Individual and Simultaneous Voltammetric Determination of Ultra-Trace Environmental Contaminant Dihydroxybenzene Isomers Based on a Composite Electrode Sandwich-like Structure

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Individual and Simultaneous Voltammetric Determination of Ultra-Trace Environmental Contaminant Dihydroxybenzene Isomers Based on a Composite Electrode Sandwich-like Structure

Ziad Khalifa,* Khalid Hassan, Mohamed Fathi Abo Oura, Abla Hathoot, and Magdi Abdel Azzem

ABSTRACT: An advanced electroanalytical technique for the simultaneous assessment of environmental contaminant dihydroxybenzene isomers, catechol (CC), hydroquinone (HQ), and resorcinol (RC), has been investigated using palladium nanoparticles (PdNPs) incorporated onto a poly(1,5-diaminonaphthalene) (DAN) matrix over a glassy carbon electrode (GCE). Concurrently, these types of phenols can be assessed by the PdDAN/GCE modified electrode employing square wave voltammetry and cyclic voltammetry (CV) techniques under optimal conditions. This modified electrode has demonstrated linear responses for CC, HQ, and RC from 50.0 to 1000.0 mM; concomitantly, low detection limits of 0.22, 0.22, and 0.47 nM and low quantification limits of 0.740, 0.758, and 1.590 nM, have been, respectively, shown. Successfully, the simultaneous assessment of the three isomers in river stream water, tap water, and underground water has been implemented via the modified electrode under investigation. In comparison to reported studies, the PdDAN catalytic electrode has shown an effective sensitivity, leverage reproducibility, long-term stability, and excellent anti-interference capability for the determination of dihydroxybenzene isomers.

1. INTRODUCTION

Dihydroxybenzene isomers such as catechol (CC), hydroquinone (HQ), and resorcinol (RC) have been widely used in tanning, dye, pesticides, cosmetics, antioxidant, flavoring agents, medicines, and photography chemicals.1 International bodies such as the United Nations Environment Program, European Union (EU), and the US Environmental Protection Agency (EPA) have considered these chemicals as environmentally hazardous materials because of their great toxicity, limited degradability, and long-term negative effects on human health and the environment.2 Some of these compounds could be inadvertently released into the environment polluting ground waters and rivers during the production and usage processes, which might lead to major human and animal health problems. Hence, it has become essential to develop an easy and fast analytical method for the determination of dihydroxybenzene isomers. Moreover, these three isomers often coexist and have similar chemical structures, which make its simultaneous analysis more difficult. Hence, constructing and designing a highly sensitive and selective sensor for CC, HQ, and RC detection and discrimination are a challenging point of research.

These phenols have been determined via many chemical analysis methods and techniques, such as capillary electrophoresis, chemiluminescence, fluorescence, gas chromatography/mass spectrometry, and high-performance liquid chromatography.3–9 High cost, time consuming, sophisticated sample preparation procedures, and using hazard solvents are some of the major drawbacks of these techniques.10 However, electroanalytical techniques have attracted further attention because of its superior advantages of low cost, real-time results, high accuracy and stability, small sample size, and environmentally friendliness.11 It has been reported that the bare electrode surface modified by a thin coat of the organic polymer has got much attention because of their versatile characteristics of enhancing the electrode performance and utilization of the electrocatalytic methods on different unique applications.12 Our research group has recently reported the individual and simultaneous determination of CC, HQ, and RS on poly(1,5-diaminonaphthalene) (DAN)/glassy carbon electrode (GCE)-modified electrode.13
Dispersion of noble metal nanoparticles on conducting polymer films and in its porous matrix can effectively enhance the electrocatalytic properties, sensitivity, selectivity of such modified electrodes. Palladium metal (Pd) has been relatively abundant and inexpensive.\textsuperscript{14,15} Nevertheless, bulk palladium materials still demonstrate unsatisfactory electrocatalyst activity.\textsuperscript{16} However, such noble metal catalytic activity could be enhanced effectively by controlling its size and way of distribution on the matrix of the support material producing a modified electrode with effective stability, selectivity, and superior catalytic performance. Typical support materials have been characterized by important parameters, which are directly related to catalyst activity, such as porosity, high specific surface area, and active sites, which exert an influence on the morphology of the metal crystallites. The excellent catalytic effect of palladium nanoparticle (PdNPs) incorporated in the conducting polymer matrix returns to the hollow polymer nanospheres that act as a solid support to stabilize PdNPs.\textsuperscript{17} This leads to formation of a highly efficient and stable nanocatalyst in electro-oxidation reactions with great enhancement in the electrochemical performances.\textsuperscript{18}

In this study, Pd nanoparticles have been incorporated into the DAN polymer thin film by a convenient deposition method to examine the synergetic effect and the role of PdNPs on the sensitive simultaneous determination of CC, HQ, and RC in real samples of freshwater, groundwater, and tap water.

2. EXPERIMENTAL SECTION

2.1. Instrumentation and Chemicals. All electrochemical analyses have been performed on a PST 006 electrochemical work station from Voltalab-Radiometer Analytical equipped with Volta Master 4 software. Traditional three electrode 5.0 mL cells have been used for all measurements: silver/silver chloride (Ag/AgCl) as a reference electrode, platinum wire (Pt) as an auxiliary electrode, and 3.0 mm GCE as the working electrode. Before each preparation the working electrode surface has been rinsed with water followed by methanol to flush away any encrusted material on the surface. Wet the disk with triple-distilled water and apply a few drops of the 2.0 μm diamond polish slurry.

All chemicals used were of analytical grade and have been used as received without any further purification: 1,5-diaminonaphthalene (97%, Merck), catechol (99%, Sigma-Aldrich), HQ (99%, Merck), RC (99%, Merck), palladium (II) chloride (59%, Merck), hydrochloric acid (37%, Sigma-Aldrich), perchloric acid (70%, Sigma-Aldrich), and sodium hydroxide (Pellets, Merck). Triple distilled water has been used for all chemical preparations.

2.2. Syntheses of the PdDAN/GCE Modified Electrode. We have reported the electrochemical preparation of DAN/GCE using a cyclic voltammetry (CV) technique from a well mixed solution of 1.5 mM 1,5-diaminonaphthalene and 1.0 M HClO₄ in the potential range 0.0−800 mV at a scan rate scan rate of 20 mV/s for 15 consecutive cycles.\textsuperscript{19} Modification of DAN/GCE with PdNPs has been attained electrochemically using a CV technique by placing a freshly prepared DAN/GCE in 10 mL of homogeneous mixture 2.5 mM PdCl₂/0.1 M HClO₄ and undergo 25 cycles in the potential range −350−650 mV at a scan rate of 50 mV/s.

2.3. Testing and Analysis Procedures. For dihydroxybenzene isomers under investigation, electroanalytical studies have been performed by a square wave voltammetry (SWV) technique in a supporting electrolyte of 5.0 mM HClO₄ besides, the in-lab water samples used for calibration and testing have been prepared by adding known quantities of the analytes to 5.0 mM HClO₄. Real water samples have been collected from the local water stream of Al-Shohdaa city, Menoufia governorate, Egypt, and tested without any further processing.

3. RESULTS AND DISCUSSION

3.1. Surface Area Measurement (A) and Kinetic Studies. The effective surface area of bare GCE, DAN/GCE, and PdDAN/GCE has been measured by applying the effect of the scan rate on the standard substance,\textsuperscript{20} as shown in Figure 1. The effect of the scan rate has provided a linear relation between the peak current (Iₚ) values and the square root of the scan rate (υ₁/₂) at PdDAN/GCE that indicates a diffusion-controlled electrode reaction,\textsuperscript{20,21} as presented in Figure 2c. The surface area (A) has been calculated from the regression analysis of the linear relation, as presented in Figure 2b, and slope value of the linear line applied in a Randles- Sevcik equation.\textsuperscript{20} The surface area value has been calculated for bare GCE, DAN/GCE, and PdDAN/GCE to be 0.072, 0.113, and 0.561 cm², respectively. In a previous article, we have measured a Pd nanoparticle size (between 114.6 and 179.9).\textsuperscript{22} The correlation factor between the nanometal particle size and the obtained surface area is a negative correlation.

The peak current of both segments of 1.0 mM K₄Fe(CN)₆ in 0.1 mM KCl at PdDAN/GCE have been increased linearly with a scan rate increase and slightly shifted to positive (anodic) and negative (cathodic) potentials, where Eₚₐ = 288 mV, Eₚₜ = 109 mV, and ΔEₚ = 179 mV (Figure 2a). From eq 1, we could apply for $Iₚ/\tau = n F A C^{1/2}$ as the slope of the graph, as shown in Figure 2a, “n” is the number of electrons transferred, “A” (calculated surface area); “F” (Faraday constant); “R” (universal gas constant); and “T” (absolute temperature) have their normal values. From the calculation, surface coverage “Γ” value of PdDAN/GCE was 9.4 × 10⁻⁹ mol/cm². The moles of K₄Fe(CN)₆ redox site per unit surface area of the electrode were represented by “Γ”.\textsuperscript{21,23,24}
The electrochemical response of the modified electrode was greatly enhanced by the presence of the Pd nanoparticles in the polymer matrix that mediates the charge transfer and boosts both selectivity and sensitivity to a much lower detection limits other than the DAN/GCE itself.28,29

The analyte concentration effect on the PdDAN/GCE detection performance has been investigated by varying the concentration in the range of 0.1–10 mM for each one of the di-hydroxybenzene isomers, CC, HQ, and RC. All electrochemical responses have been recorded using SWV techniques at room temperature under optimum conditions with a scan rate of 50 mV s⁻¹, duration of 1.0 s, amplitude of 50 mV, and pulse of 25 mV.

The linear relation between the modified electrode oxidation current responses for various concentrations of each isomer has clearly been depicted in Figure 4a–c. Calibration curves have been plotted for each isomer individually, as shown in Figure 4 (a, b and c insets). In all, the oxidation peak current values have been increased linearly by increasing the CC, HQ, and RC concentrations. Table 1 presents the calculated calibration parameters of low detection limits (LODs), linear detection ranges (LDRs), low quantification limits (LOQs), and correlation coefficients (R). It is obvious that the modified electrode has been highly sensitive for the very limited quantification of CC, HQ, and RC in acidic medium.

### 3.3. Simultaneous Assessment of CC and HQ in Binary Solutions

It has been clear that CC and HQ are electro-oxidized at the close anodic potentials of 220 and 120 mV, respectively. Therefore, the sensitivity and selectivity of PdDAN/GCE for the simultaneous determination of each isomer have been investigated to determine its redox interference performance among each isomer in binary solutions.
Binary solutions have been prepared from various equal concentrations of both CC and HQ in the range 0.1−10.0 mM using 50 mM HClO₄ as the supporting electrolyte, and they have been subjected to the SWV analysis at a scan rate of 50 mV/s, as shown in Figure 5. Effectively, the modified electrode has demonstrated a magnificent independent performance in detecting each isomer in the binary mixture. Besides, the current peak intensity response varies linearly with the increase in CC and HQ concentrations with well-defined oxidation peak current intensities and uninterfered peak potential values. Table 2 presents the calibration parameters for the binary mixture of CC and HQ, such as LOD, LDR, and R.

Table 2. Determination of Calibration Parameters for CC and HQ in Binary Solutions at PdDAN/GCE

<table>
<thead>
<tr>
<th>analyte</th>
<th>CC</th>
<th>HQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_p (V)</td>
<td>0.233</td>
<td>0.120</td>
</tr>
<tr>
<td>LOD (nM)</td>
<td>0.141</td>
<td>0.138</td>
</tr>
<tr>
<td>LDR (nM)</td>
<td>0.1−10</td>
<td>0.1−10</td>
</tr>
<tr>
<td>R</td>
<td>0.99</td>
<td>0.99</td>
</tr>
</tbody>
</table>

On the other hand, sequential contrariwise binary solutions have been prepared with one isomer at a fixed concentration and the other at varying concentrations in 5.0 mM HClO₄. SWV analysis was performed at 50 mV/s for solution mixtures put together from a fixed concentration of CC of 5.0 mM and HQ at variable concentrations in the range 0.1−8.0 mM. Figure 6a illustrates the good sensitivity of PdDAN/GCE in detecting the increase in HQ concentration with stability in the CC-fixed concentration response. The HQ oxidation current peak values increased linearly with the increasing concentrations, while the CC response was stable, which demonstrated the modified electrode independent performance of both of them in various mixed concentrations.

Moreover, by fixing the HQ concentration at 5.0 mM and varying the CC concentration in the range 0.1−8.0 mM, a linear increase in the SWV response for the CC oxidation at PdDAN/GCE has been recorded while steady ones have been displayed for the fixed concentration of HQ in all preparations, as shown in Figure 6b. Detection sensitivities, LOD, LDR, and R for quantifications of both CC and HQ in various binary solutions have been displayed in Table 3.

Figure 4. SWV for various concentrations of (a) CC, (b) HQ, and (c) RC, in the range 0.1−10.0 mM in 0.05 M HClO₄ at PdDAN/GCE at a scan rate of 50 mV/s, duration of 1.0 s, amplitude of 50 mV, and pulse of 25 mV.

Figure 5. SWV for various HQ and CC concentrations in a binary mixture in the range 0.1−1.0 mM in 0.05 M HClO₄ at PdDAN/GCE and scan rate of 50 mV/s, duration of 1.0 s, amplitude of 50 mV, and pulse of 25 mV.

Figure 6. SWV for CC and HQ binary solutions recorded at PdDAN/GCE in 5.0 mM HClO₄ at a scan rate 50 mV/s, duration of 1.0 s, amplitude of 50 mV, and pulse of 25 mV for (a) fixed concentration of CC 5.0 mM and variable concentrations of HQ from 0.1 to 8.0 mM and (b) fixed concentration of HQ 5.0 mM and variable concentrations of CC 0.1−8.0 mM.
3.4. Simultaneous Assessment of CC, HQ, and RC in a Ternary Solution. Sensor selectivity and sensitivity in multicomponent solutions is an important performance of a reliable one that should be verified. Tertiary solutions from CC, HQ, and RC prepared from a range of concentrations 0.1–10.0 mM in 5.0 mM HClO₄ have been simultaneously detected at PdDAN/GC via the SWV technique at a scan rate of 50 mV/s, duration of 1.0 s, amplitude of 50 mV, and pulse of 25 mV. Figure 7 demonstrates the modified electrode sound effectiveness in selecting each isomer in the tertiary solution distinctly, in addition to its corresponding sensitivity for concentration variation from the very limited to the high levels of mixed analyte intensity. The oxidation current peak values for each isomer vary linearly with the increase in each isomers’ concentration in a pretty relationship. It has been clear that PdDAN/GCE proves its feasibility in the simultaneous determination and sensing of each isomer in mixed solutions at various concentrations with an enhancement in the oxidation current peak values with an adequate catalytic separation for each isomer in the mixture.

By analyzing the peak-to-peak potential separations between each of CC−HQ and RC−CC, they have been found to be 110 and 382 mV, respectively. This reasonable potential separation has demonstrated PdDAN/GCEs’ capabilities to recognize each of CC, HQ, and RC simultaneously in tertiary solutions. Such profound performance could be due to the presence of Pd in the polymer matrix that provides more surface area and more active sites for catalytic redox reactions, which has enhanced the sensor’s conductivity, electroactivity, selectivity, and sensitivity. Calibration parameters such as LODs, LDRs, and R for the simultaneous detection of dihydroxybenzene isomers in ternary mixtures have been calculated and presented in Table 4.

Furthermore, the electrochemical behavior of the fixed concentrations of both CC and RC of 0.05 mM in the presence of variable concentrations of HQ in the range of 0.2–8.0 mM in 5.0 mM HClO₄ have been determined at PdDAN/GC using the SWV technique under optimum conditions, as has been presented in Figure 8. The voltammetric oxidation peak current intensities of HQ have been linearly increased by increasing its bulk concentration with a correlation coefficient of 0.98, whereas the oxidation peak currents of CC and RC remain constant. For ternary mixtures of variable CC concentrations in the range 0.2–2.0 mM and fixed concentrations of both HQ and RC of 0.05 mM, a direct proportionality has been detected between the CC oxidation peak current values and its concentration with a correlation coefficient of 0.97, as shown in Figure 8b.

Concussively, the characteristic electrocatalytic responses for the detection of CC, HQ, and RC at PdDAN/GCE and other modified electrodes, as reported in the literature, have been listed in Table 6. It has been observed that PdDAN/GCE has manifested a superior catalytic performance compared with the mentioned electrodes.
3.5. Dihydroxybenzene Electrooxidation Mechanism.

The imino groups (−NH) of the polymer film (PDAN) have constructed hydrogen bonds leading to a decrease in the hydroxyl bond energy through an O−H···NH bond. Moreover, PdNPs have created more O−H···PdNPs bonds helping the electron transfer, as shown in the following scheme (Scheme 1).

![Scheme 1. Dihydroxybenzene Electrooxidation Mechanism](image)

3.6. Application in Real Samples. The PDAN/GCE sensitivity and selectivity for CC, HQ, and RC detection in real natural water samples from various sources; river stream water, tap water, and underground water have been studied. Because naturally occurring concentrations of dihydroxybenzene isomers are very low and under the current detection limit, the standard addition method has been employed in all real natural water samples tests. Equal concentrations of 50 μM from each isomer have been spiked to each sample under analysis. The results have demonstrated the effective sensitivity and selectivity of the sensor under investigation with acceptable recovery results, as listed in Table 7. It is obvious that river stream water samples got ~100% recovery for all isomers, the tap water samples displayed ~100% recovery for both HQ and RC while 97.8% for CC; however, the underground water samples recovery have 95, 98, and 100% for CC, HQ, and RC, respectively. This has proven both high selectivity and sensitivity of PDAN/GCE and its applicability as an effective sensor for the determination of CC, HQ, and RC simultaneously.

Moreover, the long-term stability of PDAN/GCE performance in detecting the three isomers in real natural water samples has been also studied using SWV under several ranges of prolonged conditions such as a scan rate 50−500 mV/s, duration of a single potential pulse 0.25−100 ms, amplitude 20−100 mV, and various time intervals of analysis range 1 h to 3 days. The three isomers have been simultaneously detected in the three water samples under investigation using the same standard addition method used before. All results have demonstrated both reproducibility and stability of the sensor oxidation current peak intensity and the oxidation potential values. The isomers CC, HQ, and RC testing results have displayed acceptable RSD values in the three samples; river stream water: 1.15, 1.03, and 1.01%; tap water: 1.18, 1.06, and 1.02%; and underground water: 1.22, 1.08, and 1.02% for each isomer, respectively. It has been obvious that the modified electrode exhibited long-term stability, high precision, and tenuous fatigue factor.

### Table 6. Electrocatalytic Determination of CC, HQ, and RC at Various Modified Electrodes

<table>
<thead>
<tr>
<th>electrode</th>
<th>method</th>
<th>linear range μM</th>
<th>LOD μM CC</th>
<th>LOD μM HQ</th>
<th>LOD μM RC</th>
<th>references</th>
</tr>
</thead>
<tbody>
<tr>
<td>graphene oxide doped</td>
<td>DPV</td>
<td>2−400</td>
<td>2.5−200</td>
<td>1.6</td>
<td>1.6</td>
<td>27</td>
</tr>
<tr>
<td>poly(3,4-ethylenedioxythiophene)/GCE</td>
<td>CV</td>
<td>0.091−98</td>
<td>0.1−49</td>
<td>0.0009</td>
<td>0.0001</td>
<td>32</td>
</tr>
<tr>
<td>poly(diallyldimethylammonium chloride)</td>
<td>CV</td>
<td>1−500</td>
<td>1−500</td>
<td>0.25</td>
<td>0.2</td>
<td>30</td>
</tr>
<tr>
<td>functionalized graphene/GCE</td>
<td>DPV</td>
<td>10−500</td>
<td>10−500</td>
<td>0.7</td>
<td>1.8</td>
<td>33</td>
</tr>
<tr>
<td>MWCNTs-PDDA-GR</td>
<td>DPV</td>
<td>2.5−400</td>
<td>2.5−100</td>
<td>2.5</td>
<td>2.5</td>
<td>34</td>
</tr>
<tr>
<td>poly(3,4-ethylenedioxythiophene)/AnE</td>
<td>DPV</td>
<td>10−500</td>
<td>1−170</td>
<td>0.16</td>
<td>0.13</td>
<td>35</td>
</tr>
<tr>
<td>graphene−doped CILE</td>
<td>CV</td>
<td>5−100</td>
<td>5−100</td>
<td>0.9</td>
<td>1.4</td>
<td>36</td>
</tr>
<tr>
<td>PANI/MnO₂</td>
<td>CV</td>
<td>1−500</td>
<td>1−300</td>
<td>0.75</td>
<td>0.75</td>
<td>37</td>
</tr>
<tr>
<td>poly(direct yellow 11)/MPGE</td>
<td>DPV</td>
<td>50−350</td>
<td>50−350</td>
<td>0.11</td>
<td>0.16</td>
<td>38</td>
</tr>
<tr>
<td>KOH-activated GSEC film</td>
<td>SWV</td>
<td>0.5−200</td>
<td>0.5−200</td>
<td>0.1</td>
<td>0.1</td>
<td>39</td>
</tr>
<tr>
<td>NDSBAC/GCE</td>
<td>CV</td>
<td>1−500</td>
<td>1−500</td>
<td>0.11</td>
<td>0.09</td>
<td>40</td>
</tr>
<tr>
<td>p-1,5-DAN/GC</td>
<td>SWV</td>
<td>0.1−100</td>
<td>0.1−100</td>
<td>0.059</td>
<td>0.034</td>
<td>13</td>
</tr>
<tr>
<td>PdDAN/GCE&lt;sup&gt;a&lt;/sup&gt;</td>
<td>SWV</td>
<td>50−1000</td>
<td>50−1000</td>
<td>0.227 nM</td>
<td>0.222 nM</td>
<td>0.477 nM</td>
</tr>
</tbody>
</table>

<sup>a</sup>In 5.0 mM HClO₄.

### Table 7. Determination of CC, HQ, and RC Simultaneously in Real Water Samples at PdDAN/GCE

<table>
<thead>
<tr>
<th>sample</th>
<th>added μM</th>
<th>found recovery μM</th>
<th>(% SD)</th>
<th>CC found recovery μM</th>
<th>(% SD)</th>
<th>HQ found recovery μM</th>
<th>(% SD)</th>
<th>RC found recovery μM</th>
<th>(% SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>river stream water</td>
<td>50</td>
<td>50</td>
<td>100</td>
<td>0.52</td>
<td>1.03</td>
<td>100</td>
<td>0.57</td>
<td>100</td>
<td>1.15</td>
</tr>
<tr>
<td>tap water</td>
<td>50</td>
<td>48.9</td>
<td>97.8</td>
<td>0.53</td>
<td>1.06</td>
<td>100</td>
<td>0.58</td>
<td>100</td>
<td>1.18</td>
</tr>
<tr>
<td>underground water</td>
<td>50</td>
<td>47.5</td>
<td>95</td>
<td>0.53</td>
<td>1.08</td>
<td>98</td>
<td>0.58</td>
<td>100</td>
<td>1.22</td>
</tr>
</tbody>
</table>

<sup>a</sup>In 5.0 mM HClO₄.
3.7. Interference Effect and Stability Studies. The interfering effect of very high concentrations of various cations and anions existing in natural water samples on the simultaneous assessment of CC, HQ, and RC has been investigated. Accordingly, various mixtures of CC, HQ, and RC containing 1.0 mM of each isomer have been tested in the presence of variable very high concentrations of interfering ions. In laboratory, anion and cation solutions have been prepared in triple-distilled water containing 1000-fold of K⁺, 1000-fold Cl⁻, 500-fold SO₄²⁻, 500-fold Cu²⁺, 500-fold urea, 250-fold Na⁺, and 250-fold F⁻ have been spiked with 1-fold concentration of CC, HQ, and RC and tested at PdDAN/GCE by SWV under optimum conditions. By comparing the gained results in the presence of interfering ions with the previous ones in its absence, no significant variations have been observed in both oxidation peak currents and potential value of the determination of isomers, just a signal change ≤5%. This has confirmed the modified electrode anti-interference capability toward the simultaneous assessment of CC, HQ, and RC.

4. CONCLUSIONS

According to this study, a simple and sensitive electroanalytical system for the simultaneous assessment of CC, HQ, and RC has been developed employing a new modified electrode, namely, PdDAN/GCE. Combining the advantageous features of DAN and PdNPs, a composite film has been constructed on the surface of GCE forming a unique thin polymer film. Under the optimum conditions, the PdDAN/GC electrode has shown excellent selectivity and sensitivity properties and is capable of separating the three isomers’ oxidation peaks. The invented electroanalytical sensor has exhibited resplendent electrocatalytic responses toward dihydroxybenzene isomer oxidation at very small concentrations. PdDAN/GCE could be further used for the multicomponent analysis in environmentally hazardous pollutant control and chemical industry. LOD of CC, HQ, and RC have been as low as 0.22, 0.22, and 0.47 nM, respectively.

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The authors declare no competing financial interest.

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