



Fabrication of 4-methoxyphenol chemical sensor with graphene oxide conjugated binary $\text{Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ nanocomposite by linear sweep voltammetry

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ABSTRACT

Combining binary metal nanoparticles (MNPs) with two-dimensional materials can create innovative nanocomposites with unique physical and chemical properties, which are particularly useful for developing efficient electrochemical sensing systems. This study presents a unique approach for detecting and validating the hazardous substance 4-Methoxyphenol (4-MP) electrochemical approach with conjugated nanocomposite (NC). This approach utilizes an electrochemical sensor constructed on a glassy carbon electrode (GCE), modified with hybrid composite material including graphene oxide (GO) conjugated binary yttrium oxide (Y_2O_3) and cobalt oxide (Co_3O_4) as GO@ $\text{Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs. After preparing the NCs using the solid-state chemical method, various techniques were used to characterize the materials by using various techniques including Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray Spectroscopy (EDS), Fourier-Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Ultraviolet-Visible Spectroscopy (UV/Vis), Brunauer-Emmett-Teller Surface Area Analysis (BET), and Transmission Electron Microscopy (TEM). Cyclic voltammetry (CV), linear sweep voltammetry (LSV), and impedance spectroscopy (EIS) were used to examine the electrochemical characterization and sensing application of the fabricated electrodes. Under standard laboratory circumstances, we used LSV to measure the 4-MP detection limit, which linear dynamic range (LDR) from 0.67 to 2.08 M. Based on the calibration curve's slope, the sensor's sensitivity was found to be $2.9 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$. It was calculated the limit of quantification (LOQ) of 0.19 M and a lower limit of detection (LOD) of 0.057 M. Compared to other modified electrodes for 4-MP detection, the composite electrode demonstrated superior electrocatalytic performance. The GO@ $\text{Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs sensor demonstrates excellent selectivity, even among several interfering substances and metal ions. For optimization, different phosphate buffered saline (PBS) solutions with pH values ranging from 5.7 to 8.0 were used to evaluate the sensor activity. The sensor's effectiveness in detecting unknown 4-MP concentrations was tested in various real-samples, including seawater, industrial wastewater, tap water, and well water, using a standard addition method. This study introduces a new approach for developing an electrochemical sensor aimed at monitoring environmental chemicals. The sensor incorporates cobalt nanoparticles on carbon materials to introduce the inorganic-carbon composite materials for the safety in environmental and healthcare applications on a large scale.

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1. Introduction

The electrochemical detection of organic pollutants, particularly phenolic compounds, has attracted considerable attention owing to its prevalent occurrence in industrial effluents and the environment, posing substantial risks to human health and ecosystems. Among these compounds, 4-MP is of particular concern due to its extensive use in the pharmaceutical, agricultural, and cosmetic industries, leading to its frequent detection in water bodies. Thus, developing selective and sensitive sensors for the identification of 4-MP is very necessary [1,2]. GO integrated with metal oxide nanocomposites has garnered interest in the development of electrochemical sensors due to its unique structural, electrical, and catalytic properties. These materials provide significant promises for sensor development owing to their distinctive characteristics. GO, a monolayer substance obtained from graphite, has a substantial surface area, superior conductivity, and many reactive sites, making it an optimal choice for sensor applications. When mixed with metal oxides including Co_3O_4 and Y_2O_3 , the composite material can offer enhanced electrochemical performance due to synergistic effects [3–5]. Co_3O_4 is a spinel-type oxide with remarkable redox properties, making it highly effective for catalytic applications. It has been extensively used in sensors owing to its superior electrochemical activity and stability. Y_2O_3 is recognized for its exceptional thermal stability, mechanical strength, and distinctive electrical characteristics, which may further improve the performance of the composite material. The combination of GO, Co_3O_4 , and Y_2O_3 ($\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$) creates a novel nanocomposite that leverages the strengths of each component, resulting in a highly efficient sensor material for the detection of 4-MP [6,7]. Both the medical and industrial fields make extensive use of phenol and its derivatives. Natural decomposition, human waste, oil refineries, and pharmaceutical production are further sources of these phenolic chemicals [8].

Generally, 4-MP has use in several sectors, primarily as an intermediate in making agrochemical products and as a polymerization inhibitor in the petrochemical industry. In addition, it functions as a stabilizer for adhesives, sealants, and toners and inks, and it is a leather and textile industry addition. However, even minimal contaminants of phenolic compounds during their production are toxic. As a result, these compounds often contaminate waste, as well as fresh water, and, on occasion, a variety of foods [9]. 4-MP can seriously irritate the eyes and is harmful to aquatic life, such as bacteria and fish. The degradation and toxicological impacts of phenol derivatives and their byproducts represent substantial environmental issues. These issues pose serious risks to ecosystems and human health [10]. Because phenolic chemicals are harmful even at low quantities, it is essential to monitor them in water in real time. Various methods exist for the detection of phenol derivatives in water, including electrochemical approaches [11], capillary electrophoresis [12], gas chromatography (GC) [13], and liquid chromatography (LC) [14]. Sometimes spectrophotometry and LC are used in combination with electrochemical techniques [15]. Routine environmental monitoring is not a good fit for these technologies because of the extensive and time-consuming sample pre-treatments [16]. It is critical to create 4-MP detectors that are quick, cheap, dependable, and very sensitive. These sensors can detect very low concentrations of 4-MP in water, which is crucial for determining the substance's environmental effect. Electrodes composed of GCE, carbon paste (CP), and often platinum are typically used in the detection of phenol derivatives [17].

GCEs are often modified prior to their use as sensors. This can involve adding surfactants to help accumulate phenol derivatives or using nanocomposites and nanoparticles. On the other hand, a platinum electrode may readily oxidize phenolic compounds, the responses are often unclear, making platinum electrodes unsuitable for precise electrochemical studies [18]. To solve this issue, we need to enhance electrodes with nanocomposites that have many active sites, creating reliable electrochemical detectors for phenolic chemical detection. This

technique thoroughly evaluated $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs that were synthesized using a simple solid-state chemical procedure. The samples were then analyzed using FESEM coupled with EDS, XPS, XRD, UV/vis., and FT-IR spectroscopy. In addition, a 4-MP chemical sensor was made using a GCE surface that was produced using $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs. At room temperature, the $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs were tested for their electrochemical potential with respect to 4-MP. The oxidation of 4-MP was reported to be very selectively and sensitively detected by $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs, with a low detection limit. The findings indicate that NCs provide significant potential for the detection and quantification of 4-MP. This is the first work that we are aware of utilizing carbonaceous phases, such as GO, to enhance the current collecting characteristics of a $\text{Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ electrode in a 4-MP detection. This work is distinctive, given GO was modified by attaching $\text{Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ nanoparticles via a solid-state approach. It has been shown that high-quality nanostructured electrodes may have quick electron transfer kinetics and an outstanding storage capacity.

This paper presents the development of an electrochemical sensor using a $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs for the detection of 4-MP. The synthesis of the nanocomposite involves a straightforward and cost-effective procedure, and the resulting material exhibits excellent sensitivity, selectivity, and stability. The electrochemical performance of the fabricated sensor was evaluated using a variety of methodologies, including LSV and CV. The results demonstrate the superior analytical capabilities of the $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs sensor in detecting 4-MP, highlighting its potential for practical applications in environmental monitoring and public health protection.

2. Experimental Sections

2.1. Materials and methods

The chemicals utilized in this research were sourced from Merck and included potassium dihydrogen phosphate (KH_2PO_4), dipotassium hydrogen phosphate (K_2HPO_4), cobalt (III) oxide (Co_3O_4), sodium hydroxide (NaOH), hydrochloric acid (HCl), potassium ferrocyanide ($\text{K}_4[\text{Fe}(\text{CN})_6]$), potassium ferricyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]$), and anhydrous yttrium(III) chloride (YCl_3). Additionally, high-purity GO was obtained from Sigma-Aldrich. All chemicals were of analytical grade and employed as received without any further purification. For solution preparation, deionized water was utilized, and pH adjustments were made using NaOH and HCl . A 0.1 M phosphate buffer solution (PBS) was formulated by combining KH_2PO_4 and K_2HPO_4 salts. For the preparation of the $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs via a solid-state method, Y_2O_3 (99 % purity), Co_3O_4 (99 % purity), and graphene oxide (GO) (98 % purity) were used, all procured from Sigma-Aldrich. To synthesize the nanocomposite, 1.0 g of the metallic salt was combined with NaOH in a stoichiometric ratio. This mixture was ground in a granite mortar and pestle for 15 min, followed by annealing at 600°C for a duration of 6 h. This process allowed for the effective integration of the components, yielding a nanocomposite suitable for subsequent applications.

2.2. Preparation of $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs by solid-state method

A solid-state technique was used to synthesize the $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs. Initially, 1.0 g each of Co_3O_4 and Y_2O_3 nanoparticles were thoroughly mixed and ground into a uniform powder. Subsequently, 0.001 g of GO and sodium hydroxide pellets were incorporated into the powder and thoroughly mixed for 10–20 min until homogeneously blended. After that, the paste was moved to a ceramic dish and heated at $500\text{--}600^\circ\text{C}$ for 5–6 h.

Once it has cooled to normal room temperature, the dried mixture was ground into fine powder to form the nanocomposites. Formation of the successful nanocomposites confirmed by different characterization techniques.

2.3. Fabrication of GCE using $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs

We fabricated the working electrode (WE) for the sensor by exchanging GCE with synthesized NCs. To create this modified GCE, we dissolved $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs in an ethanol solution, then applied a thin layer of the mixture onto the GCE's surface and allowed it to dry under controlled conditions. To ensure the durability of the layer, we added a few drops of binding agent 5 % nafion solution to the GCE. After applying this solution, we placed the modified GCE for dry at room temperature or heated at 35 °C for an hour, followed by another drying phase. For the construction of the electrochemical sensor, we used Metrohm Auto lab components. The configuration included an Ag/AgCl (Saturated KCl) electrode serving as the reference electrode, a platinum wire functioning as the counter electrode, and the modified glassy carbon electrode as the working electrode. We performed electrochemical studies on 4-MP solutions, diluted in a pH 7.0 buffer to attain concentrations between 0.67 and 2.08 M. The sensor's sensitivity, LOD, LDR, stability, and pH influence on 4-MP analysis were all assessed using linear sweep voltammetry in the experiment.

2.4. Characterization of $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs

To investigate the crystalline structure of the nanocomposite samples, we employed powder X-ray diffraction (XRD) using an AXS-D4 Endeavour system, testing various types of radiation. For a comprehensive analysis of the size, shape, morphology, and overall structure of the samples, we utilized two electron microscopes: the JEOL-6300F operating at 5.0 kV and the JEOL JEM-2100F-UHR running at 200.0 kV. The identification of functional groups within the samples was achieved through Fourier-transform infrared spectroscopy (FTIR) using the KBr pellet method, covering a spectral range from 400 to 4000 cm^{-1} , facilitated by a Perkin Elmer Spectrum 100. To gain insights into the elemental composition and binding energies, we conducted X-ray photoelectron spectroscopy (XPS) with a 200R-VGESCALAB after degassing the samples. Surface area and pore size measurements of the nanocomposites were performed via Brunauer-Emmett-Teller (BET) analysis using a Quanta-chrome analyzer (NOVA 4200) at 77 K, following a 12-hour degassing at 200 °C. This nitrogen adsorption data allowed us to accurately calculate the surface area of the samples.

Further morphological assessment and elemental distribution were conducted using field emission scanning electron microscopy (FESEM) on an FEI Quanta-250, as well as high-resolution transmission electron microscopy (HRTEM) with a JEOL JEM-3000F, which included energy-dispersive X-ray spectroscopy (EDX) for detailed elemental analysis. In addition, we carried out UV–visible spectroscopic analysis of the nanocomposites using a Jasco V-650 spectrophotometer to explore their optical properties. Overall, these techniques provided a comprehensive characterization of the nanocomposite samples, enabling a thorough understanding of their structural and functional attributes.

3. Results and Discussion

3.1. FESEM and EDS analysis

The FESEM images in Fig. 1 show the structure of the $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs, which is a combination of GO, Co_3O_4 , and Y_2O_3 . In Fig. 1(a) and (b), the GO sheets appear wrinkled and layered, providing a large surface area. On these sheets, the Co_3O_4 and Y_2O_3 nanoparticles are spread across the surface, forming a rough, granular texture resulting from their smaller size and high surface energy. Under higher magnification, you can see these particles clustering together, creating a porous and interconnected structure. This porosity and rough texture likely contribute to the composite's improved electrochemical performance, making it useful for applications like catalysis or sensing. In the figures, the material is recognized as NCs due to the combination of these three components.

We used energy-dispersive X-ray spectroscopy (EDS) and scanning electron microscopy (SEM) to analyze $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs and the results are shown in Fig. 1. The SEM images confirm that the synthesized materials are indeed nanocomposites, (SEM and EDS). Fig. 1(c) provides a detailed view of the nanocomposite structure, displaying irregularly shaped particles with slight agglomeration. These particles are spread across a 5.0 μm scale, indicating their nanoscale dimensions and rough surface, which can enhance the material's catalytic surface area. The EDS analysis in Fig. 1(d) reveals that the nanocomposite consists of 7.85 % cobalt (Co), 7.51 % yttrium (Y), and 22.64 % oxygen (O), confirming the successful synthesis of the $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs. The high oxygen content reflects the presence of graphene oxide and metal oxides, while

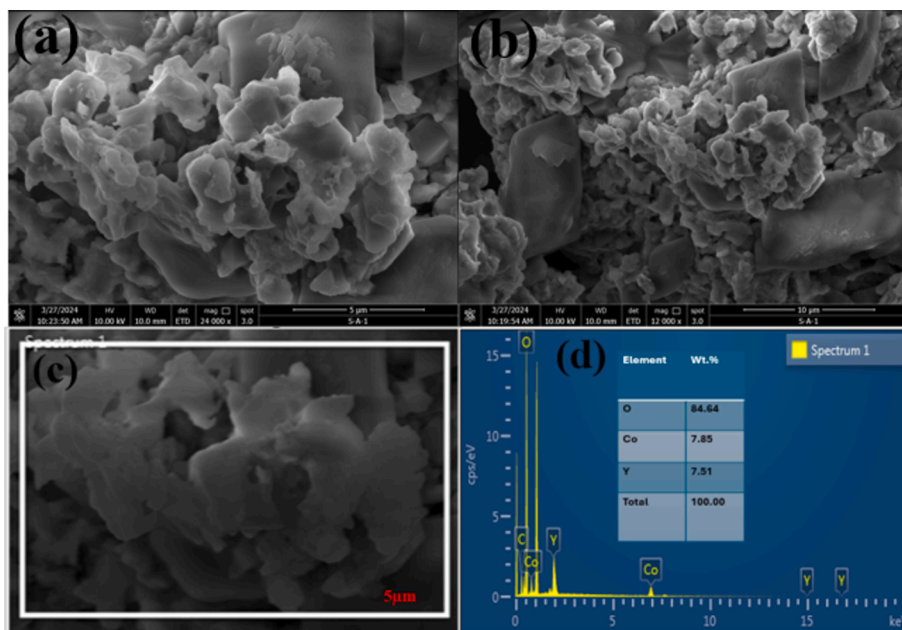


Fig. 1. Morphological analysis with FESEM and Elemental investigation of $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs (a) 5.0 μm , (b) 10.0 μm , (c) EDS Image, and (d) Weight percentage elemental composition.

the cobalt and yttrium confirm the incorporation of Co_3O_4 and Y_2O_3 , key materials for the intended electrochemical applications.

3.2. TEM analysis

The TEM images of the $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs in Fig. 2(a–c) display a structure like what was observed in the FESEM analysis. The $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs at 0.2 μm and 50.0 nm provides low-to-high-resolution view of the crystalline structure seen in Fig. 2(a and b). In Fig. 2(a), you can see Co_3O_4 nanoparticles attached to this interconnected Y_2O_3 structure like cluster. When GO nanoparticles are added to the Co_3O_4 and Y_2O_3 mixture, they bind to the surface and give more active sides for electrochemical reaction. In Fig. 2(b), showing layered thin sheet-like structure correspond the GO provides high surface area and platform for the attachment of the Co_3O_4 and Y_2O_3 nanoparticles. The smooth, transparent regions in the image are typical of GO, showing its thin, sheet-like nature. This results in the $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs taking on a nanosheet-like configuration. It can be seen distinct lattice fringes (0.27 nm), which indicate well-ordered crystal structures (Fig. 2c). These fringes likely belong to the Co_3O_4 and Y_2O_3 nanoparticles. The clear lattice lines (0.27 nm) demonstrate good crystallinity, which is essential for efficient electrochemical performance, especially in catalytic applications like 4-MP detection.

3.3. Functional, optical and structural analyses of $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NC

An Agilent-Cary 630 equipment was used for Fourier transform infrared spectroscopy (FTIR) analysis to investigate the chemical structure and molecular interactions of the produced nanocomposite. Using KBr pellets, the measurements were conducted in the 400–4000 cm^{-1} wavenumber range. Fig. 3(a) displays the Fourier transform infrared spectra of the Y_2O_3 nanocomposites that were produced at a calcination temperature of 600 $^\circ\text{C}$. The synthesized nanocomposite exhibited a prominent peak in the 880–920 cm^{-1} wavenumber region. The peaks observed at 910 cm^{-1} are indicated in the Y-OH stretching mode. The FTIR spectra of Y_2O_3 exhibited a notable reduction in the strength of hydroxyl and carbonate groups [19]. The absorption spectra of graphite exhibited peaks at 3646 cm^{-1} for O-H stretching and at 1740 cm^{-1} for C = C stretching [20]. Additionally, the FTIR spectra of the Co_3O_4 nanoparticles indicated two distinct peaks at 572 and 1370 cm^{-1} , which correspond to the Co^{3+} -O and Co^{2+} -O stretching vibration modes,

respectively. According to the spinel structure of the Co_3O_4 nanoparticles, these peaks are the consequence of the tetrahedral and octahedral sites [21].

The UV–Visible spectrum of $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs exhibits a distinct absorption peak around 301 nm shown in Fig. 3(b). This peak is caused by electronic transitions associated with the surface plasmon resonance of the Co_3O_4 nanoparticles and the interaction between the GO and Y_2O_3 in the composite. The presence of this peak suggests effective integration of the materials, enhancing their optical properties for potential applications in sensing and catalytic systems [22].

The phases and structures of the graphene oxide nanocomposites ($\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs), Y_2O_3 , and Co_3O_4 were determined by powder XRD, as seen in Fig. 3(c). When processing the data, the PAN-Analytical Library was of assistance. According to JCPDS card numbers 41–1487 and 41–1488, graphite usually shows strong peaks in XRD patterns at 23.2° and 51.2° 2θ angles, which correspond to crystallographic planes (002) and (004) for hkl values, respectively [23,24]. According to JCPDS#71–0099, the (222), (400), (411), and (440) crystallographic planes are equivalent to the (XRD) pattern of Y_2O_3 , which shows clear and sharp peaks at 29.6° , 33.62° , 35.52° , 48.51° , and 57.74° , respectively [25]. The (111), (311), (400), and (511) planes of cobalt oxide (Co_3O_4) are matched by the XRD peaks at 18.9° , 36.8° , 44.8° , and 59.3° in the sample, as per JCPDS card no. 42–1467 [26]. There are no peaks from contaminants such iron hydroxide complexes when comparing the XRD pattern of the material with these standard patterns. In summary, the XRD pattern of the $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs shows broad peaks due to the nanoscale size of the particles. Specific peaks can be matched to standard patterns using hkl values and JCPDS numbers to verify the existence of Graphite, Co_3O_4 , and Y_2O_3 phases in the nanocomposite.

3.4. Surface analysis of $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs by BET

The BET technique was used at 77 K with a 3Flex analyzer (Micromeritics, USA) to measure the surface area, pore volume, and pore size of the $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs. The specific surface area was determined to be 21.257 m^2/g using BET theory, which is based on the nitrogen adsorption–desorption isotherm (Figure S1a). Figure S1b illustrates a type IV isotherm characterized by a hysteresis loop, indicating the existence of mesopores. A pore volume of 0.049 cm^3/g and a pore size of 13.845 Å were determined. The use of an alkaline solution helped reduce the chemical precursors, encouraging the formation of surface

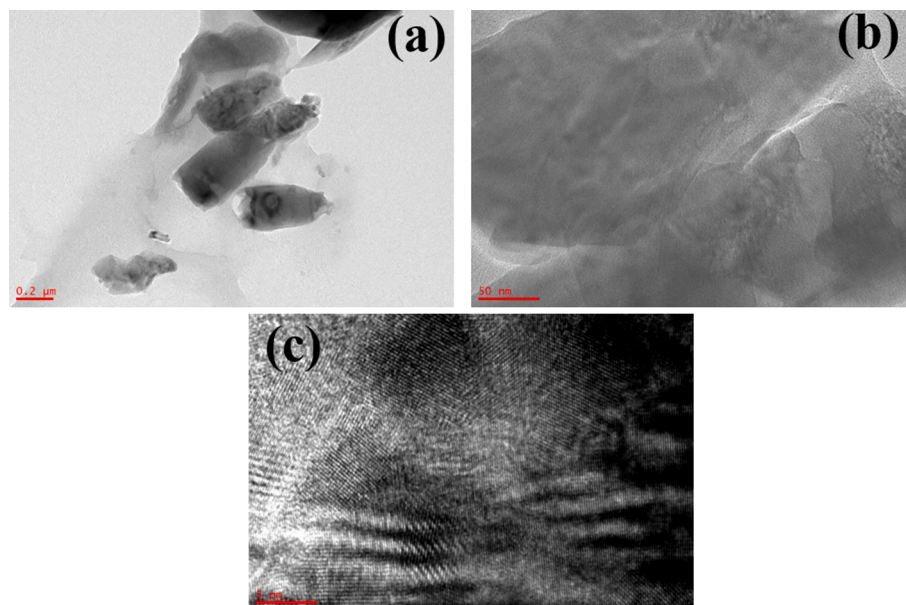


Fig. 2. TEM study of the $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs structural morphology high-to-low magnification (a) 0.2 μm (b) 50 nm, and (c) 5.0 nm.

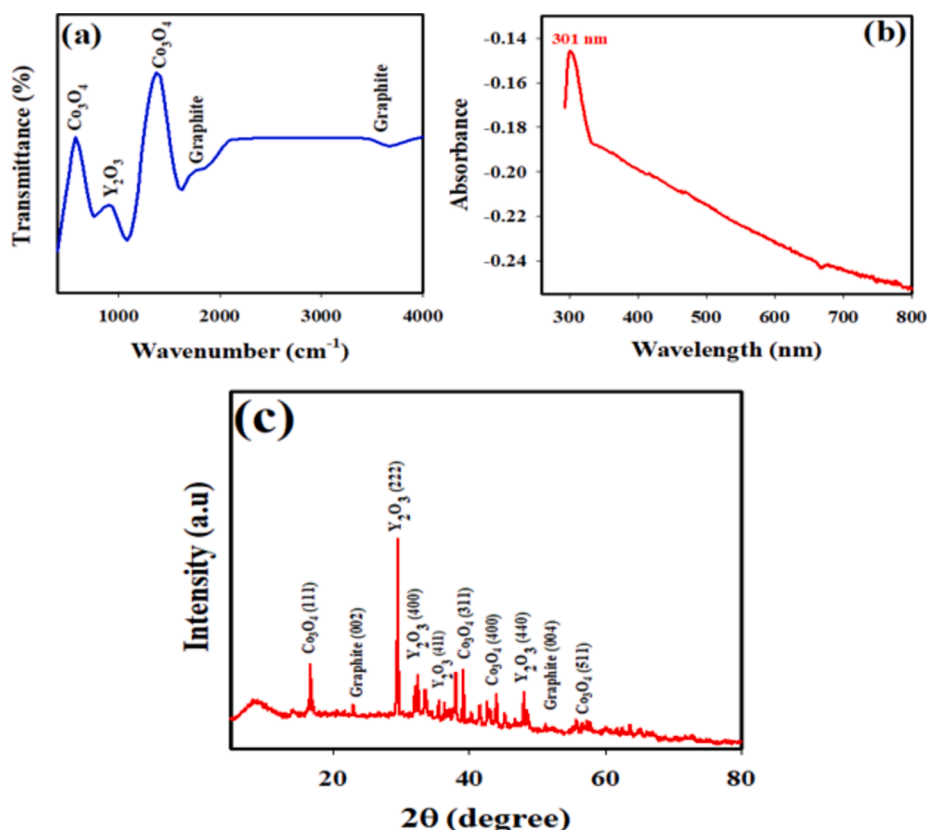


Fig. 3. (a) Spectrum of FT-IR and (b) GO@Co₃O₄/Y₂O₃ NCs UV-visible spectrum, and (c) XRD illustration of GO@Co₃O₄/Y₂O₃ NCs.

cavities in the nanocomposite.

3.5. Electrochemical characterization of GO@Co₃O₄/Y₂O₃ NCs

The electrochemical oxidation of 4-MP was investigated using CV and EIS in a 0.1 M PBS solution. To assess the performance of the newly developed nanocomposite, CV experiments were conducted in a solution of 0.1 M potassium hexacyanoferrate K₄[Fe(CN)₆]. GCE exhibited a potential gap of + 0.23 V; however, the GCE modified with the nanocomposite displayed a reduced potential difference, with the oxidation peak occurring at + 0.35 V and the reduction peak at + 0.12 V, as illustrated in Fig. 4. This result suggests that the nanocomposite-coated GCE possesses superior electron transport characteristics compared to the bare GCE.

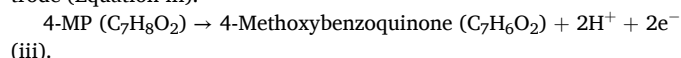
Fig. 4(a) illustrates that the GCE modified with the GO@Co₃O₄/Y₂O₃ NCs achieved the highest oxidation current among all tested electrodes, demonstrating its effectiveness. When assessed in a 0.1 M K₄[Fe(CN)₆] solution, GO@Co₃O₄/Y₂O₃ NCs GCE exhibited the most elevated oxidation potential. To further understand the interaction between the molecules and the working electrode surface, cyclic voltammetry was performed at scan rates ranging from 10 to 500 mV/s in the K₄[Fe(CN)₆] solution. As shown in Fig. 4(b), the peak currents exhibited a consistent increase with the scan rate during both oxidation and reduction phases, indicating a diffusion-controlled process. This behavior signifies that the modified electrode is highly sensitive and effective for the detection of electroactive species. Moreover, Fig. 4(c) reveals a distinct linear correlation between the current and the square root of the scan rate, which reinforces the diffusion-driven nature of the electrochemical process. This conclusion is further supported by the corresponding equations, which reinforce the electrode's effectiveness in electrochemical sensing applications (Equation (i-ii)).

$$\begin{aligned} \text{ip} &= 85.94(\text{S.R})^{0.5} - 108.81; R^2 = 0.9960; \text{oxidation K}_4[\text{Fe}(\text{CN})_6] \text{ (i).} \\ \text{ip} &= -77.37(\text{S.R})^{0.5} - 183.62; R^2 = 0.9910; \text{reduction K}_4[\text{Fe}(\text{CN})_6] \text{ (ii).} \end{aligned}$$

Fig. 4(d) illustrates the changes in the electrochemical reaction as 4-MP concentrations increase from 0.025 to 1.47 mM. With higher 4-MP levels, the current rises, demonstrating the strong electrochemical activity of the GO@Co₃O₄/Y₂O₃ NCs in oxidizing 4-MP. The strong linear correlation between current and 4-MP concentration, especially at higher concentrations, shows that these nanocomposites are highly sensitive and effective in detecting 4-MP, even at elevated levels. This suggests their potential for accurate monitoring in environments where 4-MP is present in larger amounts, making them a reliable tool for applications requiring precise detection of this compound. Additionally, their performance at higher concentrations highlights the robustness of the nanocomposites, which could be useful in real-world scenarios where 4-MP levels may vary significantly.

3.6. Electrochemical characterization of GO@Co₃O₄/Y₂O₃ NCs with 4-MP

For the electrochemical detection of 4-methoxyphenol (also called p-methoxyphenol or p-hydroxyanisole) using GO@Co₃O₄/Y₂O₃ NCs, the process usually involves oxidizing the 4-MP at the surface of the electrode (Equation iii).



The oxidation of 4-methoxyphenol into 4-methoxybenzoquinone (a type of quinone) involves the release of protons (H⁺) and electrons (e⁻). These electrons are transferred to the GO@Co₃O₄/Y₂O₃ NCs GCE, which helps in detecting the reaction electrochemically. The presence of Co₃O₄ and Y₂O₃ likely boosts the catalytic efficiency and enhances the sensitivity of the GO matrix, making the electrode more effective for this process.

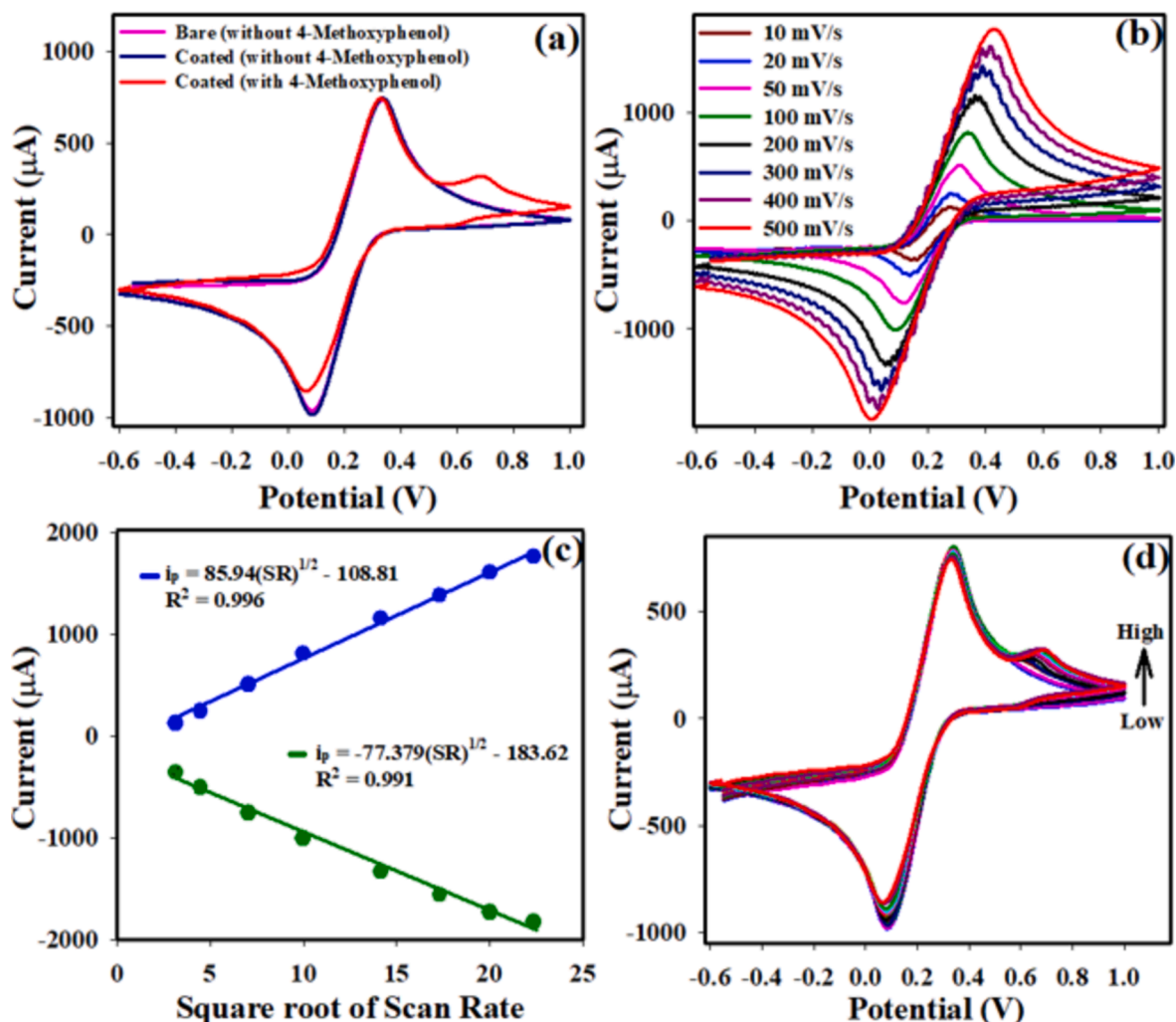


Fig. 4. GO@Co₃O₄/Y₂O₃ NCs electrochemical cyclic voltammetry characterization, (a) Coated (without 4-MP), bare (without 4-MP) and coated (with 0.1 mM 4-MP) electrochemical oxidation of 0.1 M K₄[Fe(CN)₆] at 100 mV s⁻¹ scan rate, (b) Coated GO@Co₃O₄/Y₂O₃ NCs cyclic voltammograms at different scan rates ranging from 10 to 500 mV s⁻¹, (c) The square root of SR versus peak current, and (d) different concentrations from 0.025–1.47 mM.

3.7. EIS study for fabricated GO@Co₃O₄/Y₂O₃ NCs GCE

We also examined the stability of the GO@Co₃O₄/Y₂O₃ NCs coating on a glassy carbon electrode utilizing 5 % Nafion as a binder by electrochemical testing. The electrode, which was coated with the nanocomposite material, tested in 0.1 M potassium hexacyanoferrate(II) (K₄[Fe(CN)₆]) solution. As shown in Figure S2(a), after 50 cycles, the results showed little to no change in performance. This indicates that the electrode is highly stable and is likely to perform reliably when used with other substances for analysis.

The EIS investigation aimed to deepen the understanding of the catalyst's performance in the electro-oxidation process of 4-MP. EIS serves as an effective technique for probing subtle alterations occurring at the interface between the electrode and electrolyte during electrochemical reactions. By employing this method, researchers can monitor the surface characteristics of an electrode modified with an electrocatalyst in real-time, providing valuable insights into the interfacial dynamics throughout the reaction. This real-time analysis is crucial for optimizing catalyst design and performance, ultimately enhancing the efficiency of the electro-oxidation process [27]. An EIS experiment was performed by applying a 10.0 mV perturbation across a wide frequency spectrum, ranging from 0.01 Hz to 100,000 Hz. The experiment was carried out in a 1.0 mM solution of 4-MP in a 0.1 M phosphate-buffered saline (PBS) environment, with a constant applied potential of 1.0 V.

This setup allows for an in-depth analysis of the electrochemical properties of the 4-MP solution, enabling insights into its behavior under varying frequencies.

This material is expected to demonstrate minimal charge transfer resistance (R_{ct}) and exceptional electrical conductivity at the interface between its surface and the electrolyte. This inference is supported by the Nyquist plot, which reveals a reduced semicircle in the high-frequency domain, indicating effective charge transfer dynamics and favorable electrochemical performance [28]. The electrical conductivity of GO@Co₃O₄/Y₂O₃ NCs is essential for their functionality in oxidizing or reducing analytes. To assess their performance, EIS was performed in a 0.1 M Fe(CN)₆^{3-/4-} solution, using a phosphate buffer maintained at pH 7.0. The results revealed that the semi-circle corresponding to the GO@Co₃O₄/Y₂O₃ NCs exhibited a lower impedance (95.8 Ohms) compared to that of the bare GCE, which recorded a higher value of 398.7 Ohms, as illustrated in Figure S2(b) and detailed in the EIS data presented in Figure S2(c). This reduction in impedance signifies that the GO@Co₃O₄/Y₂O₃ NCs possess a lower charge-transfer resistance (R_{ct}), indicating an enhanced ability for charge transfer during the electrochemical detection process of the analyte. Such improvements are critical for optimizing sensor performance and sensitivity in analytical applications.

3.8. Detection of 4-MP by LSV with $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs

One of the most well-known methods for the sensitive electrochemical detection of organic contaminants is LSV. In this study, we applied LSV to measure low concentrations of 4-MP in a conductive solution with a pH of 7.0. The performance of GCE was evaluated both

with and without various coatings. These included thin films of $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$, $\text{Co}_3\text{O}_4/\text{Y}_2\text{O}_3$, and Co_3O_4 nanoparticles. Comparisons were made to assess how the coatings improved 4-MP detection. As shown in Fig. 5(a), the electrodes' electrochemical activity was compared using LSV. The $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs GCE produced a much stronger peak in comparison to the other GCE electrodes (bare, coated),

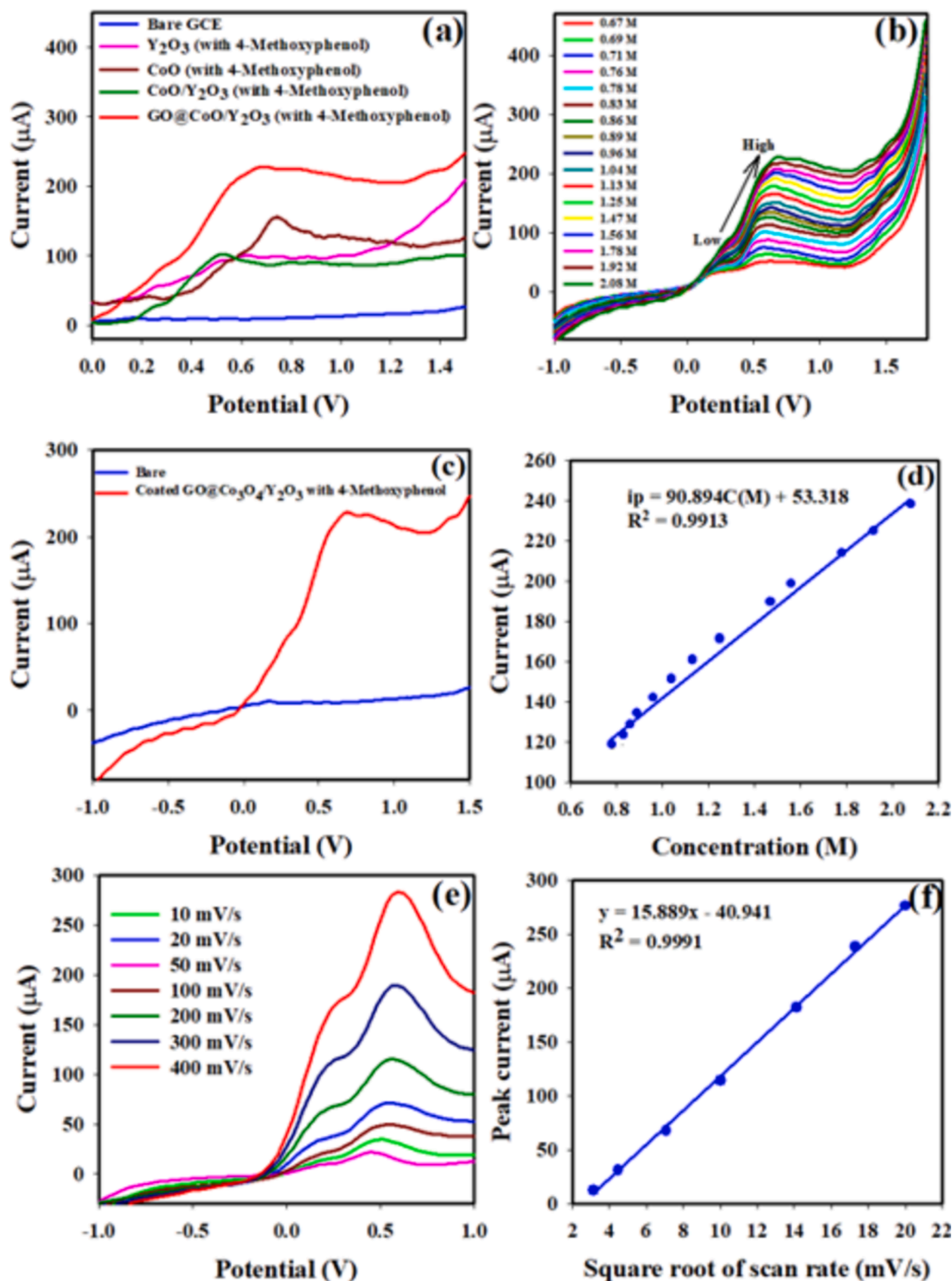


Fig. 5. Analyzing 4-MP levels in conductive buffer solution using LSV, (a) Coated and bare GCE analysis, (b) LSV different concentrations of 4-MP, (c) $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs/GCE coated vs. bare GCE, (d) calibration of 4-MP sensor (e) LSV of $\text{GO@Co}_3\text{O}_4/\text{Y}_2\text{O}_3$ NCs GCE at scan rates from 10 to 500 mV/s, and (f) Square root of scan rate vs. peak current linear fitting.

suggesting that this coating is highly efficient for 4-MP detection. A range of 4-MP solutions were prepared, with concentrations between 0.67 M and 2.08 M, in a conductive buffer at pH 7.0 and tested using LSV, as displayed in Fig. 5(b). Furthermore, Fig. 5(c) demonstrated that the WE, enhanced with the constructed NCs, exhibits a more prominent peak. This indicates that the NCs are highly selective in detecting 4-MP. With the elevation of 4-MP concentration, the peak current correspondingly rises. This means that during the LSV electrochemical process, 4-MP molecules undergo oxidation when they encounter the surface of the working electrode, which is made of GO@Co₃O₄/Y₂O₃ NCs GCE.

The linear detection range (LDR) of the sensor refers to the range of 4-MP concentrations it can accurately measure. In Fig. 5(d), the graph illustrates the relationship between the electrical current at the peak and the increasing 4-MP concentrations. The slope of this graph indicates how responsive the sensor is to changes in 4-MP levels, which essentially reflects the sensor's sensitivity. For this sensor, the sensitivity has been determined to be 2.9 $\mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$, showing how much the current changes for each unit increase in 4-MP concentration per square centimeter of the sensor's surface area. This high sensitivity demonstrates the sensor's capability for precise detection of 4-MP even at low concentrations.

$$i_p = 90.894 (M) + 53.318 \text{ (iii)}.$$

The oxidation peak current for 0.1 M 4-MP on the GO@Co₃O₄/Y₂O₃ NCs sensor increases when the scan rate increases from 10 to 500 mV/s, as shown in Fig. 5(e). The results indicate that oxidation process depends on how quickly the electrode surface interacts with the 4-MP, indicating a process that encompasses both electrocatalysis and adsorption [29]. The regression equation displayed in Fig. 5(f) is represented as $I_{pa} = 15.889(\text{SR})^{1/2} - 40.941$, with a strong correlation value of 0.9991.

The acidity (pH) of the conductive electrochemical sensing medium plays a crucial role in the experiment. To determine the optimal pH for the buffer solution, an experiment was performed, as illustrated in Figure S3(a). The findings revealed that the peak current in the LSV analysis was highest at a pH of 7.0 when using a 4-MP concentration of 2.08 M. This suggests that the buffer solution's neutral pH creates the most favorable conditions for electrochemical sensing, possibly due to enhanced electron transfer and better stability of the sensing material at this pH. Based on this, pH 7.0 is the most favorable condition for detecting 4-MP using LSV.

In Figure S3(b), the bar chart depicts the present current (μA) at max potential, around 0.58 V, across different pH levels. The bars show that the current increases with rising pH, reaching its highest at pH 7.0, where it peaks at approximately 188 μA . Repeatability and reproducibility are key factors in assessing the dependability of an electrochemical sensor. The GO@Co₃O₄/Y₂O₃ NCs GCE sensor was evaluated for 4-MP detection under consistent conditions, specifically at pH 7.0 with a 4-MP concentration of 2.08 M. As displayed in Figure S3(c), the results from 10 consecutive measurements showed little variation, demonstrating the sensor's excellent stability. Reproducibility is a crucial measure of how reliable the fabricated electrodes are for repeated use.

We prepared six identical GCE modified with GO@Co₃O₄/Y₂O₃ NCs to assess the repeatability of the electrocatalyst, as shown in Figure S3 (d). Using the same experimental conditions, we then performed LSV experiments on all six electrodes. Although the anodic currents showed some variation, with the highest peak current observed for GCE-5, the relative standard deviation (RSD) was 3.97 %. This indicates that the sensor electrodes can be reproduced with good reliability.

3.9. Optimization of GO@Co₃O₄/Y₂O₃ NCs fabricated electrode

We performed selectivity experiments using LSV measurements to evaluate the applicability of the newly built electrocatalyst. The GO@Co₃O₄/Y₂O₃ NCs was applied to a GCE, and various biomolecules such as L-glutamic acid, lactic acid, urea, creatinine, 4-chlorophenol,

thiourea, melamine, and H₂O₂ five times higher concentrations were added to 4-MP in a 0.1 M PBS solution. For urea and hydrogen peroxide, concentrations were doubled.

Notably, the 4-MP (shown in red) exhibits a distinct and strong current response, indicating a high level of sensitivity and selectivity for this compound. In contrast, the other substances show much lower current responses, suggesting minimal interference in detecting 4-MP. This highlights the effective selectivity of the GO@Co₃O₄/Y₂O₃ NCs for 4-MP even in the presence of potential interfering agents. The results demonstrated that all examined biomolecules elicited minimum to no current response at around 1.0 V, hence confirming the nanocomposite's pronounced selectivity for the electro-oxidation of 4-MP ions. Repeating the experiment yielded consistent results, as illustrated in Figure S4(a). This conclusion is reinforced in Figure S4(b), where a bar graph highlights 4-MP substantially higher current response compared to the other analytes.

The study investigated the impact of 4-MP using LSV analysis to assess possible interference from other substances. 4-MP concentration of 2.08 M was tested alongside eight similar compounds. The electrochemical behavior of 4-MP detection using GO@Co₃O₄/Y₂O₃ NCs was examined in two parts. The first part focused on the effect of 4-MP in the presence of other ions, and the findings are shown in Figure S4(c), which is a graph based on LSV data. The response of the sensor in the presence of various potential interfering ions, including Zn²⁺, K⁺, Ba²⁺, HCO₃⁻, Mg²⁺, SO₄²⁻, Cd²⁺, and Ca²⁺, over a potential range from -1.0 to 1.5 V. The current (measured in μA) shows a clear and distinguishable peak at around 1.4 V for GO@Co₃O₄/Y₂O₃ NCs, while the other interfering ions exhibit minimal influence on the current response and the sensor exhibited an adequate response to 4-MP, indicating that the detection was not affected by interference. Figure S4(d) presents a bar graph comparing the current responses for 4-MP in the presence of different ions (Zn²⁺, K⁺, Ba²⁺, HCO₃⁻, Mg²⁺, SO₄²⁻, Cd²⁺, and Ca²⁺). The current values remain consistent across all ions, suggesting that none of the tested ions substantially affect the electrochemical detection of 4-MP. This underscores the sensor's capability to reliably detect even when faced with complicated mixtures that may contain interfering substances. The use of GO@Co₃O₄/Y₂O₃ NCs in this context ensures enhanced selectivity and sensitivity, makes it a highly effective material for detecting 4-MP through electrochemical methods. The stable current response across different ions suggests robust interference tolerance, essential for real-world applications where various ions may be present. This study confirms that the developed nanocomposite sensor is effective for detecting 4-MP, with excellent selectivity and resistance to common electrochemical interferences.

The GO@Co₃O₄/Y₂O₃ NCs based sensor shows outstanding results for detecting 4-MP through electrochemical methods. It remains highly selective for 4-MP, even in the presence of other common ions such as sulfate, calcium, potassium, magnesium, cadmium, and zinc, which could interfere with the detection process. The sensor's ability to produce a current response consistently highlights its impressive sensitivity and quick detection of 4-MP. To confirm the effectiveness of this sensor, its performance metrics, including the LDR and LOD, were compared with recent studies, as shown in Table 1 [30–34]. These comparisons reveal that the GO@Co₃O₄/Y₂O₃ NCs/GCE outperforms other substrates used for electron sensing.

3.10. Validity of sensor probe in real samples

In this study, we detected 4-MP in sea water, well water, tap water and industrial waste samples using a GO@Co₃O₄/Y₂O₃ NCs sensor through standard methods. We performed three runs for each concentration level and averaged the results to determine the 4-MP concentration (Figure S5). The results, presented in Table 2, show recovery rates between 99.91 % and 100.32 %, with relative standard deviations (RSDs) below 1 %. These results correspond with the conventional curve methodology, demonstrating the sensor's accuracy. This indicates that

Table 1Evaluation of the newly prepared GO@Co₃O₄/Y₂O₃ NCs sensor by electrochemical approaches with various nanocomposites in the detection of 4-MP.

Modified Electrodes	Techniques	LOD	Linear range	Sensitivity	Ref
PPy/CNT/HRP/AuE/PPy-films	I-V	1.06 μM	1.6–81.6 μM	50 $\text{nA}\mu\text{M}^{-1}$	[30]
3D G-Micropillar	CV	50 nM	50 nM to 2 μM	3.9 $\mu\text{A}\text{mM}^{-1}\text{cm}^{-2}$	[31]
MWCNT/Nafion	I-V	90 nM	0.2–1.6 μM	7.0 $\mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$	[32]
NiS ₂ -CNT NCs/GCE	I-V	30.0 $\pm$ 0.02 pM	0.01 nM to 10.0 mM	0.633 $\mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$	[33]
CPE/GDP	ASV	5.0 μM	5.0–40 μM	42.0 $\text{nA}\mu\text{M}^{-1}$	[34]
GO@Co ₃ O ₄ /Y ₂ O ₃ NCs GCE	LSV	0.0574 M	0.67–2.08 M	2.889 $\mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$	Present Work

Table 2Analyzing environmental samples using GO@Co₃O₄/Y₂O₃ NCs sensor probe.

Measured 4-MP concentration by GO@Co ₃ O ₄ /Y ₂ O ₃ NCs (M)						
Real Samples	Added 4-MP conc. (M)	R1 (100 μL)	R2 (200 μL)	R3 (300 μL)	Average Recovery	RSD (%) (n = 3)
Industrial waste	2.08	2.077	2.099	2.084	100.32	0.53
Tap water	2.08	2.083	2.075	2.080	99.96	0.19
Sea water	2.08	2.078	2.086	2.074	99.97	0.29
Well water	2.08	2.077	2.080	2.078	99.91	0.07

the sensor may be efficiently used in practical applications [35–43].

Finally, the novelty of this innovative work lies in the development and application of a 4-MP chemical sensor using GO-conjugated Co₃O₄/Y₂O₃ nanocomposite, engineered for high sensitivity and selectivity via LSV. This innovative approach controls the synergistic properties of the GO-Co₃O₄/Y₂O₃ nanocomposite, combining the high conductivity and large active surface area of graphene oxide with the catalytic activity and stability of the binary metal oxides (Co₃O₄ and Y₂O₃). The hybrid structure not only enhances electron transfer rates but also provides specific binding sites, allowing for precise detection of 4-MP at low concentrations. This dual-component design is an advancement over conventional single-metal oxide sensors, offering improved sensitivity, stability, and reusability. By validating this sensor in real sample scenarios, the study sets a foundation for scalable, cost-effective sensors that could be employed in both environmental and healthcare applications where phenolic compound monitoring is critical. This study may introduce as an excellent initial effort in developing a chemical 4-MP sensor probe capable of detecting unsafe and carcinogenic pollutants on a broad scale, with the aim of safeguarding public health and preserving the environment.

4. Conclusion

This study introduced a highly selective electrochemical sensor for detecting 4-MP by modifying GCE with a thin layer of GO@Co₃O₄/Y₂O₃ NCs bound with 5 % Nafion to enhance adhesion. The nanocomposite was synthesized using a solid-state technique and analyzed through various characterization methods, including UV–vis, BET, FTIR, FESEM, TEM, EDS, and powder XRD. These techniques provided detailed insights into the material's elemental makeup, surface area, functional groups, and optical properties. The resulting GO@Co₃O₄/Y₂O₃ NCs-modified sensor demonstrated exceptional sensitivity, low detection limits, strong linearity, good repeatability, and reliable stability. Furthermore, the sensor was effectively tested on wastewater samples spiked with 4-MP, proving its practical applicability for environmental monitoring.

CRediT authorship contribution statement

Mohsin Saeed: Writing – original draft, Methodology, Investigation, Formal analysis. **Hadi M. Marwani:** Writing – review & editing,

Supervision, Resources, Methodology, Investigation. **Muhammad Fazle Rabbee:** Writing – review & editing, Software, Resources, Methodology, Investigation. **Sulaiman Y. Alfaifi:** Writing – review & editing, Resources, Methodology, Investigation, Formal analysis. **Mohammad Mizanur Rahman Khan:** Writing – review & editing, Methodology, Investigation, Formal analysis. **Mohammed M. Rahman:** Writing – review & editing, Supervision, Resources, Methodology, Conceptualization.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.microc.2024.112231>.

Data availability

Data will be made available on request.

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