



Multi-walled carbon nanotube wrapped rare earth tungstate nanosheet composites for selective and rapid detection of sulfadiazine

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ABSTRACT

Multi-walled carbon nanotube wrapped rare earth tungstate nanosheet composites are developed for the ultra-sensitive and selective electrochemical detection of sulfa drug, sulfadiazine (SAN) as they exhibit high levels of toxicity towards public health and ecosystem. Here, we synthesized Gadolinium tungstate decorated with multi-walled carbon nanotubes ($Gd_2WO_6/MWCNT$) through hydrothermal processing and characterized by XRD, SEM, EDX, TEM, and EIS measurement to investigate the phase purity, morphology, and interfacial property. Gd_2WO_6 is a double perovskite that has high oxygen surface exchange kinetics and the MWCNT possesses high catalytic capability and a larger surface area contributes to the efficient sensing ability. The $Gd_2WO_6/MWCNT$ possessed a great electrical conductivity owing to the synergism between the Gd_2WO_6 and MWCNT. The synergistic effect increases the surface area, ionic and electrical conductivity which increases the current response of SAN. Under optimum conditions, the $Gd_2WO_6/MWCNT/GCE$ displays a broad linear of 0.01 – 671 μM and a LOD level of 2 nM (S/N ratio: 3) with a sensitivity of 0.371 $\mu A \mu M^{-1} cm^{-1}$. The analytical applicability of the proposed electrode modifier leads to a promising sensor for SAN detection in human urine and water samples with appreciable results.

1. Introduction

In dealing with environmental pollution, renewable energy sources and green technologies are being explored in order to address the ever-increasing energy demands [1]. Tremendous focuses on pharmaceutical products, which results in high environmental problems. In pharmaceutical fields, it has grown in antibiotic drugs commonly used in animal husbandry for the prevention and to treat bacterial diseases. Its persistence in the environment, high consumption, and huge variety make it an important class of water pollutant [2]. Sulfadiazine (SAN), a sulfa-based drug also known as sulfonamides is a type of antibiotic. Its potential broad spectrum 4-amino-N-pyrimidine-2-yl-benzenesulfonamide is extensively used in veterinary, and human intakes [3] with remedial properties employed for the treatment of chancroid, toxoplasmosis, nocardiosis, wound sepsis, etc. It is also used to treat infections of the urinary tract, malaria, infections on the ear, meningitis, burns, and

toxoplasmosis [4]. With its growing usage, SAN has been found in environments to have an impact on human health, there were several residue limits in China and Europe. To safeguard the safety of animal products and protect consumers, European Union legislation set a safe limit for sulfonamides in animal-origin consumables at 100 g Kg^{-1} . [4]. In China, for the aquatic system, the maximum permitted level of SAN is 0.014 – 0.28 $\mu g/Kg$ and the maximum admirable level in milk at 0.07 ppm have set by international regulations [5]. These drugs spread in the environment and spread toxicity and serious public health hazards [6,7]. Thus, it is essential to choose a sensitive and selective method for the detection of SAN. Currently, SAN has been detected by numerous technique including capillary electrophoresis [8], liquid chromatography-mass spectrometric [9], fluometric [10], high-performance liquid chromatography [11], and UV-visible spectrometry [12]. These approaches are reliable but are not real since they rely on expensive instruments and longtime analysis. The electrochemical

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method becomes more advantageous than other analytical methods for trace-level detection due to its inherent properties such as sensitivity, fast response, and low cost. Since the drugs are electroactive compounds they can be electrochemically detected. Electrochemical sensor-based nanomaterials have become widely used as nanotechnology has advanced, bringing advantages over electrodes such as enhanced mass transport and shorter times in nanoscale dimensions.

Tungstates are a large class of inorganic materials exhibiting physical properties and technology applications in various fields such as supercapacitors [13], hydrogen evolution [14], oxygen evolution [15], photocatalysis [16], and so on. Rare earth-based tungstates have aroused great interest in many fields nowadays. Amidst gadolinium tungstate ($\text{Gd}_2(\text{WO}_6)_3$), possesses remarkable properties such as ferroelectricity, laser host, catalysis, and low toxicity [17,18]. Due to its excellent mechanical strength as well as chemical and thermal stability, gadolinium tungstate (Gd_2WO_6) has been demonstrated to be an admirable material. [19]. Gd_2WO_6 belongs to the monoclinic crystal system with a space group of C_2/c containing Gd^{3+} ions [20]. Numerous efforts have been made to enhance the surface morphology of the material. M Rahimi et al synthesized $\text{Gd}_2(\text{WO}_4)_3$ and processed photocatalytic study [17], F Lei et al synthesized $\text{Gd}_2\text{WO}_6:\text{Eu}^{3+}$ for the luminescence study [18], K selvakumar et al synthesized $\text{Gd}_2\text{WO}_6/\text{ZnO}/\text{bentonite}$ for the degradation of ciprofloxacin and Bisphenol A [21]. However, a flake like Gd_2WO_6 (Gd_2WO_6) was synthesized by the facile hydrothermal method which has improved the good electrical conductivity, high surface area, and improved charge transport.

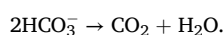
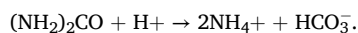
Research has begun to focus on increasing the conductivity of rare earth tungsten oxide. Linkers like graphene, graphene oxide, reduced graphene oxide, conducting polymers, multi-walled carbon nanotubes, single-walled carbon nanotubes, and quantum dots were proven to be effective in enhancing conductivity [22–27]. Carbon nanotubes (CNTs) have garnered significant interest across various scientific and technological domains owing to their exceptional characteristics, including high aspect ratio and distinctive electrical, chemical, and mechanical properties [28]. The outstanding electronic characteristics imply that CNTs have the potential to enhance electron transfer rates when employed as an electrode. [29]. Because of its unique qualities such as superior conductivity, high surface area, and strong mechanical strength, multi-walled carbon nanotubes (MWCNT) can significantly improve the transmission of electrons between the electrode surface and analytes [30,31]. Nowadays, several kinds of composites have been prepared by cooperating MWCNTs for enhancing electrochemical performance. Wenhao Peng et al prepared $\text{NiMn}_2\text{O}_4/\text{MWCNT}$ as electrode material for improved specific capacitance [32]. The instigation of MWCNT into metal oxides effectually enhances the electrocatalytic performance as a result of its specific physicochemical characteristics [33–35].

As far as we know, this is the first investigation on the electrochemical detection of SAN by utilizing the synergism between $\text{Gd}_2\text{WO}_6/\text{MWCNT}$. This state-of-the-art preparation of $\text{Gd}_2\text{WO}_6/\text{MWCNT}$ by hydrothermal approach lends a hand to the formation of well-defined morphology. This proposed sensor material possesses high structural stability that leads to the fast transfer of charge between the electrode and electrolyte. In this present work, Gd_2WO_6 , MWCNT, and $\text{Gd}_2\text{WO}_6/\text{MWCNT}$ were employed as different electrode modifiers. Whereas, the incorporation of MWCNT with the rare earth tungsten oxide will achieve an exceptional electrochemical performance owing to its unique properties. The synergism between the Gd_2WO_6 and highly conductive MWCNT promotes the trace-level detection of SAN and is also applicable in real-life samples. Accordingly, the verdicts of this work provide insight into the constructive detection of SAN to be achieved in clinical applications.

2. Experimental

2.1. Preparation of $\text{Gd}_2\text{WO}_6/\text{MWCNT}$

The precursors and instruments used were described briefly in the [supplementary section](#) (SI). The $\text{Gd}_2\text{WO}_6/\text{MWCNT}$ composite was prepared by the facile hydrothermal method. In this typical procedure, 0.1 M of $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ were liquified in 30 ml of DI H_2O separately. Then 0.6 g of urea was dissolved in 30 ml of DI H_2O . As accordingly, urea is being used in the reaction to assist the synthesis of metal oxides. Urea as the precipitation agent is utilized in the formation of micron size. The adequate way of urea usage to synthesize amorphous and crystalline metal oxide form a uniform shape particle from an aqueous media [32,33]. The urea hydrolysis is described as:



Followed by the addition of 0.01 g of MWCNT and stirred for about 30 min. The suspension was transported to autoclave and reserved for 12 h at 180 °C. After, Teflon was cooled and the obtained precipitate was washed. Finally, the resultant product was dried upto 24 h. Hence the product was labelled as $\text{Gd}_2\text{WO}_6/\text{MWCNT}$. For the comparative study, the same procedure was followed without adding MWCNT. Schematic illustration of synthesis of $\text{Gd}_2\text{WO}_6/\text{MWCNT}$ was represented in [Scheme 1](#).

3. Result and discussion

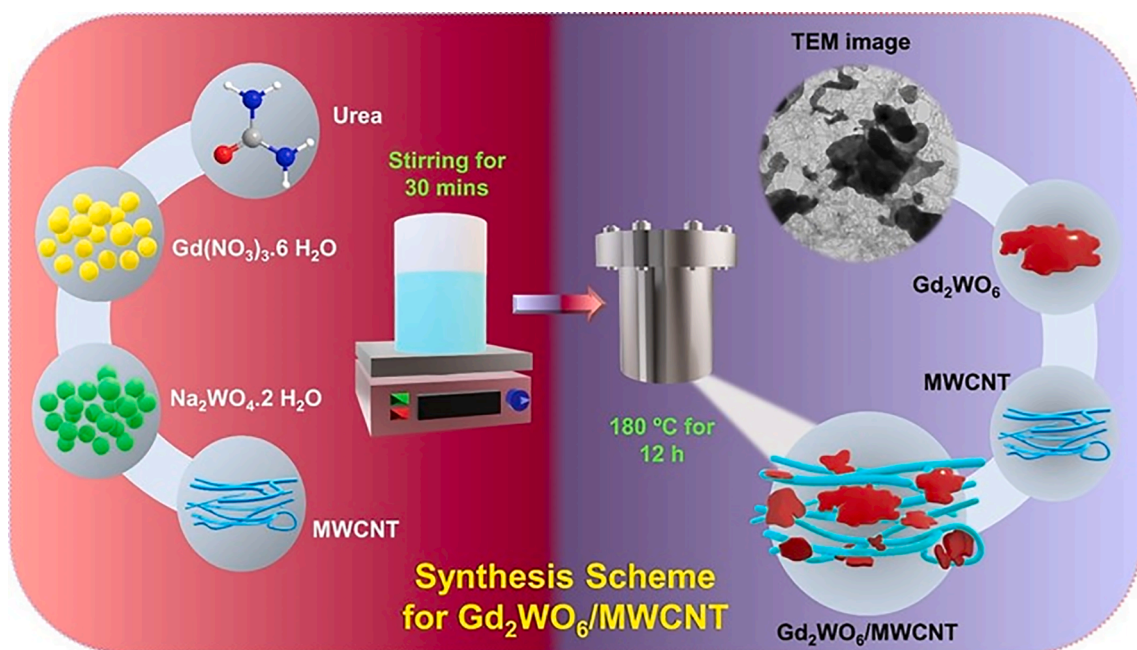
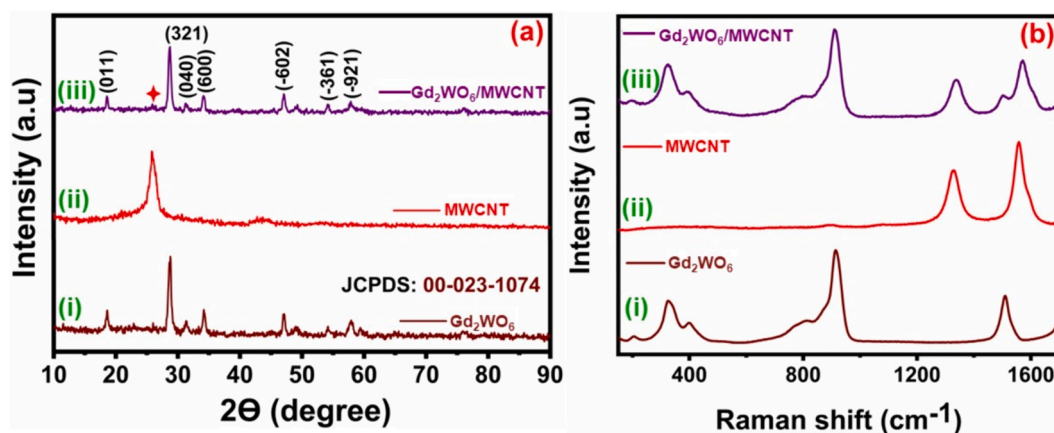
3.1. Structure and morphological characterization

To study the crystalline phase of the materials, XRD characterization method was utilized. The $\text{Gd}_2\text{WO}_6/\text{MWCNT}$ findings XRD pattern was displayed in [Fig. 1a\(i\)](#) to confirm the crystal structure. The obvious diffraction peaks of Gd_2WO_6 at $2\theta = 18.6, 28.6, 31.3, 34.2, 47.0, 54.1$, and 57.8 have coincided with the (011), (321), (040), (600), (-602), (-361), and (-921) crystal planes of Gd_2WO_6 (JCPDS.No: 00–023–1074) [21]. [Fig. 1a\(ii\)](#) shows the XRD peak of MWCNT which shows a peak at 25.8 and 43.3 assigned to the (002) and (100) plane of the graphite [34,35]. The crystalline size was calculated as 20.43 nm by using the Scherrer's equation. [Fig. 1a\(iii\)](#) shows the XRD peak of $\text{Gd}_2\text{WO}_6/\text{MWCNT}$, it was observed that all the individual peaks of Gd_2WO_6 and MWCNT were shown. The results indicated the successful formation of the $\text{Gd}_2\text{WO}_6/\text{MWCNT}$ composite.

Raman spectroscopy technique was widely employed for the analysis of MWCNT as it provides information about the degree of disorder. [Fig. 1b](#) depicts the Raman spectra image of Gd_2WO_6 , MWCNT, and $\text{Gd}_2\text{WO}_6/\text{MWCNT}$ respectively. In Raman spectra of Gd_2WO_6 , the peak at 325.4 cm^{-1} resembles to the bending or stretching vibrations in W-O bonds. The bands at 913.4 cm^{-1} ascribed to the symmetric stretching mode of $\text{A}_1(\nu_1)$ [36]. The band at 1509 cm^{-1} , owing to the oxygen stretching vibration [37]. It was noticed that the MWCNT displays a strong peak at 1557 cm^{-1} and a weak peak at 1328.5 cm^{-1} , the intensity ratio was estimated to be 0.85 [38]. The Raman spectra of $\text{Gd}_2\text{WO}_6/\text{MWCNT}$ display similar peaks of Gd_2WO_6 and MWCNT, the intensity ratio was calculated to be 0.86 for composite higher than that of MWCNT demonstrates the decreased fraction of ordered carbon. The crystallite size was further calculated from a modified Tuinstra–Koeing relation equation [39] with the help of intensity ratio (I_D/I_G) obtained from Raman spectra,

$$La(\text{nm}) = (2.4 \times 10^{-10}) \lambda^4 (I_D/I_G)^{-1} \quad (1)$$

The obtained crystallite size for $\text{Gd}_2\text{WO}_6/\text{MWCNT}$ was 22.27 nm and it was in agreement with the calculated crystallite size from XRD. The obtained results further confirm the successful formation of $\text{Gd}_2\text{WO}_6/\text{MWCNT}$.

Scheme 1. Graphical representation of Gd₂WO₆/MWCNT preparation.Fig. 1. (a) XRD pattern and (b) Raman spectra of Gd₂WO₆, MWCNT, and Gd₂WO₆/MWCNT.

MWCNT as a composite material.

Fourier transforms infrared (FTIR) spectroscopy has been studied to identify the functional group of the as-synthesized nanomaterials. The FTIR of the Gd₂WO₆/MWCNT (Fig. 2a) was exhibiting an absorption peak at 532.2, 794.5 cm⁻¹ belonging to the W-O symmetric and asymmetric stretching and O-W-O symmetric and asymmetric deformation vibration in tungstate groups [21]. Some of the characteristics of Gd₂WO₆ was observed at 1450.2, and 1604.4 cm⁻¹. The peak at 3694.9 cm⁻¹ belongs to the stretching mode of the O-H group, and the peak at 1720.1 cm⁻¹ is due to the C = C stretching mode [40]. The peak at 1457.96 cm⁻¹ corresponds to the C-O stretching vibration associated with the defects in multi-walled carbon nanotubes [41]. Thus, the results confirm the successful formation of the Gd₂WO₆/MWCNT composite.

By using photoelectron spectroscopy (XPS), the chemical states of the prepared composite Gd₂WO₆/MWCNT was investigated. The survey spectrum in Fig. 2(b) demonstrates the presence of Gd, W, O, and C in the hydrothermally synthesized composite. The XPS spectra of Gd are displayed in Fig. 2(c). Gd 4d_{5/2} is responsible for the peak at 144.8 and Gd_{3/2} corresponds to the peak at 150.1 eV [42], which indicates the state of Gd is + 3. Fig. 2(c) depicts the deconvoluted XPS distinctive peak of

W⁶⁺ related to W 4f_{7/2} and 4f_{5/2} are located at 39.7, and 37.6 eV [21]. The XPS spectrum of O 1s was shown in Fig. 2(d), detected at 531.4, 530.1, and 529.1 eV corresponds to the O-C = O, C = O, and Gd-O/W-O [42]. The peaks that appeared at 289.4, 288.2, 287.2, 286.4, and 285.3 eV corresponds to the π-π*, -COO, >C = O, -C-O, and C = C/ C-C [43].

Representative FE-SEM images of synthesized Gd₂WO₆ in Fig. 3(a,b) illustrates the formation of a nanosheet-like architecture. Fig. 3(c) depicts the FE-SEM images of MWCNT reflecting their orthodox nanotubular structure. Fig. 3(d,e) portrays the low and high-magnification FESEM images of the Gd₂WO₆/MWCNT composite. The FESEM image of Gd₂WO₆/MWCNT confirms that the Gd₂WO₆ sheets were wrapped with the MWCNT tubes. Moreover, the wrapping of MWCNT does not seem to affect the nanosheet like surface topology of Gd₂WO₆. Thus, the uniformity of the nanosheets and well-ordered CNTs swathed around them enables the Gd₂WO₆/MWCNT composite to promote effective charge transfer resulting in effective electrochemical oxidation of SAN.

Furthermore, the surface morphology, size distribution, and interatomic spacing of the prepared Gd₂WO₆/MWCNT composite were analyzed by HRTEM. Detailed structural analysis of TEM, HRTEM, and elemental mapping was scrutinized in Fig. 4. Gd₂WO₆ displays a sheet-

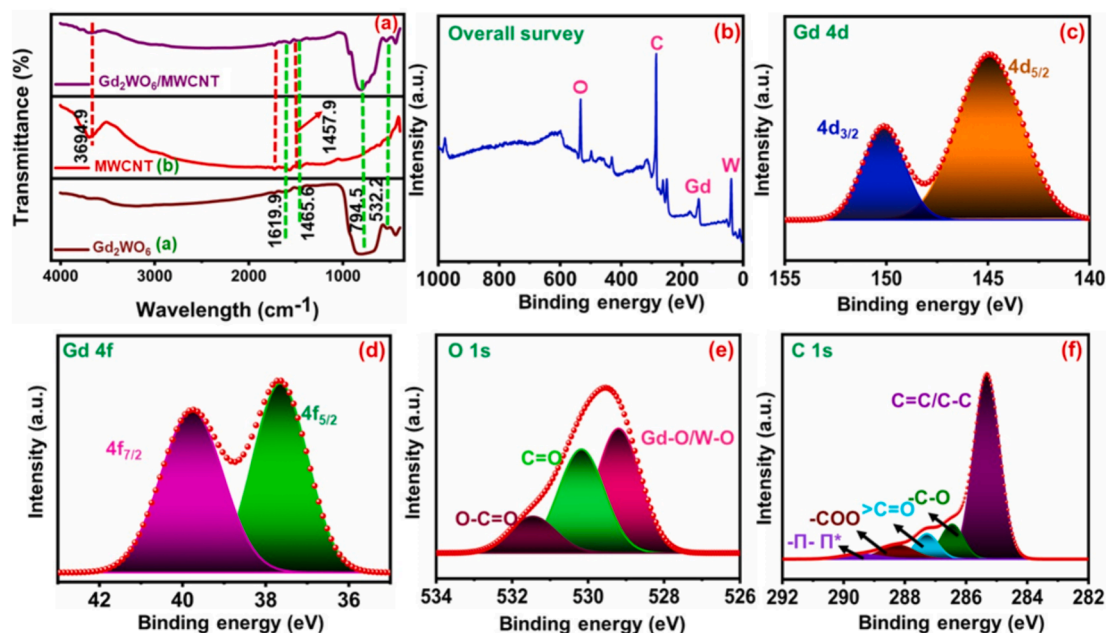


Fig. 2. (a) FTIR spectra of Gd₂WO₆, MWCNT, and Gd₂WO₆/MWCNT, (b) XPS survey spectra, high-resolution spectra of (c) Gd 4d, (d) W 4f, (e) O 1s, and (f) C 1s.

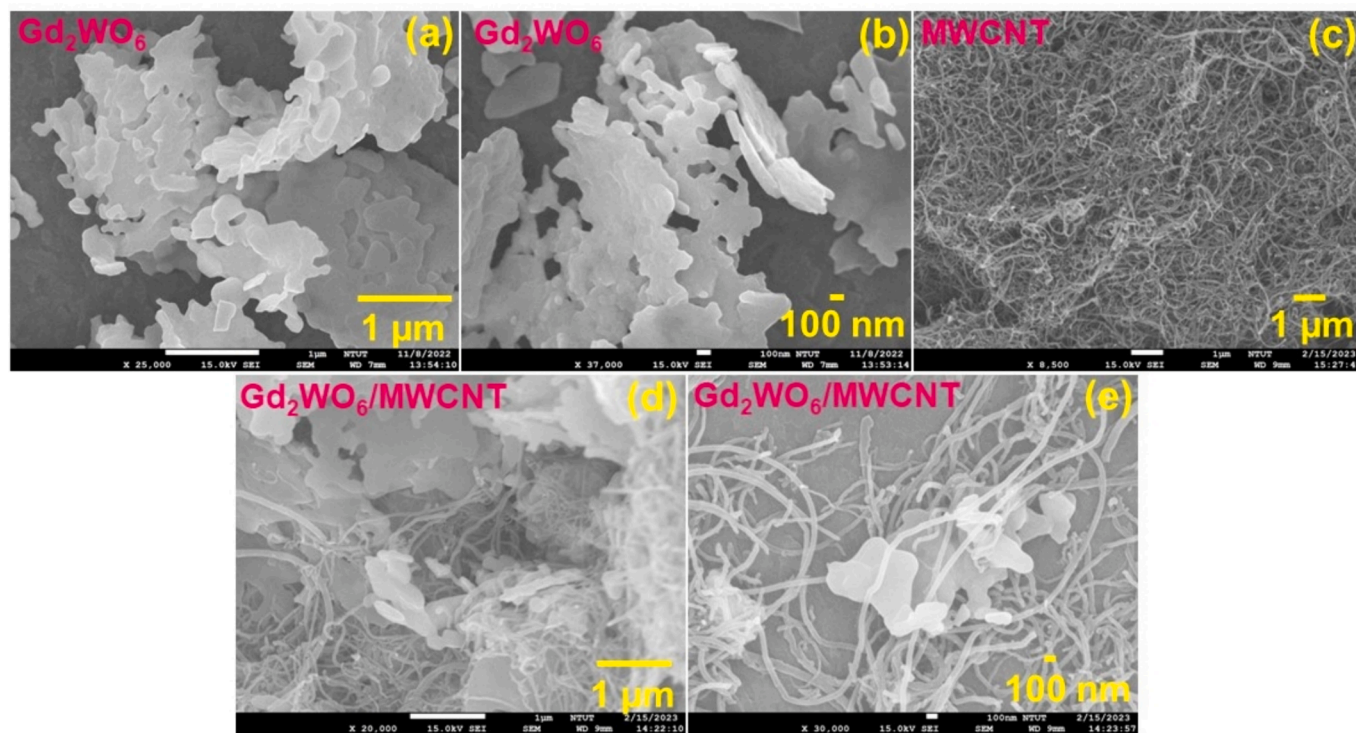


Fig. 3. FESEM images (a-b) Gd₂WO₆, (c) MWCNT, and (d-e) Gd₂WO₆/MWCNT.

like morphology in Fig. 4(a-c) which is in accordance with the FESEM images result. In addition to surface morphology, the elemental mapping showcased in Fig. 4(d-g) implies concrete evidence that the synthesized Gd₂WO₆/MWCNT composite comprises of homogeneously distributed Gd, W, O, and C elements. The SAED pattern of Gd₂WO₆/MWCNT in Fig. 4(h) illustrates the (040), and (321) planes which concurs the XRD results. In Fig. 4(i) the lattice fringes of Gd₂WO₆/MWCNT with the interplanar distance of 0.326 nm correspond to the (321) plane. These characterization data have indicated that the Gd₂WO₆/MWCNT composite was synthesized as a stable structure.

Analyzing the FESEM and HRTEM results, after the wrapping of Gd₂WO₆ with MWCNT has shown evidence that a uniform dispersion of elements has occurred, resulting in the enhanced structural stability of the composite, which will be significantly enhance the signal strength for the electrochemical sensing of SAN by virtue of the increased surface area to volume ratio.

3.2. Electrochemical behavior of Gd₂WO₆/MWCNT/GCE

As an effective method, the EIS technique has been used to examine

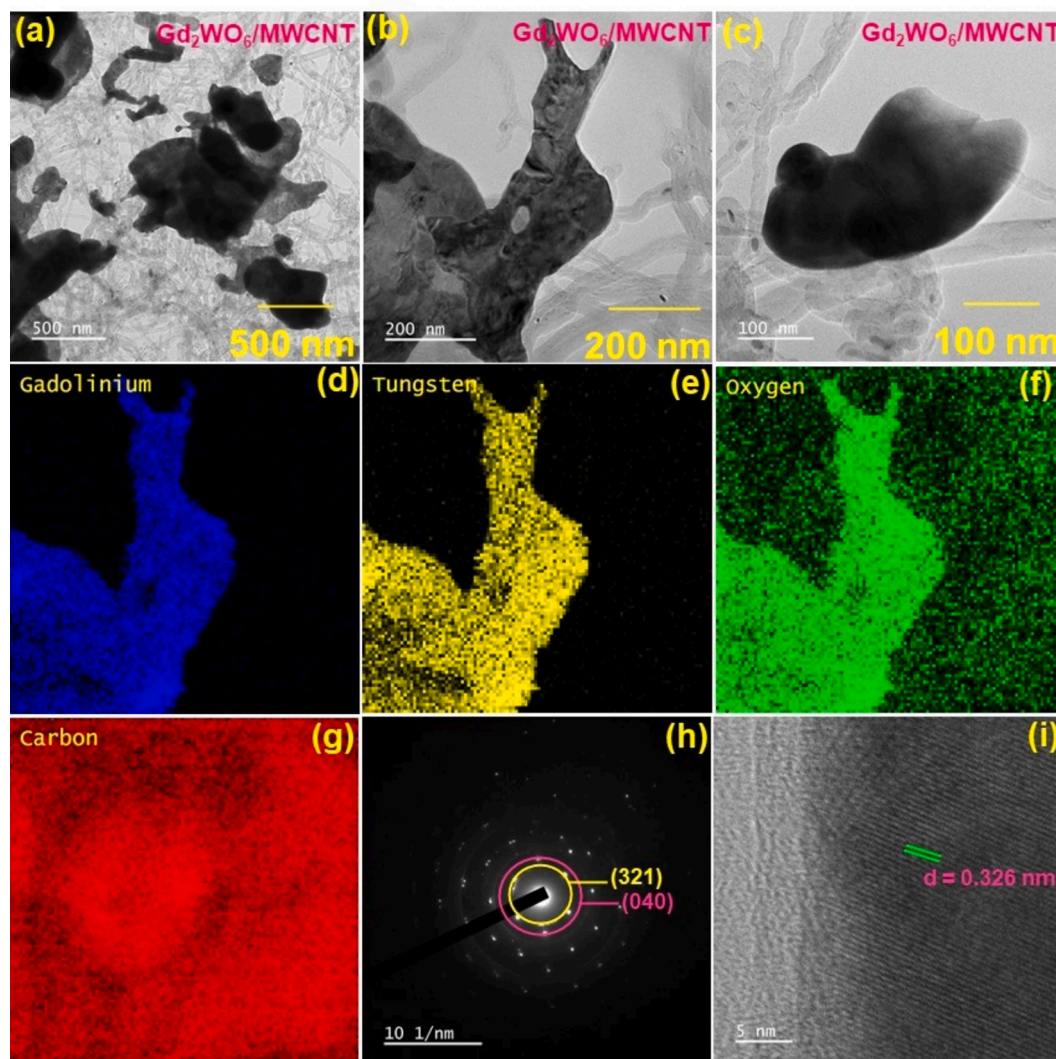


Fig. 4. (a-c) TEM images of $\text{Gd}_2\text{WO}_6/\text{MWCNT}$ at different magnifications, (d-g) elemental mapping of Gd, W, O, and C, (h and i) HR-TEM images of $\text{Gd}_2\text{WO}_6/\text{MWCNT}$.

the interfacial properties of the sensing platform. EIS data is typically represented through either Nyquist plots or Bode plots. Bode plots illustrate the frequency response of a system, showcasing both gain (magnitude) and phase information separately. On the other hand, Nyquist plots amalgamate gain and phase in a single complex plane representation. While Nyquist plots are more intricate than Bode plots, they are widely utilized in electrochemistry due to their heightened sensitivity to subtle changes. Additionally, Nyquist plots provide a direct means of deducing certain parameters from the plot itself [44]. Fig. 5a reveals the Nyquist plots in the frequency range of 100 kHz to 10 MHz are fitted by the Randle's circuit model of different modified electrodes in 0.1 M KCl and 5 mM of $[\text{Fe}(\text{CN})_6]^{3+/4+}$. Fig. 5a illustrates the electron transfer ability (R_{ct}) shows a downward trend after independently modifying the bare GCE, $\text{Gd}_2\text{WO}_6/\text{GCE}$, MWCNT/GCE , and $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$. The R_{ct} value of bare GCE, $\text{Gd}_2\text{WO}_6/\text{GCE}$, MWCNT/GCE , and $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$ was calculated to be 636, 261.3, 222.6, and 56.1 Ω . Amongst them, $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$ shows smaller semi-circle results in smaller R_{ct} values. Subsequently, the charge transfer coefficient (K_s) was calculated from equation (2) to examine the resistivity possessed by electrode modifiers [45].

$$R_{ct} = \frac{RT}{n^2 F^2 K_s C} \quad (2)$$

The calculated K_s of bare GCE, $\text{Gd}_2\text{WO}_6/\text{GCE}$, MWCNT/GCE , and $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$ are 0.836×10^{-8} , 2.037×10^{-8} , 2.391×10^{-8} , and 9.487×10^{-8} respectively. Among these various electrodes, $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$ possess higher K_s value which indicates the low resistivity and fast mobility of electrons in the electrode/electrolyte system. From the results, it was evidenced that the $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$ shows excellent electrical conductivity, owing to the structural advantages and the good conductivity of Gd_2WO_6 and MWCNT with the synergetic effect of the $\text{Gd}_2\text{WO}_6/\text{MWCNT}$ compositions.

Furthermore, the cyclic voltammetry (CV) curves display the pair of peaks for each case, whereas amongst them $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$ significantly outplays under identical conditions, indicating the better electrocatalytic activity of the as-synthesized composite in Fig. 5(b). Furthermore, the ΔE_p value between the anodic and cathodic peaks for bare GCE, $\text{Gd}_2\text{WO}_6/\text{GCE}$, MWCNT/GCE , and $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$ was estimated using the formula $\Delta E_p = E_{p,c}/E_{p,a}$ to be 184, 139, 122, and 111 mV. Low current was obtained for the bare GCE owing to the poor electron transport in the ferri-cyanide solution. The $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$ produces increased redox peak current and a slight shift in potential due to the high content of $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$ undergoing the gaining of electrons and the redox reaction with $[\text{Fe}(\text{CN})_6]^{3+/4+}$ compared with other modified electrodes. In contrast, the $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$ modified electrode involves quick electron transfer due to

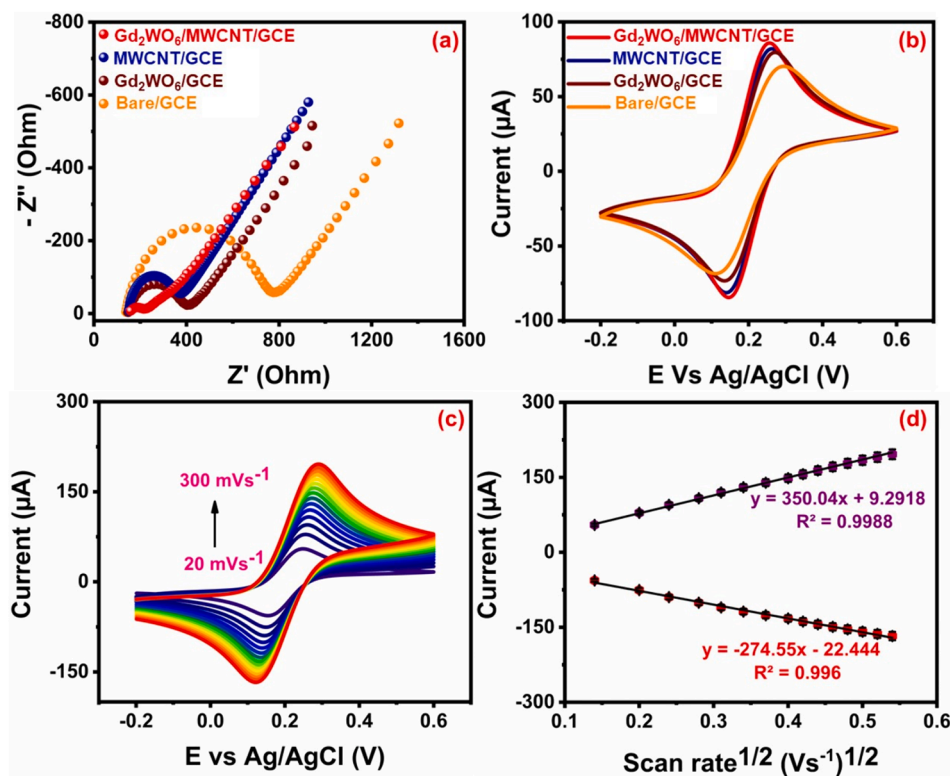


Fig. 5. (a) EIS plot and (b) CV of modified electrodes, (c) CV's of $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$ at different scan rates.

the electron-conducting nature of MWCNT, which becomes more advantageous for electron transport in the $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$ modified electrode.

Fig. 5(c) depicts the voltammetry response of $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$ by varying scan rates from 20 – 300 mV/s. From the figure, it was evidenced that as the scan rate increases the current response gets increased. Fig. 5(d) displays with a regression equation, provides the linear plot for $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$'s current response to the square

root of the scan rate ($I_{pa} = 350.04 v^{1/2} + 9.2918$, $R^2 = 0.9988$, $I_{pc} = -274.55 v^{1/2} + 22.444$, $R^2 = 0.9960$, respectively). The electrochemical active surface area (EASA) was calculated by using the Randles – Sevcik equation [46,47],

$$I_p = (2.69 \times 10^5) n^{3/2} D^{1/2} A v^{1/2} C \quad (1)$$

Using equation (1) EASA was calculated to be 0.079, 0.125, 0.133, 0.156 cm^2 for bare GCE, $\text{Gd}_2\text{WO}_6/\text{GCE}$, MWCNT/GCE , and $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$.

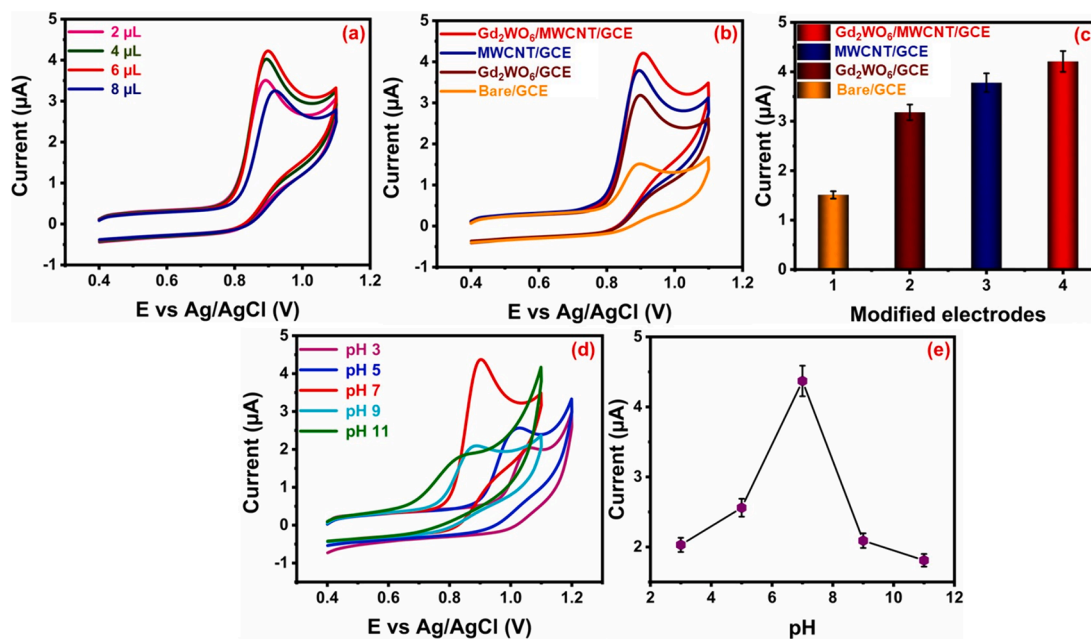


Fig. 6. CV response of $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$ contains 75 μM of SAN (a) different loading catalyst, (b) different modified electrodes, (c) corresponding bar diagram of current response of different modified electrodes, (d) different pH (3 – 11), (e) correlating plot of current response for the varied pH.

MWCNT/GCE. The results confirm the greater electrocatalytic activity and good conductivity of the Gd₂WO₆/MWCNT/GCE owing to the charge transfer kinetics among the redox couples resulting from the synergistic effect.

3.3. Electrochemical detection of SAN with Gd₂WO₆/MWCNT/GCE

3.3.1. Effect of loading catalyst

The amount of loading catalyst plays a major role in efficient electrochemical sensing performance. The CV current response of Gd₂WO₆/MWCNT/GCE was investigated in 0.1 M PBS containing 75 μM of SAN (Fig. 6a). The results illustrate that upto 6 μL, the current response increases and starts decreasing as the intensity dropped at 8 μL. The reason might be attributed to the thickness of Gd₂WO₆/MWCNT/GCE. As a result, 6 μL of Gd₂WO₆/MWCNT/GCE was considered as a loading catalyst concentration for further electrochemical sensor detection of SAN. Table.S1 represents the average loading amount of the Gd₂WO₆/MWCNT on the GCE surface.

3.3.2. Influence of different modified electrodes

The CV response of bare GCE, Gd₂WO₆/GCE, MWCNT/GCE, and Gd₂WO₆/MWCNT/GCE was verified by adding 75 μM of SAN to 0.1 M PBS solution to demonstrate the electrochemical behavior. From Fig. 6b, it was evidenced that the current response of bare was low due to the poor electrocatalytic activity [48]. Fig. 6c represents the bar diagram of the current response of different modified electrodes. When the GCE was modified with Gd₂WO₆ it shows an increased current. The MWCNT-modified GCE shows a slight raise in current as well as a slight shift in potential. Gd₂WO₆/MWCNT/GCE has an appealing peak current with a slight potential shift. The incorporation of Gd₂WO₆ with MWCNT further enhances the fast electron transferability with the sensing ability toward SAN detection.

3.3.3. Influence of pH value

The dependence of oxidation peak potential was investigated using the CV response of different pH studies in 0.1 M PBS. Fig. 6d depicts the response of Gd₂WO₆/MWCNT/GCE of different pH values of PBS (3, 5, 7, 9, 11) in presence of 75 μM of SAN. The results demonstrate that the peak current of Gd₂WO₆/MWCNT/GCE increases until the pH rises from 3 to 7. After pH 7, the peak current decreases as the pH increases from 9 to 11 which is owing to the fact that the amide and amino group in SAN has pK_a values 6.5 and 1.65 respectively [49]. Fig. 6e outlines the bar diagram of the current response of different pH. Linear plot of pH vs potential of Gd₂WO₆/MWCNT/GCE represented in S1. The results illustrate that pH 7 is suitable for further electrochemical sensor studies for SAN detection. Additionally, in the Nernst equation the slope value was employed [50],

$$B = \frac{-2.3025mRT}{nF} \quad (2)$$

where 'm' and 'n' describes the number of protons and electrons, 'B' defines the slope value, 'R' is the gas constant, 'T' describes the room

temperature in kelvin, and 'F' describes the faraday's constant. Calculating the m/n ratio of SAN was determined to be 0.5, confirming that the oxidation pathway of SAN involves an equal number of protons and electrons. Scheme 2 depicts the electrooxidation mechanism of SAN in which two electrons and two protons were involved in the overall mechanism [49].

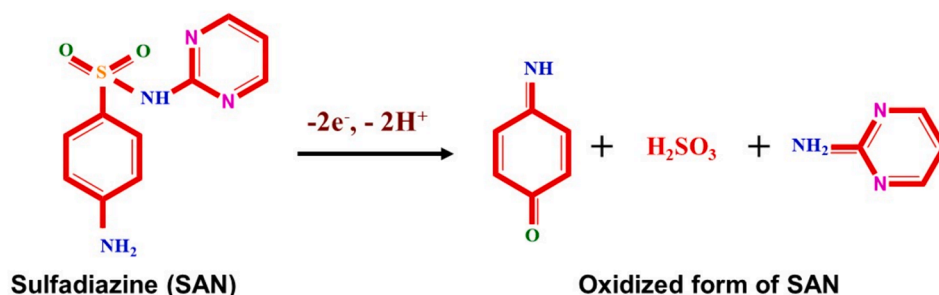
3.3.4. Effect of concentration and scan rate

The effect of varying concentrations of analyte on sensing properties can be verified by investigating the dependence on concentration. The CV response of Gd₂WO₆/MWCNT/GCE in 0.1 M PBS of different concentrations of SAN 15 – 150 μM at a scan rate of 0.05 mV/s. As visualized in Fig. 7a, a distinguishable and sharp peak of SAN was obtained as the concentration of SAN increased. Gd₂WO₆/MWCNT/GCE composite increases electrolyte transport and quick electron transfer speeds up the electrochemical process, and improves peak current, allowing for better signal detection proves the antifouling property [51]. Fig. 7b displays a linear plot of the current response which was extended to higher concentration SAN with a linear regression equation $I_{pa} = 0.0454 (\mu M) + 0.5587$, $R^2 = 0.9953$ respectively. The superior electrocatalytic activity and sensing of Gd₂WO₆/MWCNT/GCE were attributed to the large surface area and synergism between the Gd₂WO₆ and MWCNT in the composite. Thus, these results indicate the Gd₂WO₆/MWCNT/GCE as a suitable candidate electrode for SAN detection in environmental samples.

The scan rate was investigated to verify the absorption or diffusion-controlled process of the electrode process. The CV response of Gd₂WO₆/MWCNT/GCE in 0.1 M PBS in the presence of 75 μM of SAN with a scan rate range of 20 – 300 mV/s (Fig. 7c). The results in Fig. 7d indicates the linear increase in current as the scan rate increases. The linear relationship between the anodic peak current and scan rate was expressed with correlation regression, $I_{pa} = 18.496 (Vs^{-1}) + 3.2446$, $R^2 = 0.9953$ respectively. Fig. 7e indicates the linear plot of log of current vs log of scan rate with correlation regression, $I_{pa} = 0.3604 (Vs^{-1}) + 1.0981$, $R^2 = 0.9701$ respectively [52–54]. These results evince the rapid oxidation detection of SAN on Gd₂WO₆/MWCNT/GCE, owing to the adsorption-controlled process with a slight shift in the peak potential [55].

3.4. Analytical performance of SAN

Differential pulse voltammetry (DPV) is considered the most sensitive and accurate electrochemical method to examine the analyte at low concentrations. Fig. 8a displays the DPV response of Gd₂WO₆/MWCNT/GCE after incubation of different concentrations of SAN in 0.1 M PBS at a scan rate of 0.05 mV/s. As depicted in Fig. 8a the peak current as the concentration increases from 0.01 – 200 μM; 200 – 671 μM. The anodic peak current gradually increases as the concentration increases with a slight shift in positive potential. Fig. 8b depicts the calibration plot of different concentrations of SAN against the DPV current response (inset represent the calibration plot for low concentrations of SAN). The linear regression equation demonstrated as $I_{pa} = 0.026 \text{ SAN } (\mu M) + 8.5176$, R^2



Scheme 2. Electro-oxidation mechanism of sulfadiazine (SAN).

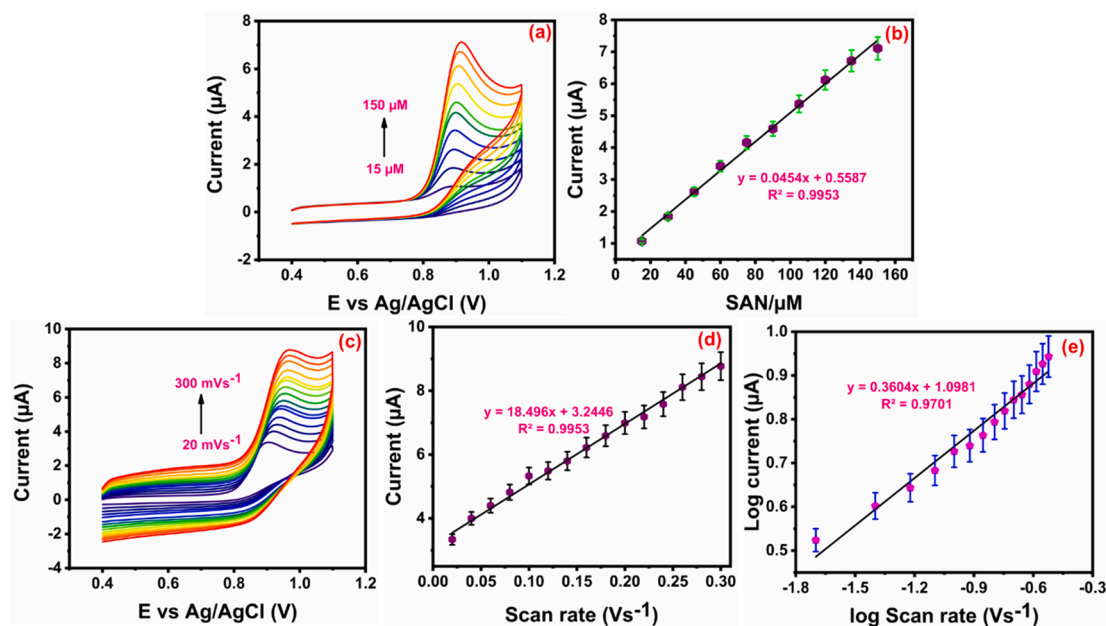


Fig. 7. (a) CV profile of Gd₂WO₆/MWCNT/GCE for different SAN concentrations (15 μM – 150 μM), (b) corresponding linear plot of SAN concentrations against current response, (c) CV profile of Gd₂WO₆/MWCNT/GCE for different scan rates, (d) comparable linear plot of current response against scan rate, and (e) comparable linear plot of log of current response against log of scan rate.

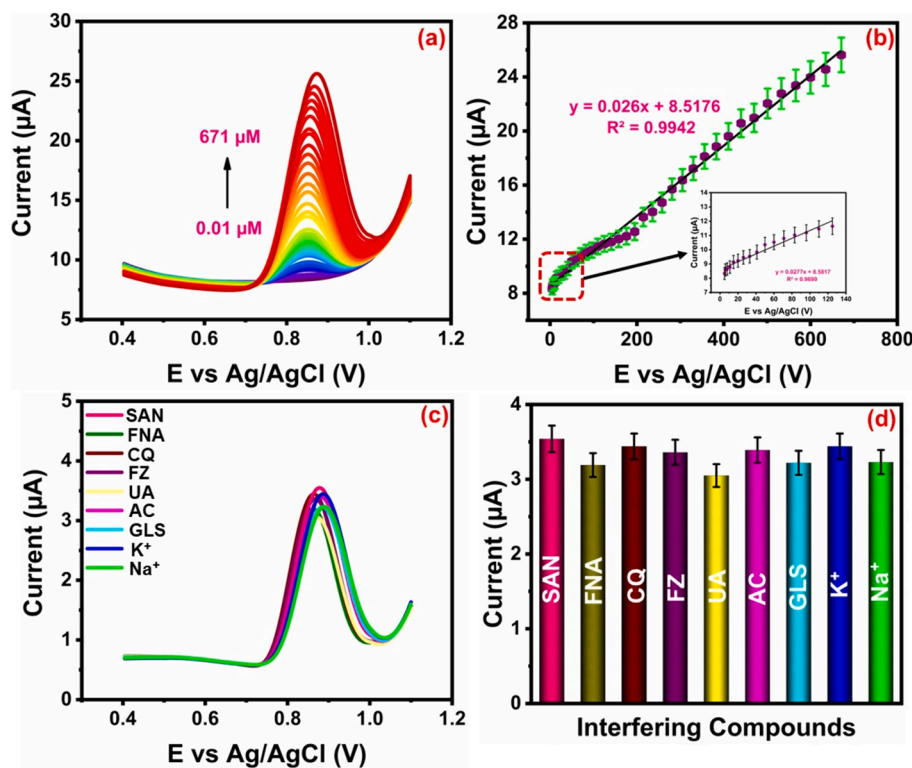


Fig. 8. (a) DPV response of Gd₂WO₆/MWCNT/GCE at several concentrations of SAN, (b) linear relationship between current response and SAN concentrations, (c) DPV response of anti-interfering ability of Gd₂WO₆/MWCNT/GCE with the existence of 10 μM of SAN along with interfering compounds, (d) corresponding bar image of interfering compound's current response.

= 0.9942, respectively. Based on the equation $LOD = 3 s/q$ [56], the LOD of Gd₂WO₆/MWCNT/GCE was calculated to be 2 nM and sensitivity to be 0.371 μA μM⁻¹. Thus, as-constructed sensor exhibits a wider linear range and low LOD than the other previously reported literature depicted in Table.S2. This overview emphasizes the promising response of Gd₂WO₆/MWCNT/GCE for the detection of SAN. Such

excellent behavior is owing to the synergetic effect between the Gd₂WO₆ and MWCNT. The unique properties and specific features of Gd₂WO₆/MWCNT/GCE provides high surface area, active sites, and favored nanostructure.

3.5. Interference, Reproducibility, and stability

The selectivity of the newly constructed electrochemical sensor is an important parameter. Selectivity can help to improve sensor precision and avoid making incorrect decisions in real-time diagnosis. The ability of the anti-interference at $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$ has been scrutinized containing 10 μM of SAN with 10 fold concentration of several interfering drugs such as flufenamic acid (FNA), clioquinol (CQ), furazolidone (FZ), also with biological compounds uric acid (UA), ascorbic acid (AC), glucose (GLS), and with hard and soft acid and bases K^+ , and Na^+ by DPV technique depicted in Fig. 8c. The current response of $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$ in the existence of interfering reagents was compared with the current response for the SAN detection in Fig. 8d. The results conclude that the interfering compounds have a negligible current response towards SAN detection. The results indicate the $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$ can be successfully used for SAN detection.

For practical use, the prepared sensor should be reproducible and stable in real-time applications. The reproducibility of $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$ towards the detection of SAN was verified by the distinct current response of three different electrodes. Fig.S2a depicts the DPV response of three distinct electrodes. The relative standard deviation (RSD) of the peak oxidation current was estimated as 1.46 % indicating the appreciable reproducibility of $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$. Moreover, $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$'s stability was studied both before and after storage using DPV in 0.1 M PBS contains 100 μM of SAN. Fig.S2b displays the DPV response of $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$ after storing it for 12 days. As shown in Fig.S2b, the fabricated electrode retained 95 % of the initial current after 12 days of storage. The above results demonstrate the $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$ has reproducibility and good stability for the electrochemical sensor detection of SAN.

3.6. Real sample analysis

To evaluate the potential of the prepared sensor $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$ in real samples, urine sample from human, and river water sample were determined. SI clarifies the real sample preparation. Initially, the blank current was noted without the addition of SAN, after a known concentration of SAN (10, 20, and 30 μM) was injected. The CV response of $\text{Gd}_2\text{WO}_6/\text{MWCNT}/\text{GCE}$ was depicted in Fig.S3(a&b) of human urine and water samples. Table.S3 displays the found and recovery percentage. We envisioned that the proposed material can be utilized for the identification of SAN in human urine and water samples.

4. Conclusion

A new electrode material of Gd_2WO_6 decorated with MWCNT synthesized by hydrothermal method. Gd_2WO_6 has a strong synergetic bond with the MWCNT which improves the overall conductivity of $\text{Gd}_2\text{WO}_6/\text{MWCNT}$, resulting as an excellent electrocatalyst for SAN detection. This is the first report based on rare earth tungstate with a carbon composite on their electrochemical behavior. Owing to the higher active sites and good electron transport $\text{Gd}_2\text{WO}_6/\text{MWCNT}$ used for the detection of SAN shows a broad range of 0.01 – 671 μM , a low LOD of 0.002 μM , excellent anti-interfering ability, and good stability. Moreover, the sensing material was efficiently applied to quantify the SAN in human urine and water samples and obtained recovery results of 99.1 – 98.3 % and 99 – 98.2 %, showing the sensor has feasibility in real-time analysis. The results pave the way for the rare earth tungstate-based sensors which can be used as promising candidates for the detection of various environmental contaminants and further applications.

CRediT authorship contribution statement

Santhiyagu Sahayaraj Rex Shanlee: Conceptualization, Supervision, Methodology, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Sundaresan Ruspika:**

Conceptualization, Supervision, Methodology, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Shen-Ming Chen:** Supervision, Project administration, Investigation, Funding acquisition, Conceptualization. **Ramachandran Balaji:** Conceptualization, Writing – original draft, Visualization. **Ying-Chih Liao:** Supervision, Resources, Formal analysis. **Narendhar Chandrasekar:** Software, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2024.152179>.

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