

ABSTRACT

This work reports on the synthesis of antimony oxide nanoparticles by hydrothermal method, acid treatment of multi-walled carbon nanotubes, and synthesis of MWCNT-AONP nanocomposite modified on screen-printed carbon electrode towards detection of serotonin in tomatoes. The synthesized nanomaterials were all characterized with x-ray diffraction (XRD) spectroscopy, scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, ultraviolet-visible (UV-vis) spectroscopy, and transmission electron microscopy (TEM). The electrochemical experiments were performed utilizing square wave voltammetry (SWV), and cyclic voltammetry (CV) methods. The SPCE-MWCNT-AONP modified electrodes showed better electron transport and improved current response towards detection of 5-HT when compared to other electrodes studied. The sensitivity, limit of detection (LoD) and limit of quantification (LoQ) at the SPCE-MWCNT-AONP modified electrode towards 5-HT detection was 0.2863 $\mu\text{A}/\mu\text{M}$, 24.6 nM, and 74 nM respectively, with linearity from 0.016 to 0.166 μM ($R^2 = 0.9851$) utilizing SWV. Furthermore, the proposed sensor showed good reproducibility and excellent anti-interference behavior. Real-sample analysis of 5-HT in tomatoes showed excellent recoveries ranging from 91.32 to 108.28%, with an average RSD (%) value of 2.57 ($n = 3$).

Keywords: Serotonin, Multi-walled carbon nanotube, Antimony oxide nanoparticle, Cyclic voltammetry, Electrochemical

INTRODUCTION

Neurotransmitters (NTs) are important endogenous chemical messengers that monitor and facilitate communication between nerve cells and the entire body [1]. Serotonin (5-HT) is a monoamine NTs involved in regulating body temperature, mood, muscular contraction, bowel motility, bladder control, and endocrine regulation, etc [2]. However, abnormal levels of 5-HT in the body have been reported to cause insomnia, migraine, anxiety, schizophrenia, bipolar disorder, and unexpected infant mortality [2,3]. Therefore, monitoring and evaluation of these NTs in the body is of great importance. Due to its medical, chemical, and pharmaceutical importance, techniques such as electrochemical (voltammetry), sol-gel, capillary electrophoresis (CE), high-pressure liquid chromatography (HPLC), High-pressure liquid chromatography (HPLC) with colorimetry, and mass spectrometry (MS) have been carried out to detect 5-HT in bodily fluids [4-7]. From listed techniques, only electrochemical techniques have seen growth in their popularity towards detecting 5-HT. Electrochemical techniques are found to be highly sensitive, simple, time-saving, offer rapid analysis, and increase the sensing ability of NTs inside living entities [8]. Carbon nanotubes (CNTs)-metal oxide nanoparticles (MONPs) nanocomposites have been extensively used towards the detection of monoamine NTs, due to the synergistic effect between the two materials. MWCNTs have unique mechanical, structural and electronic properties, enabling ease of electron transfer [9]. Acid treatment of CNTs helps eliminate end caps, which generates defect sites and attaches oxygen functional group alleged to assist with adsorption and electron transfer [10]. Antimony oxide nanoparticles (AONPs) have a higher refractive index, higher abrasive resistance, higher proton conductivity, outstanding mechanical strength and higher absorbability [11].

MATERIALS AND METHODS

The chemicals listed below were acquired and used as the manufacturers delivered them. Sigma Aldrich (USA) provided antimony trichloride (99%) (SbCl_3), MWCNTs (O.D. $\times$ L.D. $\times$ L $10 \text{ nm} \times 1 \text{ mm} \times 4.5 \text{ nm} \times 0.5 \text{ nm} \times 3-6 \mu\text{m}$) (98%), serotonin hydrochloride powder ($\geq 98\%$), ascorbic acid (99.5%), sodium hydroxide (98%) (NaOH), hydrochloric acid (32%) (HCL), and N, N-dimethylformamide (99%) ($\text{C}_4\text{H}_9\text{NO}$). Toluene was acquired from the SA-ARCHEM Pty Ltd (RSA) (99%). Distilled water was utilized throughout to prepare chemicals. The Dropview 8400 software programme from Metrohm DropSens Pty Ltd (RSA) was used to conduct electrochemical experiments at $25 \pm 1^\circ\text{C}$. A PBS buffer (pH 7) solution was used as a supporting electrolyte throughout the experiment. Ultraviolet-visible (UV-vis) spectroscopy was acquired from Agilent technology, Cary series, Fourier transform infrared (FTIR) spectroscopy from Agilent technology, Cary 600 series, USA, x-ray diffraction (XRD) spectroscopy from Bruker-AXS, Madison, USA, transmission electron microscopy (TEM), and scanning electron microscopy (SEM) were used to characterize all prepared nanomaterials, AONPs, f-MWCNTs, and MWCNT-AONP nanocomposite.

EXPERIMENT

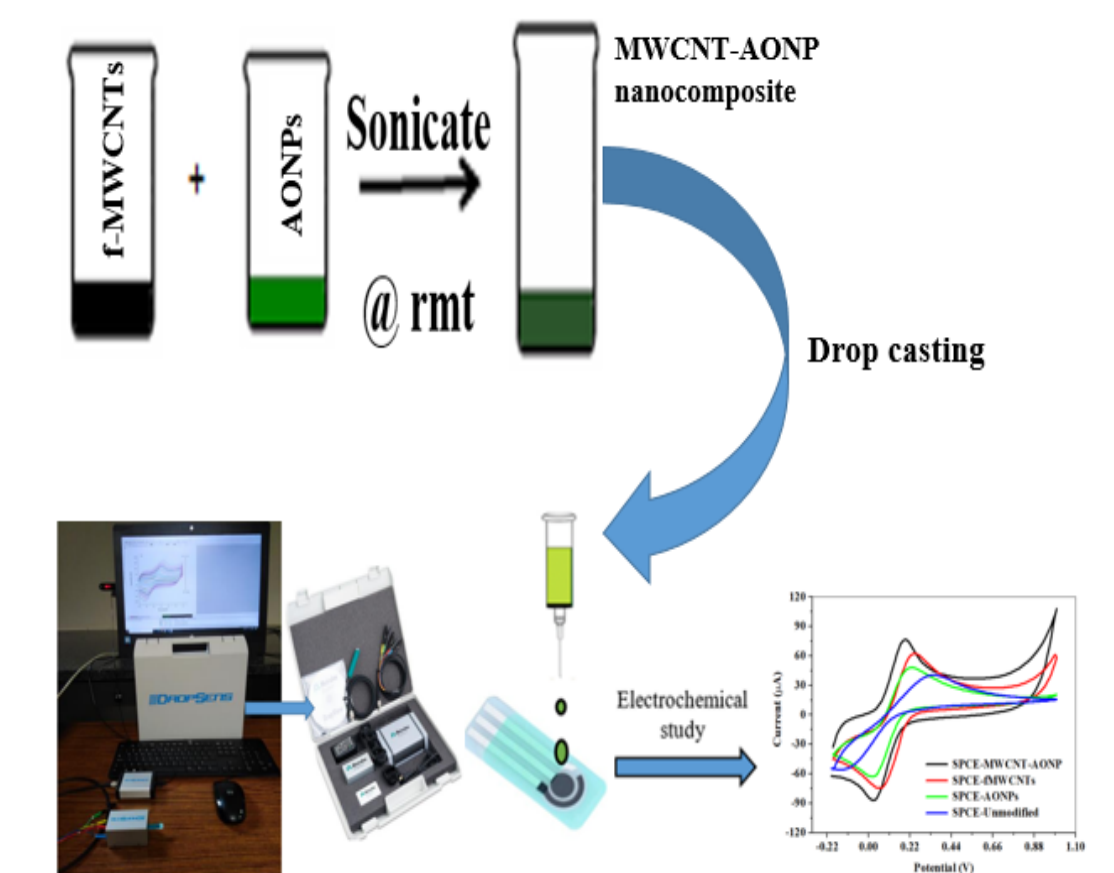


Fig. 7. SWV curves in (a) 1 mM AA and various concentration of 5-HT (100 – 545 μM) produced in 0.1M PBS (pH 7) buffer solution, and (b) corresponding linear calibration plot.

Real-sample analysis

Table 1: Detection of 5-HT in tomatoes

Sample	Added (μM)	Detected (μM)	Recovery (%)	RSD (%)
Tomatoes	400	433.11	108.28	3.20
	600	547.92	91.32	2.60
	900	923.66	102.63	1.90

$n = 3$; RDS (%) = 2.57

RESULTS

Spectroscopic characterization

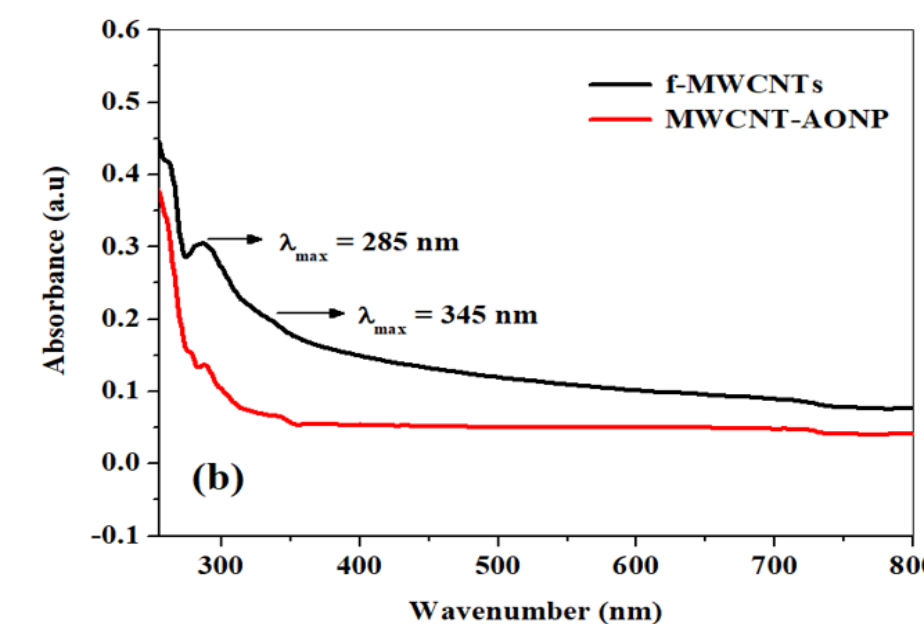


Fig. 1: UV-vis spectra of f-MWCNTs and MWCNT-AONP nanocomposites

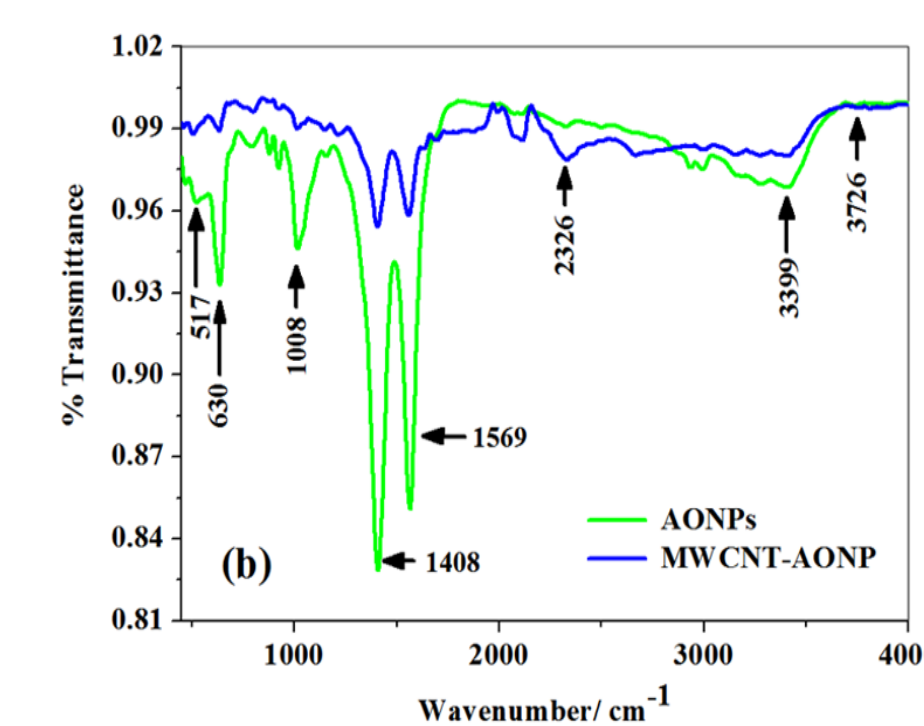


Fig. 2: FTIR spectra of AONPs and AONP-MWCNT nanocomposites.

Electrochemical characterization

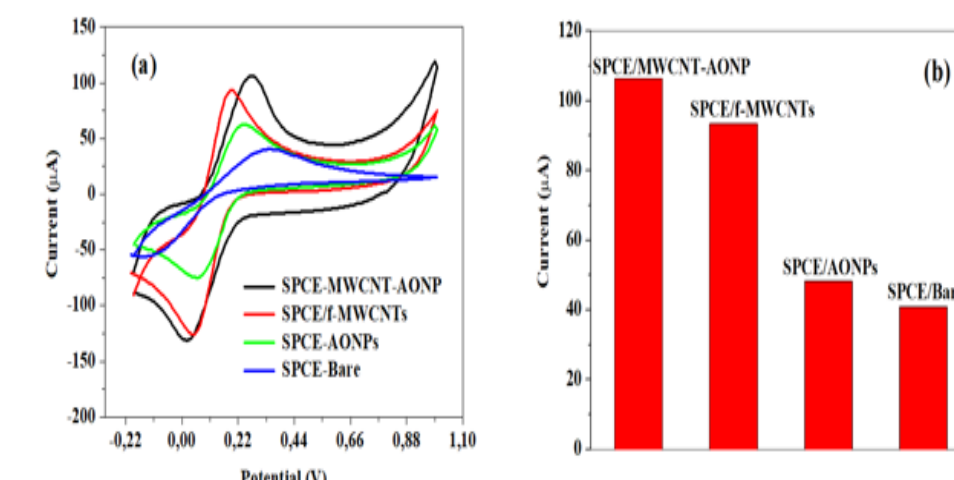


Fig. 5: (a) Cyclic voltammograms for modified electrodes in 5 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ solution prepared in 0.1 M PBS (pH 7) at a scan rate of 25 mVs^{-1} (b) comparative current response between electrodes.

Interference study

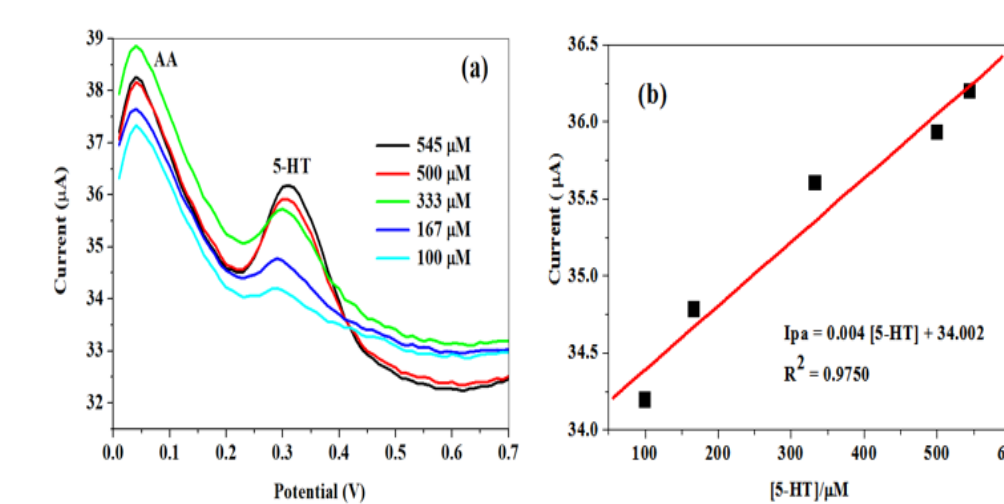


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RESULTS - CON'T

Morphological characterization

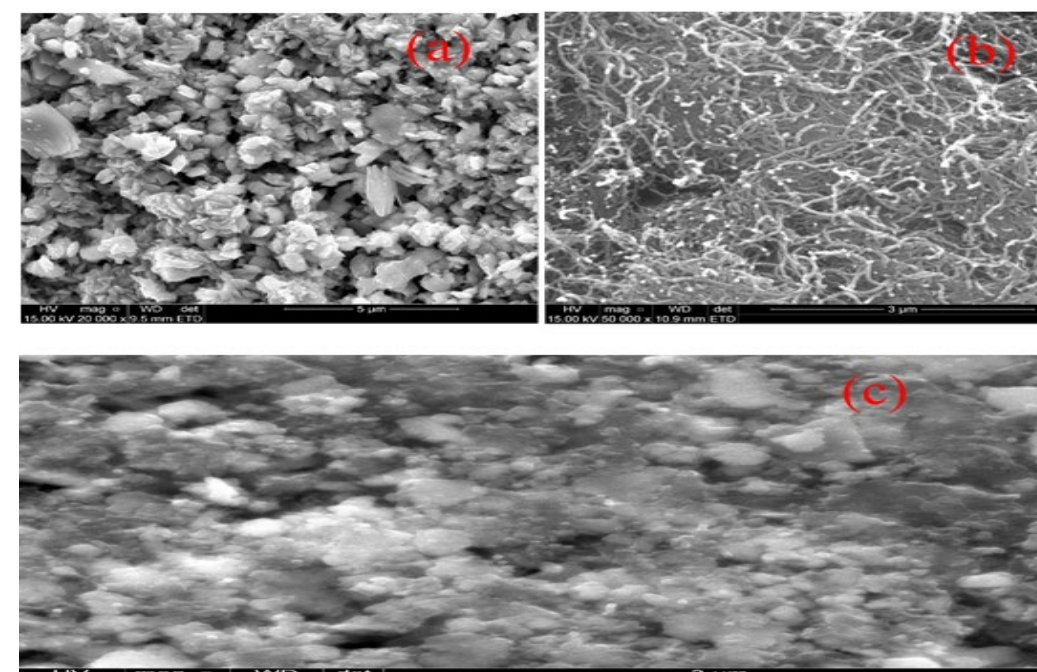


Fig. 3: SEM images of (a) AONPs, (b) f-MWCNTs, and (c) MWCNT-AONP nanocomposite

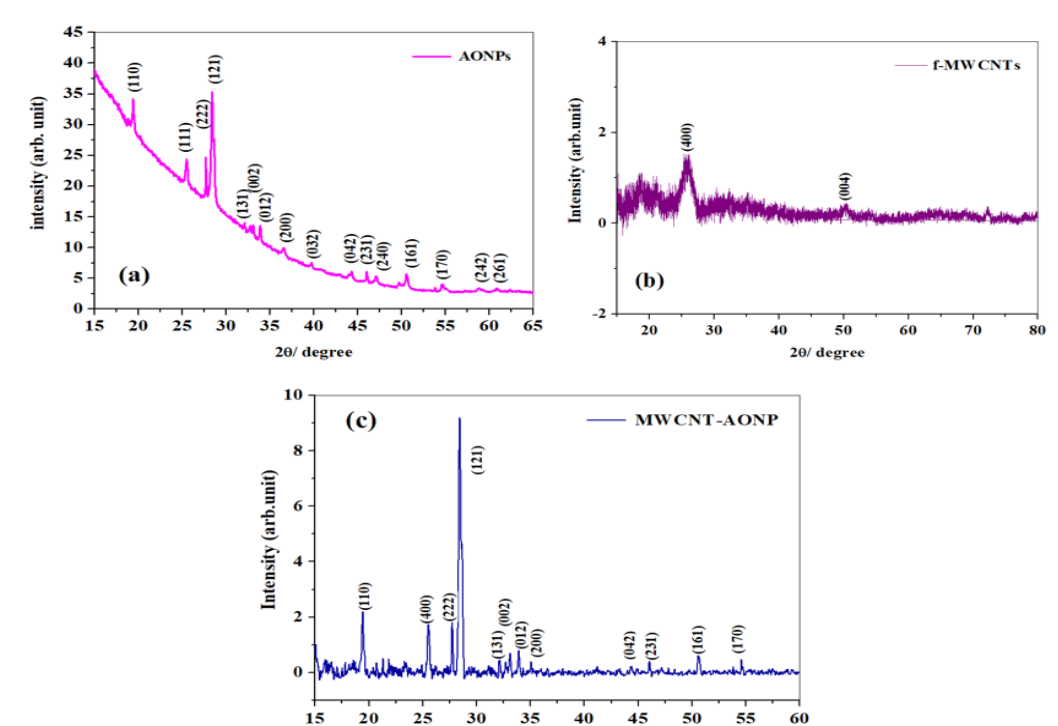


Fig. 4: XRD spectra of (a) AONPs, (b) f-MWCNTs, and (c) MWCNT-AONP nanocomposite

Electrocatalysis experiment

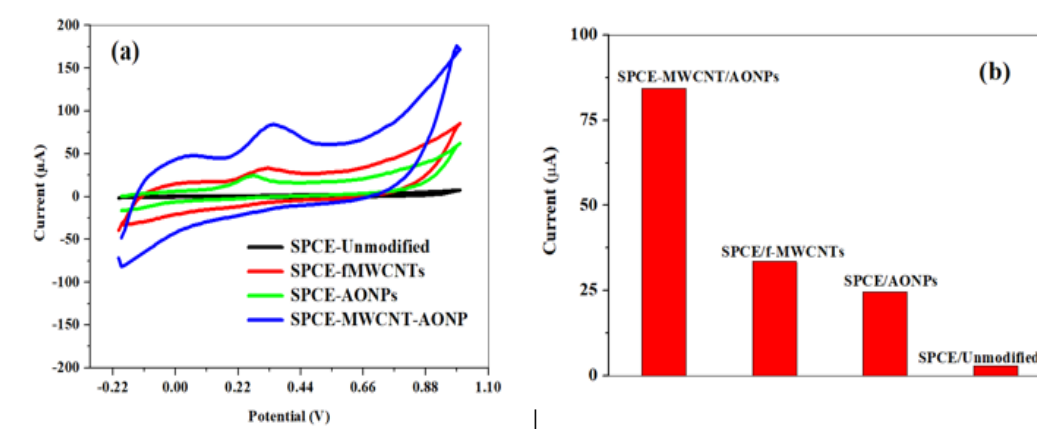


Fig. 6: (a) Comparative cyclic voltammograms for modified and unmodified electrodes in (a) 0.1 mM 5-HT prepared in 0.1M PBS (pH 7) buffer solution at a scan rate of 25 mVs^{-1} (b) comparative current response between modified and unmodified electrodes.

Electroanalysis experiment

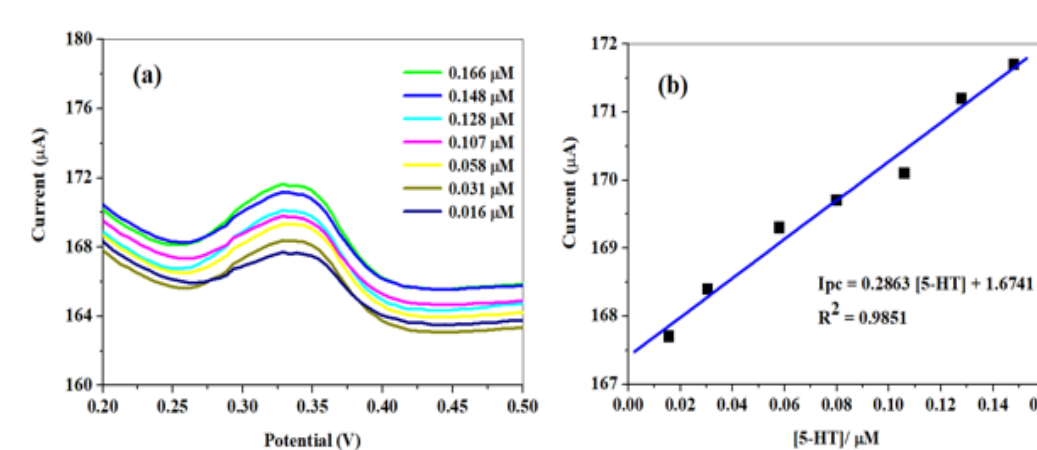


Fig. 8: SWV of SPCE-MWCNT-AONP modified electrode in (a) 0.016 to 0.116 μM 5-HT prepared in 0.1M PBS (pH 7) buffer solution (b) corresponding linear plots.

Stability and reproducibility study

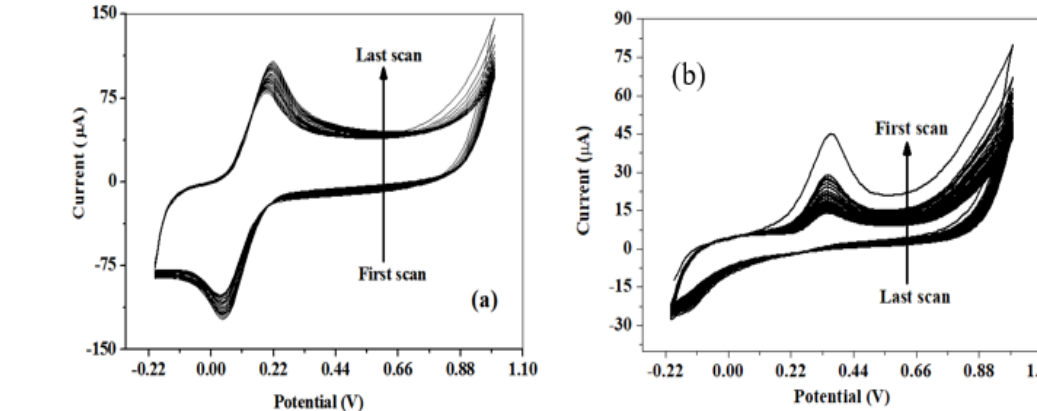


Fig.9: Reproducibility study at SPCE-MWCNT-AONP in (a) 5 mM $\text{Fe}(\text{CN})_6^{3-/4-}$; (b) 0.1 mM 5-HT prepared in 0.1M PBS (pH 7) buffer solution at a scan rate of 25 mVs^{-1} .

RESULTS - CON'T

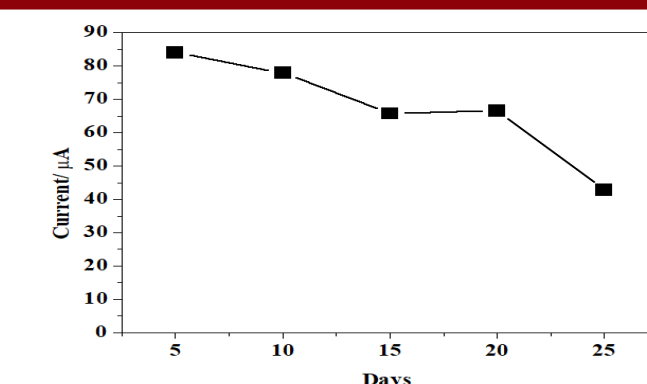


Fig. 10: Shelf-life study at the nanocomposite modified electrode

DISCUSSION

The synthesized nanomaterials and nanocomposite were positively confirmed using spectroscopic and morphological techniques in Fig 1-4. Fig 5 shows that the SPCE-MWCNT-AONP electrode exhibits better redox potentials, faster electron transfer kinetic compared to other electrodes. Furthermore, the electrodes showed a decrease in active surface area in this manner, the SPCE-AONP-MWCNT (0.716 cm^2) > SPCE-f-MWCNTs (0.346 cm^2) > SPCE-AONPs (0.123 cm^2) > SPCE-Bare (0.054 cm^2) electrode. The SPCE-AONP-MWCNT modified electrode had about thirteen times larger active surface area than the bare electrode. The SPCE-AONP-MWCNT exhibited an enhanced electrocatalytic response to 5-HT compared to other electrodes use. The current response decreased in this manner, the SPCE-AONP-MWCNT ($84.13 \mu\text{A}$) > SPCE-f-MWCNTs ($33.49 \mu\text{A}$) > SPCE-AONPs ($24.40 \mu\text{A}$) > SPCE-Bare ($2.89 \mu\text{A}$) electrode as displayed in Fig 6. The current response at the SPCE-AONP-MWCNT modified electrode was 29 times bigger than that at the bare electrode. A greater current response to 5-HT noticed at the SPCE-AONP-MWCNT modified electrode implied excellent biocompatibility of the nanocomposite with the analyte, and better electrocatalytic activity at the electrode compared to other fabricated electrodes. Furthermore, the reaction of 5-HT at the proposed electrode were diffusion-controlled. The fabricated electrode exhibited excellent anti-interference behavior even at fixed concentrations, as demonstrated by distinctive visible peaks of each analyte and a broad peak-to-peak separation of 367.90 mV between two analytes as represented in Fig 7. The sensitivity, limit of detection, the limit of quantification of the nanocomposite modified electrode towards detecting 5-HT was 0.2863 $\mu\text{A}/\mu\text{M}$, 24.6 nM, and 74 nM, respectively with linearity from 0.016 to 0.166 μM ($R^2 = 0.9851$) as demonstrated in Fig 8. The acquired LoD and LoQ values for the proposed electrode were comparable to those from Literature. From Fig 9 (a) It was noticed that the anodic current peak increased by 26.39 % while the cathodic current peak decreased by 17.71 %. This increase in anodic current peak could be attributed to the increased electroactive surface area of the probe solution with interactions over time. In a similar manner, Fig 9 (b) revealed that the 5-HT anodic current peak decreased by 68.32 % and had an RSD (%) = 34.45. Fig 10 shows the nanocomposite modified electrode reached half of its initial current response after 25 days. Table 1 shows the applicability of the fabricated sensor towards the detection of 5-HT in tomatoes. For detection of 5-HT in tomatoes, the proposed electrode showed good recoveries ranging from 91.32 to 108.28 % with an average RSD (%) value of 2.57 ($n = 3$). This study suggests that the modified electrode is suitable for 5-HT detection in real samples.

Conclusions

In conclusion, electrochemical detection of 5-HT at the SPCE-MWCNT-AONP nanocomposite modified electrode has been achieved. The synthesized nanomaterials and nanocomposites were positively confirmed using FTIR, XRD, UV-vis TEM, and SEM. Electrochemical studies were performed utilizing SWV and CV techniques. The electrocatalytic reduction peak of 5-HT was carried out using the CV technique and the reduction peak at the SPCE-MWCNT-AONP electrode was observed at 0.33 V with a reduction current of 84 μA . The sensor further demonstrated good selectivity and anti-interference behavior. Real sample analysis was conducted and it was shown that the sensor has potential for real application in the field. The proposed novel electrochemical sensor platform is of high interest for monitoring 5-HT and its therapeutic use.

References

- Yang L and Beal M F. *Mol. Biol.* **793** 401-15
- Tavakolian-Ardakani Z, Hosu O, Cristea C, Mazloum-Ardakani M and Marazza G. *Sensors.* **19** 2037.
- Hasanzadeh M, Shadjou N and Omidinia E. *J. Neurosci. Methods.* **219** 52-60
- Manjunatha JG, Swamy B K, Deraman M and Mamatha G P. *Int. J. Pharm. Pharm. Sci.* **5** 355-362.
- Salimi A, MamKhezri H and Hallaj R. *Talanta.* **70** 823-832.
- Zhang X, Fuller RR, Dahlgren RL, Potgieter K, Gillette R and Sweetler J V. *J. Anal. Chem.* **369** 206-211
- Xiao R, Beck O and Hjendahl P. *J. Clin. Lab. Anal.* **58** 505-510
- Campeau P M, Bernard G and Clayton P T. *Mol. Genet. Metab.* **92** 189-197
- Wang Z H, Liang Q L, Wang Y M and Luo G A. *J. Electroanal. Chem.* **540** 129-134
- McCreery R L 2. *Chem. Rev.* **108** 2646-2687.
- Falcaro P, Ricco R, Yazdi A, Imaz I, Furukawa S, Maspoeh D, Ameloot R, Evans J D and Doonan C J. *Coord. Chem. Rev.* **307** 237-254.

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