Int. J. Electrochem. Sci., 12 **(2017)** 7446 – 7456, doi: 10.20964/2017.08.145

International Journal of
ELECTROCHEMICAL
SCIENCE
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Determination of Non-Steroidal Anti-Inflammatory Drug (NSAID) Azathioprine in Human Blood Serum and Tablet Samples Using Multi-Walled Carbon Nanotubes (MWCNTs) Decorated Manganese Oxide Microcubes Composite Film Modified Electrode

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Received: 10 May 2017 / *Accepted:* 14 June 2017 / *Published:* 12 July 2017

The development of sensor for azathioprine (ATP) determination is extremely important as its excess level in blood imposes carcinogenic threats. A sensitive, selective, reproducible and durable azathioprine sensor was demonstrated using a nanocomposite composed of Mn_3O_4 micro cubes and multi-walled carbon nanotubes (MWCNTs/Mn_3O_4 MCs). The composite was prepared through a facile hydrothermal method and its morphology, elemental, impedance and electrochemical properties were studied. The MWCNTs/Mn_3O_4 MCs was modified on the screen-printed electrode, and the resulting modified electrode displayed excellent electrocatalytic ability towards ATP and the reduction peak current was related to the concentration of ATP. The working range was 0.045-2530 µM and the detection limit was 4.3 nM (± 2.53). The method was successfully applied to the determination of ATP in spiked samples of human blood serum and tablets.

Keywords: Analytical Science; Multi-walled carbon nanotubes; Hybrid materials; Manganese oxide; Modified electrode; Signal amplification; Biochemistry.

1. INTRODUCTION

Manganese oxide (MnO_x) based nanocomposites have been reported to exhibit prominent electrochemical properties and they were extensively applied in supercapacitors [1], batteries [2] and sensors. MnOx materials are low cost, abundant on earth crust and highly stable [3]. MnOx can be prepared in wide range of shapes such as, needles, tubes, particles, plates and wires in a multi-valent states like MnO, Mn_2O_3, MnO_2, Mn_3O_4 and MnOOH [4]. Recent years seen steady interest in the preparation of Mn_3O_4 incorporated graphene composites mainly for energy applications [5-7]; Mn_3O_4 nanoparticles/reduced graphene oxide (RGO) [8], graphene oxide (GO)-Polymer-Mn_3O_4 hybrid [9], N-doped RGO/Mn_3O_4 nanoparticles [10]. Virtually, all reports focused on energy applications; nonetheless, MWCNTs/Mn_3O_4 microcubes (MCs) based composite has never been explored in electrochemical sensing applications. In recent years, many analytical methods have been developed for the ATP determination like, gas chromatography (GC) [11], high performance liquid chromatography (HPLC) [12], spectrophotometry [13], flow injection analysis [14], capillary zone electrophoresis [15], and chemiluminescence [16]. Although, these methods are highly sensitive but it is not convenient in practical use because they are very expensive, tedious, time consuming and required pretreatment of sample preparation. Contrary, the electrochemical methods used for an alternative detection method due to the advantages especially easy to use, selective method, less time consuming, cost effective and applicability [17-19]. Eventhough, an unmodified bare screen printed carbon electrodes (SPCE) exhibit low sensitivity and high overpotential towards ATP determination. Therefore, the chemically modified electrode is more preferable and important to the detection of ATP. Recently, MWCNTs based nanocomposite modified SPCE used for the electro chemical detection of ATP due to the inherent redox activity.

Our research group is continuously developing MWCNTs-based composites for sensing applications [20-22]. Herein, we have explored the preparation of electrochemically active Mn_3O_4 micro cubes networks embedded in MWCNTs as a composite and employed it in ATP sensing (**figure 1**). The preparation of the MWCNTs/Mn_3O_4 MCs hybrid composite is simple, reproducible, does not require any hazardous reducing agents. The MWCNTs/Mn_3O_4 MCs film modified screen-printed carbon electrode (SPCE) exhibited large electrochemical active area, excellent electrocatalytic ability and offered outstanding sensing characteristics, which are superior over existing methods.

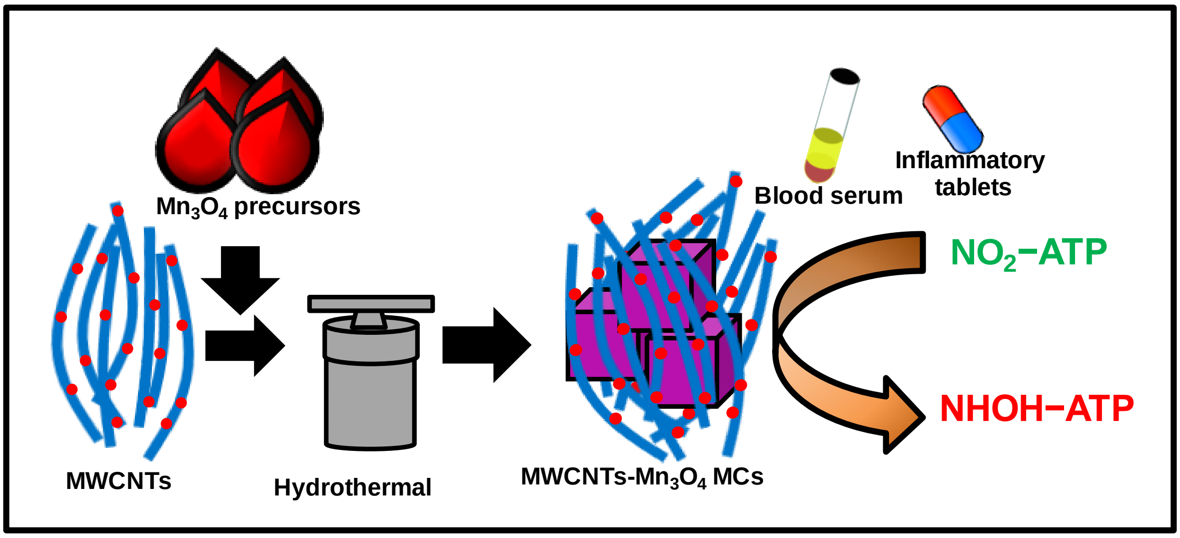

Figure 1. synthesis of MWCNTs/Mn_3O_4 MCs for the determination of ATP in human blood serum and tablet samples

2. EXPERIMENTAL

2.1 Materials and Instrumentation

Multiwall carbon nanotube (MWCNT) (powder, <20 µm), manganese(II) sulfate mono hydrate ($MnSO_4{\cdot}H_2O$), thiourea ($CS(NH_2)_2$) and azathioprine tablet (50mg) were purchased from Sigma-Aldrich (http://www.sigmaaldrich.com/taiwan.html) and used as received. The SPCEs were purchased from Zensor R&D Co., Ltd., Taipei, Taiwan (http://www.zensor.com.tw/index_en.html). All the reagents used were of analytical grade and used without any further purification. The supporting electrolyte used for the electrochemical studies was 0.1 M phosphate buffer (PB), prepared using Na_2HPO_4 and NaH_2PO_4 and the pH was adjusted either using H_2SO_4 or NaOH. Prior to each experiment, the electrolyte solutions were deoxygenated with pre-purified nitrogen gas for 15 min unless otherwise specified. All assays were performed in triplicate, and the results reported are the average of at least three experiments. The error is calculated from standard deviation of these three readings.

The electrochemical measurements were performed using CHI 1205A workstation. The electrochemical studies were carried out in a conventional three-electrode cell using BAS SPCE as a working electrode (area 0.2 cm^2), saturated Ag/AgCl as a reference electrode and Pt wire as a counter electrode. Amperometric measurements were performed with analytical rotator AFMSRX (PINE instruments, USA) with a rotating disc electrode (RDE) having working area of 0.24 cm^2. Scanning electron microscopy (SEM) studies were performed with Hitachi S-3000 H scanning electron microscope. Energy-dispersive X-ray (EDX) spectra was recorded using HORIBA EMAX X-ACT (Sensor + 24V=16 W, resolution at 5.9 keV). EIM6ex Zahner (Kronach, Germany) was used for electrochemical impedance spectroscopy (EIS) studies. Human serum were acquired from Chang Gung University, Taiwan and the experimental protocols were approved by the institutional Animal Ethic Committee.

2.2 Synthesis of MWCNTs/Mn_3O_4 MCs and fabrication of modified electrode

Starting from Multi wall carbon nanotubes 40mg was taken, to this thiourea (3 g) and $MnSO_4{\cdot}H_2O$ (0.01 M) were prepared separately in 40 mL water via magnetic stirring followed by ultrasonication for 15 min. Next, the $MnSO_4$ solution was slowly added dropwise into thiourea solution. The obtained mixture was stirred for 30 min to acquire a homogeneous solution and the resulting solution was transferred to a teflon–lined stainless steel autoclave and heated at 180°C for 10 h. After hydrothermal treatment, the resulting product was collected and washed with ethanol, and then dried at 40^{o}C. Then the solid was transferred to a tube furnace and heated to 400^{o}C for 2 h at a heating rate of 2^{o}C min^{-1}. Finally, the product MWCNTs/Mn_3O_4 MCs was collected. To ensure sufficient interfacial self-assembly of negatively charged MWCNT sheets on the positively charged Mn_3O_4 MCs through electrostatic interaction, thus yielding stable MWCNTs/Mn_3O_4 MCs composite. The surface of SPCE was pre-cleaned by cycling between −1.0 V and 1.2 V (vs. Ag/AgCl), in 0.1 M PB (pH 7). Next, 8 µl MWCNTs/Mn_3O_4 MCs was dropped at SPCE and dried at room temperature. As control, MWCNTs modified SPCEs were prepared.

3. RESULTS AND DISCUSSION

3.1 Surface morphological and elemental characterization

Figure 2 shows the SEM image of (A) MWCNTs, and (B) MWCNTs/Mn_3O_4 MCs. The morphological structure of MWCNTs shows a high surface. Moreover, the SEM image of MWCNTs/Mn_3O_4 MCs exhibited randomly aggregated with distinct edges and folding MWCNTs surfaces [23]. The SEM image of Mn_3O_4 MCs reveal cubic structure [24]. Besides, the SEM image of MWCNTs/Mn_3O_4 MCs shows the Mn_3O_4 MCs incorporated with the MWCNTs surface [25, 26]. MWCNTS decorated Mn_3O_4 MCs is conformed from the SEM image (B). The EDX spectra of (C) MWCNTs/Mn_3O_4 MCs shows the signal for carbon (C), oxygen (O), and manganese (Mn). The quantitative analysis shows weight of Carbon 39 %, oxygen 26 %, and manganese 25 %. Hence, the EDX spectra confirm the formation of MWCNTs/Mn_3O_4 MCs nanocomposite and finalized the composition of the elements.

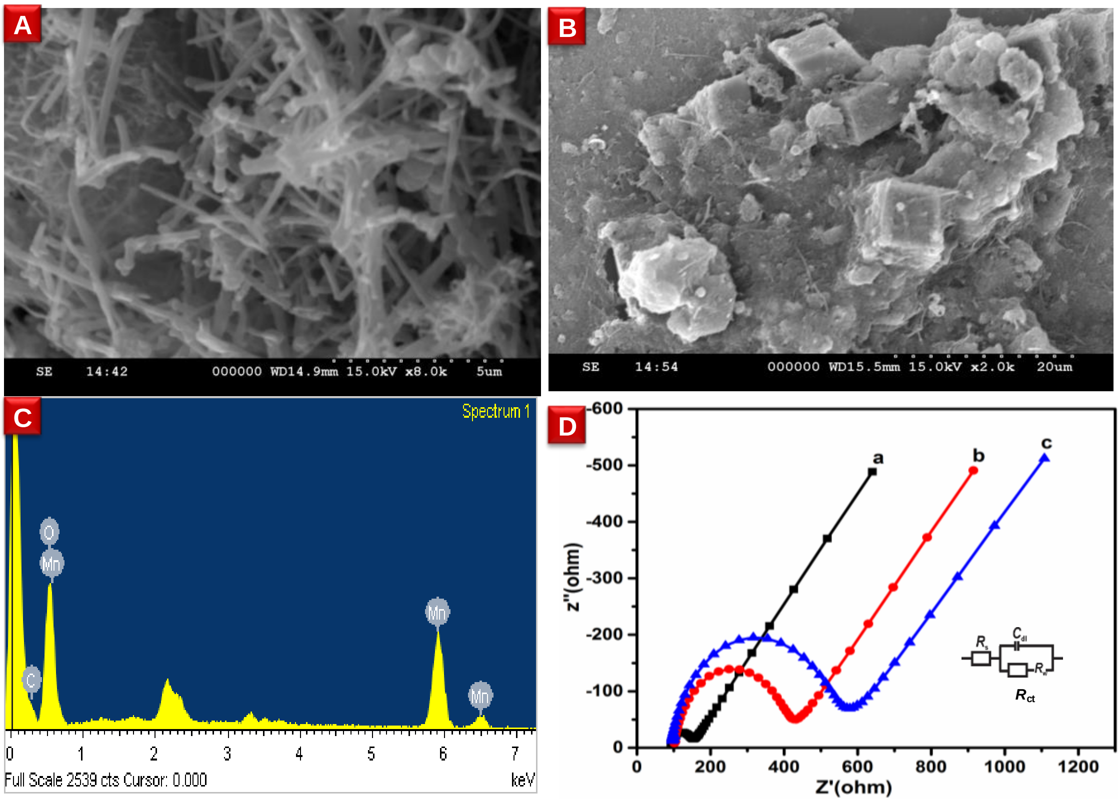

Figure 2. (A) SEM images of, MWCNTs and (B) MWCNT/Mn_3O_4 MCs. (C) EDX profile of MWCNT/Mn_3O_4 MCs. (D) EIS curves of SPCE (a), MWCNTs/SPCE (b) and MWCNT/Mn_3O_4 MCs/SPCE (c) obtained in 0.1 M KCl containing 5 mM $Fe(CN)_6^{3-/4-}$. Inset shows the randles equivalent circuit model used to fit the EIS experimental data.

3.2 Electrochemical impedance spectroscopy

The electrochemical impedance spectroscopy (EIS) has been used to monitor the electrochemical impedance changes of the different modified electrodes at the electrode and electrolyte interface. Figure. 2D shows the EIS plots of (a) bare SPCE, (b) MWCNTs, (c) MWCNTs/Mn_3O_4 MCs in 5 mM $[Fe(CN)_6]^{-3/-4}$ with 0.1 M KCl as a supporting electrolyte. Figure. 2 inset shows the randles equivalent circuit model used to fit the EIS experimental data. The charge transfers resistance (R_{ct}) of the modified electrode is corresponds to the diameter of the semi-circle in the Nyquist plot [27-29]. All the modified electrode exhibited semi circles of different diameters illustrate different R_{ct} . The higher R_{ct} value of about 497 Ω was obtained for the SPCE electrode. The MWCNTs and MWCNTs/Mn_3O_4 MCs show the R_{ct} values of 328 Ω and 68.5 Ω, respectively. However, the R_{ct} value of the MWCNTs/Mn_3O_4 MCs/SPCE was about 68.5 Ω, which proposed that the charge transfer resistance of manganese oxide was decreased due to the non-covalent interaction with MWCNTs [30-32]. Moreover, the MWCNTs enhance the electron conductivity properties at the electrode surface. The EIS results confirmed that the MWCNTs/Mn_3O_4 MCs/SPCE have higher electron conductivity properties with low charge transfer resistance than that of the other modified electrodes [33-35].

3.3 Electro catalysis of azathioprine

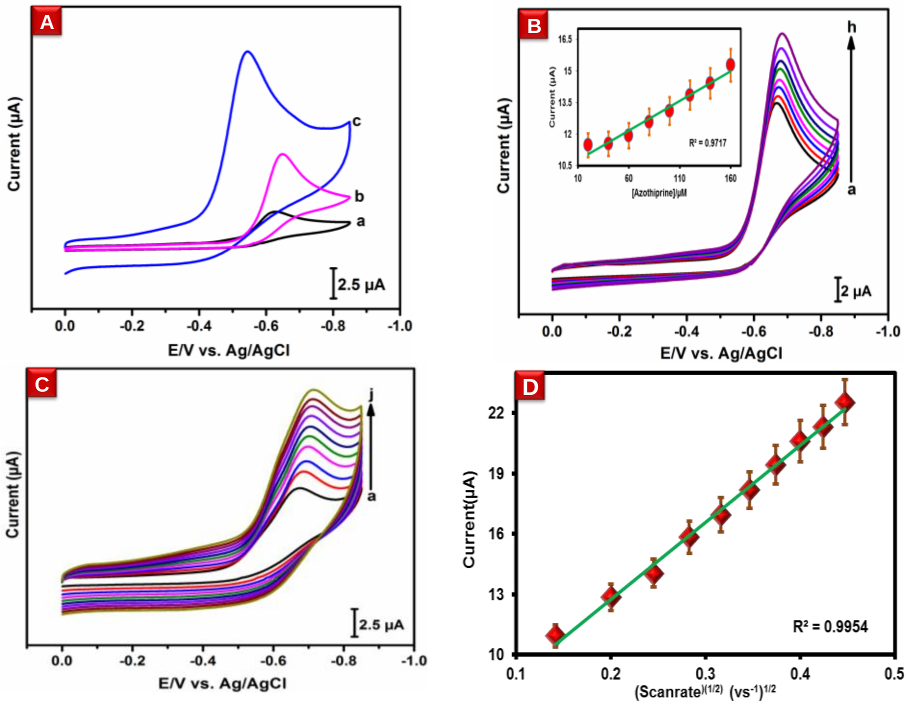

Figure 3. (A) CVs obtained at bare SPCE (a), MWCNTs (b), and MWCNT/Mn_3O_4 MCs (c) films modified SPCEs in 0.1 M buffer (pH 7) containing 5 μM ATP at scan rate of 5 mV s^{-1}**.** (B) Cyclic voltammograms obtained at MWCNT/Mn_3O_4 MCs/SPCE in 0.1 M PB (pH 7) containing ATP (a to h; 20 to 160 μM). Inset [ATP]/μM vs. current/μA. (C) Cyclic voltammograms obtained at MWCNT/Mn_3O_4 MCs/SPCE in 0.1 M buffer (pH 7) containing 5 μM ATP at different scan rates (a to j; 20 to 200 mVs^{-1}). (D) (scan rate)$^{1/2}$ $(V.s^{-1})^{1/2}$ vs. peak currents (μA).

Electrocatalytic ability of the MWCNT/Mn_3O_4 MCs/SPCE towards ATP (10 µM) reduction was investigated in phosphate buffer (pH 7) and the corresponding voltammogram is given as Figure. 3A. The first forward segment of the voltammogram displays a sharp cathodic peak at –0.56 V, which is manifested to the reduction of NO_2–ATP to NHOH–ATP [36-38]. This type of electrocatalytic behavior is consistent with the previous reported ATP sensor. The cathodic peak current is responsible for the reduction of NO_2–ATP to NHOH–ATP and compared with control electrodes. Figure 3A shows, the comparison with control electrodes (a) bare SPCE, and (b) MWCNTs/SPCE. The (c) MWCNT/Mn_3O_4 MCs modified electrode have shown significantly enhanced reduction peak current which is considerable higher than that of bare SPCE, and Mn_3O_4 MCs/SPCE. The overpotential observed at MWCNT/Mn_3O_4 MCs nanocomposite modified electrode is 110 mV, and 124 mV lower than the bare SPCE, and MWCNTs/SPCE. Also, the nanocomposite provides largely exposed electrochemically active area and synergic effect of MWCNTs and Mn_3O_4 MCs. The electrocatalytic activity enhanced due to the absorption of ATP through π- π stacking interaction between the benzene ring of ATP and π bonds of MWCNTs [39-41].

Figure 3B, displays the voltammograms obtained at MWCNTs/Mn_3O_4 MCs/SPCE towards different concentrations of ATP. The reduction peak current linearly increases with respect to different concentration ATP. Insert, exhibit the linear relation between the reduction peak current and concentration of ATP is exhibited. The effect of scan rate on the electrocatalytic behavior of ATP reduction at MWCNT/Mn_3O_4 MCs/SPCE modified electrode was investigated by varying the different scan rate from 20 to 200 mVs^{-1} Figure 3C. The reduction peak current was increased linearly with increasing the scan rates. Figure 3D, shows the linear relation between the cathodic peak current and scan rates with the corresponding linear regression equation is I_c (µA) = 0.096 ν (mVs^{-1}) + 13.61 (R^2 = 0.9954). Hence, this phenomenon indicates that the ATP reduction at MWCNT/Mn_3O_4 MCs composite modified SPCE. Which is exhibit the characteristic behavior of surface confined diffusion controlled electrocatalytic process at the modified electrode [36, 42, 43] .

3.4 Amperometric determination of ATP

Amperometric method is high precision and more sensitive method than that of the other voltammetric methods. Figure 4A shows the amperometric response of MWCNT/Mn_3O_4 MCs modified rotating electrode upon each successive addition of various concentrations of ATP into continuously stirred PB at the rotation speed 1200 RPM and the applied potential was held at -0.55 V. The amperometric sensor exhibited sharp amperometric response for each addition of ATP with regular time intreval (50s). The steady state current response of the ATP is reached within 4 sec at MWCNT/Mn_3O_4 MCs nanocomposite modified electrode, it is indicating that fast response of the reduction of ATP. The Figure 4B shows the calibration plot between the ATP concentration and amperometric current response. The linear plot displayed good linearity with slope of 0.9962 µA $µM^{-1}$. The working concentration range was linear from 0.045-2530 µM with sensitivity of 2.05 µA $µM^{-1}$ cm^{-2} and the detection limit is 4.3 nM. This indicates the outstanding electrocatalytic reduction of ATP at the MWCNTs/Mn_3O_4 MCs composite modified electrode. In addition, based on the above results

MWCNTs play a vital role in the reduction of ATP due to electron-rich environment, higher electron transfer nature and well reduction properties. In addition, the high surface area of Mn_3O_4 MCs used to provide more active surface for an interaction with MWCNTs. Therefore, the MWCNsT/Mn_3O_4 MCs composite play a significant role for the selective detection of ATP. The important parameters of sensor, such as LOD and linear range were compared with previously reported modified electrodes and shown in Table 1. The analytical performance of the MWCNTs/Mn_3O_4 MCs modified electrode is better than previously reported sensor electrodes.

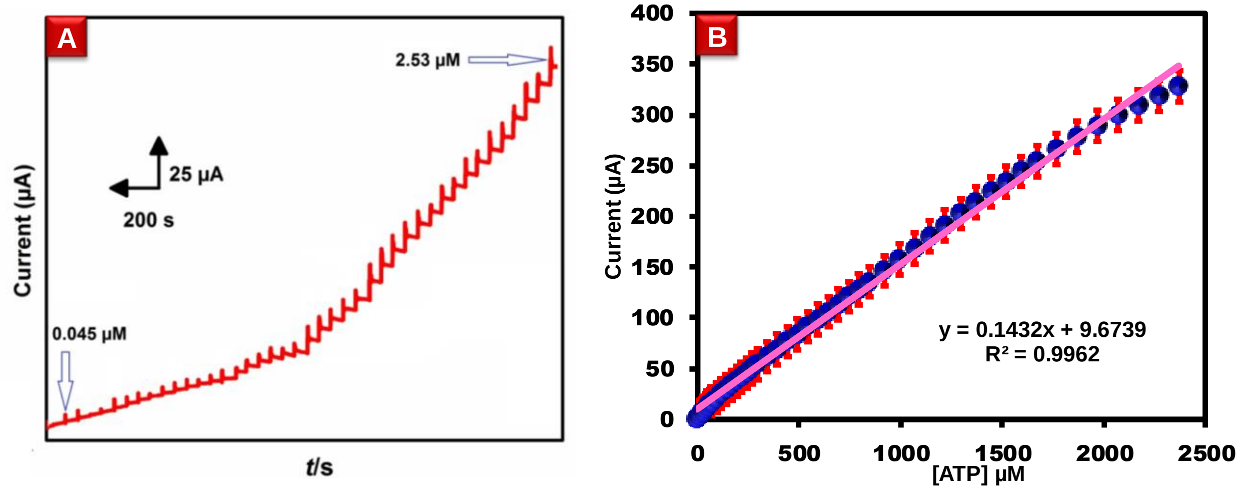

Figure 4. (A) Amperometric response of MWCNT/Mn_3O_4 MCs film modified electrode for each sequential additions of ATP into 0.1 M PB (pH 7). The rotation speed = 1200 RPM. (B) Plot of [ATP]/μM vs. current (μA). E_{app}= - 0.55 V (vs. Ag/AgCl).

Table 1. Comparison of analytical parameters for the determination of ATP at MWCNTs/Mn_3O_4 **MCs** film modified electrode with reported works

Electrode	Linear range (μM)	LOD (μM)	Electrolyte	Methods	Ref.
[a]Ag NPs@Graphene/[b]PGE	0.1–100	0.068	PB (pH 6)	Cyclic voltammetry	[38]
Au/Au-[c]NA electrode	0.095–900	0.027	PB (pH 7.4)	Differential pulse voltammetry	[44]
[d]NDG/[e]CS/[j]GCE	0.2–100M	0.065	PB (pH 7)	Cyclic voltammetry	[36]
[f]MIP-[g]SPE	0.01–2.5	0.08	–	Solid-phase extraction	[45]
[h]CNP/[i]N/[j]GCE	0.2–50	0.08	PB (pH 6)	Cyclic voltammetry	[37]
MWCNTs/Mn_3O_4Mcs/SPCE	0.45–2530		PB (pH 7)	Amperometry	This work

[a]AgNPs= silver nano particle, [b]PGE= Pyrolytic graphite electrode, [c]NA= Nano array, [d]NDG= Nano diamond graphite, [e]CS=chitosan, [f]MIP=Nano- molecule imprinted polymers, [g]SPE= solid phase extraction [h]CNP= Carbon nano particle, [i]N= Nafion, [j]GCE= Glassy carbon electrode.

3.5 Selectivity, stability, repeatability and reproducibility studies

Selectivity of the MWCNTs/Mn_3O_4 MCs modified electrode is more important to the detection of (a) ATP in presence of common interferrants analysts (Figure 4). The tested interferrants are acetaminophen, buspirone, Cetirizine, hydroxyzine, dopamine, amitriptyline, alprazolam, amlodipine, atorvastatin, and nimesulide. As shown in the selectivity studies, the modified electrode has delivered excellent current response to ATP, eventhough it shows negligible response to other interferrants analyte. The possible reason for the selectivity is different redox potentials and different adsorption sites on the surface of MWCNTs/Mn_3O_4 MCs modified electrode. While the adsorption of ATP could be significantly higher than that of the other interfering species. In order to determine storage stability of the MWCNTs/Mn_3O_4 MCs modified electrdoe in presence of 5 µM ATP was monitored every day. The electrode delivered good consistent amperometric response to ATP during two weeks of storage period. About 97.14% of initial response current was retained after two weeks of its use, which is indicating the acceptable stability of the modified electrode. Moreover, the repeatability and reproducibility of the modified electrode were tested. The MWCNTs/Mn_3O_4 MCs modified electrode exhibits appreciable repeatability with RSD of 4.87% for five repeatitive measurements using single modified electrode. On the otherhand, the electrode exhibits good reproducibility with RSD of 5.77% for five independent measurments carried out in five independent modified electrodes. Therefore, the modified electrdoe have well selectivity, stability, repeatability and reproducibility studies.

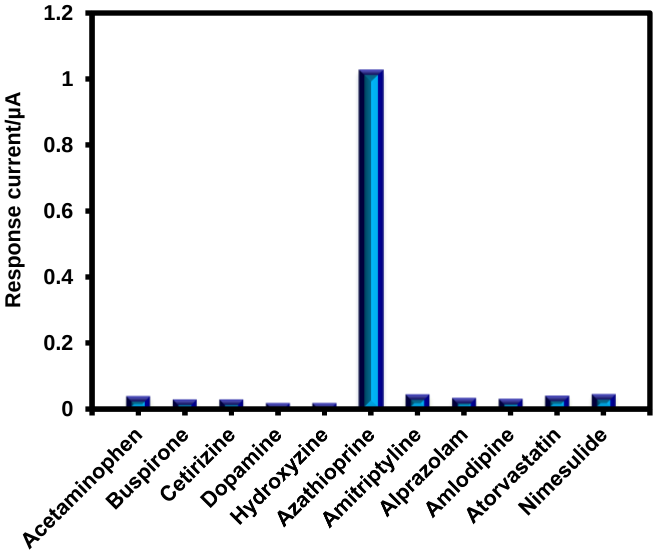

Figure 5. Amperometric response of MWCNTs/Mn_3O_4 MCs film modified electrode for additions of ATP and interferrants analysts into 0.1 M PB (pH 7). The rotation speed = 1200 RPM.

3.6 Real sample analysis

The practical feasibility of the method was demonstrated in human serum and rat brain serum samples. the human serum was spiked with known amounts of ATP and amperometry was performed (Table 2). First, 3 ml serum sample was diluted to 10 ml by adding phosphate buffer (pH 7). Next, amperometry experiments were carried out using MWCNTs/Mn_3O_4 MCs and following similar optimized experimental conditions. The found and recovery values are in acceptable range. Hence, the MWCNTs/Mn_3O_4 MCs could be applicable for the real-time ATP sensing applications.

Table 1. Real-time determination of ATP in human serum and ATP tablet samples using MWCNTs/Mn_3O_4 MCs film modified electrode

Samples	Added/µM	Found/µM	Recovery/%	*RSD/%
Human serum	10 µM	10.31 µM	103.1	3.63
ATP Tablets	20 µM	20.32 µM	103.6	3.48

* Relative Standard Deviation of 3 individual measurements

4. CONCLUSIONS

A highly sensitive, selective, stable, reproducible and durable nitrite sensor was demonstrated using a robust nanocomposite, MWCNTs/Mn_3O_4 MCs. The nanocomposite was prepared via facile hydrothermal method and its successful formation was revealed by SEM, EDX, mapping, EIS and electrochemical methods. The MWCNTs/Mn_3O_4 MCs/SPCE showed outstanding electrocatalytic ability towards ATP reduction and the sensor performance was either superior or comparable to the previous works. The assay procedure was simple, fast, and reproducible. The method was successful in the determination of ATP spiked in human serum and ATP tablet samples, thus holds great potential in health safety and biological analysis.

ACKNOWLEDGEMENT

This work was supported by the National Science Council and the Ministry of Education of Taiwan (Republic of China) and National Taipei University of Technology, Taipei, Taiwan.

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