Herein, a Barium tungstate ($\text{BaWO}_4$) and Graphitic carbon nitride (GCN) based new electrochemical sensor ($\text{BaWO}_4$/GCN/GCE), for the detection of diphenylamine (DPA). Nearly oval-shaped $\text{BaWO}_4$ was anchored on the GCN sheets by a worthwhile and simple hydrothermal route. Cyclic voltammetry (CV) and Differential pulse voltammetry (DPV) were used to scrutinize the electrochemical performance of DPA on $\text{BaWO}_4$/GCN/GCE. The prepared sensor exhibited phenomenal electrocatalytic action towards the detection of DPA. Moreover, the $\text{BaWO}_4$/GCN sensor exhibiting good sensitivity of $1.51267 \, \mu\text{A} \, \mu\text{M}^{-1} \, \text{cm}^{-2}$ with the low detection limit (LOD) of 1 nM and a broader linear range from 0.001 to 533 µM for DPA detection under the improved experimental conditions. Furthermore, the effect of storage duration on the $\text{BaWO}_4$/GCN sensor’s CV response reveals the improved stability. Owing to these extraordinary analytical advantages, the as-produced sensor was applied to analyse the DPA level in apple juice with satisfactory results.

**Keywords:** Diphenylamine, Graphitic carbon nitride, scheelite, electrochemical sensor, cyclic voltammetry.
1. INTRODUCTION

Fungicides are commonly used worldwide to protect the postharvest decay of crops from pathogens[1]. The anti-oxidant, Diphenylamine (DPA) is used as an anti-scald agent. Usually, at the time of storage, the fruit's skin undergoes some kind of distortion called Scald[2]. DPA, which is widely used in fruits to store it for prolong duration on cooled air and controlled atmosphere as an inhibitor[3]. The post-harvest treatment of DPA prevents the fruits (apple and pears) from the scald[4]. And also treated after the harvesting to maintain its color at the time of storage. During the transportation of fruits, it preserves the fruits and maintains their freshness. DPA was used in pharmaceuticals to synthesis its derivatives and also to prepare photography chemicals[5]. Moreover, for the nitrocellulose explosives and single, double, and triple base propellants in missiles, it is used as a stabilizer[6]. DPA has poor solubility in water and has superior solubility in organic solvents. Even though washing of apple and pear on water, it may stick on the apple and pear[7]. DPA has high reactivity, due to the imine H-atom, which is readily electrophilically substituted[5]. People who consume food products with DPA are hazardous to health and it has severe risks like bladder diseases, eczema, hypertension, and it damages the Red Blood Cells (RBC)[8]. So, the level of DPA is regulated by the European Union, and it has permitted the DPA with the level of 5mg Kg\(^{-1}\) for apples and 10mg Kg\(^{-1}\) for pears[9]. For determining DPA, various methods are available, such as fluorescence, spectrofluorometric technique, and high-performance liquid chromatography, tandem mass spectrometric, and electrochemical techniques[10]. Among these methods, Electrochemical sensors have been considered as an attractive and effective method due to their modest price, ease of sample preparation, effective way with rapid detection, a broad range of detection, low level of detection limit, high level of selectivity, and sensitivity towards the analyte[11].

Graphitic carbon nitride (GCN) is a non-metal semiconductor with N-atom substituted graphitic-conjugated layer assembly made up of repeating heptazine units bound through the 3° amines[12]. The electronic property of GCN was influenced by the lone pair present in the N- atom. Layers of GCN with the distance of \(d = 3.26 \text{ Å}\), it is 3% high dense packing than graphite \(d = 3.35 \text{ Å}\)[13]. It is one of the carbonaceous materials with electron-rich properties, multiple surface functionalities, and connected with the H-bonding[14]. Because of its mechanical, unique optical, and physicochemical properties[15], GCN has recently been suggested as a potential material for solar water splitting[16], SERS sensing[17], visible-light photocatalytic hazardous pollutant degradation[18], optoelectronics[19], and bioimaging[20] applications. The intrinsic structure of GCN contains an abundance of uniform nitrogen coordinators, which provides more number of metal coordination sites as a catalytically active sites throughout the electrocatalytic process[21]. This means that suitable modification will greatly increase the electrocatalytic function of GCN.

The scheelite type AWO\(_4\) (A = Ca, Sr, and Ba) has more active surface areas. In which the alkali earth metal coordinated with the eight oxygen atoms and the tungstate coordinated with the four-oxygen atom[22]. The scheelite type metal tungstate is promising candidate and attracted towards the various fields like solid-state laser system[23], scintillator[24], and energy storage[25] materials and mostly used as photocatalyst[26]. Many research groups are interested in barium tungstate (BaWO\(_4\)) crystals because of its potential applications in batteries[27], capacitors[28], photocatalysis[29], electrochemical
sensors[30], and photoluminescent materials[31]. BaWO₄ is one of the semiconductor, it comes under the scheelite group of crystallized tetragonal arrangement with the I4₁/a space group, in which eight O-atoms linked to the Ba-atom and the tetragonal coordination of W-atom connected to O-atoms; hence, clusters of [BaO₈] and [WO₄] units are combined to form the BaWO₄ crystal[28]. To prepare this material, various methods have been suggested, including microwave-assisted[32], Co-precipitation[33], Czochralski method[34], sol-gel technique[35], and hydrothermal synthesis[36].

In this study, we successfully prepared BaWO₄/GCN nanocomposite by using thermal polymerization and hydrothermal method. Further, BaWO₄/GCN nanocomposite was used as the electrode material to detect the level of DPA. The formation of a Barium tungstate nanoparticle decorated on Graphitic carbon nitride was analyzed by spectroscopic and analytical techniques. Working electrode (GCE) has modified by the as prepared Barium tungstate nanoparticle decorated on Graphitic carbon nitride nanocomposite for detection of DPA. The proposed sensor provides excellent selectivity with the greater sensitivity, and quick response to detect DPA in apple juice. Here in this work, we report the modified electrode of BaWO₄/GCN to have a large electrode active surface area and high electrical conductance for the detection of diphenylamine.

2. EXPERIMENTAL SECTION

2.1. Materials and Electrolyte

Diphenylamine((C₆H₅)₂NH), Melamine (C₃H₆N₆, 99%), Barium nitrate (Ba(NO₃)₂, ≥99%), Acetic acid (CH₃COOH, ≥99%), Sodium tungstate dihydrate (Na₂WO₄·2H₂O, ≥99%), Sodium hydroxide (NaOH, 98%), Hydrochloric acid (HCl, 36.5–38.0 %), potassium chloride (KCl, 99.0-100.5%), potassium ferrocyanide (K₄[Fe(CN)₆]), Potassium ferricyanide (K₃[Fe(CN)₆]), All the chemicals were purchased from Sigma-Aldrich and used exactly as obtained. As a supportive electrolyte, phosphate buffer (PB) with 0.1 M was prepared by homogeneously mixed with Na₂HPO₄ and NaH₂PO₄ in distilled water (DW), and the electrolyte pH was modified with HCl and NaOH. Throughout the experiment, the required solutions were prepared with the deionized water (DI) and ethanol. All of these chemicals used in the experimentations were of standard analytical grade, and all over the electrochemical experiments were conducted at ambient temperature and the phosphate buffer were purged with N₂ gas before each experimentation.

2.2. Preparation of GCN

GCN was synthesized by the thermal polymerization of melamine. Briefly, 2 g of melamine was ground well to get a uniform mixture with the mortar and pestle. The grounded mixture was transformed into an enclosed alumina boat, it was pyrolyzed in a low oxygen horizontal quartz furnace at 550 °C for 3 h with the heating rate of 2 °C min⁻¹. Then the resulted granules were placed inside the quartz furnace for naturally cooled down to room temperature and treated with 1M HCl for 12 h and showered thrice.
with DI water. The washed product was desiccated at 60 °C overnight in the oven. The obtained yellow sample of GCN was ground well into a fine material for further usage.

2.3. Preparation of BaWO₄

For the synthesis of BaWO₄, 4 mmol of (Ba (NO₃)₂), 4 mmol Na₂WO₄.2H₂O, and 5ml of CH₃COOH added to the 100 ml beaker, then 45 ml of DI water was added and for 1h the mixture was stirred. After the obtained homogeneous solution pH was tuning to 12 by the addition of 0.1M NaOH. Then, the obtained mixture was then shifted to a Teflon-lined autoclave with the volume of 100 ml and it was held at 180°C for 24 h. Then, it is allowed to cool down to the room temperature, followed by centrifugation to collect the product. Finally, the obtained product was washed thrice with DI and C₂H₃OH. Then, the product was desiccated at 60 °C overnight and named BaWO₄.

2.4. Preparation of BaWO₄/GCN

5 mg of as-synthesized BaWO₄ and 10 mg of GCN were suspended in 30 ml of DI water and sonicated for 30 minutes. After that, the resulting mixture was centrifuged, rinsed with water, and dried for 12 hours at 50°C. Finally, the obtained product was named BaWO₄/GCN.

![Scheme 1](image)

**Scheme 1.** Graphically illustrated the preparation of BaWO₄/GCN composite by thermal polymerization and hydrothermal method.

2.5. Instrumentation

The chemical valence state of as-synthesized BaWO₄/GCN composite was studied by X-ray photoelectron spectroscopy (XPS) using Thermo ESCALAB 250 instrument. The crystallinity of the
prepared composite was determined by using powder X-ray diffraction (XRD) with an XPERT-PRO spectrometer with the monochromatized Cu-Kα radiation (λ = 1.54 Å). Morphology of as-synthesized composite was obtained by Field emission scanning electron microscopic (FE-SEM) using Hitachi S-3000 microscope. Electrochemical conductivity of prepared sample has measured using Electrochemical impedance spectroscopy (EIS), and Cyclic voltammetry instrument (CHI 1205a) and Differential pulse voltammetry instrument (CHI900) (U.S.A) were used to perform the electrochemical measurements. Both electrochemical experiments were carried out with a three-electrode device that included a glassy carbon electrode (GCE) as a working electrode (working electrode surface area of 0.071 cm²), reference electrode as saturated Ag/AgCl, and a platinum wire as a counter electrode.

2.6. Preparation of the modified electrode

GCE’s surface was washed with 0.05µm of α-alumina (α-Al₂O₃) powder over the silicon carbide paper and rinsed under the DI water flow to remove the encrusted particle from the GCE surface, along with ethanol wash and dried. Later, 1mg of as-prepared composite dispersed in 2 ml of water and sonicated for 30 minutes. 6 µL of composite suspension was loaded on GCE surface by drop cast method and it was dried at 50°C for 15 minutes. Further, it can be utilized to the electrochemical investigation.

3. RESULT AND DISCUSSION

3.1. Morphological characterization of BaWO₄ and BaWO₄/GCN composite

![Figure 1](image)

Figure 1. (a-c) High and low magnifying FESEM image of BaWO₄, (d and e) FESEM image of BaWO₄/GCN nanocomposite.
The structural morphology of the as-synthesized BaWO$_4$, BaWO$_4$/GCN nanocomposite were examined by FESEM. Low and high magnifying FESEM images of BaWO$_4$ nanoparticles (Fig.1a-c) clearly shows the random distribution with morphology nearly the oval shape and has a smooth surface. Arrangement of nanoparticles were lower in aggregation and arranged uniformly with average particle size of 750-800 nm. FESEM images of BaWO$_4$/GCN nanocomposite in Fig.1d and e shows that BaWO$_4$ nanoparticles are randomly and grown on the GCN surface, and the GCN sheets in the composite were not perfectly smooth, it was observed to be wrinkled. Moreover, BaWO$_4$ and GCN combined to form tightly and less aggregated nanostructure. Nanostructured BaWO$_4$ has effective intercalation to the GCN sheets leads to the structural constancy of the composite due to the cation-π interaction of the GCN and BaWO$_4$. We surely estimated that the interaction of BaWO$_4$ and the GCN should be accountable to the intrinsic benefits of the greater electrochemical property of the BaWO$_4$/GCN electrode material. Fig.2. (a-f) depicts the FESEM-EDX mapping of BaWO$_4$/GCN composite, it confirmed that the presented elements are equally distributed in the composite material such as Barium (Ba), Tungsten (W), Oxygen (O), Carbon (C), Nitrogen(N). The weight percentage of presented elements was confirmed by EDX (Fig.3) shows Ba, W, O, C and N were presented with 20.5, 25, 22, 14.2, and 18.3%, respectively.

**Figure 2.** (a-f) FESEM-EDS mapping of BaWO$_4$/GCN nanocomposite (a) mixed color of Ba, W, O, C, N (b) N (blue dots), (c) O (green dots), (d) C (yellow dots), (e) Ba (red dots), (f) M (violet dots).
3.2. Structural characterization of BaWO$_4$ and BaWO$_4$/GCN composite

The crystalline phase of GCN, BaWO$_4$, and BaWO$_4$/GCN were examined by powder X-ray diffraction displayed in fig.4. Diffraction peak obtained at the $2\theta = 26.2^\circ$, corresponding to (002) planes for the stacking peak of the interplanar continuous repeating tris-triazine network of typical GCN. Interestingly, the high-intensity diffraction peaks for BaWO$_4$ of the following planes (101), (112), (004), (202), (211), (204), (220), (116), (215), (132), (224), and (008) are corresponding to the standard tetragonal unit cell of BaWO$_4$ (JCPDS 72-0746)[37], were also observed in our BaWO$_4$/GCN composite. Diffraction peaks of BaWO$_4$/GCN composite were observed similar to that of BaWO$_4$ with lower intensity after the addition of GCN, which results confirms the successful formation of BaWO$_4$/GCN nanocomposite. Size of the particle was determined from the Debye-Scherrer equation. ($D=K\lambda/ (\beta \cos \theta)$;
\( \lambda \) is the wavelength of Cu-K\( \alpha = 1.54178 \) Å, D is the crystallite size; K is the Scherrer constant =0.89, \( \theta \) is the XRD peak position, \( \beta \) signifies the full width at half-maximum (FWHM). The calculated average particle size of the BaWO\(_4\) was \( \approx 800 \) nm. Consequences for the XRD pattern of BaWO\(_4\)/GCN composite, typical peaks for BaWO\(_4\) and GCN with the good intensity. Hence, the attained outcomes established that the effective combination of BaWO\(_4\)/GCN high purity nanocomposite.

![Figure 5](image_url)

**Figure 5.** (a) XPS overall survey spectra. (b) High-resolution spectra of C 1s, (c)N 1s, (d) O 1s, (e) Ba 3d, and (f) W 4f region for BaWO\(_4\)/GCN nanocomposites.

The chemical composition and chemical state of the composite were examined by the XPS. Fig.5 (a) shows the overall survey spectrum of BaWO\(_4\)/GCN, displayed peaks at corresponding binding energies of Ba, W, O, C, and N. Fig.5 (b) shows the C1s spectrum, which attributed to GCN at the binding energies at 285.9, 288.9, and 291.2 eV corresponding to the C-C/C=C, N-C=N, and O-C=O respectively[38]. Fig.5 (c) Shows that the N1s spectrum of GCN with the binding energies at 401.6, 402.5, 403.6 eV conforming the graphitic-N, pyrrolic-N, and pyridinic-N respectively[39]. The high-resolution O1s spectrum shows two peaks in Fig.5 (d) binding energies at 534.6 and 536.1eV respectively[40]. Ba 3d Spectrum shown in Fig.5 (e) Which displays double peaks with the binding energies of 785.3 and 800.7eV corresponding to the 3d\( _{3/2} \) and Ba 3d\( _{5/2} \) energy states respectively[41]. Fig.5 (f) displays the W 4f high-resolution spectrum, which exposed double peaks at the binding energies of 34.1 and 41.6eV and its agreeing to the energy states of 4f\( _{7/2} \) and W 4f\( _{5/2} \) respectively[42]. The obtained results confirmed the presence of Ba 3d, C 1s, O 1s, W 4f, and N1s, in the BaWO\(_4\)/GCN composite.
3.3. Electrochemical Impedance spectroscopic (EIS) studies

The charge transmission ability of the prepared electrocatalyst are examined by the EIS technique. The EIS performance of bare GCE, BaWO₄/GCE, GCN/GCE, and BaWO₄/GCN/GCE in 0.1M KCl solution containing 5mM of K₃[Fe(CN)₆] and K₄[Fe(CN)₆] and the equivalent Nyquist plot are resulted in (Fig. 6a). Randle's equivalent circuit was used to fit Nyquist plots, which are shown in the inset of Fig.6a. The charge transfer resistance (Rct) observed due to the faradic reaction that occurred among the electrode and electrolyte is described by the semicircle, which was noticed at the higher frequency region. The Rct values were calculated to be 866.9, 818.28, 408.403, and 381.93Ω for bare GCE, BaWO₄/GCE, GCN/GCE, and BaWO₄/GCN/GCE respectively.

![Figure 6](image)

Figure 6. (a) Nyquist plot of bare GCE, BaWO₄/GCE, GCN/GCE, and BaWO₄/GCN/GCE with the inset of Randles Equivalent circuit, (b) CV profile of bare GCE, BaWO₄/GCE, GCN/GCE, and BaWO₄/GCN/GCE at the scan rate 50 mV s⁻¹, (c) CV response of BaWO₄/GCN/GCE at the scan rate as of 20 to 300 mV s⁻¹, and (d) linear plot of obtained current versus scan rates. All of these experimentations were performed in 5mM [Fe (CN)₆]₃⁻/₄⁻ containing 0.1 M KCl solution.

And the obtained results display that the BaWO₄/GCN modified GCE has high charge conductivity as compared to the other modified and bare GCE, BaWO₄, GCN modified GCE shows less Rct value comparing to the bare GCE, this finding showed that the integration of GCN and BaWO₄ significantly decrease the resistivity during electron transport, and the synergistic effect can effectively decrease the charge transfer resistance, resulting in a desirable charge transfer resistance (Rct) of the BaWO₄/GCN nanocomposite in the [Fe (CN)₆]₃⁻/₄⁻ system.
Also, cyclic voltammetry (CV) was performed to attain a better understanding of the BaWO₄/GCN/GCE nanocomposite, as shown in Fig. 6b. The BaWO₄/GCN/GCE nanocomposite has a higher electrochemical redox peak current than the GCN and BaWO₄ catalysts. The high redox peak current attained for the BaWO₄/GCN/GCE composite, due to its high specific surface area and the active sites also increased by the interaction of BaWO₄ nanoparticle and GCN layers, therefore BaWO₄/GCN nanocomposite had excellent electrocatalytic activity. The BaWO₄/GCN modified GCE has relatively higher redox peak current (Ip) with the very smaller peak-to-peak separation (ΔEp) than the other modified GCE and bare GCE; The higher (Ip) and lower ΔEp of BaWO₄/GCN suggest rapid electron transfer in [Fe (CN)₆]³⁻/⁴⁻ system.

The catalytic kinetics of BaWO₄/GCN nanocomposite was investigated at various scan rate ranging from 20 to 300 mV s⁻¹. As displayed in Fig.6c, the observed redox peak current of BaWO₄/GCN/GCE increased, when the scan rate increased from 20 to 300 mVs⁻¹, showing the polarization curve of an aqueous electrolyte and the quick electron transfer kinetics of electrode. Fig. 6d. shows a linear regression of Ip and Ipc peak current versus the square root of the scan rate, with coefficients (R²) of 0.9986 and 0.9904, respectively. The Electrode Active Surface Area (EASA) of the BaWO₄/GCN/GCE was calculated using the Randles–Sevcik equation (1)

\[
I_{pa} = (2.69 \times 10^5) n^{3/2} AC \frac{1}{2} v^{1/2}
\]

Where ‘A’ is the active surface area of the electrode, ‘Ipa’ is the peak current value, ‘D’ denotes the electrolyte diffusion coefficient, ‘C’ is the ferricyanide solution concentration, ‘n’ represents the number of electrons involved in the redox reaction, and ‘v’ stands for the scan rate (V s⁻¹). EASA was calculated from the slopes of ‘Ip’ vs. square root of scan rate (mV s⁻¹) in Fig. 6d. The measured EASA for the bare GCE, BaWO₄/GCE, GCN/GCE, and BaWO₄/GCN/GCE were 0.96, 0.124, 0.135, and 0.156 cm² respectively. The higher EASA of BaWO₄/GCN/GCE is predicted to support the electrochemical reaction with DPA.

3.4. Electrochemical detection of DPA

![Figure 7](image-url)

Figure 7. (a) The CV current response of 100 µM of DPA at BaWO₄/GCN/GCE electrode with different amount of catalyst (BaWO₄/GCN) coating on GCE (4, 6, and 8 µL), and (b) the corresponding bar diagram for peak current versus the amount of BaWO₄/GCN catalyst loading on GCE (µL).
The effect of BaWO$_4$/GCN/GCE nanocomposite concentration on the surface of the working electrode towards the electrochemical oxidation of DPA was examined in CV measurement by variable the covering concentration of BaWO$_4$/GCN/GCE. Fig. 7a shown the CV current response of GCE was modified with different concentrations of BaWO$_4$/GCN nanocomposite 4 µL, 6 µL, and 8 µL with the addition of 100 µM DPA in 0.1 M (pH7) PB solution at a scan rate of 50 mV s$^{-1}$. As related to altered GCE with other concentrations, the GCE modified with BaWO$_4$/GCN 6 µL has a higher current response. As a result, an electrode with a concentration of 6 µL was used for further electrochemical investigation. Fig. 7b expressions the bar graph for CV current response versus catalyst dosage (µL).

![Figure 7a](image1)

![Figure 7b](image2)

**Figure 8.** (a) CV profile of bare GCE, BaWO$_4$/GCE, GCN/GCE, and BaWO$_4$/GCN/GCE in the presence of 100 µM DPA with 0.1 M PB (pH 7.0) with the scan rate 50 mV s$^{-1}$, (b) the dependence bar diagram for oxidation current response for DPA over different modified GCEs, (c) CV responses of BaWO$_4$/GCN/GCE at different concentration of DPA (20-100 µM) with 0.1 M PB (pH 7.0) with the scan rate 50 mV s$^{-1}$. (d) The linear calibration plot for oxidation peak current Vs concentration of DPA.

Initially, CV was performed to inspect the electrochemical response of DPA using different modified and unmodified GCE. The electrochemical oxidation of DPA with bare GCE, BaWO$_4$/GCE, GCN/GCE, and BaWO$_4$/GCN/GCE in 100 µM DPA with 0.1 M PB (pH 7.0) at a scan rate of 50 mV s$^{-1}$ was shown in Fig. 8a. Bare GCE had a low peak current ($I_{pa}$) for the electrochemical detection of DPA, demonstrating that the bare GCE had a low number of catalytic active sites. The BaWO$_4$/GCN altered
The electrode has a higher $I_{pa}$ than the other modified electrodes, this is because the BaWO$_4$/GCN composite on the electrode surface enhances the catalytic active sites by increasing the quick electron transfer.

**Scheme 2.** The overall electrochemical oxidation mechanism of DPA on the BaWO$_4$/GCN/GCE.

**Figure 9.** (a) CV response of BaWO$_4$/GCN/GCE at various scan rates (20-300 mVs$^{-1}$) in 0.1 M PB (pH 7.0) contained 100 µM of DPA. (b) The dependence plot for peak current versus scan rates. (c) CV responses of BaWO$_4$/GCN/GCE at different pH (3.0 to 11.0) of PB with the addition of 100 µM DPA with 0.1 M PB (pH 7.0) with the scan rate 50 mV s$^{-1}$, and (b) the corresponding linear plot for different pH (3.0-11.0) versus potential and current.
As a result, BaWO$_4$/GCN has more catalytically active sites than other comparative catalysts. The synergetic effects of BaWO$_4$ nanoparticle interact with the GCN layer improves the electrocatalytic activity and excellent conductivity. Fig.8b displays the bar diagram for oxidation peak current response for DPA over different modified and unmodified GCE.

Fig. 8c displays the CV curves of BaWO$_4$/GCN/GCE at different DPA concentrations (20 to 100 µM) with 0.1 M PB (pH 7.0) with scan rate of 50 mV s$^{-1}$. The oxidation current response of DPA increased gradually with the increasing DPA concentration from 20 to 100 µM. Which demonstrates the rapid electron transfer of BaWO$_4$/GCN/GCE nanocomposite. Fig. 8d shows the linear plot of oxidation peak current versus concentration of DPA, which displays a good linear regression equation with the coefficient $I_{pa} = -0.3266$ (µM) -3.1126, and $R^2$ = of 0.991 respectively.

A different scan rate study was done to demonstrate the electrocatalytic kinetic performance of BaWO$_4$/GCN/GCE towards DPA by CV analysis. Fig.9a depicts CV responses of BaWO$_4$/GCN/GCE for 100 µM of DPA in 0.1 M PB (pH 7.0) with various scan rates (20 to 300 mV s$^{-1}$). The $I_{pa}$ gradually increased as the scan rate increased, and the plot shows a strong linear relationship between the scan rate and the $I_{pa}$. The resulted plot (Fig.9b) displays the coefficient and linear regression of $I_{pa} = -37.604(V s^{-1}) - 2.4441$, $R^2 = 0.993$ respectively. It exposes the electrocatalytic oxidation of DPA at the BaWO$_4$/GCN/GCE process as the adsorption-controlled process.

Electrocatalytic property of BaWO$_4$/GCN/GCE also relates to the pH value of PB. CV analysis was performed with several pH ranges (3.0, 5.0, 7.0, 9.0, and 11.0) of PB containing 100 µM DPA at a scan rate of 50 mV s$^{-1}$ to better understand the electrocatalytic performance of BaWO$_4$/GCN/GCE shown in (Fig. 9c). As we have shown in Fig.9 when increasing the pH of PB the anodic peak potential ($E_{pa}$) shifted towards a negative direction. Fig. 9d shows the linear plot between pH versus $E_{pa}$, and oxidation peak current response with the linear regression equation and coefficient were $E_{pa} = -0.0396 pH + 0.8465$ and $R^2 = 0.9946$ respectively. The obtained slope value is -0.039 V pH$^{-1}$, which is closer to a theoretical value of -0.059 V pH$^{-1}$, indicating that the electrochemical oxidation reaction occurs at electrode surface which involves an equal amount of protons and electrons[43].

3.5. Determination of DPA by DPV analysis

BaWO$_4$/GCN/GCE sensor’s reliability for detecting DPA was tested using DPV analysis. Under 0.1 M PB (pH 7.0), the DPV response of BaWO$_4$/GCN/GCE to continuous dose of various concentrations of DPA (0.001–533 µM) is exposed in Fig. 10a. The $I_{pa}$ response increased rapidly following each addition of DPA. The obtained current response of BaWO$_4$/GCN/GCE was linearly scaled with the wide concentration of DPA present in Fig. 10b. $I_{pa}$ (µA) = 0.1074 [DPA] (µM) +13.979 and the coefficient ($R^2$) of 0.9958 can be found as linear regression equation. The limit of detecting (LOD) was calculated to be 0.0010 µM by the standard equation, LOD = 3 S/$q$, where ‘$q$’ is the slope value (0.1074 µA µM$^{-1}$) from the calibration plot, and ‘S’ is the standard deviation obtained from the five measurements of the blank signal (0.00003729 µA). Meanwhile higher sensitivity was obtained to be 1.5126 µA µM$^{-1}$ cm$^{-2}$. In addition, as shown in Table 1, the analytical parameters of the BaWO$_4$/GCN/GCE sensor for DPA sensing were compared to the analytical parameters of other
recorded DPA sensors in terms of linear range, sensitivity, and LOD. It can be noted that the suggested BaWO₄/GCN/GCE sensor’s LOD and linear range were lower and extensive than those of previous stated DPA sensing materials.

Figure 10. DPV response of the BaWO₄/GCN/GCE with various concentration of DPA (0.001-533 µM) in 0.1 M PB (pH 7.0), (b) the linear plot for Iᵦ response versus concentration of DPA, (c) the DPV current response of BaWO₄/GCN/GCE for 100 µM containing some potential interfering species, in 0.1 M PB (pH 7.0), and (d) The related bar plot of relative error (%) of current Vs interfering molecules.

Table 1. Comparisons of the BaWO₄/GCN/GCE linear range, sensitivity, and limit of detection for electrochemical detection of DPA with previously reported electrodes.

<table>
<thead>
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<th>Electrodes</th>
<th>Method of detection</th>
<th>Linear range (µM)</th>
<th>LOD (µM)</th>
<th>Sensitivity (µA µM⁻¹ cm⁻²)</th>
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<td>2.32</td>
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<td>DPV</td>
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<td>Peak Potential (mV)</td>
<td>Recovery (%)</td>
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<tr>
<td>--------------------------</td>
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</tr>
<tr>
<td>PMo12@GO/GCE</td>
<td>DPV</td>
<td>0.05-400</td>
<td>0.006</td>
<td>14.52</td>
<td>[50]</td>
</tr>
<tr>
<td>CuC2O4/GCE</td>
<td>DPV</td>
<td>0.005-55.65</td>
<td>0.00267</td>
<td>NR</td>
<td>[51]</td>
</tr>
<tr>
<td>h-C- gCN</td>
<td>DPV</td>
<td>0.008-682</td>
<td>0.009</td>
<td>NR</td>
<td>[52]</td>
</tr>
<tr>
<td>La2(WO4)3/SPCE</td>
<td>DPV</td>
<td>0.01-58.06</td>
<td>0.0024</td>
<td>1.021</td>
<td>[53]</td>
</tr>
<tr>
<td>RGO/Fe3O4-IL-MIP</td>
<td>DPV</td>
<td>0.1-30</td>
<td>0.05</td>
<td>NR</td>
<td>[54]</td>
</tr>
<tr>
<td>BaWO4/GCN/GCE</td>
<td>DPV</td>
<td>0.001-533</td>
<td>0.0010</td>
<td>1.51267</td>
<td>This work</td>
</tr>
</tbody>
</table>

aGCE: glassy carbon electrode; b molecularly imprinted polymer-based carbon paste electrode; c poly (3, 4-ethylenedioxythiophene); d carbon interlaced nanoflake-assembled Magnesium,nickel,sulphide microspheres; e functionalized carbon nano fiber; f Screen printed carbon electrode; g graphene oxide; h carbon-rich graphitic carbon nitride; i reduced graphene oxide; j ionic liquids; k differential pulse voltammetry; l Linear sweep voltammetry; m not reported.

3.6. Selectivity study of BaWO4/GCN/GCE

The anti-interfering capability of an electrochemical sensor is a noticeable analytical parameter to their practical examination. The action of other electroactive species is frequently obtained under physiological conditions at an applied working potential. Hence, selectivity of as-fabricated BaWO4/GCN/GCE was studied with the DPV technique against consecutive dose of 100 µM DPA and 10-fold excess concentration of interfering molecules such as Catechol (CT), Dopamine (DOP), Hydro Quinone (HQ), Glucose (GLU), Uric acid (UA), under in 0.1 M PB (pH 7.0) (Fig.10c). From the DPV responses, the peak current response and peak potential were unaffected by the inclusion of a 10-fold excess concentration of interfering molecules. Moreover, no supplementary peak responses were observed for added interfering molecules. The corresponding relative error (%) of current recovery versus interfering molecules was given in Fig.10d and the recovery current of DPA was obtained in the range of 94.5-97.5 %. The obtained results indicate the outstanding selectivity of the BaWO4/GCN/GCE sensor for the electrochemical oxidation of DPA.

3.7. Stability, repeatability, and reproducibility studies

![Figure 11](image-url)  
Figure 11. (a) The CV current response of 100 consecutive cycles of BaWO4/GCN/GCE electrode in the 5mM of [Fe (CN)6]3-/4- with 0.1M KCl solution with the scan rate 50 mV s−1, (b) 100 consecutive cycle of BaWO4/GCN/GCE electrode in the 0.1M PB (pH 7) with scan rate 50 mV s−1.
The cyclic stability of modified BaWO₄/GCN/GCE investigated by CV analysis using 5mM of [Fe (CN)₆]³⁻/⁴⁻ solution having 0.1M KCl solution and also in 0.1 M (pH7.0) PB, 100 consecutive cycles were performed with the BaWO₄/GCN modified GCE shown in Fig.11a and b. Fig.12a shows the bar diagram of 5 different electrodes versus the current response, relative standard deviation (RSD) was calculated to be 2.62 %, which shows the excellent reproducibility of the BaWO₄/GCN electrode. The obtained results exposed the outstanding stability of our proposed BaWO₄/GCN electrode. The long-term electrochemical stability of the BaWO₄/GCN sensor was assessed by CV response of BaWO₄/GCN electrode towards 100 µM of DPA in 0.1 M PB (pH 7.0) for 25 days displayed in Fig. 12b, the current responses have been measured every 5 days intervals after the electrode is stored in the refrigerator at 4°C. The BaWO₄/GCN electrode retained 96.4 % of current from its first day and the RSD value is 2.4 %, the obtained result revealed the outstanding long-term stability of our proposed BaWO₄/GCN electrode. The repeatability of the BaWO₄/GCN electrode was explored by five consecutive repeatable measurements using a single BaWO₄/GCN electrode in 0.1M PB (pH 7.0) containing 100 µM DPA. The bar diagrams depicted in Fig. 12c show the current response of the BaWO₄/GCN electrode for repeatable measurement of DPA and the RSD is calculated to be 2.35%, evident the excellent repeatability of the BaWO₄/GCN electrode. These results evidence that the strong interfacial interactions and electrical contacts between BaWO₄ and the GCN layers provide structural stability of the composite. Moreover, the reusability and durability of the proposed electrode related to their stability due to the effective Ba and W cation-π interaction of the GCN.

3.8. Real sample analysis

To evaluate DPA in the apple juice sample (Fig.8), the practical applications and viability of the fabricated sensor were evaluated. The juice sample was bought at a Taipei local market and diluted 10 times in 0.1 M PB (pH 7.0). A known concentration of DPA was added to the pre-treated apple juice sample in DPV analysis under optimum conditions by the standard addition method. The prepared BaWO₄/GCN sensor to detect the concentration of DPA in different samples before and after spiking,
the obtained results are summarized in Table 2. The results of recoveries, which ranged from 99.8% to 102.4 %, were outstanding, indicating that the prepared sensor can be used as an efficient and reliable sensing tool for DPA determination in real samples. It's conceivable that the prepared sensor would be able to detect DPA in both commercial and lab samples, with reasonable recovery rates. Finally, these findings support the hypothesis that the proposed sensor can be used to determine DPA in real samples in a convenient, accurate, sensitive, and feasible manner.

![Figure 8. DPV response of spiked DPA in (a) Apple juice.](image)

**Table 2.** Determination of DPA in apple juice sample at BaWO₄/GCN/GCE.

<table>
<thead>
<tr>
<th>Real sample</th>
<th>Added (µM)</th>
<th>Found (µM)</th>
<th>Recovery (%)</th>
<th>RSD*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apple juice</td>
<td>5.00</td>
<td>5.12</td>
<td>102.40</td>
<td>2.67</td>
</tr>
<tr>
<td></td>
<td>10.00</td>
<td>9.98</td>
<td>99.80</td>
<td>2.15</td>
</tr>
<tr>
<td></td>
<td>15.00</td>
<td>15.10</td>
<td>100.60</td>
<td>2.67</td>
</tr>
</tbody>
</table>

*Measurement of three experiments (n=3).

4. **CONCLUSION**

In summary, BaWO₄/GCN nanocomposite was successfully prepared in this work by the facile hydrothermal route and thermal polymerization method be used to construct an electrochemical sensor for sensitive and selective detection of DPA in the PB solution as well as in the real sample of apple juice with satisfactory results. The high surface area of BaWO₄/GCN for DPA adsorption, excellent conductivity, and perfect interfacial contact between BaWO₄ nanoparticle and GCN layer for fast
electron transport all contributed to the greater performance of modified electrode. Moreover, the obtained results show the proposed electrochemical sensor exhibits good sensitivity 1.51267 μA μM$^{-1}$ cm$^{-2}$, a wide linear range (0.001-533 μM), and an excellent limit of detection (LOD) 1 nM. Besides, the BaWO$_4$/GCN sensor revealed long-term stability and, good reproducibility as well as high selectivity, therefore BaWO$_4$/GCN composite was promising sensor material to detect DPA in real samples such as fruits, vegetables, and pharmaceutical samples.

ACKNOWLEDGEMENT
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References
506–511.
42. Y. Wu, J. Yang, Y. Lin, J. Xu, Molecules, 24 (2019).

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