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Preparation of ZnO@SiO₂-n-propyl-NH₂ functionalized with benzoylthiourea-Cu(II) for the simultaneous detection of hydroquinone and catechol

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ABSTRACT

This study presents the synthesis of nanocomposites, consisting of ZnO@SiO₂-n-propyl-NH₂ functionalized with benzoylthiourea-Cu(II) using sol-gel method. The electrochemical properties of the composite were evaluated for the detection of catechol (CC) and hydroquinone (HQ) through differential pulse voltammetry (DPV). The electrochemical performance of the sensor was evaluated by cyclic voltammetry (CV), differential pulse voltammetry (DPV), and electrochemical impedance spectroscopy (EIS). The modified electrode exhibited excellent electrocatalytic activity and reversibility towards the oxidation of both Catechol (CC) and Hydroquinone (HQ) in a 5x10⁻⁸M acetate buffer solution (pH = 7.0). The relationship between the oxidation peak current of CC and its concentration was found to be linear in the dynamic range from 2.5 x 10⁻⁸ to 1.5 x 10⁻⁷ M, while a similar linear relationship was observed for the oxidation peak current of HQ within the range of 2.5 x 10⁻⁸ to 1.5 x 10⁻⁷ M. The detection limits (S/N = 3) for CC and HQ were determined to 5 10⁻⁸M.

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1. INTRODUCTION

Hydroquinone (HQ) and catechol (CC) represent two significant isomeric phenolic compounds widely utilized in various industries including cosmetics, pesticides, flavoring agents, antioxidants, secondary coloring agents, and photography chemicals [1-3]. Consequently, these compounds can easily enter the environment as pollutants during manufacturing and application processes.

Furthermore, they pose a significant risk to both environmental ecosystems and human health, even at minimal concentrations [4]. Given their structural and property similarities, accurately and simultaneously determining these isomers presents a considerable challenge [5-7]. Thus, there is a pressing need to develop a highly sensitive and selective analytical method capable of concurrently detecting HQ and CC. To date, several methodologies such as high-performance liquid chromatography (HPLC) [8], spectrophotometry [9], and electro-chemiluminescence [10] have been employed for the simultaneous determination of HQ and CC. Among these techniques, electrochemical methods stand out as favorable and attractive due to their rapid response, cost-effectiveness, simplicity, time efficiency, high sensitivity, and excellent selectivity, which are advantageous for detecting phenolic compounds [4]. However, conventional electrodes like gold and glassy carbon electrodes (GCE) fail to resolve these phenolic isomers due to the overlapping oxidation peaks they exhibit [11]. Various inorganic materials have garnered attention due to their versatile applications such as catalysts, humidity and gas sensors, and energy storage devices [12-13]. These compounds represented as MO_4 (where M stands for Ni, Co, Zn, Mo, Mn, Fe, Si, etc.), have recently gained prominence as advanced electrode materials in electrochemical applications due to their remarkable electrocatalytic properties [14-15]. Particularly noteworthy is the combination of ZnO, SiO₂, APTES, and an aromatic compound, which acts as an electro-attractant, presenting a promising electrode material. This material capitalizes on the significant electrochemical activity of Si and the high electrical conductivity of ZnO [16-17].

In our investigation, the resulting material, ZnO@SiO₂-n-propyl-NH₂-BTU-Cu(II), demonstrated high specific surface area, long-term stability, and porous structures that are capable of absorbing catechol and hydroquinone by electroanalytical oxidation. The modified electrodes exhibited exceptional sensitivity, exhibiting an exceptional detection limit for catechol and hydroquinone.

2. RESEARCH METHOD

2.1. Materials and Reagents.

Benzoyl chloride (C₇H₅COCl), potassium thiocyanate (KSCN), tetraethyl orthosilicate (TEOS), (3-aminopropyl) triethoxysilane (APTES), potassium chloride (KCl), zinc oxide (ZnO), ethanol (EtOH), sodium hydroxide (NaOH), hydrochloric acid (HCl), toluene (C₆H₅CH₃), acetone (C₃H₆O), copper(II) chloride (CuCl₂), potassium hexacyanoferrate(III) (K₃[Fe(CN)₆]), potassium hexacyanoferrate (II) trihydrate (K₄[Fe(CN)₆·3H₂O]), Catechol (CC), Hydroquinone (HQ) were purchased from Sigma-Aldrich. All solutions were prepared with water (resistivity 18.2 mΩ cm). Phosphate buffer (0.1 M) solution was prepared by dissolving monosodium dihydrogen phosphate trihydrate (NaH₂PO₄·2H₂O) and disodium hydrogen phosphate dodecahydrate (Na₂HPO₄·12H₂O), both obtain from Merck, in water.

2.2 Preparation of ZnO@SiO₂-n-propyl-NH₂-BTU-Cu (II)

KSCN (5 mmol) was added to a solution of benzoyl chloride (5 mmol) in dry acetone and then refluxed for 30 min to result in benzoyl isothiocyanate. In the next step, 1 g of ZnO@SiO₂-APTES NPs was added for reaction with benzoyl isothiocyanate in dry toluene and stirred in the reflux conditions for 5 h. The obtained product was collected by washing with distilled water, acetone

and dry toluene and then dried at 80 °C for 12 h. Finally, $\text{HAuCl}_3 \cdot 3\text{H}_2\text{O}$ (1.5 mmol) was added in one portion to a solution of $\text{ZnO}@ \text{SiO}_2\text{-n-propyl-BTU}$ NPs (1 g) in water (50 mL) and was stirred continuously for 6h at ambient temperature to anchor Cu(II) onto the surface of $\text{ZnO}@ \text{SiO}_2\text{-n-propyl-BTU}$ NPs. The resultant nanocomposites were washed with distilled water and ethanol to remove the unattached substrates. It was dried subsequently under vacuum.

3. RESULTS AND ANALYSIS

3.1. Preparation of modified electrodes

The glassy carbon electrode (GCE) surface was manually polished with a 0.03 μm alumina powder using emery paper, rinsed with distilled water, and then ultrasonically cleaned in ethanol for 5 minutes to obtain a reproducible state. Electrochemical pretreatment involved cyclic voltammetry in 0.5 M NaOH at a scan rate of 50 mV/s, ranging from 0 to 1.4 V as required. To prepare the composite ($\text{ZnO}@ \text{SiO}_2\text{-n-propyl-NH}_2\text{-BTU-Cu (II)}$), 2.0 mg of the composite was ultrasonically dispersed in 1 mL of ethanol to form a homogeneous solution. Subsequently, 5 μL of this composite solution was deposited onto the GCE surface and dried at room temperature, resulting in the formation of the modified electrode ($\text{ZnO}@ \text{SiO}_2\text{-n-propyl-NH}_2\text{-BTU-Cu (II)}/\text{GCE}$).

3.2. Electrochemical characterization

The electrochemical behavior of the modified and unmodified electrode in a 0.1 M KCl solution containing 5.0 mM $\text{Fe(CN)}_6^{4-/3-}$ was investigated using cyclic voltammetry and electrochemical impedance spectroscopy (EIS). As shown in **Figure 1a**, a reversible redox peak was observed in bare GCE. Upon modification of the GCE with the composite $\text{ZnO}@ \text{SiO}_2\text{-n-propyl-NH}_2\text{-BTU-Cu (II)}$, significantly increased anodic and cathodic currents were observed, indicating improved electrochemical performance. This enhancement can be attributed to the composite's high specific surface area and enhanced electrical conductivity resulting from the synergistic effects of the negatively charged hydroxyl groups (-OH) on the silica surface and repulsive interactions with the negatively charged redox also can be attributed to the presence of the aromatic group of benzoyl thiourea-Cu (II).

The EIS spectra of the bare electrode and the $\text{ZnO}@ \text{SiO}_2\text{-n-propyl-NH}_2\text{-BTU-Cu (II)}$ modified electrode were analyzed, revealing distinct features in **Figure 1b**. These spectra exhibited a semicircle and a linear portion. The semicircle diameter observed at higher frequencies corresponds to the charge transfer resistance (R_{ct}), while the linear segment at lower frequencies is indicative of the diffusion process. As depicted in **Figure 1b**, it is evident that the bare electrode has an R_{ct} value of 144 Ω , whereas the modified electrode shows a lower value of 2500 Ω . This notable reduction in the R_{ct} value is due to the improved electron transfer at the modified electrode in comparison to the bare electrode. Moreover, the agreement between the cyclic voltammetry (CV) data and the results obtained from electrochemical impedance spectroscopy (EIS) further supports these findings.

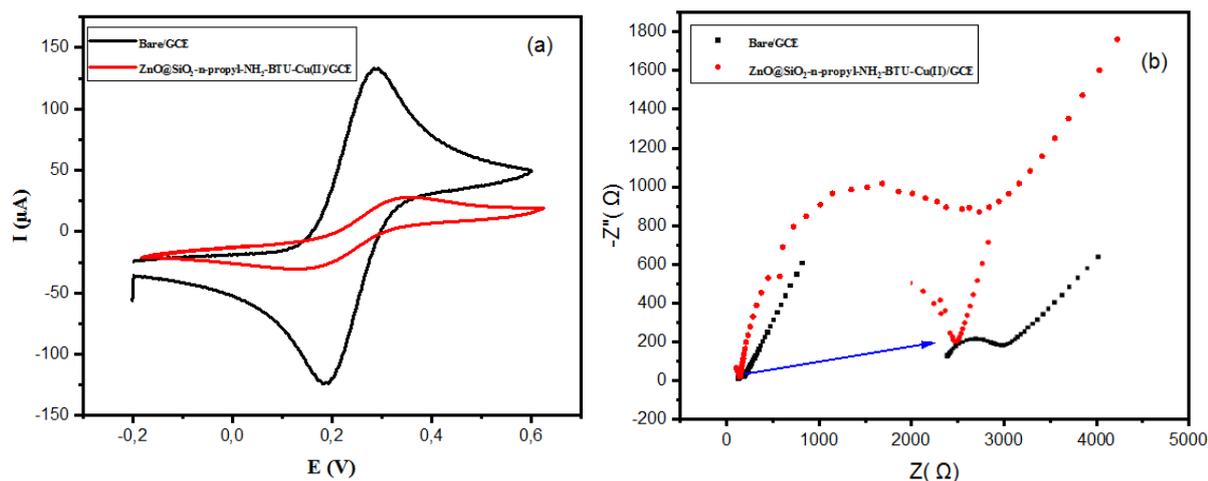


Figure 1. (a) Cyclic voltammograms, and (b) Nyquist plots of bare and modified GCE by ZnO@SiO₂-n-propyl-NH₂-BTU-Cu (II) in 0.1 M KCl solution containing 5 mM [Fe(CN)₆]^{3-/4-} at scan rate of 100 mV s⁻¹.

3.3. Simultaneous detection of catechol and hydroquinone using ZnO@SiO₂-n-propyl-NH₂-BTU-Cu (II) /GCE.

Under the optimum conditions, HQ and CC ions were determined by the DPV method using ZnO@SiO₂-n-propyl-NH₂-BTU-Cu (II) modified electrode for different ion concentrations from 2.5 10⁻⁸ to 1.5 10⁻⁷ M.

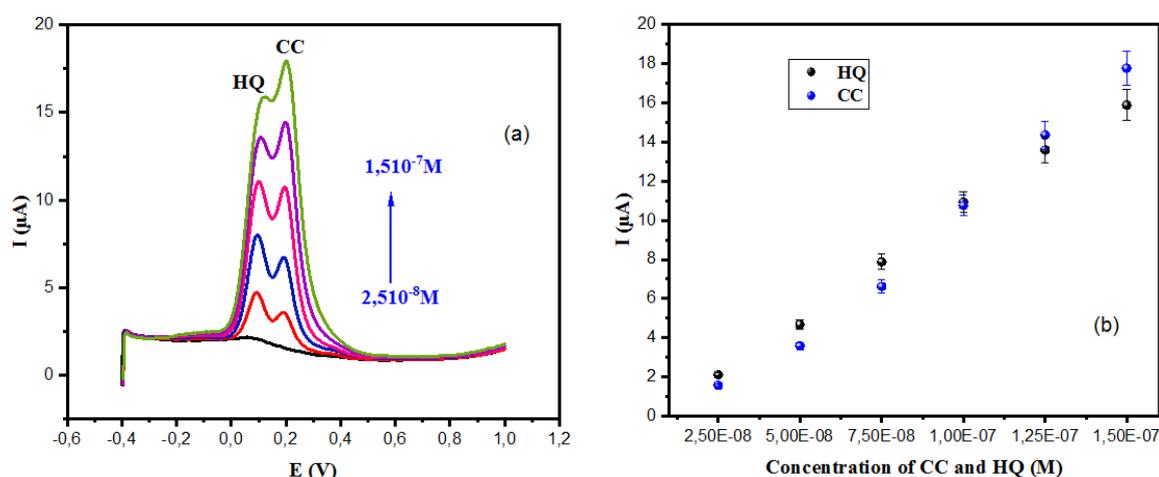


Figure 2. Differential pulse voltammograms of different concentrations of HQ and CC at ZnO@SiO₂-n-propyl-NH₂-BTU-Cu (II) /GCE in 0.1M PBS buffer solution (pH 7).

Figure 2 illustrates a notable trend wherein the response peak currents of the tested molecules exhibit a consistent increase corresponding to the concentration of the added molecules. Additionally, distinct response peaks indicative of HQ and CC emerge at potentials of 0.1 V and 0.2 V, respectively. Notably, an impressive low detection limit of 5 × 10⁻⁸ M was achieved for both HQ and CC. Moreover, the oxidation peak currents demonstrate a proportional relationship with the concentration of HQ and CC within a broader range spanning from 2.5 × 10⁻⁸ to 1.5 × 10⁻⁷ M. Comparatively, the analytical performance of the modified electrode across various tested ions

aligns favorably with findings from other referenced modified chemical electrodes (refer to Table 1). This underscores the robustness and reliability of our approach. Importantly, our electrode exhibits heightened sensitivity in the detection of HQ and CC ions, marking a significant advancement in this domain.

Table 1 Performance comparison of the fabricated electrode for HQ and CC detection with other electrodes

Electrodes	Methods	Linear range (μM)		Determination limit (M)		Reference
		HQ	CC	HQ	CC	
CS/MWCNTs/PDA/AuNPs	DPV	1×10^{-7} – 1×10^{-5}	1×10^{-7} – 1×10^{-5}	3×10^{-8} 51×10^{-6}	4.71×10^{-8}	[18]
poly/GO	DPV	3×10^{-7} – 1×10^{-4}	2×10^{-7} – 1×10^{-4}	0.0 8.5×10^{-5}	8×10^{-8}	[19]
CNTs	CV	2.9×10^{-6} 1.4×10^{-3}	3×10^{-6} – 1×10^{-3}	2.91×10^{-6}	1.47×10^{-6}	[20]
PEDOT/GO	DPV	2×10^{-6} – 4×10^{-4}	2×10^{-6} – 4×10^{-4}	1.61×10^{-6}	1.61×10^{-6}	[21]
N-GCE	DPV	5×10^{-6} – 2.6×10^{-4}	5×10^{-6} – 2.6×10^{-4}	2×10^{-7}	2×10^{-7}	[22]
AuNPs/Fe ₃ O ₄ /APTES/GO	I-T	3×10^{-6} – 1.1×10^{-4}	2×10^{-6} – 1.4×10^{-4}	1.1×10^{-6}	8×10^{-7}	[23]
LDHF	DPV	1.2×10^{-5} – 8×10^{-4}	3×10^{-6} – 1.5×10^{-3}	9×10^{-6}	1.2×10^{-6}	[24]
CH ₂ CH ₂ NH ₆ Poly/MWNTs	DPV	1×10^{-5} – 4.8×10^{-4}	3×10^{-5} – 1.1×10^{-4}	1.6×10^{-6}	5.8×10^{-6}	[25]
H-NiAl/LDHs	I-T	1×10^{-8} – 1.4×10^{-4}	1×10^{-8} – 4×10^{-4}	0.0 3×10^{-6}	3×10^{-8}	[26]
ZnO@SiO ₂ -n-propyl-BTU-Cu(II)	DPV	2.51×10^{-8} – 1.5×10^{-7}	2.51×10^{-8} – 1.5×10^{-7}	5×10^{-8}	5×10^{-8}	This work

4. CONCLUSION

A doped and functionalized silica matrix with a high specific surface area was successfully prepared by a simple technique at 40°C for use as an electrochemical sensor for the simultaneous determination of HQ and CC by DPV. Well-defined oxidation peaks were observed, which is attributed to the large specific surface area and a large number of recognition sites on the ZnO@SiO₂-n-propyl-BTU-Cu(II) surface, and the ZnO@SiO₂-n-propyl-BTU-Cu(II)-modified electrode also exhibited a lower detection limit. Based on the results obtained, it is clear that the ZnO@SiO₂-n-propyl-BTU-Cu(II) electrode has great potential for isomer determination

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