The 56th International October Conference on Mining and Metallurgy
22-25 October 2025, Bor Lake, Bor, Serbia
www.ioc.tfbor.bg.ac.rs

DOI: 10.5937/IOC25409T *Review paper*

CARBON-BASED ELECTROCHEMICAL SENSORS MODIFIED WITH METAL OXIDE NANOPARTICLES

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Abstract
Carbon-based electrochemical sensors are of great importance in analytical chemistry due to their high conductivity, chemical stability and cost-effectiveness. They are widely used for the detection of various analytes, including heavy metals, biomolecules and pharmaceutical compounds. Since the electrochemical sensors can be easily modified with different materials to improve their sensitivity and selectivity, they offer advantages over other traditional analytical techniques. Among these modifiers, metal oxide nanoparticles are of particular importance due to their large surface area, catalytic activity and good electrochemical properties. Their incorporation into carbon electrodes improves detection limits, reproducibility and stability, making them very effective for advanced sensing applications.

Keywords*: carbon paste electrode, electrochemical sensors, metal oxide nanoparticles, electrochemical methods*

1. INTRODUCTION

Various analytical methods can be used to determine and quantify different target analytes, including high-performance liquid chromatography or spectrophotometric methods. However, electrochemical methods are attracting increasing attention from researchers as they provide rapid results, are easy to handle and are cost-effective compared to analytical methods. In addition, electrochemical methods have good sensitivity to the target analyte and the ability to modify the electrode surface can also offer some notable advantages in electrochemical reactions [1,2]. Electrochemical sensors enable the highly sensitive detection of various analytes, including biomolecules, pharmaceutical substances and environmental pollutants [3]. Due to the low background current and the good electrical conductivity, electrochemical activity and porous structure, carbon paste electrodes (CPEs) can be used for the determination of these compounds [4]. In addition, the carbon paste electrodes are inexpensive and easy to manufacture, they work in wide potential window and offer flexibility in optimizing the composition of the paste, which can improve the sensitivity and selectivity of the sensor [5,6,7]. This article provides a brief overview of the literature in which modified CPEs have proven successful for the detection and determination of various target analytes.

2. MODIFIED CARBON-BASED SENSORS

CPEs can be modified with various materials to improve their sensitivity, selectivity and stability. The most commonly used modifiers include polymers, enzymes, complex metal ligands and metal oxide nanoparticles. Metal oxide nanoparticles such as ZnO, TiO_2, Fe_3O_4 and CeO_2 are particularly important as they have a large surface area, good conductivity and catalytic activity, making them ideal for improving the electrochemical performance of sensors [2,8,9]. According

to Parvin et al. [4], metal nanoparticles improve the detection limit of the target analyte and facilitate electron transfer. Compared to organic modifiers, nanoparticles of metal oxides are more resistant to chemical changes under aggressive conditions, enable higher adsorption of analytes and better electrochemical activity [8]. Various techniques such as electropolymerization, physical adsorption, covalent bonding and electrodeposition can be used to modify the sensor surface with metal oxide nanoparticles [10].

Farhan et al. [11] and Zoubir et al. [12] developed a CPE sensors modified with ZnO nanoparticles (ZnO NPs) and tested them for the determination of difloxacin HCl and hydroxychloroquine, respectively. Both research groups came to the conclusion that the ZnO nanoparticles improve the active surface of the electrode and provide more catalytically active sites as well as contribute to a better electron transfer compared to the unmodified CPE. The results obtained are shown in Table 1. In addition to ZnO NPs, Fe_2O_3 and CuO NPs were also used as modifiers for CPE and the resulting sensor was tested for the determination of paracetamol (PA) and dopamine (DA) [13] as well as for guanine, adenine and thymine [14]. By comparing the cyclic voltammetry curves of PA and DA (Figure 1) in phosphate buffer solution at the bare carbon paste electrode (BCPE) and at the iron oxide modified carbon paste electrode (IOCPE), enhanced anodic and cathodic peaks were observed for both PA and DA at the IOCPE. This behavior indicates the catalytic effect of Fe_2O_3 NPs. After 120 days, the experiments were repeated and the developed IOCPE showed good stability and sensitivity to PA and DA [13].

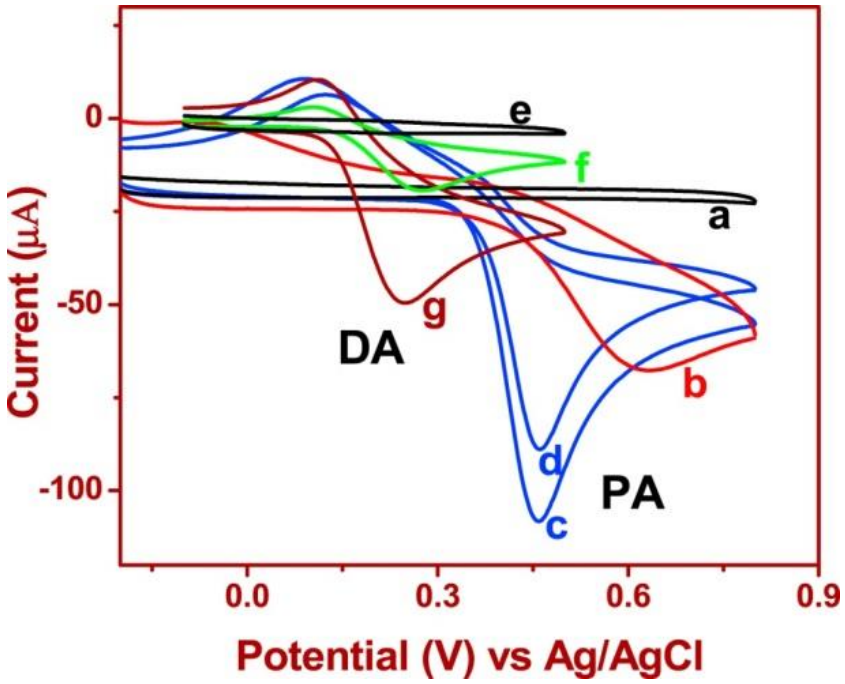

Figure 1. CV's of: (a) and (e) buffer at IOCPE; 1 mM PA at (b) BCPE; (c) and (d) IOCPE; and 1 mM DA at (f) BCPE; (g) IOCPE at scan rate of 100 mV s^{-1} ((d), (e), (f) and (g) obtained at IOCPE after 120 days). Reprinted from [13]

Nano-cobalt (II,III) oxide was also used as a modifier for CPE and the sensor thus developed was tested for the determination of caffeine in 0.01M H_2SO_4 in the presence of sodium dodecyl sulfate (NCOMCPE/SDS) [1]. The detection limit obtained for caffeine is shown in Table 1. The authors indicated that SDS was adsorbed on the NCOMCPE surface due to hydrophobic interactions between the SDS molecules and the hydrophobic binder in the carbon paste, resulting in a threefold higher sensitivity for caffeine. It was also found that the best electrocatalytic activity for caffeine oxidation was observed in highly acidic solutions (pH 0.75) and electron transfer was faster than in media with higher pH values. Apart from metal oxide nanoparticles, Mahanthappa et al. [16]

synthesised CuS nanoparticles by co-precipitation and used them as a modifier for CPE. The resulting CuS NPs MCPE was used for the determination of caffeine in acetate buffer solution. The authors concluded that the applied modifier contributed to the shift of the caffeine oxidation potential towards a negative value compared to the bare CPE and that the oxidation peak was improved. The detection limit obtained is shown in Table 1.

Table 1 - Modified carbon paste electrode as electrochemical sensor for determination of different target analytes

Modifier	Target analyte	Medium	Electrochemical method	Concentration range	LOD	Real sample	Ref
Nano-cobalt (II,III) oxide	Caffeine	0.01M H_2SO_4 in the presence of SDS	DPV	5.0– 600 μM	0.016 μM	Commercial samples	[1]
ZnO NPs	Difloxacin HCl	/	Potentiometric titration	6.3×10^{-6}–10^{-2} M	6.3×10^{-6} M	Pharmaceuticals formulation	[11]
ZnO NPs	Hydroxychloroquine	PBS pH 7.0	SWV	1×10^{-3} – 0.8×10^{-6} M	1.33×10^{-7} M	Human urine and pharmaceutical samples	[12]
Fe_2O_3 NPs	Paracetamol	0.1M PBS pH 7.0	DPV	2–150 μM	1.16 μM	Pharmaceutical samples	[13]
	Dopamine		SWV	2–170 μM	0.79 μM		
CuO NPs	Guanine	PBS	DPV	1–80 μM	0.687 μM	/	[14]
	Adenine			1–80 μM	0.472 μM		
	Thymine			1–210 μM	0.111 μM		
TiO_2/Fe_3O_4/MWCNTs nanocomposite	Morphine	PBS pH 7.0	SWV	2.5×10^{-8} – 6.0×10^{-4} M	1.5×10^{-8} M	Urine and pharmaceutical samples	[15]
CuS NPs	Caffeine	0.1 M ABS pH 7.0	DPV	2–120 μM	0.0186 μM	Commercial tea and coffee samples	[16]

LOD – limit of detection; SWV – square wave voltammetry; DPV – differential pulse voltammetry, PBS – phosphate buffer solution, ABS – acetate buffer solution, / – no data.

According to the results in Table 1, the prepared modified CPEs were successfully used for the determination of compounds of interest in various real samples with acceptable recoveries. In addition, the effect of interference on modified sensors has been studied by adding different ions such as Na^+, K^+, Li^+, Ca^{2+}, Ba^{2+}, Mg^{2+}, Cl^-, Br^-, SCN^-, NO_3^-, ClO_4^-, SO_4^{2-} and sugars such as glucose, fructose and sucrose [13,15,16]. The results obtained in these studies show that interferences have no influence on the current peak and the potential peak of the target analytes.

3. CONCLUSIONS

Carbon-based electrochemical sensors are important tools for testing various compounds such as nucleic acids and pharamceutical compounds in different media. The importance of metal oxide nanoparticles for the development of electrochemical sensors is also presented in this article. Various research groups have shown that ZnO, Fe_2O_3 and Co(II, III) oxide nanoparticles can be successfully used as modifiers for CPE. The developed sensors have proven their applicability in various media including acidic aqueous solutions (pH 0.75) and buffered media (phosphate and acetate buffer solutions). It has been shown that the use of these nanoparticles as modifiers enables fast electron transfer and more sensitive determination of the target analytes due to their catalytic effect and the larger surface area of the modified electrodes.

ACKNOWLEDGEMENTS

The research presented in this paper was done with the financial support of the Ministry of Science, Technological Development and Innovation of the Republic of Serbia, within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor, according to the contract with registration number 451-03-137/2025-03/200131.

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