



Efficient detection and validation of 4-Methoxyphenol chemical based on binary oxides intercalated ZnO-CdO nanocomposite by electrochemical approach

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ABSTRACT

In this approach, nanoscale binary doped materials was prepared by solid state method as Zinc oxide intercalated Cadmium oxide nanocomposites (ZnO-CdO NCs) and then practically implemented for the validation and electrochemical analyses using linear sweep voltammetry (LSV) and cyclic voltametric (CV) methods. Out of all the substances that were causing interferences, the constructed sensor probe showed selectivity towards 4-methoxyphenol (4-MP) due to the molecular interaction onto the intercalated surfaces of ZnO-CdO NCs. The chemical sensor exhibited enhanced electrochemical characteristics, such as higher sensitivity, a wide linear dynamic range (LDR), lower limit of detection (LOD), and good stability in detecting the specific compound 4-MP. For their optical, elemental, functional, morphological, and structural properties, the calcined ZnO-CdO NCs were analyzed using FTIR, UV, FESEM, EDS, XPS, TEM, and XRD techniques, respectively. In sensor fabrication, a flat GCE was constructed by applying a thin layer of NCs using a 5 % Nafion binder as a chemical coating agent. The calibration graph exhibited a linear relationship with a high coefficient of determination ($r^2 = 0.9680$) throughout a broad range of 4-MP concentrations (0.22–7.5 μM). The sensitivity and limit of detection (LOD) were determined to be $1.5189 \mu\text{Amm}^{-1} \text{cm}^{-2}$ and $0.01091 \mu\text{M}$ respectively. The synthesis of ZnO-CdO NCs by solid-state method is a promising approach for developing a phenolic sensor in a broad scale by electrochemical approach. The 4-MP sensor has demonstrated a promising performance using ZnO-CdO NCs by LSV and CV methods. This significantly impacts the identification of hazardous phenolic chemicals by electrochemical methods in the environmental and healthcare sectors, hence ensuring safety.

1. Introduction

There has been a growing need for electrochemical 4-MP sensors that are very sensitive and dependable in recent years. To address this requirement, much endeavor has been dedicated to the development and design of electrodes with large surface areas and favorable physico-

chemical characteristics. The study on nanoscale ZnO and CdO is rapidly gaining popularity because of its distinctive characteristics and wide variety of applications, especially in computing systems, sensor technology, and optical and electrical properties [1–4]. Scientists have been attracted to inorganic substances like metal oxide nanoparticles due to their low density, expansive surface area, and distinctive optical

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properties. Moreover, these nanoparticles made of metal oxides exhibited enhanced efficacy in several applications, including catalysis and sensing. ZnO nanoparticles are favored by materialists due to their many characteristics, such as a wide bandgap, piezoelectric properties, and their application in UV/blue emission devices [5–7]. Nanocrystalline ZnO has superior performance compared to bulk crystals due to quantum confinement phenomenon. On the contrary, CdO at the nano scale is a semiconductor with a significant energy gap and reduced electrical resistance. This oxide is recommended due to its inclusion of a component that is commonly utilized in electroplating baths and contributes to the coloring process [8,9]. Phenol and its derived compounds have widespread use in the therapeutic and manufacturing sectors. Phenolic chemicals are also generated by biological breakdown, human excrement, refined petroleum products, and drug industries [10]. 4-Methoxyphenol is utilized in many sectors, mostly as mediators to produce agricultural chemicals and as blockers of monomer polymerization in the petroleum sector. Additionally, it serves as an additive in the composition of inks and toners, in addition to being used in additives, sealing compounds, and resins for the leather and apparel sectors. 4-MP is a phenolic compound widely used in various industries, including pharmaceuticals, cosmetics, and as a stabilizer in polymers. Despite its utility, 4-MP poses environmental and health risks due to its toxicity and potential bioaccumulation, making its detection crucial for environmental monitoring and safety assessment.

Even minute quantities of phenolic chemicals emitted during manufacture have been shown to be hazardous. Therefore, they are often present in both polluted and clean water sources, and on occasion, they have also been detected in various food samples [11]. 4-MP is known to induce severe ocular annoyance and is also toxic to marine organisms, including sharks and whales. Furthermore, the prospective deterioration and harmful influences of phenol based derived compounds, together with their bio-breakdown byproducts, are a significant ecological concern that might pose a substantial risk to ecosystems and human prosperity [12]. Hence, the continuous check of phenolic compounds in water-based solutions is crucial due to their inherent toxicity, which persists even at minimal concentrations. Phenol derivatives in water can be determined using different techniques such as electrochemical methods [13], capillary electrophoresis (CE) [14], gas chromatography (GC) [15], liquid chromatography (LC) (often combined with LSV and CV techniques) [16], and spectrophotometry [17]. However, thus mentioned techniques require pre-treatment of the test substances, that is a complicated and time-arduous process. As a result, they are not appropriate for regular ecological examining [18]. Hence, the imperative need arises for the advancement of 4-MP sensors that possess high sensitivity, reliability, affordability, and rapid response time. This is crucial for accurately evaluating the environmental consequences of 4-MP and detecting even minute and extremely small quantities of it in water-based substances. Phenol derivatives sensing commonly involves the use of platinum (Pt), carbon paste and GCEs [19,20]. Typically, GCEs undergo modifications prior to their use as sensors. For instance, they can be treated with surfactants to allow for the accumulation of phenol derivatives. Alternatively, they can be manufactured using nanocrystals (NCs) and nanoparticles (NPs). Phenolic chemicals undergo oxidation readily on a platinum electrode, but this process consistently produces uncertain or unclear results, making it unsuitable for electrochemical investigations [11]. To address this issue, it is required to modify the electrodes using nanocomposites that have a high number of active sites. This will enable the development of electrochemical sensors that are practical for detecting phenolic chemicals.

ZnO-CdO composites have garnered attention in sensor applications due to their unique physicochemical properties. ZnO is a well-known semiconductor material with high sensitivity and excellent chemical stability, while CdO enhances conductivity and electron mobility due to its narrow band-gap [20]. When combined, the ZnO-CdO composite exhibits synergistic effects, such as improved charge transfer efficiency, enhanced active surface area, and greater stability under

electrochemical conditions. These attributes make ZnO-CdO composites highly suitable for the sensitive and selective detection of phenolic compounds like 4-MP. Recent studies have demonstrated that ZnO-CdO composites effectively address limitations of single-component materials, such as low sensitivity and poor selectivity. Moreover, the ease of synthesis, cost-effectiveness, and ability to tune their properties further underline their potential in sensor development. By leveraging these advantages, ZnO-CdO-based sensors can provide accurate, reliable, and efficient detection of 4-MP, even at low concentrations.

Binary ZnO-CdO nanocomposites were effectively synthesized using a straightforward solid-state process. These nanocomposites were thoroughly analyzed using several techniques including Field Emission Scanning Electron Microscope (FESEM) with Fourier Transform Infrared Spectroscopy (FT-IR), Energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and Ultraviolet-visible spectroscopy (UV/vis). In addition, an electrochemical probe for 4-MP was created using a binary ZnO-CdO NCs produced GCE surface. The electrochemical characteristics of the ZnO-CdO compound in relation to 4-MP were assessed under normal room circumstances. The study revealed that binary ZnO-CdO nanocrystals showed a remarkable ability to selectively and sensitively detect the oxidation of 4-MP, with a low detection limit. The results indicate that the combination of ZnO and CdO in a binary form has significant promise for use in detecting and quantifying 4-MP. As far as we know, this is the first work that has utilized cadmium oxide to enhance the current collecting characteristics of a ZnO electrode in a sensor for detecting 4-MP. This work is distinctive since it involved the functionalization of CdO by attaching ZnO nanoparticles employing the solid-state method. Demonstrations have shown the effectiveness of high-quality nanostructured electrodes in terms of storage capacity and electron transfer kinetics.

2. Experimental sections

2.1. Materials and methods

Cadmium(II) nitrate [$\text{Cd}(\text{NO}_3)_2$], Zinc(II) nitrate [$\text{Zn}(\text{NO}_3)_2$], potassium ferrocyanide [$\text{K}_4[\text{Fe}(\text{CN})_6]$], dipotassium hydrogen phosphate (K_2HPO_4), potassium ferricyanide [$\text{K}_3[\text{Fe}(\text{CN})_6]$], hydrochloric acid (HCl), sodium hydroxide (NaOH), and Potassium dihydrogen phosphate (KH_2PO_4) utilized in this study were procured from Merck. No additional purification was conducted on the remaining chemicals; solutions were prepared utilizing deionized water. The substances under consideration were of analytical grade. To adjust the pH, HCl and NaOH were used, and KH_2PO_4 and K_2HPO_4 salts were used to make 0.1 M phosphate buffer solutions (PBS). The ZnO-CdO nanocomposite was synthesized using the solid-state method with zinc nitrate [$\text{Zn}(\text{NO}_3)_2$; ~99 % purity; Sigma Aldrich] and cadmium nitrate [$\text{Cd}(\text{NO}_3)_2$; 99 % purity; Sigma Aldrich]. To conduct the experiment, a granite mortar and pestle was used to triturate a stoichiometric mixture of 1.0 g of metallic salt and NaOH for 15 min. The mixture was then annealed at 600 °C for 7 h.

This study employed powder XRD diffractometers (AXS D4 Endeavors) subjected to various radiation types to analyze the crystalline structure of the Y/Fe-MWCNT nanocomposite samples. The investigation of size, form, morphology, and structure was conducted using 5.0 kV (JEOL-6300F) and 200.0 kV (JEOL JEM-2100F-UHR). The functional group analysis was performed utilizing Fourier-transform infrared spectroscopy (FTIR) via the KBr pellet method, employing a Perkin Elmer (Spectrum 100) instrument within the 400–4000 cm^{-1} range. The shape and elemental composition of the ZnO-CdO nanocomposite were analyzed using FESEM (FEI Quanta-250) with EDS. The JascoV-650 spectrophotometer was employed for UV-visible spectral analysis. To analyze the binding energies (eV) among elemental Zn, Cd, and O, the X-ray photoelectron spectroscopy (XPS) investigation was executed for ZnO-CdO nanocomposite on a K- $\alpha 1$ spectrometer (Thermo scientific, K- $\alpha 1$ 1066) with an excitation radiation source (A1 K $\alpha 1$, Beam spot size =

300.0 μm , pass energy = 200.0 eV, pressure- 10^{-8} torr).

2.1.1. Fabrication of electrode by ZnO-CdO nanocomposite

By incorporating ZnO-CdO nanocomposite into GCE, the working electrode the principal component of the suggested sensor was created. A thin layer of a ZnO-CdO nanocomposite slurry in ethanol was applied to a freshly cleaned GCE surface, and then the electrode was allowed to dry in a controlled laboratory environment to create the functioning electrode. After the nanocomposite layer on the GCE was coated with multiple drops of 5 % Nafion adhesive, which increased its stability and prolonged the electrode's usable life, it was let to dry at room temperature. A Metrohm Autolab Potentiostat was used for all electrochemical experiments. Working electrode: GCE, reference electrode: Ag/AgCl (Saturated KCl), and counter electrode: Pt wire made up the electrochemical cell. Seawater from Jeddah, industrial water from Jeddah, and well water from Abha were the real samples used. A concentration of 1.0 g/L was observed for all species that interfered.

3. Results and discussion

3.1. Optical and structural analysis of nanocomposites

Fig. 1(a) displays the UV–vis absorption spectrum of the CdO/ZnO nanocomposite. The graph plots the normalized absorption of the photocatalyst versus the wavelength. This spectrum is captured within the wavelength range of 200 to 800 nm. Remarkably, the CdO/ZnO nanocomposite exhibits a nearly identical absorption profile characterized by a sharp absorption edge within the wavelength range of 360–400 nm. This region corresponds to the band gap energy of ZnO. The CdO/ZnO nanocomposite exhibits two distinct absorption peaks: one at 320 nm, corresponding to ZnO, and another at 389 nm, corresponding to CdO. The lack of impurity energy level transitions is indicated by the fully decreased absorbance curves after 570 nm for all systems [21]. The FTIR spectrum is utilized to provide further evidence for the creation of metal

oxides and to determine the specific sorts of functional groups present on their surface. Typically, most metal oxides could absorb radiation in the low-energy infrared (IR) range, namely below 1000 cm^{-1} [22]. The FTIR spectra of the CdO/ZnO nanocomposite, as depicted in Fig. 1(b), exhibits a prominent multiple peak. This peak comprises individual peaks at 444, 589, 659, 723, and 828 cm^{-1} , that correlate with the values to the vibrations of Cd-O and Zn-O bonds within the composite. These values closely align with those described in reference [23–25].

The ZnO-CdO nanocomposite X-ray diffraction (XRD) patterns with JCPDS card numbers 36-1451 and 05-0640 are displayed in Fig. 1(c). The indices of (100), (002), (101), (102), and (110) for wurtzite hexagonal ZnO were determined to be responsible for the peaks observed at 31.49, 34.25, 36.08, 47.47, 56.45, and 62.81 in the XRD pattern of ZnO nanoparticles. The presence of CdO cubic peaks at 33.08, 38.36, and 55.22 etc. in the XRD pattern of the ZnO-CdO nanocomposite was recognized as (111), (200), and (220), respectively, confirming the development of the nanocomposite. The absence of any non-ZnO-CdO distinctive XRD peaks in the corresponding XRD patterns leads these investigations to the conclusion that the generated ZnO-CdO nanocomposite structures were pure [26].

3.2. Morphological and elemental study of nanocomposites

Fig. 2(a–b) displays the SEM of ZnO and CdO-ZnO nanocomposite at three different sizes: 10 μm , 3 μm , and 500 nm. The electron micrographs of CdO-ZnO exhibit a three-dimensional hexagonal structure bearing the length edge of 110 nm and height of 140 nm. The hexagonal structures are evenly dispersed and spaced apart, providing ample room for 4-MP molecules to react with Cd^{2+} and Zn^{2+} ions. The elemental analysis findings of the ZnO-CdO nanocomposite, as depicted in Fig. 2(c), confirm the nanosheet shape of the generated material. The elemental analysis obtained from EDS revealed the presence of just Zn, O, and Cd, which is presented in the Fig. 2(d–e). The ZnO-CdO nanocomposite consists of 37.78 % Zn, 44.79 % O, and 17.43 % Cd in terms of

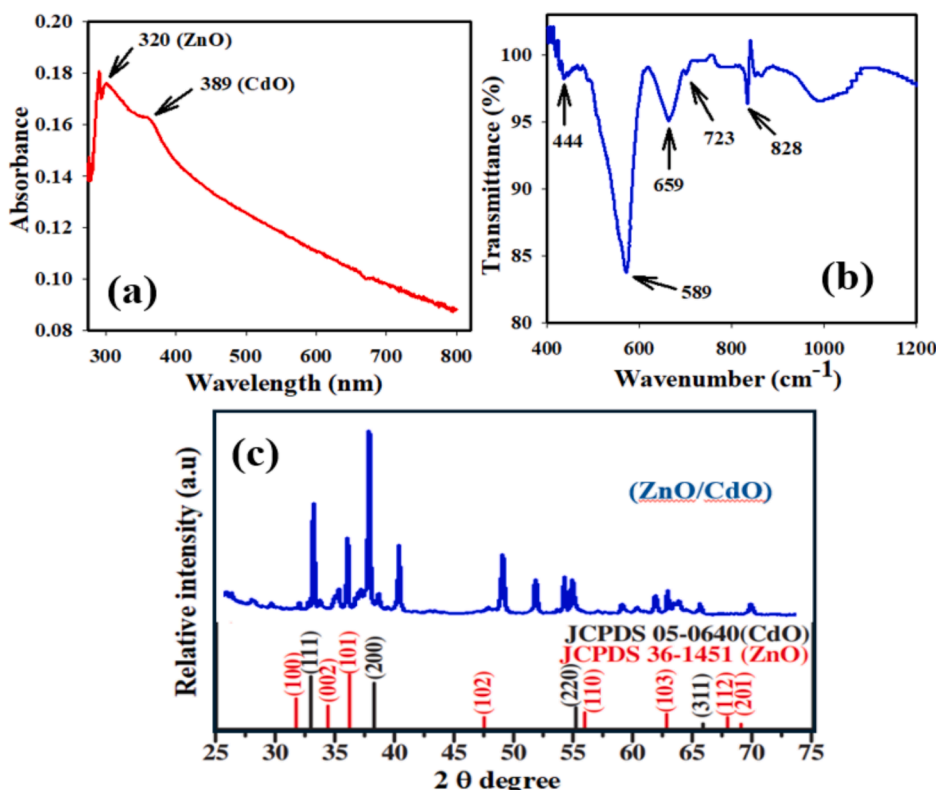


Fig. 1. (a) Ultraviolet–Visible absorption, (b) FT-IR, and (c) XRD spectra of ZnO-CdO nanocomposite.

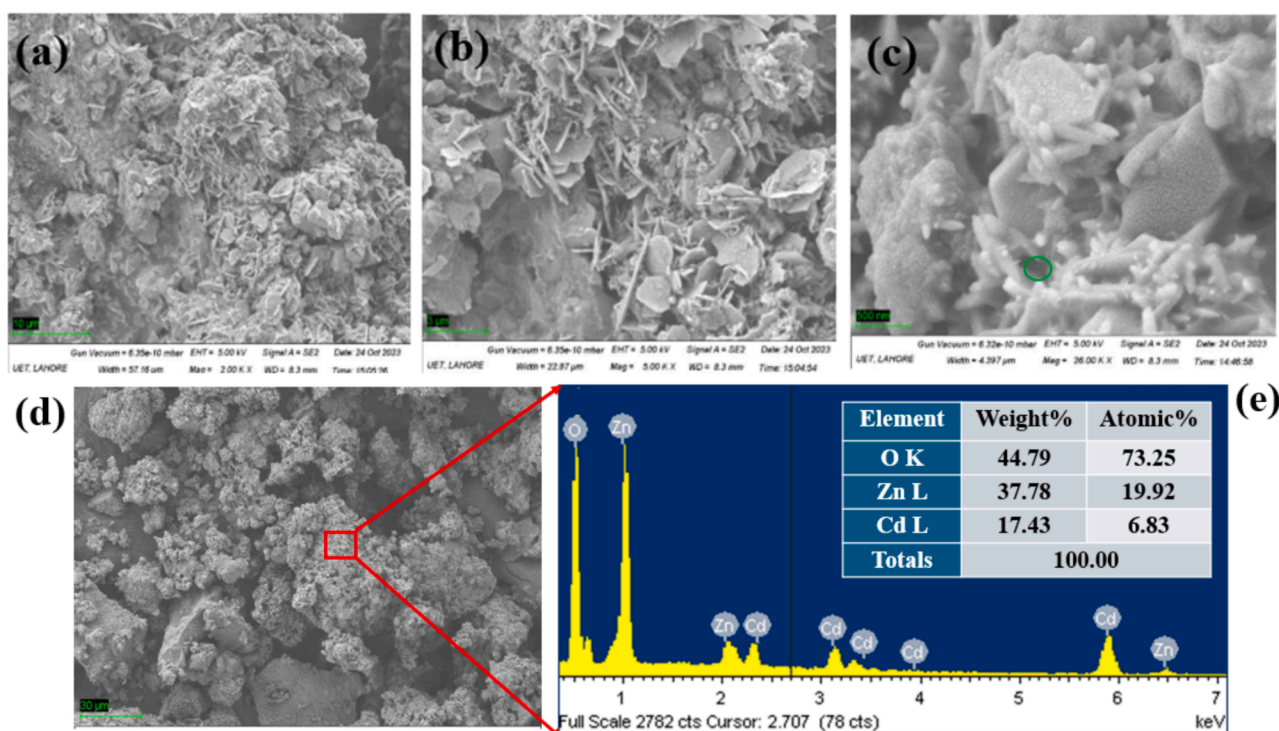


Fig. 2. Morphological and elemental analysis. (a–c) SEM images of the ZnO-CdO nanocomposite's structural morphology from lower to higher resolution, (d) Images of ZnO-CdO nanocomposite microstructure validated by EDS, and (f) ZnO-CdO nanocomposite elemental compositions investigated by EDS.

elemental composition (Fig. 2e-inset).

3.3. XPS study of ZnO-CdO nanocomposite

In this section, Fig. S1(a) represents an X-ray photoelectron spectroscopy (XPS) spectrum of the Zn2p core level. XPS is a surface-sensitive technique widely used to investigate the elemental composition and electronic states of materials. The Zn2p core level typically displays two distinct peaks corresponding to the spin-orbit splitting of the 2p orbital into Zn2p_{3/2} and Zn2p_{1/2}. These peaks arise due to spin-orbit coupling, where the *p* orbitals split into two states with different energy levels. The binding energy difference (ΔE) between these peaks is approximately 23.0 eV, a characteristic value for zinc-containing compounds such as ZnO or metallic Zn. The position and shape of the peaks provide essential information about the oxidation state and chemical environment of zinc in the sample. The graph shows two notable peaks around 1020–1045 eV, which likely correspond to the Zn2p_{3/2} and Zn2p_{1/2} transitions. The higher intensity of the left peak (Zn2p_{3/2}) is consistent with its lower binding energy compared to Zn2p_{1/2}. The binding energy values around 1020–1045 eV align with literature-reported values for zinc species, where ZnO (Zn²⁺ state) typically has a Zn2p_{3/2} peak at ~1022.1 eV and Metallic Zn exhibits a lower binding energy near ~1022.1 eV. The high intensity of the signal suggests a significant zinc presence, while the specific binding energies provide insight into its oxidation state [27].

The Cd 3d core level typically exhibits spin-orbit splitting due to the interaction between the electron's spin and orbital angular momentum. This splitting divides the Cd3d signal into two distinct peaks as Cd3d_{5/2} (The peak with the lower binding energy, typically located around 405–406 eV) and Cd3d_{3/2} (The peak with the higher binding energy, usually around 411–412 eV). The energy separation (ΔE) between the two peaks is approximately 5.8 eV, which is characteristic of cadmium in its oxidized states, such as Cd²⁺. Fig. S1(b). The observed symmetry, positions, and relative intensities of the peaks indicate the presence of cadmium in a single predominant oxidation state, likely Cd²⁺, commonly found in compounds like cadmium oxide (CdO) [28]. Fig. S1

(c) exhibits O1s XPS spectrum, with a binding energy peak at approximately 531.8 eV, suggests the presence of surface oxygen species, lattice oxygen, or hydroxyl groups. Based on the binding energy (near 531.8 eV), the peak can be attributed to the following chemical states as Oxygen in metal oxides (ZnO & CdO) where oxygen forms lattice bonds (O²⁻) and Surface hydroxyl groups or adsorbed water often appear slightly above 531.8 eV due to hydrogen bonding [3].

Peaks corresponding to Zn2p are prominently observed in the spectrum, typically around the binding energies of 1020–1045 eV, with the Zn 2p_{3/2} peak near 1022.1 eV and the Zn2p_{1/2} peak around 1045.0 eV. These peaks confirm the presence of Zn in the material, primarily in the Zn²⁺ oxidation state, consistent with the formation of ZnO. The Cd3d region reveals peaks near 405–412 eV, with the Cd3d_{5/2} peak typically around 406.1 eV and the Cd3d_{3/2} peak near 411.9 eV. These peaks confirm the presence of Cd, predominantly in the Cd²⁺ state, which is characteristic of CdO. The O1s peak is observed around 529–532 eV. Deconvolution of the O 1s peak often reveals contributions from lattice oxygen (associated with ZnO and CdO bonds) near 51.8 eV. Fig. S1(d).

3.4. TEM analysis of ZnO-CdO nanocomposite

Transmission Electron Microscopy (TEM) is a powerful analytical tool used to investigate the structural and morphological properties of ZnO-CdO nanocomposites at the nanoscale which is presented in the Fig. S2. Here, it provides high-resolution images [Fig. S2(a–b)] that reveal the overall morphology of the ZnO-CdO nanostructures. It typically shows the formation of distinct ZnO-CdO nanomaterials as doped nanomaterial, indicating the successful synthesis of the binary doped composite. It exhibits spherical disc-shape shape structures, depending on the solid-state synthesis method at higher temperature. It also provide evidence of the interaction between ZnO and CdO, where images demonstrate a good doping, which is essential for the enhanced structural and morphological properties of the ZnO-CdO nanocomposites. The lattice spacing of ZnO and CdO are measured from the magnified TEM images as 0.25 nm and 0.27 nm respectively, which are presented in the Fig. S2(c,d).

3.5. Electrochemical characterization of ZnO-CdO/GCE sensor

The CV measurement was employed in an ideal setting to detect 4-MP at varying concentrations using ZnO-CdO/GCE. The current responses of 4-MP are shown in Fig. 3(a) for a range of 0.22 to 7.3 μM . An increase of 4-MP consistently results in a higher CV peak current. The electrochemical oxidation of 4-MP was tested on the as-fabricated electrode using CV methods in a phosphate buffer (0.1 M) having 6.5 pH. The voltammograms obtained using bare GCE, ZnO/GCE, CdO/GCE, and ZnO-CdO/GCE are displayed in Fig. 3(b) at a potential scan rate of 100 mVs^{-1} . A series of μM solutions of 4-MP are used as the test analyte. Bare GCE showed an oxidation peak, CdO-modified GCE, and ZnO-modified GCE in the potential window of around 0.3 V. At anode, the ZnO-CdO/GCE electrode demonstrates a more robust electrochemical reaction rate compared to the unmodified glassy carbon electrode within the same potential area. The ZnO-CdO/GCE depicts a prominent peak structure with a significant rise of anodic current at 0.3 V potential, that is substantially lesser than its rivals at roughly 0.092 V. The ZnO-CdO nanocomposite appears to possess improved detection and catalytic performance for the 4-MP electro-oxidation series, as evidenced by the notable enhancement of current intensity and the substantial reduction of overpotential. Fig. 3(b) shows that the ZnO-CdO/GCE electrode has a higher oxidation current, and a higher capacitance current compared to the ZnO/GCE, CdO/GCE, and unmodified GCE electrodes. An increase in capacitive current can result from a higher surface area, which could be caused by the incorporation of CdO into the produced nanocomposite [29]. The approach can increase the catalytic surface area, make numerous new active sites, and improve the target analyte's interaction with the as-fabricated electrocatalyst [30,31].

The purpose of the EIS study was to learn more about the catalytic

performance of the catalyst throughout its production in 4-MP electro-oxidation. As an adaptable strategy for assessing the interfacial characteristics of the modified ZnO-CdO/GCE, the EIS is a valuable tool for understanding the subtle fluctuation of the interaction between surface and electrolyte characteristics during the electrochemical migration [32,33]. The EIS Nyquist curve was obtained in respect to 7.5 μM 4MP in 0.1 M PBS, with a related potential of 1.0 V, and a signal amplitude ranging from 10^{-2} to 105 Hz. At the interface between surfaces and solutions, strong electrical conductance, or a slight electron transfer hindrance, was shown by an EIS Nyquist plot exhibiting a reduced semicircle diameter in the high-frequency zone [34]. Here, in the identical experimental setup, the naked GCE shows larger charge transfer impedance and slower electron transfer rates, indicating decreased catalytic efficacy. Fig. 3(c) shows that the semicircle diameter of the increased frequency area was smaller in ZnO-CdO modified GCEs, indicating that the 4-MP electrochemical oxidation process was more catalytically effective. This discovery highlights the potential for ZnO-CdO nanocomposite to enhance surface-solution interface conductivity, which could potentially facilitate heterogeneous electron transport and nitrite electro-oxidation. Using the ZnO-CdO electrocatalyst may result in lower overpotential and outstanding oxidation efficiency, which could be attributed to the synergistic coupling effect. In addition, by increasing the number of electron transfer channels and the effective surface area, CdO is expected to enhance the electro-oxidation of 4-MP catalytic performance. The result is an increase in the total number of active catalytic sites.

An electrochemical reaction occurring on the surface of the ZnO-CdO/GCE electrode was examined by altering the scan rate (10–500 mV s^{-1}) in a solution of 0.1 M $\text{M}_3(\text{Fe}(\text{CN})_6)/\text{K}_4(\text{Fe}(\text{CN})_6)$ made in 0.1 M of PBS. As seen in Fig. 3(d), the scan rate has a direct correlation with the

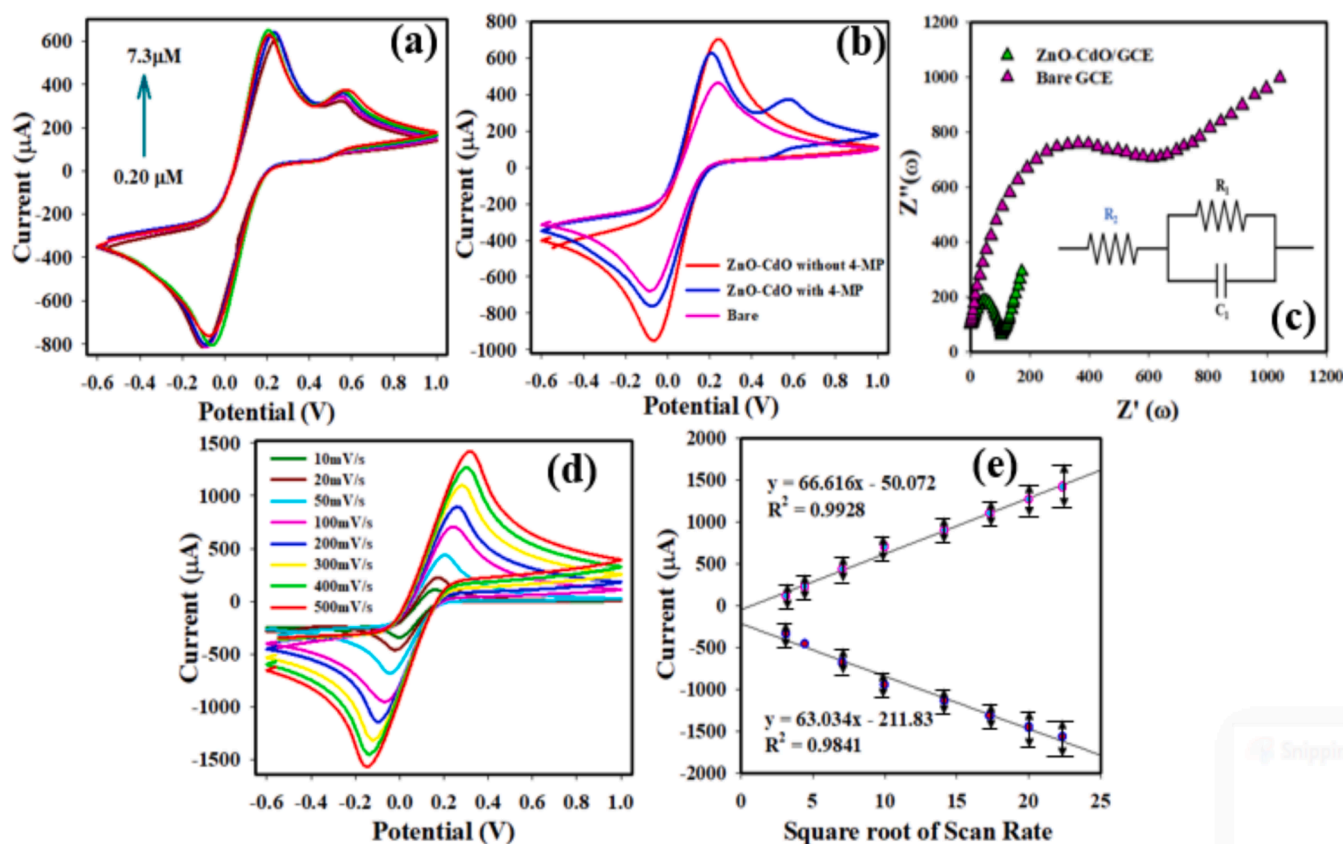


Fig. 3. (a) CV Concentration variation (0.20–7.3 μM), (b) Control using CV by containing of bare GCE, Coated ZnO-CdO/GCE without/with 4-MP and ZnO-CdO/GCE in 7.5 μM 4-MP solution at a scan rate of 100 mVs^{-1} , (c) Nyquist plot of EIS for bare GCE and modified ZnO-CdO/GCE, (d) Cyclic Voltammograms of coated ZnO-CdO/GCE at the scan rate from 10 to 500 mVs^{-1} (e) Peak current versus the square root of the scan rate.

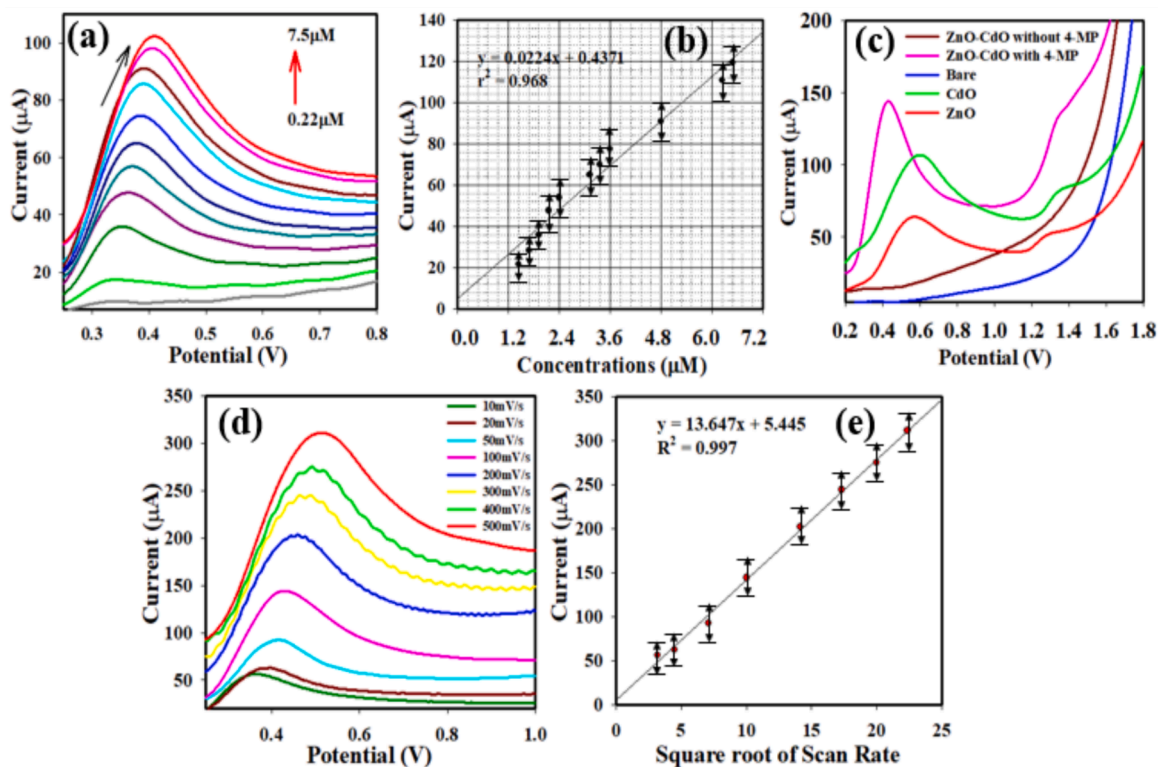


Fig. 4. Detection of 4-MP by electrochemical approach. (a) LSV of ZnO-CdO/GCE with 0.22 to 7.5 μM concentration range, (b) Calibration curve: peak current vs the 4-MP concentration, (c) Control containing LSV of bare/GCE, Coated ZnO-CdO/GCE without 4-MP, Coated ZnO/GCE, Coated CdO/GCE, coated ZnO-CdO/GCE in 7.5 μM 4-MP solution (pH = 6.5) at a scan rate of 100 mVs^{-1} , (d) LSVs of coated ZnO-CdO/GCE at the scan rate from 10 to 500 mVs^{-1} , and (e) Peak current vs. the square root of the scan rate.

peak currents. The linearity demonstrated in the Fig. 3(e) plot of the square root of the scan rate vs peak current yielded the regression equation that follows.

$$I_{\text{pa}} = 0.0054 v^{1/2} - 0.0004 (R^2 = 0.9928)$$

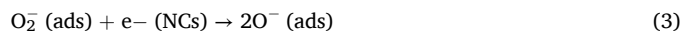
$$I_{\text{pc}} = 0.0048 v^{1/2} + 0.0003 (R^2 = 0.9841)$$

An indication that the ZnO-CdO/GCE have a common mechanism controlled by control diffusion is the linear relationship between the square root of the scan rate and the peak currents.

3.6. Detection mechanism of 4-MP with fabricated ZnO-CdO NCs/GCE

The interior resistance of the manufactured nanocomposite sensor reduces as the electron communication properties increase. This is a fundamental property of nanomaterials under room settings [35–39]. The adsorption of oxygen has a crucial role in influencing the electrochemical characteristics of the ZnO-CdO NCs/GCE. The adsorption of oxygen ions eliminates the conducting electrons and enhances the conductivity of ZnO-CdO nanocomposites. The surface of ZnO-CdO NCs adsorbs and ionizes the dissolved O_2 present in the interior of solution or

the surrounding atmosphere's surface air. The following equations (Eqs. (1)–(3)) can be used to describe this process.



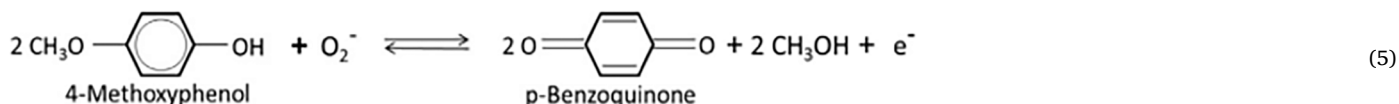
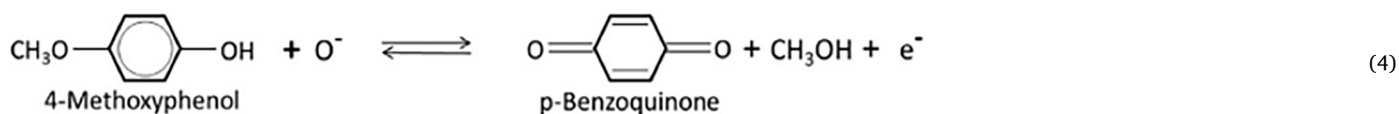
The 4-MP detecting mechanism of the ZnO-CdO nanocomposite probe is derived from the oxidation of 4-MP occurring at the exterior of the ZnO-CdO NCs. These reactions took place in the liquid/air junction or nearby surroundings of the bulk system because of low hauler amount, that initially raises the hindrance of the surface area of the electrode. The surface of ZnO-CdO NCs is chemically bound to highly reactive oxygen species (O_2^- and O^-) at room temperature. The amount of these chemically attached oxygen species mostly relies on the surface area of the ZnO-CdO nanocomposite. The high response of ZnO-CdO/GCE to 4-MP can be related to the oxidation of 4-MP by adsorbed oxygen species, specifically O_2^- and O^- . As the amount of oxygen adsorbed on the probe surface increases, the oxidizing potential also increases, leading to a quicker oxidation of 4-MP. The oxidation rate of 4-MP in

Table 1

Evaluation of the newly prepared CdO-ZnO/Nafion/GCE sensor by electrochemical approaches with various nanocomposites in the detection of 4-MP.

Modified Electrodes	Techniques	LOD (μM)	Linear Dynamic range	Sensitivity	Ref
PPy/CNT/HRP/AuE/PPy-films	I-V	1.06	1.6–81.6 μM	50.0 $\text{nA}\mu\text{M}^{-1}$	[44]
3D graphene micropillar	CV	50.0	50.0 nM to 2 μM	3.9 $\mu\text{A}\text{mM}^{-1}\text{cm}^{-2}$	[45]
MWCNT/Nafion	I-V	90.0	0.2–1.6 μM	7.0 $\mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$	[46]
NiS ₂ -CNT NCs/GCE	I-V	30.0 $\pm$ 0.02	0.01 nM to 10.0 mM	632.9224 $\mu\text{A}\text{mM}^{-1}\text{cm}^{-2}$	[47]
ZnO-CdO/Nafion/GCE	LSV	0.0198 μM	0.22 to 7.5 μM	1.518 $\mu\text{A}\text{mM}^{-1}\text{cm}^{-2}$	Present Work

ZnO-CdO NCs was much higher than that of other compounds, even when the surface area and circumstances were kept comparable [40–43]. When 4-MP undergoes a reaction with the oxygen that is adsorbed on the surface and/or inside the ZnO-CdO NCs, it is oxidized to p-benzoquinone. This reaction also results in the release of free electrons into the conduction band. These processes are described by Eqs. (4)–(5).



3.7. Detection of 4-MP with ZnO-CdO NCs by LSV

To determine the 4-MP detection efficiency of the recently synthesized ZnO-CdO electrocatalyst, an LSV experiment was performed in a 0.1 M phosphate buffer solution with 4-MP concentrations ranging from 0.22 to 7.5 μM , while keeping the scan rate constant at 100 mVs^{-1} . Fig. 4(a) demonstrates that the anodic current rises as 4-MP is introduced successively to the reaction medium, indicating the electrochemical sensing ability of the ZnO-CdO/GCE. There are a few possible reasons why 4-MP injections cause an increase in oxidation current. One is that free charges are more accessible, and another is that the ZnO-CdO/GCE bears outstanding charge abilities. All the way from 0.22 to 7.5 μM , the correlation between peak current and 4-MP concentration was a straight line.

Based on the fitting equation: $I_{\text{pa}} = 0.0224x + 0.4371$ [4-MP], the graph in Fig. 4(b) shows a linear relationship between I_{pa} and 4-MP concentration. With a r^2 value of 0.9680, this correlation is statistically significant. After that, we used Eq. (6) to determine the LOD.

$$\text{LOD} = 3\sigma/\text{m} \quad (6)$$

With σ : Blank electrolyte standard deviation and m : Slope of the calibration curve.

According to the published studies and as shown in Table 1, the values obtained with different electrodes are like, and sometimes smaller than, the determined value of 0.01091 μM . ZnO-CdO GCE has a lot of promise due to its low cost, ease of manufacturing, and lack of further preparatory requirements. Because of this, it might be used as a substitute for materials made using the other method. As illustrated in Fig. 4(c), a range of coated GCEs were utilized as control experiment. These included bare GCE, coated ZnO/GCE, coated CdO/GCE, coated ZnO-CdO/GCE with 4-MP as a target, and coated ZnO-CdO/GCE without 4-MP. The scanning rate was 100 mVs^{-1} and the pH was 6.5. The LSV profiles of the ZnO-CdO/GCE sensor are shown in Fig. 4(d) for 7.5 μM 4-MP at 10, 20, 50, 100, 200, 300, 400, and 500 mV/s . The scan rate has a positive correlation with the oxidation peak current, as shown in Fig. 4(e), indicating that the oxidation reaction is controlled by adsorption as an electrocatalytic process.

With a correlation coefficient of 0.997, the regression equation is given by $I_{\text{pa}} = 13.647 \text{ Scan rate (mV)} + 5.445$.

3.8. pH optimization and Interference study

It is impossible for the ZnO-CdO/GCE sensor probe to produce the identical electrochemical response to the 4-MP analyte, regardless of

how precisely the pH of the phosphate buffer solution is calibrated. Because of this, getting the pH right is essential for getting the most electrochemical output from the sensor. Thus, the produced sensor was used to test 4-MP in buffer solutions with pH values ranging from 5.7 to 7.5. Results of a pH-dependent electrochemical investigation of 7.5 μM 4-MP at applied potentials ranging from -1 to $+1.8$ V are shown in Fig. S3(a & b). In a pH 6.5 analysis of 4-MP, the ZnO-CdO/GCE sensor showed the most significant electrochemical reaction. This means that a

pH of 6.5 is optimal for electrochemical nitrite oxidation using the sensor probe. Through the use of LSV, we evaluated the 4-MP detection selectivity of ZnO-CdO/GCE. Fig. S3(c) and Fig. S3(d) show the introduction of 4-MP and other possible interferences to a buffer solution containing 0.1 M PBS (pH = 6.5). These substances include 4-aminophenol (4-AP), 4-aminoantipyrene (4-AAP), Lactic acid (LA), Creatinine, Citric acid (CiA), Cholic acid (ChA), Anisic acid, and Thiourea. However, the results show that even at concentrations far greater than 4-MP, the present-day alterations are less than 1 %. The 4-MP detector constructed using the ZnO-CdO/GCE sensor possesses exceptional selectivity and anti-interference properties, as shown by the data reported earlier.

3.9. Reproducibility, repeatability, and selectivity analyses

Sensor reproducibility, repeatability, and selectivity tests were carried out to guarantee the generated material's reliability with respect to acceptable assertions. Making four independent GCE electrodes with the same modification parameters allowed us to further test the material's repeatability. The as-fabricated sensor electrode can be replicated with only a slight change in the anodic current at these four electrodes, according to successive repeats of the LSV experiment performed under the identical experimental conditions. As seen in Fig. 5(a), reliability is key to the sensor's design. To evaluate the reproducibility of the sensor in detecting 4-MP concentration, ten replicate voltametric tests were carried out in PBS (pH 6.5) with ZnO-CdO/GCE. Here is Fig. 5(b). We investigated the ZnO-CdO/GCE electrode's selectivity employing LSV measurement in the manifestation of numerous compounds. At an optimal pH of 6.5, the interfering species K^+ , Ca^{2+} , Mg^{2+} , CO_3^{2-} , Ag^+ , SO_4^{2-} , and NO_3^- were introduced individually to 0.1 M PBS at a concentration five times higher than the 4-MP concentration. Even though the voltametric response was either nonexistent or extremely weak for all of the examined interfering chemicals, the current rose sharply following the addition of 4-MP to the reaction mixture [Fig. 5(c&d)].

3.10. Validation of real samples by electrochemical approach

In this method, 4-MP was detected in sea, tap, and well water samples by electrochemical methods adding ZnO-CdO/GCE according to the standard technique. We conducted three runs of each concentration experiment and then averaged the results to obtain a 4-MP concentration. Table 2 shows the results of the inspection of the real sample. There is a recovery rate ranging from 99.68 % to 99.99 % and RSDs are below 2 %. The findings corroborate the standard curve procedure, suggesting the sensor's accuracy. This opens the possibility of using the sensor in

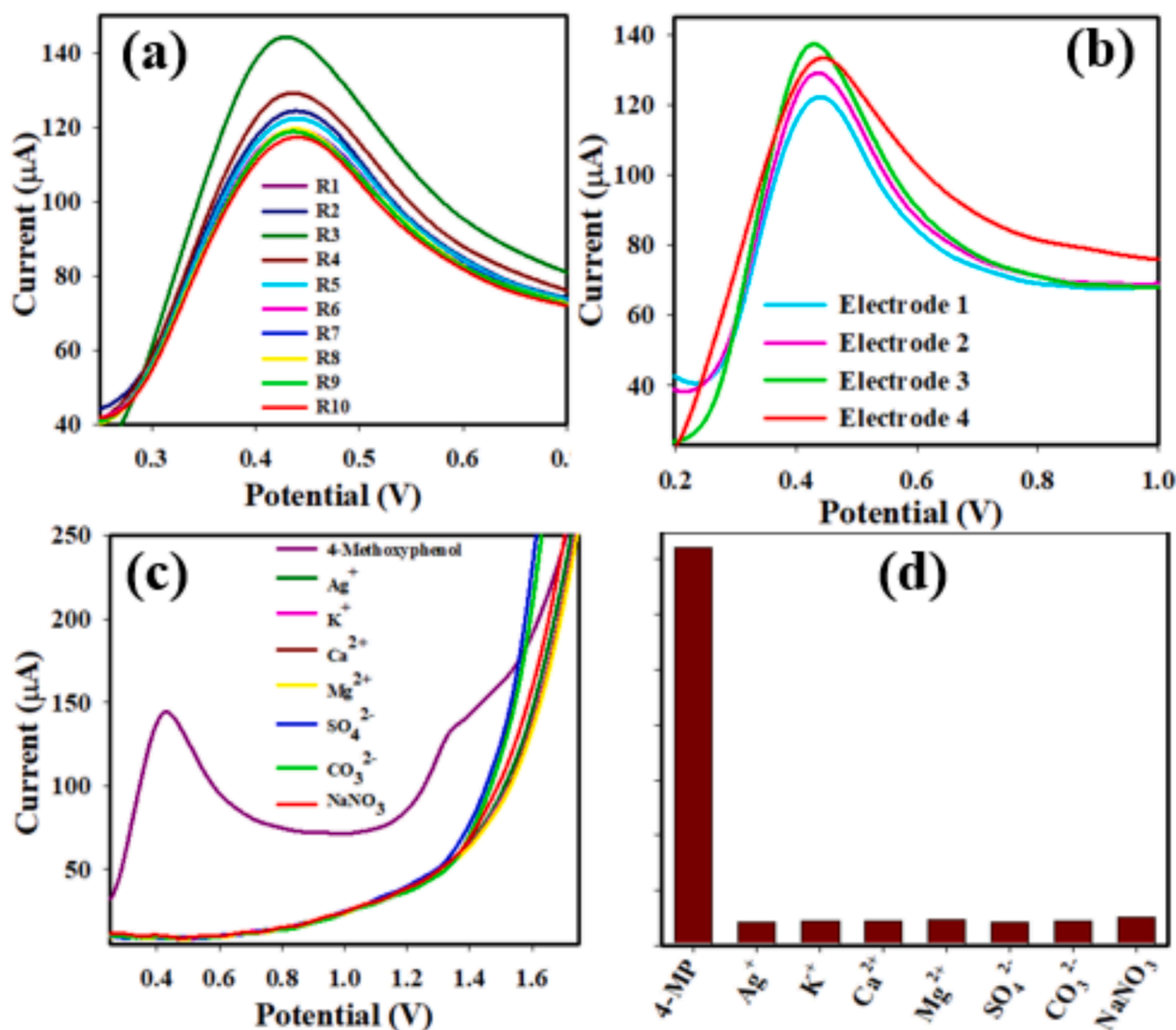


Fig. 5. Optimization of ZnO-CdO/GCE electrode by electrochemical method. (a) Find the LSV using same electrode over the course of ten repeated measurements, (b) Response of four prepared electrodes to LSV (7.5 μ M), (c) Selectivity data, and (d) Selectivity bar image.

Table 2

Validation of ZnO-CdO/GCE electrochemical sensor with collected real samples by electrochemical techniques.

Real Sample	Added 4-MP Conc. (μ M)	Measured 4-MP Conc. by ZnO-CdO NCs/GCE (μ M)			Average Recovery	RSD (%) (n = 3)
		R1	R2	R3		
Sea water	7.5	7.5	7.55	7.39	99.70	1.58
Tap water	7.5	7.3	7.48	7.55	99.99	0.72
Well Water	7.5	7.4	7.51	7.49	99.68	1.25

real-world applications.

4. Conclusion

This study encapsulated GCE with a thin layer of calcined ZnO-CdO nanocomposite using a 5 % Nafion adhesive, resulting in a selective 4-MP chemical electrochemical sensor. In the beginning, the ZnO-CdO nanocomposite was created using the solid-state method and then

analyzed using several conventional methods. These included imaging by UV/vis., FTIR, SEM, EDS, TEM, XPS, and XRD (for elemental, surface area, morphological, functional, and optical observations). In tests conducted using PBS (buffer solution), a realistic application medium, the suggested sensor consistently measured 4-MP levels. It is very good at being sensitive, linear, precise, repeatable, and stable. More than that, it's a reliable sensor for 4-MP detection in recovery-contaminated wastewater samples taken from actual samples. Hence, our findings could provide a solid basis for developing a chemical sensor probe that can identify dangerous substances in large scale, which would be great for public health and environmental preservation.

CRedit authorship contribution statement

Umer Shahzad: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Hadi M. Marwani:** Writing – review & editing, Supervision, Methodology, Investigation, Formal analysis. **Muhammad Fazle Rabbee:** Writing – review & editing, Resources, Methodology, Investigation, Formal analysis. **Maha G. Batterjee:** Writing – review & editing, Resources, Methodology, Investigation, Formal analysis. **Jehan Y. Al-Humaidi:** Writing – review

& editing, Methodology, Formal analysis. **Zahoor Ahmad:** 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, Investigation, Formal analysis, 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.2025.113171>.

Data availability

Data will be made available on request.

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