

Recent advances in electrochemical modified Electrodes for sensing phenol derivatives

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ABSTRACT

Enzymless electrode is a device combines a material component and electrochemical transducer, used for the detection of an analyte. Nanomaterials are widely used in sensing areas due to its high positive effect on the response of enzymeless based electrode, it could be used as transduction element or immobilized onto the surface of electrochemical transducers, their presence increases sensitivities and gives a lower detection limits and enhance the kinetic performance of sensors. In this work, we report the effect of the most recent nonmaterial used for electrochemical detection, catalytic effect of various nanoparticles such as, nanomaterials, gold nanoparticles, conducting polymer, carbon nanotubes, and metal oxide immobilized on the surface of electrochemical transducers (platinum electrode, Carbon electrode and Gold electrode) is intensively analyzed. A comparative study of the nanoparticles effect on the analytical performance of sensor for the detection of phenolic compounds is also presented and discussed.

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Introduction

Electrochemical sensors are very powerful tools for monitoring analytes such as phenolic compounds. These tools are mainly constituted by transducers for real-time measurement of electrochemical reactions of analytes in aqueous medium. Therefore, the fast charge transfer factor are considered important during the construction of sensors. Hence, electroanalytical performance of sensors are mainly dependent on the presence of nanomaterials in sensing platforms. Moreover, optimization of experimental parameters is essential to give a very sensitive and stable response before the construction of sensors (Scheme 1). The aim of this work is to discuss the advantage of the presence of different nanomaterials and conducting polymers in sensing platforms and their effect on the electroanalytical performance for sensing phenolic compounds.

Electrochemical sensors for the detection of phenolic compounds

Glassy carbon electrode was extensively used as an electrochemical transducer for monitoring nitrophenol; it could be modified with zinc [1, 2] or graphene [3,4,5] oxide nanoparticles or with the use of multi wall carbon nanotubes [6, 7]. Various graphene materials (GR, Go, rGo) were assembled with molecular imprinting polymers (MIPs) [8], β -cyclodextrin [9, 10].

It was showed by [11] that the modification of glassy carbon electrode surface with single-walled carbon nanotube enhances the sensitivity of p-cresol sensor ($94.9 \mu\text{A}/\mu\text{M}$) but the combination of reduced graphene oxide and multi walled carbon nanotube can extend the linear range of p-cresol detection (from $5 \mu\text{M}$ to $430 \mu\text{M}$) [12]. Multiwall carbon nanotubes (MWCNTs) were also combined with silver nanoparticles (AgNPs) to form stable film for the simultaneous voltammetric determination of hydroquinone and catechol (stability 95.4% 4 weeks) deposited at the surface of glassy carbon electrode [13]. An electrochemical sensor based on titanium dioxide and multi-walled carbon nanotubes (MWCNTs) developed for the simultaneous determination of hydroquinone and catechol displays a detection limit of ($\text{LOD}=0.8$) [14]. A sensor for electrochemical detection of hydroquinone (HQ) and catechol (CC) was prepared using atomic layer deposition (ALD) to modify glassy carbon electrode with nanocomposite film composed of nickel oxide (NiO) and carbon nanotube (CNT) ($\text{LOD}=2.5 \mu\text{M}$) [15]. A novel multielectrode array using multiwall carbon nanotubes (MWCNTs) was designed by [16] for the electrochemical sensing of catechol ($\text{LOD}=0.2 \mu\text{M}$). Graphene nanosheets were used for the modification of glassy carbon electrode surface combined with ionic liquid [17], titanium dioxide [18] or with poly(4-vinyl pyridine) [19], it was observed that the best analytical performance of modified glassy carbon electrode in terms of sensitivity ($660 \mu\text{A}/\mu\text{M}$) and stability (99 % 2 months) was obtained using graphen nanosheets combined with poly(4-vinyl pyridine).

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Table 1. Analytical performance of electrochemical sensors for the detection of phenolic compounds

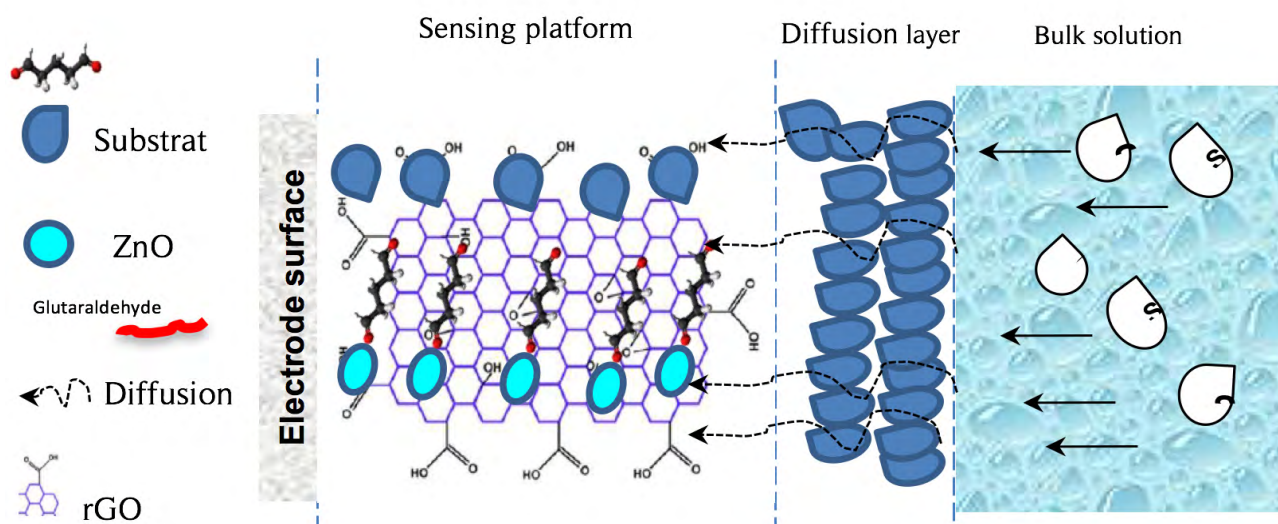
Modified Electrode surface	Sensitivity	Linear Range	L.O.D.	pH	Stability (%)	Ref.
Nitrophenol						
ZnO/GCE	0.40435 $\mu\text{A}/\mu\text{M}\cdot\text{cm}^2$	10 – 1000 μM	13 μM	7.0	60 % 1 month	[1]
Meso-ZnCO ₂ O ₄ /GCE	0.318 $\mu\text{A}/\mu\text{M}\cdot\text{cm}^2$	1 – 4000 μM	0.3 μM	7.0	N.R.	[2]
G-Cs/GCE	1.091 $\mu\text{A}/\mu\text{M}$	0.1 – 140 μM	0.09 μM	3.0	90 % 1 month	[3]
MWCNTs/GCE	6.202 $\mu\text{A}/\text{mM}$	2 – 4000 μM	0.4 μM	5.0	N.R.	[6]
AuNPs@MWCNTs/GCE	1.72 $\mu\text{A}/\mu\text{M}\cdot\text{cm}^2$	0.01 – 50 μM	N.R.	6.0	N.R.	[7]
Chlorophenols						
MIPs/Go/GCE	1.295 $\mu\text{A}/\mu\text{M}$	0.004 – 10 μM	0.5 nM	6.0	98.6 % 10 days	[8]
β -CD/G/CPE	N.R.	0.4 – 77 μM	0.09 μM	5.5	N.R.	[9]
HP- β -CD-G NR/GCE	1.12 $\mu\text{A}/\mu\text{M}$	0.01–16 μM	4 nM	6.0	87.6 (6 weeks)	[10]
Catechol						
SWCNTs/GCE	135.08 $\mu\text{A}/\mu\text{M}$	100 nM – 2 μM	2.3 nM	7.2	N.R.	[11]
AgNPs/MWCNTs/GCE	N.R.	20 – 260 μM	0.20 μM	3.0	95.4 % 4 weeks	[13]
rGo-MWCNTs/GCE	0.07 $\mu\text{A}/\mu\text{M}$	5.5 – 540 μM	1.8 μM	7.0	95.5 % 20 days	[12]
TiO ₂ /MWCNTs/ GCE	78.15 $\mu\text{A}/\text{mM}$	1.5 μM –0.3 mM	0.8 μM	7.0	96.3 % 10 days	[14]
NiO ₂ /CNTs/GCE	0.1964 $\mu\text{A}/\mu\text{M}$	10 – 400 μM	2.5 μM	7.0	97.2 % 3 weeks	[15]
MWCNTs/SPCE	0.04 $\mu\text{A}/\mu\text{M}$	1 – 100 μM	0.2 μM	5.4	N.R.	[16]
Hydroquinone						
Gs/BMMPF6/GCE	N.R.	0.5 – 50 μM	0.01 μM	5.0	93 % 2 weeks	[17]
Gs-TiO ₂ /GCE	0.1341 $\mu\text{A}/\mu\text{M}$	0.5 – 100 μM	0.087 μM	7.0	95 % 2 weeks	[18]
Gs-P4VP/GCE	660 $\mu\text{A}/\mu\text{M}$	0.1 – 10 μM	8.1 nM	2.5	99 % 2 months	[19]

Recent advances in electrochemical sensing for phenolic compounds

A ternary nanocomposites electrode prepared by [20] for the detection of caffeic acid using chlorophyll as reductants and stabilizers (stability =93 % 30 days) with a very wide linear range (from 19 to 1869 μM) [21]. Constructed a novel electrochemical sensor for the determination of caffeic acid in wine samples using screen printed electrode modified with cobalt oxide microballs due to its roughed surface and high crystallinity and large surface area. A low detection limit for the determination of caffeic acid in red wine samples (4 nM) was obtained using synthesized hierarchical mesoporous graphite oxide (HMGO) via carbonization method [22]. A novel electrochemical sensing platform for the detection of dopamine in urine sample was prepared by [23] based on the use of kiwi skin and zinc chloride nanoparticles, the biosensor exhibited a very stable response (99.06 % during 30 days) and wide linear concentration range (from 2 μM to 2000 μM). [24] Have reported the formulation of flexible plastic electrodes for electrochemical sensing of dopamine, the sensor displays a very long term stability response about 93.2 % during 6 months. An electrochemical sensor based on the synthesis of novel ZnO nanoclusters covered with reduced graphene oxide

was constructed by [25], the sensor was applied for electrocatalytic detection of BPA tissue paper samples that displays a low detection limit (2.1 nM). A lowest detection limit for electrochemical sensing of Bisphenol A in milk powder and water samples (80 nM) was obtained by [26], the sensor was constructed using gold nanoparticles (AuNPs) electrodeposited on the surface of a glassy carbon electrode (GCE) combined with a mixture of a thiolated DNA sequence. Several efforts were devoted for the development of electrochemical sensors for monitoring hydroquinone [17,18], some of them successfully applied to obtain a very stable response for monitoring hydroquinone in tap and lake water samples [19] (99 % during 2 months) or in urine sample of a healthy man [27], the sensors provides a very stable response (98 % during 5 months).

Recently, electrochemical sensors applied for monitoring catechol display a wide linear range [26-28] but most of them provide a low stability response compared with other phenolic compound based sensors. [31] have prepared a novel electrochemical sensor for the determination of catechol based on the modification of glassy carbon electrode with zinc and aluminum oxide ceramic nanofibers deposited onto the mixture of graphene oxide and gold nanoparticle using chitosan as film forming agent (LOD = 3.1 μM).



Scheme 1. Material based platforms of an electrochemical sensor with diffusion of substrate.

Nitrophenol based sensors prepared using different materials such as conducting polymer of Poly(3,4-ethylenedioxythiophene) [32], silver nanodendrites [33] or with using CoMnO₃ nanosheets [34] provide a good stability response (91.3 % during 30 days). An electrochemical sensor for the detection of nitrophenol using glassy carbon electrode modified with hydrogel matrix containing spherical shaped gold nanoparticles (AuNPs) was decorated with multi-walled carbon nanotubes (MWCNTs) [7].

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Conclusion

In this work, the use of different nanomaterials and conducting polymers in electrochemical sensing platforms that have been recently explored using a variety of transducers was briefly discussed. The advantage of the most important materials used in the modification of electrode surface in order to enhance its electrocatalytic activity for monitoring phenolic compounds were showed, and their effect on the analytical performance of sensor was mentioned. The combination of conductive nanomaterial and some conducting polymers ensure an excellent and fast response with longest stability.

Table 2. Recent advances in electrochemical sensing for phenolic compounds

Modified Electrode surface	Sensitivity	Linear Range	Limit Of Detection	pH	Stability (%)	Ref.
Caffeic acid						
Au@ α -Fe ₂ O ₃ @rGo/GCE	315 μ A/ μ M.cm ²	19 – 1869 μ M	0.098 μ M	7.0	93 % 30 days	[20]
Co ₃ O ₄ /SPCE	1.276 μ A/ μ M.cm ²	0.2 – 272 μ M	48 nM	7.0	91.52 % 4 weeks	[21]
HMGO/GCE	0.429 μ A/ μ M.cm ²	0.01 – 608 μ M	4 nM	7.0	96.45 % 1 month	[22]
Dopamine						
ZnCl ₂ -CF/GCE	0.0511 μ A/ μ M	2 – 2000 μ M	0.16 μ M	7.0	99.06 % 30 days	[23]
PE	0.0384 μ A/ μ M	10 – 550 μ M	3 μ M	6.8	93.2 % 6 months	[24]
Bisphenol A						
ZnO.NCs/rGo/SPCE	3.4266 μ A/ μ M.cm ²	0.05 – 1332 μ M	2.1 nM	7.0	97.7 % 1 month	[25]
PPy/@p-63/AuNPs/GCE	N.R.	0.5 fM – 5 pM	80 aM	7.0	93 % 30 days	[26]
Hydroquinone						
Gs/BMMPF6/GCE	N.R.	0.5 – 50 μ M	0.01 μ M	5.0	93 % 2 weeks	[17]
Gs-TiO ₂ /GCE	0,1341 μ A/ μ M	0.5 – 100 μ M	0.087 μ M	7.0	95 % 2 weeks	[18]
Gs-P4VP/GCE	660 μ A/ μ M	0.1 – 10 μ M	8.1 nM	2.5	99 % 2 months	[19]
SnO ₂ /SnS/CPE (DPV)	1.8 μ A/ μ M.cm ²	1 – 85 μ M	0.2 μ M	4.0	98 % 5 months	[27]
Nitrophenols						
PEDOT-PSS/ITO	0.1921 μ A/ μ M 0.1902 μ A/ μ M 0.1290 μ A/ μ M	0 – 80 μ M	4.55 μ M 4.59 μ M 4.51 μ M	4.0	N.R.	[32]
Au@MWCNTs/GCE	1.72 μ A/ μ M.cm ²	10 nM – 50 μ M	N.R.	6.0	N.R.	[7]
AgNDs/GCE	1.970 μ A/ μ M.cm ²	20 – 1380 μ M	1.76 μ M	5.0	95.3 % 30 days	[33]
CoMnO ₃ /GCE	2.458 μ A/ μ M.cm ²	0 – 249 μ M	10 nM	7.0	91.3 % 30 days	[34]
Catechol						
AuNPs/ZnO Al ₂ O ₃ /Go.Cs	0.17 μ A/ μ M	0.5 – 40 μ M	3.1 μ M	3.0	93.1 % 1 week	[31]
PANI nanorods/CPE (CV)	49.68 μ A/ μ M.cm ²	5 μ M – 100 mM	2.1 μ M	7.0	N.R.	[28]
Pdnano@Cs/ITO	N.R.	25 – 600 μ M	2.99 μ M	7.0	N.R.	[29]
CD-CA-f-PEDOT:PSS	0.36327 μ A/ μ M	0.05 – 200 μ M	0.0275 μ M	7.4	N.R.	[30]

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Conflicts of interest

Authors declare no conflict of interests.

Notes

The authors declare no competing financial interest.

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