



Highly sensitive and selective serotonin sensor based on gamma ray irradiated tungsten trioxide nanoparticles



A.C. Anithaa^a, K. Asokan^b, C. Sekar^{a,*}

^a Dept. of Bioelectronics and Biosensors, Alagappa University, Karaikudi 630003, TN, India

^b Materials Science Division, Inter-University Accelerator Centre, New Delhi 110067, India

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ABSTRACT

This work investigates the sensitive and selective electrochemical method for determining serotonin (5-HT) using gamma ray irradiated tungsten trioxide (GI-WO₃) nanoparticles. WO₃ NPs synthesized by microwave irradiation method was subjected to gamma ray irradiation under different doses (0–150 kGy) and the products were characterized by powder XRD, HRTEM, Raman and UV–vis spectra. The experimental results demonstrated that the 100 kGy irradiation on WO₃ NPs led to significant changes in morphology, crystal structure and improvement in specific surface area and fast electron transfer rate which enhanced its electrocatalytic activity greatly. Cyclic voltammetry and differential pulse voltammetry studies of GI-WO₃ NPs modified glassy carbon electrodes (GCE) exhibited improved electrocatalytic activity towards the oxidation of 5-HT in a phosphate buffer solution (PBS, pH 7.0). The kinetic parameters such as diffusion coefficient, electron transfer coefficient and heterogeneous electron transfer rate constant involved in the oxidation of 5-HT at the 100 kGy GI-WO₃/GCE indicate the suitability of the fabricated electrode for the detection of 5-HT. Under the optimized conditions, the oxidation peak currents were linearly proportional to 5-HT concentration over a wide linear range of 0.01–600 μM, with the lowest detection limit of 1.42 nM (S/N = 3). The fabricated 5-HT sensor showed an excellent anti-interference ability against potentially coexisting electroactive species, long-term high stability and excellent reproducibility. The proposed sensor was successfully implemented for the determination of 5-HT in human blood serum samples with good recoveries ranging from 99.2% and 102.9%.

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1. Introduction

Serotonin (5-hydroxytryptamine, 5-HT) is a redox active monoamine neurotransmitter synthesized by serotonergic neurons in the central nervous system (CNS) and enterochromaffin cells in the gastrointestinal tract. It plays a crucial role in the emotional system by regulating mood, sleep, emesis, cardiovascular function and appetite [1,2]. Low levels of 5-HT are associated with depression, anxiety, and migraines. Extremely high levels of 5-HT can manifest toxicity, liver regeneration, thermoregulation and irritable bowel syndrome [3,4]. In physiological samples, 5-HT usually coexists with higher concentrations (100–1000 times) of ascorbic acid (AA), uric acid (UA) and folic acid (FA) which strongly influences the selectivity and sensitivity of 5-HT determination [5]. Moreover, the 5-HT oxidises at almost similar oxidation potential as that of other neurotransmitters such as dopamine (DA) and epinephrine (EP),

resulting in an overlapping of voltammetric responses towards oxidation of 5-HT in mixed samples. The oxidation potential of 5-HT (0.39 V) is close to that of EP (0.20 V), DA (0.22 V), AA (0.01 V) and UA (0.33 V) [6–8]. Effective measurement of 5-HT concentration at very low levels (10^{−8} to 10^{−9} M) is of great importance in disease diagnosis and pharmaceutical applications. A variety of analytical methods including enzyme immunoassay [9], fluorimetry [10], radio-immunoassay [11], chemiluminescence [12] and mass spectrometry [13] were reported to quantify levels of 5-HT and these methods suffer from disadvantages including long analysis times, high costs, sample pre-treatment and low sensitivity. Compared to above methods, an electrochemical technique is a promising tool to meet the above requirements, but normally have low sensitivity with conventional bare electrodes. Key issues in 5-HT electrode detection are achieving better detection limits, improving selectivity and reducing electrode fouling [14].

In recent years, chemically modified electrodes are used as successful electrocatalysts because the modifiers adsorbed on the electrode surfaces achieve smart properties such as reproducible performance, good stability, high sensitivity and selectivity.

* Corresponding author.

E-mail address: Sekar2025@gmail.com (C. Sekar).

Although many modified electrodes such as double layered membrane of reduced graphene oxide/polyaniline nanocomposites modified GCE and molecularly imprinted polymers (MIES) embedded with Au NPs [15], calixarene modified GCE [16], carbon nanofiber modified GCE [17], Nafion/Ni(OH)₂-multiwalled carbon nanotubes (MWCNT) modified GCE [18], graphene nanosheets modified GCE [19], cyclodextrin modified carbon paste electrode [20] and gold nanoparticles/L-cysteine modified CGE [21], have been reported for detecting 5-HT, there is still a need to develop new method with high efficiency and convenience for the precise determination of 5-HT. Here, we propose a new strategy of using gamma ray irradiated tungsten trioxide nanoparticles (GI-WO₃ NPs) on the glassy carbon electrode (GCE) as an efficient electrocatalyst for oxidation of 5-HT.

Nanostructured WO₃ is an attractive *n*-type indirect semiconductor with optical tunable band gap ($E_g \sim 2.5\text{--}3.6\text{ eV}$), high surface-to-volume ratio, high chemical stability, good biocompatibility and quantum confinement [22]. Due to its structural flexibility, distinctive photocatalytic, electrochromic and photochromic properties, WO₃ is widely used in the field of photodegradation, smart windows, lithium-ion batteries, photoelectrocatalysis, gas sensors and biosensors [23–27]. Earlier we have successfully synthesized WO₃ NPs by microwave irradiation method and fabricated electrochemical sensors for the detection of L-dopa [28] and dopamine [29]. Gamma rays are the most energetic form of electromagnetic waves which causes lattice defects in the form of vacancies, defect clusters and dislocations leading to changes in their density and energy levels within the bandgap which can act as trapping centres [30]. When gamma ray interacts with the material, the particle energy is transferred to an atomic nucleus through defect annihilation and defect creation. The defect acts as an acceptor and surplus atom behaves like a donor which results in the changes in physico-chemical properties of the target material. Gamma irradiation of materials may also cause re-crystallization or amorphization depending on the nature of the material and localised heating caused by gamma irradiation. Though there are number of studies concerning the effects of the gamma irradiation on physicochemical properties of metal oxide semiconductors (MOS) [31–34]. There is no detailed study in the literature about the effect of gamma irradiation on the electrocatalytic behaviour of WO₃ NPs prepared by the microwave irradiation process.

In the present work, we report the effect of gamma ray irradiation (0–150 kGy) on the morphological, structural, optical and electrochemical behaviour of WO₃ nanoparticles. Cyclic voltammetry studies of 100 kGy GI-WO₃/GCE on 5-HT oxidation exhibited a remarkable catalytic performance without the use of immobilization support matrix in 0.1 M phosphate buffer solution (pH 7.0). The calibration curve obtained by differential pulse voltammetry (DPV) technique showed a wide linear concentration range (0.01–600 μM) and lowest detection limit of 1.42 nM for 5-HT determination. The application of this 5-HT sensor in human blood serum has also been demonstrated successfully.

2. Experimental techniques

2.1. Reagents

Serotonin hydrochloride, dopamine hydrochloride, Epinephrine, ascorbic acid, uric acid and folic acid were used as received from Sigma-Aldrich. Tungstic acid and 0.1 N sodium hydroxide solutions were purchased from Fischer Scientific. 0.1 M phosphate buffer solution (PBS) with different pH values were prepared by mixing the stock standard solutions of Na₂HPO₄ and NaH₂PO₄ and adjusting pH with 0.1 M H₃PO₄ or NaOH. The

solutions were prepared with de-ionized water with a resistivity of 18 M Ω /cm.

2.2. Apparatus

The WO₃ nanoparticles were subjected to gamma irradiation using 1200 gamma chamber with fluence equivalents of 5×10^{15} , 1×10^{16} and 5×10^{16} γ/cm^2 respectively. Powder X-ray diffraction (XRD) patterns were recorded using a Bruker AXS D8 advanced diffractometer with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$) in the range of 20–80°. High resolution electron microscopy (HRTEM) investigations, selected area electron diffraction (SAED) patterns and energy dispersive X-ray spectroscopy (EDS) analyses were performed using a JEOL JEM 2100 microscope operated at 200 kV. SAED patterns were marked with *d* spacing values using “Diffraction Ring Profiler” software. Raman spectra were recorded in the range 50–1000 cm^{-1} using a Confocal micro-Raman microscope (Renishaw inVia Reflex) with excitation wavelength of 514.5 nm. UV–vis spectroscopy was performed using spectrophotometer (Thermoscientific–Evolution 201) for optical studies.

Electrochemical experiments were performed with a CHI 609D electrochemical workstation (CHI, USA). A standard three electrode cell was used for the electrochemical experiments. A 3 mm diameter GCE was used as the working electrode (working area of 0.07 cm^2), platinum wire as counter electrode and Ag/AgCl as reference electrode. The electrochemical impedance spectroscopy (EIS) measurements were carried out by applying an AC potential of amplitude 10 mV over the dc potential of 200 mV in the frequency range of 100 kHz–1 Hz in 0.1 M KCl solution containing 1.0 mM [Fe(CN)₆]^{3–/4–} redox couple. The value of the charge transfer resistance (R_{ct}) was determined using Zsimpwin software simulations. The differential pulse voltammetry (DPV) measurements were performed in 0.1 M PBS (pH 7.0) in the potential region from 0.2 to 0.7 V with amplitude of 60 mV, pulse width of 0.05 s and pulse period of 0.2 s.

2.3. Synthesis of WO₃ nanoparticles

In brief, the precursor solution was prepared by dissolving 2.49 g of tungstic acid in 10 mL of sodium hydroxide to form sodium tungstate solution. To enhance the protonation process, several drops of HCl were introduced into the solution to attain the pH value of 1. The final solution was exposed to microwave (2.45 GHz) under optimum power of 180 W for 15 min and surrounding water/impurities were removed by drying at 100 °C in air. The resulted greenish yellow colored WO₃ NPs were irradiated using the gamma source 1.25 MeV ⁶⁰Co at different doses (50, 100 and 150 kGy). In order to confirm the reliability of the data obtained due to the effect of gamma irradiation, four batches (30 mg each) of WO₃ NPs were exposed to gamma rays under each dosage and the products were characterized using powder XRD and UV–vis spectroscopy.

2.4. Fabrication of modified electrodes

The WO₃ NPs suspension was prepared by dispersing WO₃ NPs (5 mg) in 1.0 mL of de-ionised water. The modified electrodes were prepared by a simple casting method. Prior to the surface coating, the GCE was polished with 0.05 μm alumina powder using a polishing cloth until the electrode surfaces had a mirror-finish and then rinsed thoroughly with de-ionised water, followed by sonication in ethanol and de-ionised water respectively. GCEs were modified by dropping a known amount of WO₃ suspension (10 μL) onto the surface and air drying it at room temperature overnight. After evaporation, a uniform and stable WO₃ film was found to have immobilized on the GCE.

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