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A low temperature synthesis of activated carbon from the bio waste for simultaneous electrochemical determination of hydroquinone and catechol





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ABSTRACT

In the present study, the simultaneous determination of hydroquinone (HQ) and catechol (CC) was investigated by using the activated carbon (AC) from dead mango leaves at a low temperature (600 °C). The synthesized AC exhibited a high surface-area of \sim 782 m² g⁻¹. The AC modified electrode exhibited a sensitive and selective detection of HQ and CC than that of other AC modified electrodes which prepared at quite higher temperatures (700 °C, 800 °C, 900 °C). The AC600 holds its high selectivity towards the potentially interfering species compared with other AC modified electrodes. The fabricated AC modified electrode showed a well defined redox peak for HQ and CC with a better peak separation compared with unmodified electrode. The AC modified electrode showed enhanced peak current response range of HQ and CC was found from 10 to 100 and 5 to 100 nM with the sensitivity 5.19 and 6.59 µA µM⁻¹ cm⁻², respectively. The limit of detection (LOD) was found as 3 nM for HQ and 2 nM for CC at the AC modified electrode, which is the lowest LOD for HQ and CC that ever been reported using carbon nanomaterials modified electrodes.

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1. Introduction

The simultaneous determination of hydroquinone (HQ) and catechol (CC) has received considerable interest due to their similar structural properties and coexistence in the environmental pollutants [1,2]. Moreover, HQ and CC certificated as high priority pollutant by the U.S Environmental Protection (EPA) Agency and the European Union (EU) due to their high toxicity and low degradability in the biological environment [2–4]. Hitherto, many methods have been employed for the simultaneous determination of HQ and CC including high-performance liquid chromatography, fluorescence, spectrophotometry and electrochemical methods [2,5–9]. Among them, electrochemical methods have widely employed for the simultaneous determination of HQ and CC owing to their simplicity and cost effectiveness with high sensitivity and selectivity [10,11]. However, the simultaneous determination of HO and CC at conventional electrodes has become a challenging task due to the overlapped redox peaks of HQ and CC [12]. To

conquer this problem, various materials have been employed for simultaneous determination of HQ and CC including graphene, carbon nanotubes, ionic liquid and mesoporous carbon [2,13–17], etc. The existing well known carbon materials can be classified as AC (0D), carbon nanotubes (CNTs) (1D), graphene (2D) and carbon foams (3D). Graphene and CNT are emerging materials that has been widely used for various potential disciplines including electrochemical sensors, battery, supercapacitor, solar cell and biological applications [18–22].

Currently, research on activated carbon (AC) from biowaste has paid a greater attention, owing to their high stability, large surface area and pore-volume ratio. Fascinatingly, the design and preparation process of AC is simple and easily adopted when compared to the preparation of graphene and CNT [23]. Recently, there has been a great interest towards the preparation of activated carbons (ACs) from various bio-wastes due to their availability and cost effectiveness. The AC has been prepared from different biowastes materials, since they are easily available, thermally stable and cost effective. Similarly, the prepared AC has exhibited a good electronic conductivity, high surface area and uniform porous nature that greatly enhanced the accumulation of charges and target

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ions easily [24–29]. As far as we know, the numerous numbers of HQ and CC sensors were developed using various modified electrodes. However, the advancement of these types of sensor at a simple electrode with either higher sensitivity or lower limit of detection (LOD) is always paid much attention to the readers of electroanalytical community.

The goal of the present study involves the simultaneous determination of HQ and CC at eco-friendly fabricated AC from the dead mango leaves at a low temperature of 600 °C. We have compared the electroactivity of the HQ and CC at different AC (AC 600, AC 700, AC 800 and AC 900) modified electrodes. The best and sensitive and selective response of HQ and CC was observed at AC 600 than that of other modified electrodes. Hence, AC 600 (AC) modified electrode was more preferred for the selective and simultaneous determination of HQ and CC. The resulting AC modified electrode displays a remarkable sensitivity along with a low detection limit and the obtained results are best among previously reported many HQ and CC sensors (Table 1).

2. Experimental

2.1. Materials

Catechol and hydroquinone were purchased from Sigma Aldrich. Potassium hydroxide (KOH) was purchased from Shimakyu's pure chemicals, Osaka, Japan. The mango leaves (*manjifera indica*) were collected from National Taipei university of Technology (Taipei, Taiwan). The supporting electrolytes were prepared by using 0.1 M of Na₂HPO₄ and NaH₂PO₄ and the pH was adjusted by NaOH or H₂SO₄. All other solutions were prepared using double distilled water.

2.2. Methods

The cyclic voltammetry (CV) and differential pulse voltammetry (DPV) studies were performed by using a CHI 900 electrochemical analyzer (CH instruments). The surface morphology of the film was studied by JEOL field-emission scanning electron microscopy. The X-ray diffraction (XRD) was carried out on a Rigaku, MiniFlex II. Raman spectra were recorded at ambient temperature in a WITeck CRM200 confocal microscopy Raman system with a 488 nM laser. N₂ adsorption–desorption isotherms and pore size distribution was studied by "Micromeritics ASAP 2020". A conventional three-electrode cell system was used with a modified glassy carbon electrode (GCE) as the working electrode with an active surface area of 0.0798 cm², an Ag/AgCl (saturated KCl) reference electrode and a platinum wire as the counter electrode.

2.3. Material synthesis

In our previous report, we have demonstrated the preparation of AC from dead mango leaves at 900 °C, which exhibited excellent capacitance ability than that of AC 700 °C, AC 800 °C [30]. Herein, the same strategy was employed to increase the surface area and porosity of AC from the mango leaves at a lower temperature (600 °C) and applied for the electrocatalytic applications. Briefly, the collected dead mango leaves washed thoroughly dried in an oven at 100 °C and finely pulverized. For the activation process, the mango leaves powder was added to 10% KOH with stirring under a N₂ atmosphere at 60 °C. The dried sample was heated in a quartz crucible at 600 °C for 12 h in a nitrogen atmosphere at a heating rate of 10 °C min⁻¹ in a tube furnace. The carbonized samples were washed with distilled water and 1 M HCl, dried at 100 °C

Table 1

Analytical performance of the AC modified electrode for HQ and CC and comparison with previously reported similar modified electrodes.

Modified electrode	Limit of detection (μM)		Sensitivity ($\mu A \ \mu M^{-1} cm^{-2}$)		Technique used	Optimum pH	Ref.
	HQ	СС	HQ	CC			
Gr ^a doped CILE ^b	1.8	7.4	-	-	DPV ^c	5	[1]
Gr-chitosan	0.75	0.75	-	-	DPV	7	[2]
Gr	0.015	0.01	-	-	DPV	4.5	[3]
GMC ^d /BMIMPF ₆ ^e	0.05	0.06	-	-	DPV	7	[10]
PCV ^f -GR/CILE	0.03	0.09	-	-	DPV	2	[11]
MWNTs ^g	0.75	0.2	-	-	DPV	4.5	[13]
MWNTs-IL ^h -Gel	0.06	0.06	-	-	DPV	7	[14]
GMC	0.03	0.03	1.09	0.43	DPV	3	[15]
EG ⁱ	0.2	0.1	-	-	DPV	5.8	[17]
Gr/MWCNTs/BMIMPF ₆	0.1	0.06	-	-	DPV	7	[34]
PEDOT ^j /Au ^k	0.01	0.009	-	-	DPV	7	[35]
$GO^{l}-MnO_{2}^{m}$	0.007	0.01	-	-	DPV	7	[36]
PTH ⁿ	0.003	0.002	1.8	1.2	DPV	7	[37]
CMK-3°-Nafion	0.1	0.1	41	52	DPV	7	[38]
ECF ^p -CPE ^q	0.2	0.4	0.054	0.059	DPV	7	[39]
AC	0.003	0.002	5.19	6.59	DPV	7	This wor

^a Graphene.

^b Carbon ionic liquid electrode.

^c Differential pulse voltammetry.

^d Graphitic mesoporous carbon.

^e 1-Butyl-3-methylimidazolium hexafluorophosphate.

- ^f Poly(crystal violet).
- ^g Multiwall carbon nanotubes.

h Ionic liquids.

ⁱ Direct electrodeposition of reduced graphene oxide.

^j Poly(3,4-ethylenedioxythiophene).

- ^k Gold.
- ¹ Graphene oxide.
- ^m Manganese dioxide.

ⁿ Poly(thionine).

- ° Mesoporous carbon.
- ^p Electrospun carbon nanofiber.

^q Carbon paste electrode.

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