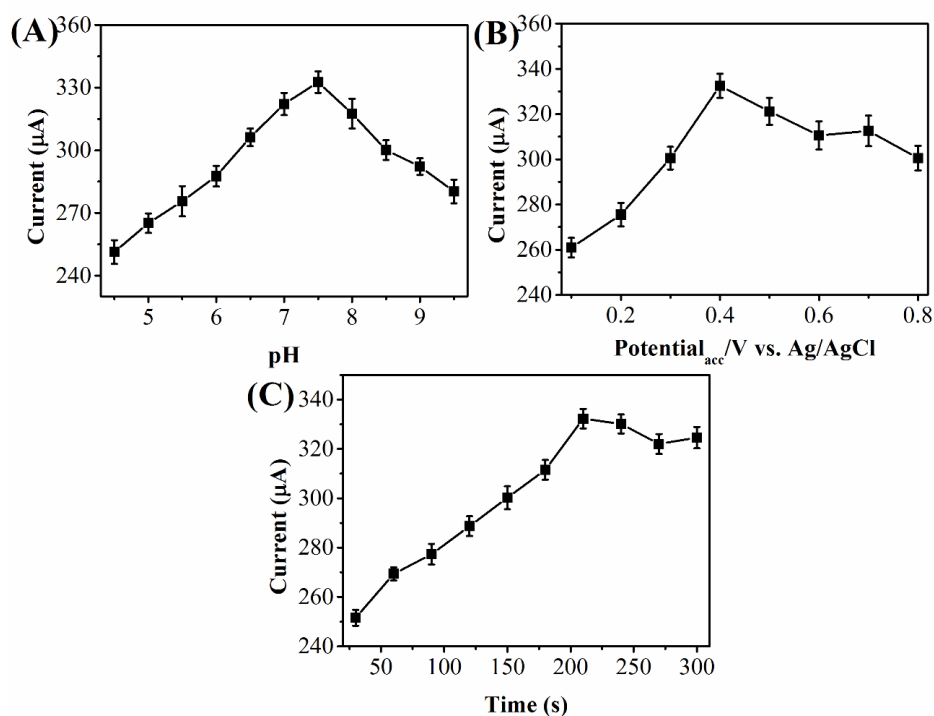

Figure 3. Effect of the (A) pH of PBS, (B) accumulation potential and (C) accumulation time on the current response of 10 μM quinoline yellow at MWCNT$_4$/ITO.

The detection performance of quinoline yellow at different pH values was investigated as well. Figure 3A shows the CVs of oxidation quinoline yellow using MWCNT$_4$/ITO at pH range from 4.5 to 9.5. As shown in Figure 3A, the oxidation peak current of quinoline yellow increases gradually with increasing the pH up to 7.5, and the maximum peak current was obtained at pH 7.5. With further increasing pH, the oxidation peak current conversely decreased. Therefore, pH 7.5 was selected as the optimum pH for the further studies.

Because the oxidation of quinoline yellow at MWCNT$_4$/ITO is controlled by adsorption, accumulation may exert great influence on the analytic sensitivity and the intensity of peak current. Figure 3B-C show the influence of accumulation potential and time toward oxidation peak current. As shown in Figure 3B, the peak current increases gradually with the increasing accumulation potential from 0.1 to 0.4 V and then decrease with further increasing potential. On the other hand, the oxidation peak current increases gradually with the increase of accumulation time from 30 to 200 s and then slowly decrease if a longer accumulation time was applied (Figure 3C). Therefore, the accumulation conditions of 0.4 V and 200 s were used in further measurements.

Potential interference to the oxidation current response of quinoline yellow from many foreign species was investigated using cyclic voltammetry under optimal experimental conditions. Experimental results showed that 100-fold excess of Na$^+$, Zn^{2+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, Cu^{2+}, SO$_4^{2-}$, NO$_3^-$, Cl$^-$ and 50-fold excess of glutamic acid, glucose, ascorbic acid, thiourea, urea, cysteine and lysine did not interfere with the analysis of quinoline yellow (peak current changes are less than ±5%). Therefore, determination of quinoline yellow in our proposed sensor is not affected by the common interferences and the selectivity of the sensor is satisfactory.
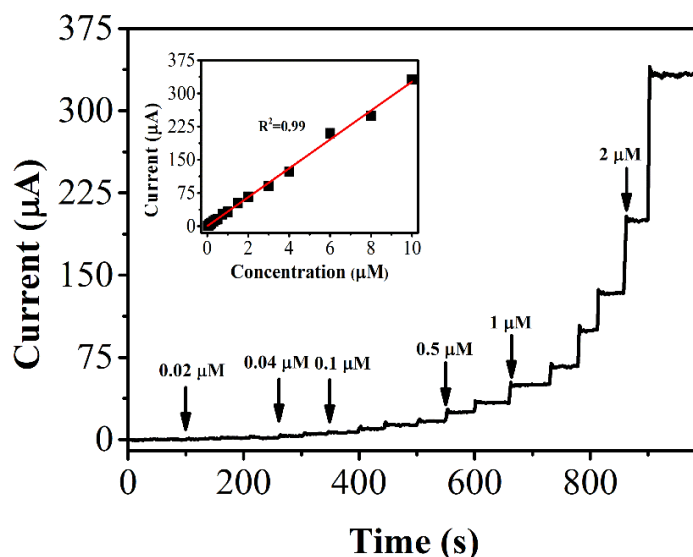

Figure 4. Amperometric response of the MWCNT$_4$/ITO for the successive addition of quinoline yellow. Applied potential: 0.79 V. Inset: the calibration curve for quinoline yellow detection using MWCNT$_4$/ITO.

The relationship between the oxidation peak current and the concentration of quinoline yellow was investigated by amperometric method under optimal experimental conditions. Figure 4 shows the

typical amperometric responses of MWCNT$_4$/ITO towards the successive addition of quinoline yellow. It can be seen that the response current increases rapidly after each addition of quinoline yellow, while returned to the steady-state within 3 s. Such an excellent response performance can be ascribed to the excellent electrocatalytic property and high conductivity of MWCNT. A linear relationship is obtained between the current response and concentration of quinoline yellow (inset of Figure 4). The linear equation can be expressed as: I (μA)= 2.189 + 32.625c (μM), R=0.998 in a concentration range of 0.02 μM to 10 μM and the detection limit was calculated as 0.004 μM based on S/N = 3. Table 1 shows the comparison of analytical performances of this quinoline yellow sensor with other quinoline yellow sensors reported previously.

Table 1. Performance comparison of the MWCNT$_4$/ITO and electrochemical sensors reported by previous reports for quinoline yellow detection.

Electrode	LOD (μM)	Linear range (μM)	Reference
Hanging mercury drop electrode	0.0021	0.0021-0.081	[34]
PVC-based graphite electrode	40	50-100	[15]
Carbon nanotubes/GCE	1.05	1.5-41	[35]
Polyvinylpyrrolidone/GCE	0.027	0.05-1	[17]
Single-walled carbon nanotubes/GCE	0.08	0.8-100	[16]
MWCNT$_4$/ITO	0.004	0.02-10	This work

In order to study the reproducibility of the electrode preparation procedure, six freshly prepared MWCNT$_4$/ITO in PBS containing 10 μM quinoline yellow. The RSD for the between electrode peak currents was calculated to be 4.71 %, suggesting a satisfactory reproducibility of the sensor preparation procedure. The stability of the quinoline yellow sensor was tested by storing the MWCNT$_4$/ITO in 4°C refrigerator for 3 weeks and then the CV was recorded. The results found that the current response remained 97.3% for 10 μM quinoline yellow detection compared with the original test, indicating excellent stability of the MWCNT film on the surface of ITO. The robustness of the proposed quinoline yellow sensor was investigated by studying the effect of small variations in PBS's pH (7.2-7.8), accumulation potential (0.38-0.42 V) and accumulation time (197-203 s) on the recovery of quinoline yellow. The results showed no significant changes of the current response. The recovery for quinoline yellow under variable conditions was in the range of 97.1%-102.6%. Therefore, the MWCNT$_4$/ITO also exhibits very good robustness.

Table 2. Determination of quinoline yellow in soft drinks by standard addition method using MWCNT$_4$/ITO.

Sample	Added (μM)	Found (μM)	Recovery (%)	RSD (%)
1	0	1.35	—	4.25
2	1	2.30	97.87	1.51
3	3	4.55	104.60	3.22
4	6	7.44	101.22	1.62

Table 3. Detection of quinoline yellow in soft drinks using HPLC and MWCNT$_4$/ITO.

Sample	Determined by HPLC (μM)	Determined by MWCNT$_4$/ITO(μM)	Recovery (%)	RSD (%)
1	1.32	1.35	102.27	1.31
2	2.27	2.30	101.32	2.33
3	4.51	4.55	100.89	1.56

The proposed sensor was used for the determination of quinoline yellow in soft drinks. As shown in Table 2, the recovery for the determination of quinoline yellow was in the range of 97.87–104.60%. In order to evaluate the accuracy, the contents of quinoline yellow in soft drinks were also analyzed by HPLC. As shown in Table 3, the results obtained by HPLC and MWCNT$_4$/ITO were in good agreement, confirming the proposed electrochemical sensor is capable for determining quinoline yellow in real samples.

4. CONCLUSION

In summary, a MWCNT modified ITO was successfully fabricated via a LbL self-assembly technique using PDDA-MWCNT and PSS-MWCNT followed by calcination process. The electrochemical property of electrode was altered by changing the bilayers of deposition cycles. Results found that the MWCNT$_4$/ITO has the best electrocatalytic performance towards oxidation of quinoline yellow. The proposed quinoline yellow sensor exhibited a linear response range from 0.02 to 10 μM and a low detection limit of 0.004 μM. In addition, the proposed sensor was successfully employed for deterring the content of quinoline yellow in soft drinks. The accuracy was confirmed by HPLC.

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