Taylor & Francis
Taylor & Francis Group

Critical Reviews in Analytical Chemistry

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/batc20

Carbon Nanomaterials-Based Novel Hybrid Platforms for Electrochemical Sensor Applications in Drug Analysis

Ahmet Cetinkaya, S. Irem Kaya, Goksu Ozcelikay, Fatma Budak & Sibel A. Ozkan

To cite this article: Ahmet Cetinkaya, S. Irem Kaya, Goksu Ozcelikay, Fatma Budak & Sibel A. Ozkan (09 Aug 2022): Carbon Nanomaterials-Based Novel Hybrid Platforms for Electrochemical Sensor Applications in Drug Analysis, Critical Reviews in Analytical Chemistry, DOI: 10.1080/10408347.2022.2109125

To link to this article: https://doi.org/10.1080/10408347.2022.2109125

 Published online: 09 Aug 2022.

 Submit your article to this journal

 Article views: 429

 View related articles

 Citing articles: 2 View citing articles

Full Terms & Conditions of access and use can be found at
https://www.tandfonline.com/action/journalInformation?journalCode=batc20

CRITICAL REVIEWS IN ANALYTICAL CHEMISTRY
https://doi.org/10.1080/10408347.2022.2109125

Taylor & Francis
Taylor & Francis Group

Check for updates

Carbon Nanomaterials-Based Novel Hybrid Platforms for Electrochemical Sensor Applications in Drug Analysis

Ahmet Cetinkaya[a], S. Irem Kaya[b], Goksu Ozcelikay[a], Fatma Budak[a], and Sibel A. Ozkan[a]

[a]Faculty of Pharmacy, Department of Analytical Chemistry, Ankara University, Ankara, Turkey; [b]Gulhane Faculty of Pharmacy, Department of Analytical Chemistry, University of Health Sciences, Ankara, Turkey

ABSTRACT

Nowadays, the rapid improvements in the medical and pharmaceutical fields increase the diversity and use of drugs. However, problems such as the use of multiple or combined drugs in the treatment of diseases and insensible use of over-the-counter drugs have caused concerns about the side-effect profiles and therapeutic ranges of drugs and environmental contamination and pollution problems due to pharmaceuticals waste. Therefore, the analysis of drugs in various media such as biological, pharmaceutical, and environmental samples is an important topic of discussion. Electrochemical methods are advantageous for sensor applications due to their easy application, low cost, versatility, high sensitivity, and environmentally-friendliness. Carbon nanomaterials such as diamond-like carbon thin films, carbon nanotubes, carbon nanofibers, graphene oxide, and nanodiamonds are used to enhance the performance of the electrochemical sensors with catalytic effects. To further improve this effect, it is aimed to create hybrid platforms by using different carbon nanomaterials together or with materials such as conductive polymers and ionic liquids. In this review, the most used carbon nanoforms will be evaluated in terms of electrochemical characterizations and physicochemical properties. Furthermore, the effect of hybrid platforms developed in the most recent studies on electrochemical sensors will be examined and evaluated in terms of drug analysis studies in the last five years.

KEYWORDS

Carbon nanomaterial; determination; drug analysis; electrochemical sensor; electrochemistry

Introduction

Drug analysis is an area that has never lost its importance from the very beginning of drug-related processes and is becoming increasingly important. Drug analysis is a broad approach that includes analytical evaluation of the safety and quality of drugs and pharmaceutical preparations and analytical determination of drugs in various media (biological, environmental, commercial, etc.).[1] For these purposes, many analytical methods are used in routine analysis and research studies. Chromatographic, spectrophotometric, colorimetric, and spectrometric methods are well-established with several advantages in sensor developments, such as high sensitivity, precision, and accuracy.[2] Nevertheless, the major drawbacks of these methods, such as expensive equipment, long analysis time, the large amount of chemicals consumption, and difficulty of use, may lead to the preference for alternative methods.[3,4]

Electrochemical techniques are highly sensitive, affordable, user-friendly, and accurate options for sensor development studies.[3,4] Electrochemical sensors provide rapid and real-time analysis, miniaturization and portable sensors, and lower chemicals and sample consumption for drug analysis.[1,2,5] However, the media in which drugs are determined; are very complex, such as biological and pharmaceutical samples containing the analyte in very low amounts and containing different substances simultaneously. Therefore, researchers always focus on improving the sensor performance in terms of selectivity, sensitivity, and efficacy.

One of the most important strategies to enhance sensor performance is to modify electrochemical sensors with various materials such as nanomaterials, mesoporous materials, and polymers. Among those materials, nanomaterials stand out with their unique properties useful for electrochemical sensors, such as excellent electronic conductivity, availability for functionalization, electrocatalytic performance, strength, stability, high surface area, and versatility.[3,4,6,7] The nanomaterials used for modification also vary widely. Among them, carbon-based ones such as graphene, carbon nanotubes (CNTs), carbon nanofibers (CNFs), and nanodiamonds, constitute a very important group.

Each carbon-based nanomaterial has unique properties that make it stand out. For example, CNFs are easily functionalized, biocompatible, and strong materials,[3,6,8] while CNTs have great electronic, thermal, and mechanical features with stability, biocompatibility, and conductivity.[4,9] Nanodiamond is another remarkable nanomaterial with excellent electrical and thermal conductivity, availability for bio-conjugation with several biological materials, chemical inertness, and versatility.[10–12] Finally, graphene and its

CONTACT Sibel A. Ozkan sibel.ozkan@pharmacy.ankara.edu.tr Faculty of Pharmacy, Department of Analytical Chemistry, Ankara University, Ankara 06560, Turkey.

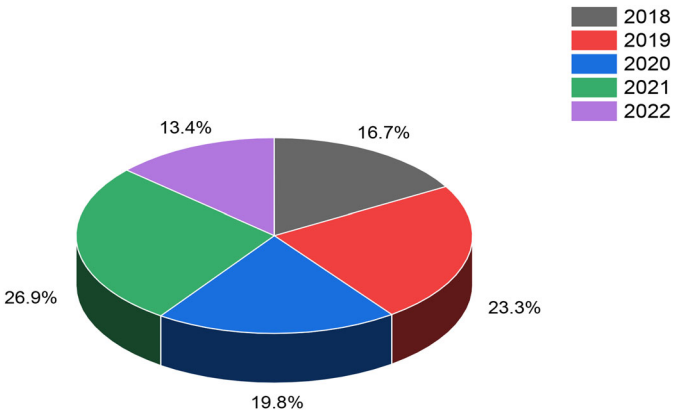
© 2022 Taylor & Francis Group, LLC

derivatives are well-known nanomaterials that are highly porous and conductive with a high surface area. They can also enhance the electrocatalytic activity of sensors.[1]

Developing hybrid platforms by using these remarkable nanomaterials together to increase the efficiency and improve the performance of electrochemical sensors is an important strategy in developing sensors for drug analysis. By combining the advantages and overcoming the disadvantages, nano-platforms for electrochemical sensors with excellent electrocatalyst effects can be created. Hybrid platforms used in electrochemical sensor development offer features and advantages that cannot be achieved with other materials alone. By this means, while developing hybrid platforms, it is aimed to take advantage of each material and eliminate its disadvantages. In this context, the most prominent effect is the synergistic catalytic effects on electrochemical determination. For example, when MWCNTs and graphene are used together, the interaction between the two materials prevents contact resistance, increasing the charge transfer rate and speed of the hybrid nanomaterial.

Similarly, using nanoparticles and graphene together is preferred for better conductivity.[13–15] Hybrid platforms can also provide many advantages during the synthesis process of nanomaterials. For example, during the preparation of various nanoparticles, the standard aggregation issue can be solved using carbon-based dots.[16]

This review evaluates the most recent and prominent electrochemical sensor applications of carbon nanomaterials-based hybrid platforms in drug analysis. Various nanoforms of carbon and the obtained electrochemical effects by combining those nanomaterials and forming hybrid platforms are discussed in detail. The percentage of published papers about the effect of hybrid platforms developed in the most recent studies on electrochemical sensors according to years are given in Scheme 1.



Scheme 1. The percentage of published papers related to most recent studies on electrochemical sensors against years.

Electrochemical characterizations and physicochemical properties of different nanoforms of carbon

The development of carbon-based nanomaterials and nanomaterials, in general, has received much attention. They are widely used in electrochemical sensors due to their ability to create sensitive and reliable electrochemical sensors capable of monitoring a wide spectrum of drug. Furthermore, carbon-based nanomaterials have attracted attention due to their strong electrical conductivity, large active surface, and other unique properties. This section will discuss the physicochemical properties of various carbon nanoforms in detail. When reviewing the literature data, diamond-like carbon (DLC), CNT, CNFs, graphene oxide (GO), reduced graphene oxide (rGO), and nanodiamonds are the most frequently encountered carbon nanoforms (Figure 1). Then, information will be given about the advantages of different carbon-based nanomaterials when considering electrochemical applications.

DLC thin films

DLC film consisting of three-dimensional structures of sp^3-C and sp^2-C is frequently used in mechanical, electronic, and optical fields.[17] DLC is preferred as a surface protection material due to its advantages, such as forming a hard surface, low friction coefficient, high wear, and corrosion resistance.[18–20] However, disruption of sp^3 bonds during film deposition causes residual stress to build up and significantly reduces the film bond strength. The performance of the DLC film is also highly affected by this irregular structure.[21] Therefore, carbon-based films have aimed to reduce internal stress, increase bond strength, and improve tribological and electrochemical properties.[22,23] Compared to other carbon-structured materials, it attracts the attention of researchers from different branches due to its features, such as being much simpler to produce, being durable, and being resistant to physical and chemical factors.[24]

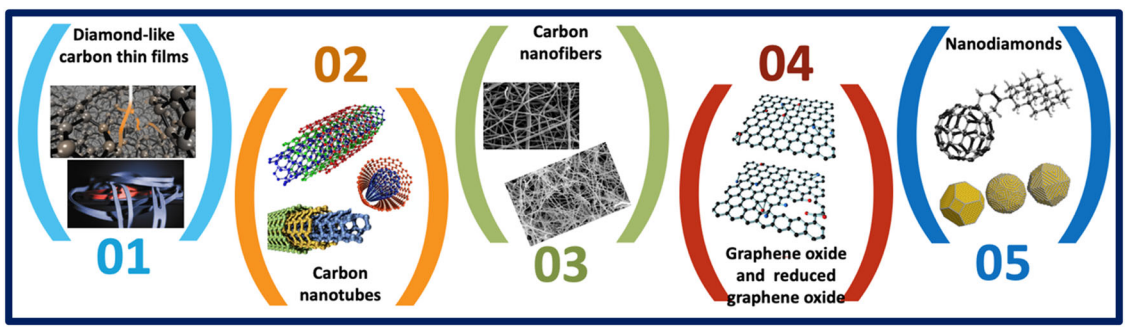


Figure 1. Schematic representation of different nanoforms of carbon.

In the study by Robertson in 2002,[25] characterization studies were carried out for DLC, and the properties of DLC films were summarized in detail. Most of the studies in the literature explained that the mechanical properties of DLC films are very important and discussed their use as a protective coating in specific applications in similar environments. In addition, it was reported that X-ray-based studies of DLC films are insufficient, and their oxygen functionalities are not well defined. Moreover, due to the surface properties of DLC thin films, it was frequently used in biosensing applications. DLC, which is important for the detection of analytes such as dopamine and ascorbic acid, is also important for electrochemical and surface characterizations. However, the uncertainty and compatibility problem in the spectra of DLCs leaves a question mark regarding surface chemistry.

Conversely, since DLC is a commercial film, defining its structure on the surface remains unclear. Therefore, the electrochemical behavior of the DLC thin film was evaluated using molecular modeling studies, spectroscopic methods like scanning electron microscopy (SEM) and Raman spectroscopy, and electrochemical methods such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). And it was important because it provided detailed chemical information in different parts of the samples.[26,27]

Riley et al. described a technique for modifying the surface of thin films containing silicon and diamond-like carbon (Si-DLC) to improve the density and development of diamond cores. Reactive ion etching (RIE) method was used to modify the surfaces of the Si-DLC films with fluorine and oxygen species. The surface properties of Si-DLC, oxygen and fluorine terminated Si-DLC (O Si-DLC) and F Si-DLC films were investigated. Studies demostrated that the carbon-carbon bond sp^2/sp^3 ratio decreased from 20.28% for Si-DLC film to 8.965% and 4.41% for O-DLC and F-DLC films, respectively. Microdiamond deposition was performed on the films using hot filament chemical vapor deposition (HFCVD). According to SEM, XRD, and Raman data for F Si-DLC and O Si-DLC films, the nucleation density of microdiamond increased, in-plane stress decreased up to 60%, and microdiamond nucleation density increased. The F Si-DLC thin film offered a better platform for diamond nucleation than the O Si-DLC film, as it had fewer sp^2 bonds and newer sp^3 regions.[28] In another study, Zhou et al. changed the microstructure and content of a series of the diamond/carbon nanowalls (D/CNWs) composite films by varying the CH_4/H_2 ratio in the gas mixture during microwave plasma enhanced chemical vapor deposition (MPCVD). As the methane concentration increased, the diamond nanoplatelets became larger and more dispersed; The CNWs got thicker as the graphene layers increased with increasing CH_4/H_2 ratio. The distinct microstructure of the D/CNWs provided a very low background current and a large potential window. The increased electrochemical activity brought about by the hydrophobic surface and many graphene edges helped the D/CNWs achieve superior electrochemical sensing capability. In contrast to standard graphite and BDD electrodes, the percent D/CNWs-3% outperformed them significantly in terms of better sensitivity and B/W ratio for simultaneous detection of Cd (II) and Pb (II) even at trace concentrations of 10 µg L^{-1}. For simultaneous measurement of Cd (II) and Pb (II), the linear range of the D/CNWs-3% electrode is 10 to 1000 µg L^{-1}. In conclusion, D/CNWs have achieved promising results as electrochemical electrode options for various trace analytes.[29]

Carbon nanotubes

CNTs, known as graphite sheets wound into cylindrical shapes, are about less than 100 nm in diameter and are a derivative of carbon fibers and fullerene. CNTs are divided into two categories based on the number of carbon layers they contain. Single-walled carbon nanotubes (SWCNTs) are hexagonally packed bundles consisting of a single sheet of graphene ranging in diameter from 0.4 to 2 nm. MWCNTs (multiwalled carbon nanotubes) are nanotubes that consist of two or more cylinders and can range from 1 to 3 nm in diameter.[30]

Electrochemical sensors have been studied extensively as a low-cost means of detecting a wide range of biological analytes with high sensitivity. Carbon-based electrodes have been widely preferred because of their low cost, high electron transfer kinetics, and biocompatibility. CNTs have been used in electrochemical sensors in recent years. CNTs have several benefits over other forms of carbon, including attractive electrical characteristics and rapid electrode kinetics.[31] As a result, CNT-based sensors have higher sensitivity, lower detection limits, and quicker electron transfer kinetics than typical carbon electrodes. Several factors must be investigated, and then, optimized to make a CNT-based sensor. The technique of nanotube production, CNT surface modification, electrode attachment method, and the presence of electron mediators can all affect electrode performance. This article analyzes electrode design strategies for selective analyte detection and emphasizes distinct biomolecules.[30,31]

Carbon nanofibers

CNFs are used in different fields such as chemical industry and materials science due to their high electrical conductivity, large surface area, good chemical stability, nanoscale diameter, and mechanical properties. CNFs are synthesized in different ways, such as chemical vapor deposition (CVD), electrospinning, templating, drawing, and phase separation.[32] The carbon structures and morphologies of CNFs are synthesized in different ways. CNFs can be classified in three ways according to the state of the graphene layers. The position of the graphene layers obliquely to the fiber axis is called herringbone, the position perpendicular to the fiber axis is called platelet, and the position parallel to the growth axis is called the strip. High graphite-containing CNFs can be used harmoniously with a wide variety of polymer processing methods. CNFs have exceptional mechanical qualities and high electrical and thermal conductivity that allow them to be used in a wide variety of matrices, including ceramic,

metal, thermoplastic, and thermoset.[33–35] Moreover, CNFs have a unique surface state that allows surface functionalization and other surface modification approaches to convert nanofibers into a master polymer.[36]

Graphene oxide and reduced graphene oxide

The promise to design and manufacture innovative nanostructures with advanced properties using cutting-edge techniques is a very important prospect for nanotechnology. Graphene (GR) is a two-dimensional, single-layer structure with a honeycomb-like structure made of atoms joined by sp^2 bonds, giving it extraordinary abilities. GR was first announced as a new material in 2004. GR is the latest member of the multidimensional family of carbon nanomaterials. GR received much attention because of its extraordinary electrical, thermal, and optical properties.[37–41] GR has an excellent conductive surface with a large surface area and it is outstanding support for the deposition of catalytic nanoparticles (NPs).[37,38] Unlike CNTs, GR is a low-cost, nontoxic material. These materials synthesized from graphite offer more electroactive sites by increasing the surface area to immobilize biomolecules. Graphene oxide (GO) is a nanomaterial suitable for the production of versatile, functional materials through covalent or non-covalent approaches due to its unique surface properties, large surface area, and layered nature. In recent years, studies on the functionalization of graphene oxide materials for medical and industrial applications have increased.[42] The only difference between graphene oxide and graphene is that GO includes –OH, –COOH, –CO, and epoxy groups. These groups increase the interlayer distance, resulting in a more hydrophilic layer. As a result, GO is a graphene sheet that has been oxygenated. When GO is partially reduced, it forms a reduced graphene-like sheet termed reduced graphene oxide (rGO).[43] GR and GO are used in nanoelectronics,[44] sensors,[45] nanocomposites,[46] batteries,[47] and supercapacitors[48] and they are nanomaterials that have attracted a lot of attention recently due to their wide application areas.

Nanodiamonds

Carbon materials have been extensively researched and developed in recently due to their high thermal stability and good mechanical properties.[49–53] The carbon atoms in the diamond are arranged as a version of the face-centered cubic crystal structure. Diamond is a metastable allotrope of carbon and is known for having outstanding physical properties, including the highest hardness and thermal conductivity of any bulk material. Soviet scientists in the 1960s discovered nanodiamonds by blasting an oxygen-deprived TNT/hexogen compound in inert conditions without any extra carbon source. Nanodiamonds have a diamond core and an amorphous carbon shell, giving them a complex structure. The average particle size of nanodiamonds is 4–5 nm, which allows them to exist in colloidal suspensions of individual diamond particles according to x-ray diffraction and small-angle x-ray scattering. Exploded nanodiamonds have been commercialized and are often used in polymer composites, energy, biological fluids, and environmental and electrical applications.[54] In addition, nanodiamonds exhibit unusual redox behavior and have been used with a number of electrochemical methods, including sensors, biosensors, fuel cells, and supercapacitor electrodes.[54,55]

Electrochemical effects of hybrids based on carbon nanomaterials

Combining different allotropic forms of carbon such as CNTs, graphene, carbon nanobuds, fullerenes, and nanodiamonds makes it possible to produce customized surfaces with unique properties. The combination of different allotropic forms of nanocarbon offers scientific and technological possibilities that cannot be achieved with any other element or material. Carbon is widely available in nature, and therefore, never a critical material. Due to various physicochemical properties (thermal, electrical, electrochemical, optical, biological) of nanocarbon, it is not only used alone but also can be designed as a hybrid material with different combinations. Studies with carbon-based hybrid nanomaterials started in 2015. There were many question marks regarding the processing and physiochemical properties of hybrid structures at that time. Many questions were clarified during the last couple of years with in-depth investigations. The electrochemical point of view is used in this section.[56]

As a widely used electrode material, the glassy carbon provides the suitable substrate for deposition several carbon allotropes together with hybrid materials. The combination of two or more carbon allotropes is generated to realize hybrid materials with unforeseen properties. Such an approach provides us with significant benefits: (i) electrical interconnections between various allotropes, (ii) use in the design of different devices, and (iii) integration with nanostructures. It can increase the sensitivity and selectivity largely due to the electrochemical properties of hybrid materials. Hybrid carbon-based materials have applications in a wide variety of technological and scientific fields.[57]

Hybrid nanomaterials with mechanical, electrical, thermal, and optical properties have been used in the development of electrochemical nanosensors. The combination of inorganic nanoparticles with filamentous forms of carbon attracts attention to hybrids' design. Due to the structure and morphology of hybrid nanomaterials, synergistic effects emerged. It causes lower material usage and higher productivity.[58] Numerous synthetic methodologies have been developed for the preparation of a combination of inorganic nanoparticles and carbon nanomaterials. Inorganic nanocrystals can be connected to carbon nanomaterials via covalent bonding, electrostatic interaction, π - π stacking, hydrophobic interaction, or hydrogen bonding. The sonication or simple mechanical stirring condition via a similar step-by-step self-assembly approach can be used for the preparation of nanocomposites. TiO_2/CNTs, Co_3O_4/CNTs, Au/CNTs, Au/TiO_2/CNTs, TiO_2/Co_3O_4/CNTs have been

Table 1. Latest applications of electrochemical sensors for using carbon nanomaterials-based hybrid platforms in the analysis of selected real samples.

Analyte	Modified electrode	Method	LOD	Linear range	Medium	Real sample	Recovery (%)	Sensitivity	Ref.
Paclitaxel	MWCNT-CTAB\GCE	DPV	0.0004 μM	0.01–12 μM	pH 7 PBS	Urine Pharmaceutical	99.07–102.17 99.32–102.25	0.432 $\mu A.\mu M^{-1}$	[59]
Azithromycin (AZY)	$Zn_3V_2O_8$/P-rGO/SPCE	DPV	0.0067 μM	0.099–450 μM	pH 7 PBS	Serum Urine Wastewater	NA	17.592 $\mu A.\mu M^{-1}$	[60]
Ascorbic acid Dopamine Paracetamol	Gr/CNF-AgNPs	DPV	0.029 μM 0.034 μM 0.019 μM	10.0–450.0 μM 2–320 μM 1–340 μM	pH 7 PBS	Urine Serum	98.68–102.0 100.69–103.4	0.70 $\mu A.\mu M^{-1}$ 0.81 $\mu A.\mu M^{-1}$ 0.012 $\mu A.\mu M^{-1}$	[61]
Isoprenaline	Bi_2O_3/ZnO modified electrode	DPV	0.06 μM	0.04–258.4 μM	pH 7 PBS	Pharmaceutical Urine	NA	0.022 $\mu A.\mu M^{-1}$	[62]
Cortisol	MIP/NiNCs-N-CNTs/GCE	EIS	2.37 pM	10 μM −1 nM	PBS pH 6	Saliva	94–112	7.13 $\mu A.\mu M^{-1}$	[63]
Methotrexate	GCE/CNO/Fe_3O_4@MCM-41-NH_2	DPV	3 nM	0.01–50 μM	pH 6 BRB	Serum	98.88–106.86	22.158 $\mu A.nM^{-1}$	[64]
Isoniazid	DNA/C/La^{3+}/CuO/CPE	DPV	0.035 μM	1.0–165.0 μM	0.5 M ABS	Urine Serum Pharmaceutical	97–104 97.5–102.3 97.7–103	2.69 $\mu A.\mu M^{-1}$	[65]
Dopamine	Co_3O_4@NECNFs	DPV	9 nM	0.01–100 μM	pH 7,4 PBS	Serum	NA	2.091 $\mu A.\mu M^{-1}$	[66]
Oxymorphone Heroin	ZnO/Fe_3O_4/C MHNTA/GCE	DPV	3.5 nM 4.7 nM	0.01–500.0 μM	pH 8 PBS	Serum Urine	97.6–102.0	0.210 $\mu A.\mu M^{-1}$ 0.3214 $\mu A.\mu M^{-1}$	[67]
Metronidazole	C_{60}-rGO-NF/SPE	SWV	0.21 μM	0.25 − 34 nM	pH 7 PBS	Serum Urine	94–100	NA	[68]
Morphine	SWCNTs/GCE	DPV	0.06 $\mu g.mL^{-1}$	0.2–100 $\mu g.mL^{-1}$	pH 7.4 PBS	Food samples	98.4–103.5	NA	[69]
Epirubicin	DES/Pt-SWCNT/CPE	DPV	0.8 nM	0.001–500 μM	pH 7 PBS	Pharmaceutical Dextrose saline	97.4–104.9	0.028 $\mu A.\mu M^{-1}$	[70]
Nitrofurantoin	ScMo@*f*-MCN Ncs/GCE	DPV	9.3 nM	0.01–180 μM	pH 7 PBS	Urine Serum Water	99.4–99.9	0.513 $\mu A.\mu M^{-1}$	[71]
Hydroxychloroquine	MV-CHT/CPE	DPV	0.224 nM	0.0019–194.0 mM	pH 9 BRB	Pharmaceutical Serum Wastewater	94.8–102.5 97.8–101.3 100.2–107.6	101.85 $mA.mM^{-1}$	[72]
Isoniazid	WS_2/CNTs/GCE	DPV	0.24 μM	10–80 μM	pH 7 PBS	Urine	96.9–104.5	0.023 $\mu A.\mu M^{-1}$	[73]
Paracetamol Rizatriptan	CPE/DES/SWCNT-ZrO_2	DPV	0.7 nM 9.0 nM	0.003–100 0.08–100	pH 6 PBS	Urine Pharmaceutical	96.3–105.2 98.25–106.8	0.281 $\mu A.\ \mu M^{-1}$ 0.168 $\mu A.\ \mu M^{-1}$	[74]
Paracetamol	MWCNT–LGH–EG/GCE	DPV	100 $ng.mL^{-1}$	0.100–7.51 $\mu g.mL^{-1}$	pH 10 Borate Buffer	Urine	NA	10.72 $mL.\mu g^{-1}$	[75]
Regorafenib Uric acid	Pd–Ru/rGO/GCE	DPV	5.1 nM 8 nM	0.5–300 nM	pH 7 PBS	Pharmaceutical Serum Wastewater	97.5–102 98–99 99–101	14.60 $\mu A.nM^{-1}$ 29.70 $\mu A.nM^{-1}$	[76]
Ampicillin	ErGO-SPE/AuNPs	DPV	1 pM	10 pM–1 mM	pH 7.4 PBS	Milk	96.6–104.0	NA	[77]
Methamphetamine	Fe_3O_4@PPy/ErGO/GCE	SWV	1 nM	0.005–200 μM	pH 8 BRB	Urine Serum	94.6–104.8 92.4–104.47	0.920 $\mu A.\mu M^{-1}$	[78]
Lapatinib	b-CD@C-dots/GCE	DPV SWV	85.6 nM 18.1 nM	0.199–8.59 μM 9.9 mM–6.17 μM	pH 2.5 PBS	Urine Pharmaceutical	97.22–98.66 96.40–98.53	0.980 $\mu A.\mu M^{-1}$ 0.969 $\mu A.\mu M^{-1}$	[79]

(*continued*)

Table 1. Continued.

Analyte	Modıfıed electrode	Method	LOD	Lınear range	Medıum	Real sample	Recovery (%)	Sensıtıvıty	Ref.
Sulfamethazine	Ab_2@Ag NPs@SWCNHs	LSV	0.12 ng.mL^{-1}	0.09–15 ng.mL^{-1}	pH 7.4 PBS	River water Tap water Pond water Lake water	79.25–119.25	NA	[80]
Clozapine	TA/MWCNTs/GCE	SWV	0.55 nM	0.05–0.375 μM	pH 8.0 PBS	Pharmaceutical Urine Serum	97.68–102.57 91.46–103.11 92.97–104.21	6.061 μA.μM^{-1}	[81]
Acetaminophen	UiO-66-NH_2/CNTs/GCE	DPV	9 nM	0.03–2.0 mM	pH 7.0 PBS	Serum	96.2–97.1	12.390 μA.μM^{-1}	[82]
Dipyrone Codeine	CD-HPC/CBPE	SWV	9.0 nM 9.5 nM	0.46–35 μM 0.5–38 μM	pH 7.0 PBS	River water Urine	96–106	0.038 μA.μM^{-1} 0.047 μA.μM^{-1}	[83]
Amitriptyline	FeZ-G/GCE	DPV	0.22 μM	0.5–50.0 μM 50.0–250.0 μM	0.1 M Lithium chloride solution	Pharmaceutical Urine Environmental water	95.5–99.2	1.896 μA.μM^{-1} 0.624 μA.μM^{-1}	[84]
Cyclobenzaprine	CB-BOT/GCE	DPV	0.63 μM	2.0–20.6 μM	0.10 M NaCl solution	Pharmaceutical Serum River water	NA	0.81 A.M^{-1}	[85]
Dipyrone	PtNPs/graphene/ GCE	SWV	0.142 mM	1–100 μM 100–300 μM	pH 7.0 PBS	Tap water Sewage water	99.89–101.3 99.6–101.48	0.820 mA.mM^{-1} 0.445 mA.mM^{-1}	[86]
Salbutamol	Bi_2Te_3/GCN/SPCE	DPV	1.36 nM	0.01–892.5 μM	pH 7.0 PBS	Beef extract Lamp extract Chicken extract	99.76–99.88 99.44–99.89 99.23–99.65	6.277 μA.μM^{-1}	[87]
Flutamide	ZnO-Co_3O_4@C_3N_4 NC/GCE	DPV	0.00373 μM	0.01–98.6 μM	pH 7.0 PBS	Urine Serum	98.9–99 98.3–98.5	5.331 μA.μM^{-1}	[88]
Theophylline	CNF/PSA/GCE	DPV	0.2 μM	0.6–137 μM	H_2SO_4-Na_2SO_4 (pH2.0)	Pharmaceutical	98.6–103.4	0.0423 μA.μM^{-1}	[89]
Pethidine	CSe_2NF/GCE	DPV	19,3 nM	29 nM–181.8 μM	pH 7.0 PBS	Urine Serum Saliva	99.66–102.08 99.7–100.37 97.77–97.95	12.118 μA.μM^{-1}	[90]
Nitrofurantoin	BT/CNF/GCE	Amperometry	0.005 μM	0.06–450 μM	pH 7.0 PBS	Urine Serum River water	99.3–99.8 99.3–100.1 98.2–99.1	1.76 μA.μM^{-1}	[91]
Chloramphenicol	PDA-VGCF/GCE	DPV	3 nM	0.01–142 μM	pH 7.0 PBS	Apple juice Milk Honey	98.28 99.36 97.84	NA	[92]
Dopamine	WO_2-Na_xWO_3/CSs/GCE	DPV	1.3 nM	0.004–15.4 μM 15.4–106.4 μM	pH 7.4 PBS	Rat serum Bovine serum	94.53–97.05 96.20–101.90	19.335 μA·μM^{-1} 3.151 μA·μM^{-1}	[93]
Levodopa	GCp/SWCNT-COOH@ Nd_2O_3-SiO_2	Amperometry	0.70 μM	2–52 μM	pH 7.4 PBS	Pharmaceutical Urine	97–102 94–102	275 μA.μM^{-1}	[94]
Nitrofurantoin	g-C_3N_4/PPy/GCE	DPV	0.005 μM	0.04–585.2 μM	pH 7.0 PBS	Urine Serum	96–99.85 98–99.92	7.813 μA.μM^{-1}	[95]
Theophylline	CHL-GO/CPE	SWV	4.45 nM	0.3 nM–0.5 μM	pH 6.0 PBS	Pharmaceutical	96.5–98.8	0.289 μA.μM^{-1}	[96]
Promethazine hydrochloride	$BaWO_4$/*f*-CB/SPCE	LSV	29 nM	0.03–234.73 μM 274.73–1314.73 μM	pH 7.2 PBS	Lake water	99.06–102.16	0.1619 μA.μM^{-1} 0.1032 μA.μM^{-1}	[97]

Ibuprofen	ITO|{PAH|PB/SWCNTs}$_3$/SCE	CV	NA	0.047–0.37 μM	0.2 M KCl solution	NA	NA	2532.37 $\mu A.\mu M^{-1}$	[98]
Acetaminophen	CuNC/GCE	CA	2.46 nM	0.01–921.2 μM	pH 6.0 PBS	NA	NA	0.168 $\mu A.\mu M^{-1}$	[99]
Cyadox	CuCo@CMK–8/GCE	DPV	0.26 nM	0.001–3.0 μM	pH 7.0 PBS	Fish feed	85.5–107.2	0.046 $\mu A.\mu M^{-1}$	[100]
Amlodipine	Ag-$Ce_2(WO_4)_3$@CNF/GCE	DPV	0.712 nM	0.01–130 μM	pH 7.0 PBS	Pharmaceutical Urine	95.8–97.34 95.24–96.4	0.002 $\mu A.\mu M^{-1}$	[101]
Levodopa	GP-CAc/PVC/SPE	SWV	0.06 μM	8.0–100 μM	pH 5.0 PBS	Pharmaceutical	91.5–103 94–111	0.101 $\mu A.\mu M^{-1}$	[102]
Zidovudine	DNA/Au-Pt BNPs/GO-chit/PGE	DPV	0.003 pM	0.01 pM- 10.0 nM	pH 4.8 ABS	Serum	93.3–108	0.930 $\mu A.nM^{-1}$	[103]
Nitrofurantoin Nilutamide	BZO/SCN/GCE	DPV	2 nM 6 nM	0.09–260.9 μM 0.09–189.61 μM	pH 7.0 PBS	Urine Water	98–99.50(NFT) 97–98.50(NLT) 98.70–99(NFT) 98.70–99.50(NLT)	35.73 $\mu A.\mu M^{-1}$ 12.17 $\mu A.\mu M^{-1}$	[104]
Irinotecan 5-Fluorouracil	Pd–Au/MWCNT-rGO/GCE	DPV	0.0061 μM 0.0094 μM	0.05–40 μM 0.05–75 μM	pH 9.0 BRB	Urine Serum Pharmaceutical	98.91–99.74(IRI) 98.46–99.90 (5-FU) 99.82–100.15 (IRI) 98.71–100.24 (5-FU) 97.13–102.43 (IRI) 98.06–103.19 (5-FU) 97.49–103.08(IRI) 97.91–101.27(5-FU)	0.089 $\mu A.\mu M^{-1}$ 0.0497 $\mu A.\mu M^{-1}$	[105]
Nadifloxacin	SWCNTs/CPE	DPV	0.250 μM	3.3–53.3 μM	pH 4.0 BRB	Pharmaceutical	NA	NA	[106]
Mesalazine	WS_2/rGO/GCE	DPV	0.003 μM	0–300 μM	pH 7.0 PBS	Tap water Serum Bovine serum albumin Urine	99.4–101.04 97.70–100.3 98.98–102.13 97.95–100.54	20.71 $\mu A.\mu M^{-1}$	[107]
Tryptophan	CMOF/MWCNT/GCE	DPV	0.11 μM (L-Trp) 0.16 μM (D-Trp)	0.4–19 μM	pH 6.5 PBS	Grain	NA	1.359 $\mu A.\mu M^{-1}$	[108]
Hydroquinone Chloramphenicol	Gam@rGO/GCE	DPV	0.0129 μM 0.0063 μM	0.05–0.24 μM 0.02–0.09 μM	pH 7.0 PBS	Wastewater Tap water	99–100.6 97.5–99.3	126.81 $\mu A.\mu M^{-1}$ 23.96 $\mu A.\mu M^{-1}$	[109]
Organophosphate pesticide	$SrFe_{12}O_{19}$/g-C_3N_4 /SPCE	DPV	1.4 nM	0.005–378.15 μM	pH 7.0 PBS	Grapes Orange Guava Mango Apricots Cranberry	98.6–99.2 97.8–99.6 99.0–99.4 97.6–99.2 98.8–99 98.2–99.3	19.23 $\mu A.\mu M^{-1}$	[110]
Epinephrine	OMC-NiO/GCE	DPV	0.085 nM	0.8–50 μM	pH 7.0 PBS	Pharmaceutical Serum	96.1–103.6 94.5–108.0	0.99 $\mu A.\mu M^{-1}$	[111]
Acetaminophen	Ni/C-400/GCE	DPV	0.404 nM	0.20–53.75 μM	pH 7.0 PBS	Serum Urine	97.3–108.0 105.3–107.0	1315.82 $\mu A.mM^{-1}$	[112]
Creatinine	Sb/NPC-GCE	CV	0.74 mM	0.6–1.0 μM	pH 7.0 PBS	Serum	94–100	NA	[113]
Doxorubicin hydrochloride	MWCNTs-COOH/AuNPs/GCP	LSV	6.5 pM	0.01 nM −1 μM	pH 7.0 PBS	Pharmaceutical	95.27–104.2	NA	[114]
Acetaminophen	rGFP-1/GCE	DPV	13.27 nM	1 μM–1 mM	pH 7.0 PBS	Urine	99.70–100.21	36.81 $\mu A{\cdot}\mu M^{-1}$	[115]
Ascorbic acid Sulfite Oxalic acid	Pt-Pd NPs /CHT/N-Gra/GCE	DPV	0.97 μM 5.5 μM 0.84 μM	2–400 μM 8–600 μM 1.5–500 μM	pH 4.0 PBS	NA	92.7–105	0.075 $\mu A{\cdot}mM^{-1}$ 0.026 $\mu A{\cdot}mM^{-1}$ 0.081 $\mu A{\cdot}mM^{-1}$	[116]

(*continued*)

Table 1. Continued.

Analyte	Modified electrode	Method	LOD	Linear range	Medium	Real sample	Recovery (%)	Sensitivity	Ref.
Acetaminophen	Fe-NiO@PC/GCE	AMP	0.46 nM	0.15–1652 μM	pH 7.0 PBS	Urine	97.5–99.3	47.36 μA μM^{-1}	[117]
						Pharmaceutical	97–99.6		
Promethazine hydrochloride	GO-Zn/ZnO/SPCE	DPV	0.3 nM	0,05–177.45 μM	pH 7.0 PBS	Urine	98.8–100.8	5.29 μA.μM^{-1}	[118]
						Serum	96.17–97.8		
						Pharmaceutical	99.50–101		
						River water	95.16–97.26		
Nifedipine	f-MWCNTs/ZnO/Chit/GCE	SWV	0.49 nM	1 nM–40 μM	pH 7.2 PBS	Urine	95.00–104	21.8 μA.μM^{-1}	[119]
						Serum	98.00–102		
Theophylline	GO-NC/GCE	SWV	3.12 n M	0.03 μM $_{-0.5}$ mM	pH 5.0 PBS	Pharmaceutical	94.7–97.4	2.202 μA.μM^{-1}	[120]
						Urine	95.2–99.3		
Pazopanib	CuO-M/GCE	AdSSWV	0.494 nM	0.2 nM–1 μM	pH 7.0 PBS	Pharmaceutical	101.16–102.03	33.0 A.M^{-1}	[121]
						Serum			
Acetaminophen	ZnO NPs/NH_2-MWCNTs/SPCE	DPV	1 nM	0.009–1.3 μM	pH 7.0 PBS	Urine	97.26–101.18	89.64 μA.μM^{-1}	[122]
						Serum			
						Pharmaceutical			
Chloramphenicol	Bi_2S_3@GCN/SPCE	DPV	1.2 nM	0.02–374.4 μM	pH 7.0 PBS	Fresh milk	99.28–99.80	85.33 μA.μM^{-1}	[123]
						Honey	99.02–99.66		
						Shrimp extract	99.20–99.62		
Moxifloxacin	Sγ-CD-CNF/ SC-ISE	SWV	15.0 μM	10 mM-65 μM	NA	Urine	98–102	NA	[124]
						Serum			
						Pharmaceutical			
Amitraz	CNT/Nafion/SPCE	SWV	1.0 ng mL^{-1}	0.005–1.00 μg.mL^{-1}	pH 4.5 ABS	Honey	80.26–103.63	164.98 μA.μg mL^{-1}	[125]
						Longan fruit			

NA: Not applicable, GCE: Glassy Carbon Electrode, SCE: Saturated Calomel Electrode, SPCE: Screen Printed Electrode, PGE: pencil graphite electrode, SC-ISE: solid-contact ion-selective electrode, DPV: Differential Pulse Voltammetry, EIS: Electrochemical Impedance Spectroscopy, CV: cyclic voltammetry, SWV: square-wave voltammetry, LSV: Linear scan voltammetry, CA: Chronoamperometry, AMP: Amperometry. MWCNTs: multi-walled carbon nanotubes, SWCNTs: Single-walled carbon nanotubes CNTs: carbon nanotubes, Ag_2S:Silver sulfide, Px: poloxamer, C: Carbon, CuO: Copper Oxide, NECNFs: Nitrogen-doped Electrospun Carbon Nanofibers, MRGO-Au: Magnetite reduced graphene oxide with gold, DES: Deep eutectic solvent, MV: Molybdenum vanadate, Chit/CHT: Chitosan, f-CB: functionalized carbon black, ZnO: zinc Oxide, EG: ethylene glycol, C-dots: carbon dots, SWCNHs: single-walled carbon nanohorns, Ag NPs: silver Nanoparticles, Au NDs: Au nanodendrites, $Zn(NO_3)_2$:Zinc nitrate, CD: α-cyclodextrin, CBPE:Carbon black paste electrode, HPC:Hierarchical porous carbon, TA: Tannic acid, G: Graphene, FeZ-G: İron (III)-clinoptilolite/graphite, BOT: Botryosphaeran, GCN: graphitic carbon nitrides, Bi_2Te_3: Bismuth telluride, CSe_2NF: Carbon selenide nanofilms, BT: Bizmut titanate, VGCF: Vapor-grown carbon fiber, PAD: polydopamine, CSs: carbon spheres, SWCNT-COOH: carboxylated single-wall carbon nanotubes, g-C_3N_4: graphitic carbon nitride, PPy: Polypyrrole, PTFE: polytetrafluoroethylene, CHL: Cholesterol, $BaWO_4$: barium tungstate, PAH: poly-allylamine hydrochloride, PB NPs: Prussian blue Nanoparticles, CuNC: Cu/N-doped porous carbon nanoarchitecture, CMK-8: cubic meso- porous carbon, Ag- $Ce_2(WO_4)_3$: Silver-cerium tungstate, CAc: cellulose acetate, GP: graphite powder,PVC: polyvinyl chloride,Au-Pt BNPs: Au-Pt bimetallic Nanoparticles, GO-chit: graphene oxide-chitosan, SCN: sulphur-doped graphitic carbon nitride, BZO: barium zirconate microcrystals, SBEb-CD: sulfobutyl ether-b-cyclodextrin, CFME: modified carbon fiber microelectrode, Ni-MOF: Ni based metal-organic framework, Ni/C: Nickel-doping nanoporous carbon, Sb/NPC: Nitrogen-doped porous carbon antimony, OMC-NiO: ordered mesoporous carbon/nickel Oxide, Pt-Pd NPs: Pt-Pd Nanoparticles, N-Gra: nitrogen- doped graphene nanocomposite, PC: Porous carbon, GO-Zn: Zinc graphen Oxide, GO-NC: graphene oxide – nanoclay, M: Waste masks carbon, N-CMK-5: N-doped carbon nanopipe-arrayed mesoporous carbon, OMCs: ordered mesoporous carbons, Sγ-CD: sulfated γ-cyclodextrin, PBS: Phosphate Buffer Solutions, ABS: Acetate Buffer Solutions, BRB: Britton Robinson Buffer.

given as examples of a combination of inorganic nanoparticles and carbon nanomaterials.

Electrochemical applications of carbon nanomaterials-based hybrid platforms in drug analysis

Carbon nanomaterial-based hybrid platforms are frequently used in drug analysis due to their fast electron transfer, light weight, physical and chemical stability, and high strength. Table 1 contains the latest applications (2019–2022) of electrochemical sensors modified with hybrid platforms for the detection of drugs in real samples such as biological fluids, pharmaceuticals, food, and environmental waters.

A sensor was developed by multi-walled carbon nanotube (MWCNT), and cetyltrimethylammonium bromide (CTAB) to detect the anticancer drug paclitaxel by Gowda et al.[59] Surface morphology evaluation of the proposed sensor was carried out by the AFM method. The sensor used for electrochemical detection of paclitaxel in pure and dosage form by cyclic and differential pulse voltammetry. This work revealed that MWCNT-CTAB/GCE nanocomposite enhances the electrocatalytic performance for PAC monitoring. Scan rate variation with pH 7.0 PBS in the sensor confirmed a diffusion-controlled process. MWCNT-CTAB/GCE exhibited a LDR of 0.001 to 12 µM with a LOD of 0.0004 µM. The developed MWCNT-CTAB/GCE modified sensor has been implemented for the determination of PAC in urine and pharmaceutical samples. PAC oxidation peak current was remarkably improved due to the high catalytic activity and conductivity of MWCNT. The resulting MWCNT-CTAB/GCE sensor was highly reproducible. In 2021 by Manjula et al.,[62] was developed Bi_2O_3/ZnO on glassy carbon electrode as a sensor to detect isoprenaline (IP). The prepared sensor is an effective catalyst and later used to detect β adrenoceptor agonist IP (Figure 2). CV and DPV were used for the electrochemical detection of IP. Electrocatalytic activities of the sensor were evaluated using CV. Under optimal conditions, the present sensor showed a LOD of 0.06 μM and a LDR between 0.04 μM and 258.4 μM. Finally, the developed sensor was successfully applied to the determination of IP in the pharmaceutical and urine samples.

In another work, a sensor was developed by Ghalkhani et al.[64] The sensor-modified electrode based on iron oxide nanoparticles (Fe_3O_4) functionalized with MCM-41-NH_2 and carbon nano-onion (CNO) was prepared to quantify Methotrexate (MTX) in biological samples using. LDR, LOD, and sensitivity obtained for MTX using the developed sensor were 0.01 to 50 μM, 3 nM, and 22.158 µA.nM $^{-1}$, respectively. The sensor had reasonable selectivity, reproducibility, and good stability for MTX measurement in real samples. The excellent working of this sensor has been due to the high conductivity of Fe_3O_4 NPs and CNO, and MCM's higherl adsorption capacity. One of the good properties of the prepared sensor is the excellent recovery percentage of MTX in real samples.

In 2021, Lerdsri et al.,[125] developed a sensitive electrochemical method using CNT and Nafion (a conduction polymer) to detect amitraz (N'-(2,4-dimethyl phenyl)-N-[(2,4-dimethyl phenyl)iminomethyl]-Nmethylmethanimidamide) used in veterinary. Improvement of preconcentration through electrostatic interaction between negatively charged Nafion and positively charged 2,4-dimethylaniline (2,4-DMA) revealed the high performance of the sensor and electrochemical oxidation of hydrolyzed Amitraz. CNT/Nafion/SPCE exhibited a LDR of 0.005 to 1.00 µg.mL^{-1}, and a LOD of 1.0 ng.mL^{-1}. This electrochemical sensor was used to detect

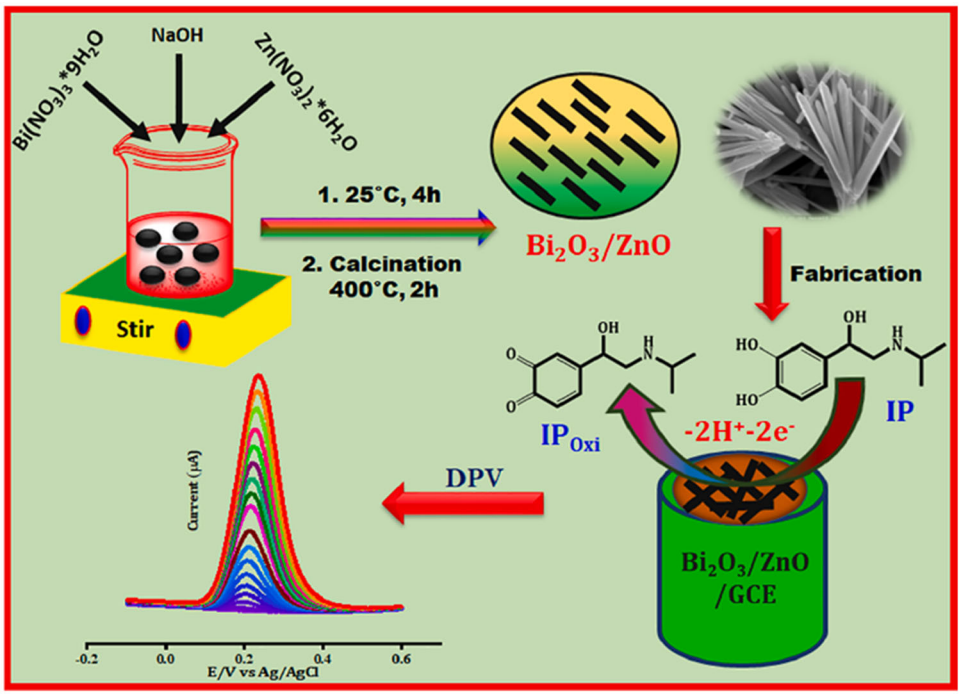


Figure 2. Schematic description of Bi_2O_3/ZnO modified electrode toward the isoprenaline oxidation. Reprinted from Ref. [62] with permission from Elsevier.

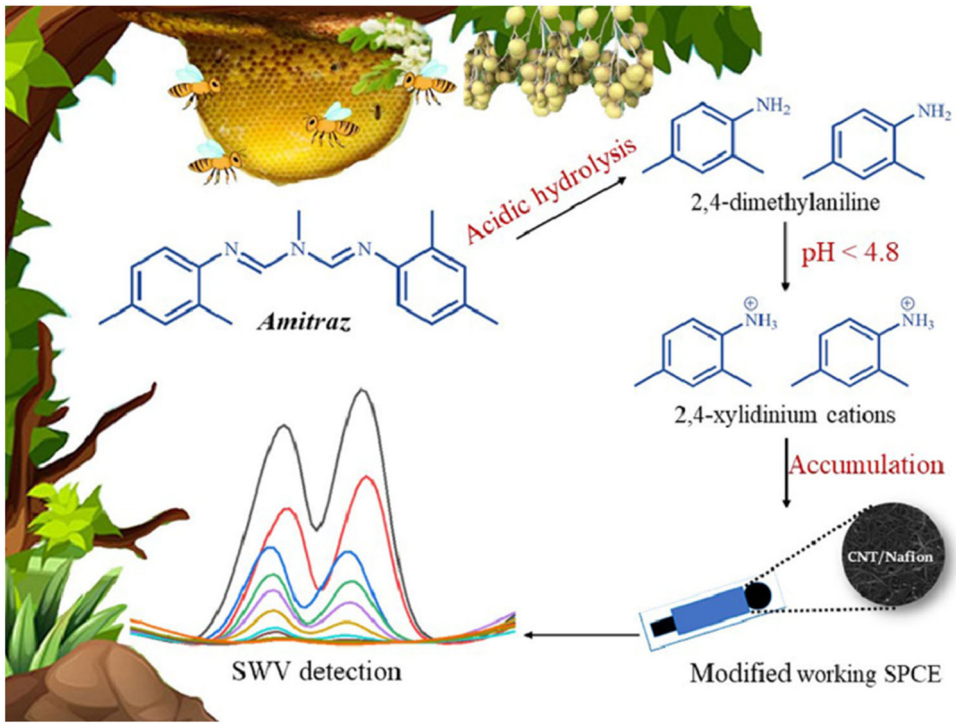


Figure 3. Schematic description of CNT/Nafion/SPCE modified electrode for amitraz determination using SWV. Reprinted from Ref. [125] with permission from Elsevier.

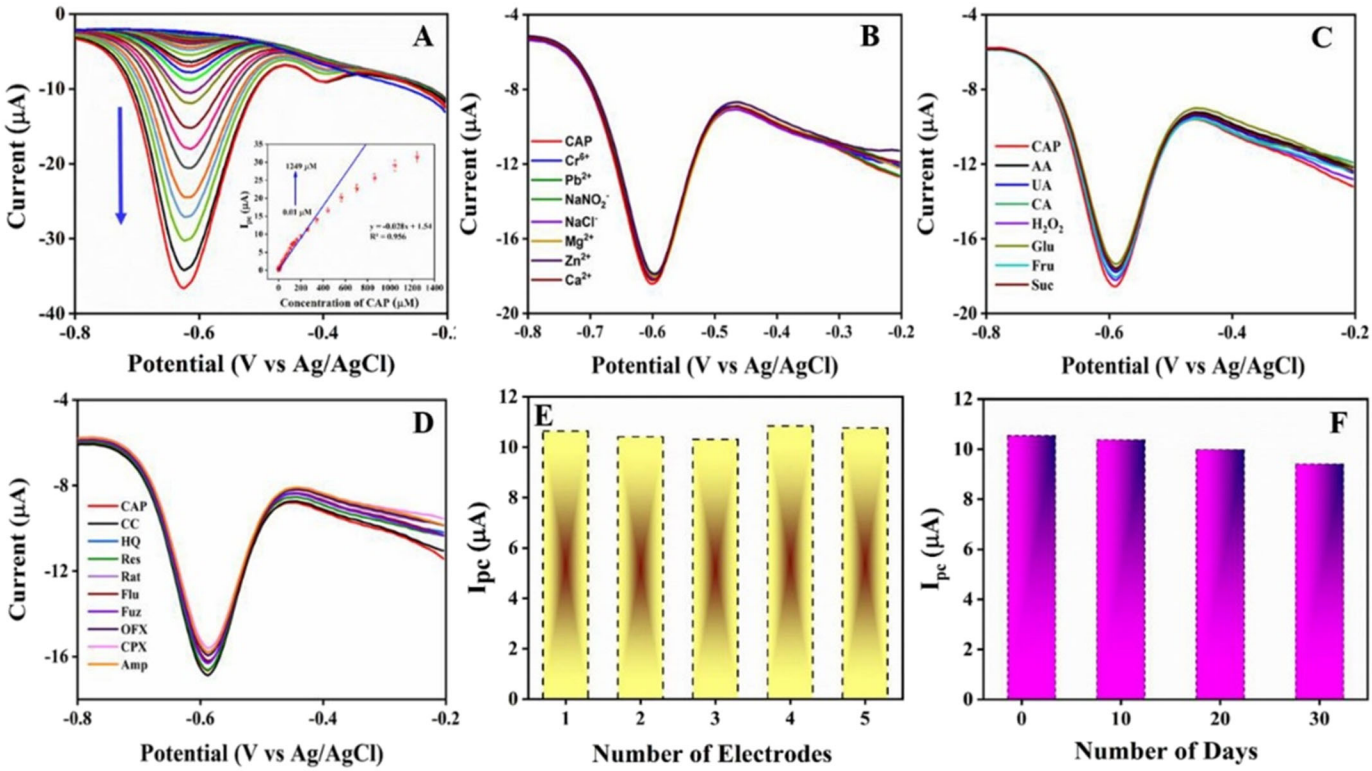


Figure 4. Schematic representation of the experimental results of the PDA-VGCF/GCE modified electrode for chloramphenicol oxidation using DPV. (A) Responses of different concentrations of CAP in DPV. (B) Biological compounds, (C) Other nitro compounds, and (D) Interference studies of PDA-VGCF/GCE with 200 μM CAP. (E) Reproducibility of CAP detection in PDA-VGCF/GCE at 200 μM CAP. (F) Storage stability of PDA-GCF/GCE to detect CAP in PBS electrolyte with 200 μM CAP. Reprinted from Ref. [92] with permission from Elsevier.

Amitraz in longan fruit and honey samples (Figure 3). Moreover, this electrochemical sensor offered good performances in terms of simplicity for manufacture, applicability, high sensitivity, reliability in practical sample analysis, and cost.

Karuppiah et al.,[92] Developed a sensor on the GCE surface using modified vapor-grown carbon fiber (VGCF) and bio-inspired polydopamine (PDA). This sensor was used to detect the antibiotic drug chloramphenicol in apple juice,

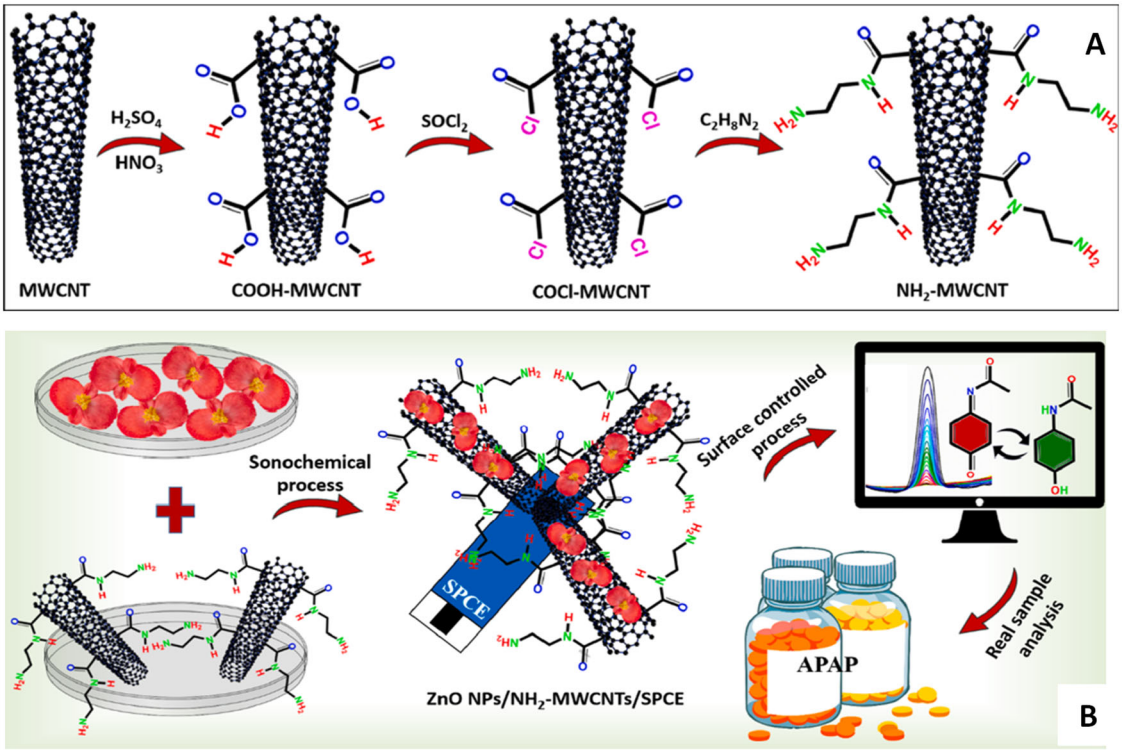


Figure 5. (A) MWCNT at surface functionalization, (B) Representation of APAP determination using ZnO NPs/NH_2-MWCNTs/SPCE. Reprinted from Ref. [122] with permission from Elsevier.

milk, and honey samples. DPV and CV methods were used to observe the electrocatalysis of CAP. According to the CV results, the PDA-VGCF modified electrode exhibited a much higher sensitivity than the bare GCE and pristine VGCF. LDR, LOD, and the higher sensitivity obtained for CAP using the developed electrochemical sensor were 0.01 to 142 μM, 3 nM, and 0.68 $\mu A \mu M^{-1} cm^{-2}$, respectively. And this sensor showed long-term stability for up to 30 days. PDA-VGCF/GCE exhibits considerable selectivity in the presence of other interfering compounds, and practical feasibility in food samples is also evaluated (Figure 4).

Furthermore, these results indicate that the as-synthesized metal-free catalyst could be a more effective electrocatalyst for pharmaceutical formulations. Balram et al.,[122] developed a sensor based on the modification on the SPCE surface with amine-functionalized multi-walled carbon nanotubes (NH_2-MWCNTs) decorated with zinc oxide (ZnO). The sensor's was used for determination acetaminophen (APAP) in real samples (Figure 5). Begonia flower-like ZnO was preoared using the arginine-supplemented aqueous solution technique and surface functionalization of MWCNTs. APAP was determined using with CV and DPV. Under optimal conditions, this sensor showed a LOD of 1 nM, a LDR of 0.009 μM to 1.3 μM and a very high sensitivity of 89.64 $\mu A \mu M^{-1} cm^{-2}$. Furthermore, the sensor showed good anti-interference features, reproducibility, high stability, practical feasibility, and repeatability.

Conclusion

Drug development, production, use, and monitoring are complex processes that involve many analyzes. In the determination of drugs, the analysis media contains many substances together, which also poses a challenge in terms of interference and selectivity. Factors such as the introduction of newly developed drugs, the prevalence of multidrug therapy in the general population, and the fact that existing preparations generally contain combined active substances increase the importance of sensor development studies. Within this scope, electrochemical sensor applications in drug analysis have gained significant popularity over the years due to the great sensitivity, rapid analysis, easy application, and affordable and portable instrumentation.

To improve the efficiency of the electrochemical sensors, developing novel hybrid platforms is a hot topic for researchers. Carbon nanomaterials show a great electrochemical performance considering the modification agents used for this purpose. Especially, the formation of hybrid platforms combining materials with different properties such as nanoparticles, nanotubes, graphitic materials, and other carbon-based materials offer enhanced conductivity, catalytic activity, and sensitivity. Furthermore, electroconductive effects obtained by synergistic effects provide advantages in electrochemical sensor studies. The acquired accelerated electron transfer and conductivity increase the sensitivity and performance of the electrochemical sensor with lower LOD values. This gives advantages that cannot be achieved with non-hybrid platforms.

When the most prominent studies in the recent literature are evaluated, it can be seen that the combination of single/multi-walled CNTs with metal and metal oxide nanoparticles is a highly preferred modification type. In addition, researchers also prefer integrating new nanomaterials with

well-known and commonly used ones, such as graphene and derivatives. Analgesic agents, antibiotics, and anticancer agents occupy the largest place in drug analysis studies. The mostly applied real samples in studies are biological fluids and pharmaceutical preparations. Furthermore, due to their sensitivity and fast measurement, the most used electrochemical methods are DPV and SWV. Although the most preferred electrode material is GCE, SPEs that offer an integrated three-electrode system has also been widely used, thanks to their ease of use, practicality, and disposability.

Future perspectives

In future applications, it is expected that newly developed nanomaterials will be used more frequently and sensors will be transformed into portable, miniaturized systems. It is expected that the newly developed carbon-based nanomaterials will be used more and more. In addition, the main goal in sensor systems today is to achieve a user-friendly and fast analysis. For this purpose, while developing novel sensors, the focus is on miniaturized and portable features. In this way, rapid sensors that allow on-site analysis for environmental samples or point-of-care testing for patients can be developed. Due to the high adaptability of electrochemical sensors to such applications and the fact that there is no need for pretreatment for the samples to be analyzed, they will be frequently preferred methods in the future.

Funding

Ahmet Cetinkaya thanks the financial support from the Council of Higher Education 100/2000 (YOK) under the special 100/2000 scholarship program and the Scientific and Technological Research Council of Turkey (TUBITAK) under the BIDEB/2211-A Ph.D. Fatma Budak thanks the financial supports from Technological Research Council of Turkey (TUBITAK) under the ARDEB/1004 Ph.D. Scholarship Programmes.

ORCID

Ahmet Cetinkaya http://orcid.org/0000-0001-5014-0907
S. Irem Kaya http://orcid.org/0000-0003-0578-5399
Goksu Ozcelikay http://orcid.org/0000-0001-7919-3236
Fatma Budak http://orcid.org/0000-0001-8935-5171
Sibel A. Ozkan http://orcid.org/0000-0001-7494-3077

References

[1] Nigović, B.; Jurić, S.; Mornar, A. Electrochemical Determination of Nepafenac Topically Applied Nonsteroidal Anti-Inflammatory Drug Using Graphene Nanoplatelets-Carbon Nanofibers Modified Glassy Carbon Electrode. *J. Electroanal. Chem.* **2018**, *817*, 30–35. 10.1016/j.jelechem.2018.03.068.

[2] Apetrei, I. M.; Apetrei, C. Highly Sensitive Voltamperometric Determination of Pyritinol Using Carbon Nanofiber/Gold Nanoparticle Composite Screen-Printed Carbon Electrode. *Int. J. Nanomed.* **2017**, *12*, 5177–5188. 10.2147/IJN.S138978.

[3] Haidyrah, A. S.; Sundaresan, P.; Venkatesh, K.; Ramaraj, S. K.; Thirumalraj, B. Fabrication of Functionalized Carbon Nanofibers/Carbon Black Composite for Electrochemical Investigation of Antibacterial Drug Nitrofurantoin. *Colloids Surf. A Physicochem. Eng. Asp.* **2021**, *627*, 127112. 10.1016/j.colsurfa.2021.127112.

[4] Li, J.; Huang, X.; Shi, W.; Jiang, M.; Tian, L.; Su, M.; Wu, J.; Liu, Q.; Yu, C.; Gu, H. Pt Nanoparticle Decorated Carbon Nanotubes Nanocomposite Based Sensing Platform for the Monitoring of Cell-Secreted Dopamine. *Sens. Actuators B Chem.* **2021**, *330*, 129311. 10.1016/j.snb.2020.129311.

[5] Anvari, L.; Ghoreishi, S. M.; Faridbod, F.; Ganjali, M. R. Electrochemical Determination of Methamphetamine in Human Plasma on a Nanoceria Nanoparticle Decorated Reduced Graphene Oxide (RGO) Glassy Carbon Electrode (GCE). *Anal. Lett.* **2021**, *54*, 2509–2522. 10.1080/00032719.2021.1875229.

[6] Liu, Y.; Fan, J.; He, F.; Li, X.; Tang, T.; Cheng, H.; Li, L.; Hu, G. Glycosyl/MOF-5-Based Carbon Nanofibers for Highly Sensitive Detection of Anti-Bacterial Drug Quercetin. *Surf. Interfaces* **2021**, *27*, 101488. 10.1016/j.surfin.2021.101488.

[7] Veera Manohara Reddy, Y.; Sravani, B.; Łuczak, T.; Mallikarjuna, K.; Madhavi, G. An Ultra-Sensitive Rifampicin Electrochemical Sensor Based on Titanium Nanoparticles (TiO_2) Anchored Reduced Graphene Oxide Modified Glassy Carbon Electrode. *Colloids Surf. A Physicochem. Eng. Asp.* **2021**, *608*, 125533. 10.1016/j.colsurfa.2020.125533.

[8] Nataraj, N.; Chen, S. M. Samarium Vanadate Nanospheres Integrated Carbon Nanofiber Composite as an Efficient Electrocatalyst for Antituberculosis Drug Detection in Real Samples. *Colloids Surf. A Physicochem. Eng. Asp.* **2021**, *617*, 126385. 10.1016/j.colsurfa.2021.126385.

[9] Kokab, T.; Shah, A.; Khan, M. A.; Arshad, M.; Nisar, J.; Ashiq, M. N.; Zia, M. A. Simultaneous Femtomolar Detection of Paracetamol, Diclofenac, and Orphenadrine Using a Carbon Nanotube/Zinc Oxide Nanoparticle-Based Electrochemical Sensor. *ACS Appl. Nano Mater.* **2021**, *4*, 4699–4712. 10.1021/acsanm.1c00310.

[10] Kumar, S.; Nehra, M.; Kedia, D.; Dilbaghi, N.; Tankeshwar, K.; Kim, K. H. Nanodiamonds: Emerging Face of Future Nanotechnology. *Carbon N. Y.* **2019**, *143*, 678–699. 10.1016/j.carbon.2018.11.060.

[11] Simioni, N. B.; Silva, T. A.; Oliveira, G. G.; Fatibello-Filho, O. A Nanodiamond-Based Electrochemical Sensor for the Determination of Pyrazinamide Antibiotic. *Sens. Actuators B Chem.* **2017**, *250*, 315–323. 10.1016/j.snb.2017.04.175.

[12] Sainio, S.; Palomäki, T.; Rhode, S.; Kauppila, M.; Pitkänen, O.; Selkälä, T.; Toth, G.; Moram, M.; Kordas, K.; Koskinen, J.; et al. Carbon Nanotube (CNT) Forest Grown on Diamond-like Carbon (DLC) Thin Films Significantly Improves Electrochemical Sensitivity and Selectivity towards Dopamine. *Sens. Actuators B Chem.* **2015**, *211*, 177–186. 10.1016/j.snb.2015.01.059.

[13] Muñoz, J.; Álvarez-Prada, I.; Lopez-Lopez, E.; Escriche, L.; Romero, N.; Sala, X.; Mas-Torrent, M.; García-Antón, J. Synthesis of 0D to 3D Hybrid-Carbon Nanomaterials Carrying Platinum(0) Nanoparticles: Towards the Electrocatalytic Determination of Methylparabens at Ultra-Trace Levels. *Sens. Actuators B Chem.* **2020**, *305*, 127467. 10.1016/j.snb.2019.127467.

[14] Sebaa, M.; Nguyen, T. Y.; Paul, R. K.; Mulchandani, A.; Liu, H. Graphene and Carbon Nanotube-Graphene Hybrid Nanomaterials for Human Embryonic Stem Cell Culture. *Mater. Lett.* **2013**, *92*, 122–125. 10.1016/j.matlet.2012.10.035.

[15] Mousavi, S. M.; Yousefi, K.; Hashemi, S. A.; Bahrani, S. *Hybrid Magnetic Nanoparticles-Carbonaceous Nanomaterials (Carbon Nanotube/Graphene)*. In *Magnetic Nanoparticle-Based Hybrid Materials*; Elsevier, Woodhead Publishing: the Netherlands, **2021**.10.1016/B978-0-12-823688-8.00024-7.

[16] Fu, Y.; Zeng, G.; Lai, C.; Huang, D.; Qin, L.; Yi, H.; Liu, X.; Zhang, M.; Li, B.; Liu, S.; et al. Hybrid Architectures Based on Noble Metals and Carbon-Based Dots Nanomaterials: A

Review of Recent Progress in Synthesis and Applications. *Chem. Eng. J.* **2020**, *399*, 125743. 10.1016/j.cej.2020.125743.

[17] Wang, Y.; Xu, J.; Ootani, Y.; Ozawa, N.; Adachi, K.; Kubo, M. Proposal of a New Formation Mechanism for Hydrogenated Diamond-like Carbon Transfer Films: Hydrocarbon-Emission-Induced Transfer. *Carbon N. Y.* **2019**, *154*, 7–12. 10.1016/j.carbon.2019.07.090.

[18] Wei, X.; Chen, L.; Zhang, M.; Lu, Z.; Zhang, G. Effect of Dopants (F, Si) Material on the Structure and Properties of Hydrogenated DLC Film by Plane Cathode PECVD. *Diam. Relat. Mater.* **2020**, *110*, 108102. 10.1016/j.diamond.2020.108102.

[19] Lu, Y.; Huang, G.; Xi, L. Tribological and Mechanical Properties of the Multi-Layer DLC Film on the Soft Copper Substrate. *Diam. Relat. Mater.* **2019**, *94*, 21–27. 10.1016/j.diamond.2019.02.019.

[20] Wei, X.; Yin, P.; Wu, J.; Nie, X.; Lu, Z.; Zhang, G. Deposition of DLC Films on the Inner Wall of U-Type Pipes by Hollow Cathode PECVD. *Diam. Relat. Mater.* **2021**, *114*, 108308. 10.1016/j.diamond.2021.108308.

[21] Shahsavari, F.; Ehteshamzadeh, M.; Amin, M. H.; Barlow, A. J. A Comparative Study of Surface Morphology, Mechanical and Tribological Properties of DLC Films Deposited on Cr and Ni Nanolayers. *Ceram. Int.* **2020**, *46*, 5077–5085. 10.1016/j.ceramint.2019.10.251.

[22] Mao, Y.; Li, Z.; Feng, K.; Guo, X.; Zhou, Z.; Wu, Y. Corrosion Behavior of Carbon Film Coated Magnesium Alloy with Electroless Plating Nickel Interlayer. *J. Mater. Process. Technol.* **2015**, *219*, 42–47. 10.1016/j.jmatprotec.2014.12.003.

[23] Tanaka, I.; Ohtgita, G.; Harada, Y. Frictional Properties of Electron Beam-Deposited a-C:Si Films. *Diam. Relat. Mater.* **2020**, *110*, 108150. 10.1016/j.diamond.2020.108150.

[24] Xiao, Y.; Sun, W.; Ma, M.; Jia, Y.; Liu, J.; Zhang, T. Diamond & Related Materials Microstructure, Wear and Corrosion Behavior of Nano-CeO_2 Doped Diamond-like Carbon (DLC) Composite Films. *Diam. Relat. Mater.* **2022**, *126*, 109087. 10.1016/j.diamond.2022.109087.

[25] Robertson, J. Diamond-like Amorphous Carbon. *Mater. Sci. Eng. R Rep.* **2002**, *37*, 129–281. 10.1016/s0927-796x(02)00005-0.

[26] Şenocak, A.; Tümay, S. O.; Ömeroğlu, İ.; Şanko, V. Crosslinker Polycarbazole Supported Magnetite MOF@CNT Hybrid Material for Synergetic and Selective Voltammetric Determination of Adenine and Guanine. *J. Electroanal. Chem.* **2022**, *905*, 115963. 10.1016/j.jelechem.2021.115963.

[27] Rodríguez-Corvera, C. L.; Laura Elías, A.; Morelos-Gómez, A.; Endo, M.; Muñoz-Sandoval, E.; López-Urías, F. Hybrid Materials Based on Pyrrhotite, Troilite, and Few-Layered Graphitic Nanostructures: Synthesis, Characterization, and Cyclic Voltammetry Studies. *Appl. Surf. Sci.* **2021**, *563*, 150327. 10.1016/j.apsusc.2021.150327.

[28] Riley, P. R.; Joshi, P.; Narayan, J.; Narayan, R. J. Enhanced Nucleation and Large-Scale Growth of CVD Diamond via Surface-Modification of Silicon-Incorporated Diamond-like Carbon Thin Films. *Diam. Relat. Mater.* **2021**, *120*, 108630. 10.1016/j.diamond.2021.108630.

[29] Zhou, M.; Zhai, Z.; Liu, L.; Zhang, C.; Yuan, Z.; Lu, Z.; Chen, B.; Shi, D.; Yang, B.; Wei, Q.; et al. Controllable Synthesized Diamond/CNWs Film as a Novel Nanocarbon Electrode with Wide Potential Window and Enhanced S/B Ratio for Electrochemical Sensing. *Appl. Surf. Sci.* **2021**, *551*, 149418. 10.1016/j.apsusc.2021.149418.

[30] Anzar, N.; Hasan, R.; Tyagi, M.; Yadav, N.; Narang, J. Carbon Nanotube - A Review on Synthesis, Properties and Plethora of Applications in the Field of. *Biomed. Sci.e. Sens. Int.* **2020**, *1*, 100003. 10.1016/j.sintl.2020.100003.

[31] Jacobs, C. B.; Peairs, M. J.; Venton, B. J. Review: Carbon Nanotube Based Electrochemical Sensors for Biomolecules. *Anal Chim Acta* **2010**, *662*, 105–127. 10.1016/j.aca.2010.01.009.

[32] Nataraj, S. K.; Yang, K. S.; Aminabhavi, T. M. Polyacrylonitrile-Based Nanofibers - A State-of-the-Art Review. *Prog. Polym. Sci.* **2012**, *37*, 487–513. 10.1016/j.progpolymsci.2011.07.001.

[33] Silvain, J. F.; Vincent, C.; Heintz, J. M.; Chandra, N. Novel Processing and Characterization of Cu/CNF Nanocomposite for High Thermal Conductivity Applications. *Compos. Sci. Technol.* **2009**, *69*, 2474–2484. 10.1016/j.compscitech.2009.06.023.

[34] Feng, L.; Xie, N.; Zhong, J. Carbon Nanofibers and Their Composites: A Review of Synthesizing, Properties and Applications. *Materials (Basel)* **2014**, *7*, 3919–3945. 10.3390/ma7053919.

[35] Lim, C. T. Nanofiber Technology: Current Status and Emerging Developments. *Prog. Polym. Sci.* **2017**, *70*, 1–17. 10.1016/j.progpolymsci.2017.03.002.

[36] Mohamed, A. *Synthesis, Characterization, and Applications Carbon Nanofibers. In* Carbon-Based Nanofillers and Their Rubber Nanocomposites; Elsevier Inc.: the Netherlands, **2018**.10.1016/B978-0-12-813248-7.00008-0.

[37] Pumera, M.; Ambrosi, A.; Bonanni, A.; Chng, E. L. K.; Poh, H. L. Graphene for Electrochemical Sensing and Biosensing. *TrAC - Trends Anal. Chem.* **2010**, *29*, 954–965. 10.1016/j.trac.2010.05.011.

[38] Yu, L. J.; Sarrami, F.; O'Reilly, R. J.; Karton, A. Reaction Barrier Heights for Cycloreversion of Heterocyclic Rings: An Achilles' Heel for DFT and Standard Ab Initio Procedures. *Chem. Phys.* **2015**, *458*, 1–8. 10.1016/j.chemphys.2015.07.005.

[39] Zhang, C.; Li, L.; Ju, J.; Chen, W. Electrochemical Sensor Based on Graphene-Supported Tin Oxide Nanoclusters for Nonenzymatic Detection of Hydrogen Peroxide. *Electrochim. Acta* **2016**, *210*, 181–189. 10.1016/j.electacta.2016.05.151.

[40] Zhao, X.; Li, N.; Jing, M.; Zhang, Y.; Wang, W.; Liu, L.; Xu, Z.; Liu, L.; Li, F.; Wu, N. Monodispersed and Spherical Silver Nanoparticles/Graphene Nanocomposites from Gamma-Ray Assisted in-Situ Synthesis for Nitrite Electrochemical Sensing. *Electrochim. Acta* **2019**, *295*, 434–443. 10.1016/j.electacta.2018.10.039.

[41] Yang, B.; Bin, D.; Zhang, K.; Du, Y.; Majima, T. A Seed-Mediated Method to Design N-Doped Graphene Supported Gold-Silver Nanothorns Sensor for Rutin Detection. *J. Colloid Interface Sci.* **2018**, *512*, 446–454. 10.1016/j.jcis.2017.10.082.

[42] Veerapandian, M.; Lee, M. H.; Krishnamoorthy, K.; Yun, K. Synthesis, Characterization and Electrochemical Properties of Functionalized Graphene Oxide. *Carbon N. Y.* **2012**, *50*, 4228–4238. 10.1016/j.carbon.2012.05.004.

[43] Ananda Murthy, H. C.; Gebremedhn Kelele, K.; Ravikumar, C. R.; Nagaswarupa, H. P.; Tadesse, A.; Desalegn, T. Graphene-Supported Nanomaterials as Electrochemical Sensors: A Mini Review. *Res. Chem.* **2021**, *3*, 100131. 10.1016/j.rechem.2021.100131.

[44] Areshkin, D. A.; White, C. T. Building Blocks for Integrated Graphene Circuits. *Nano Lett.* **2007**, *7*, 3253–3259. 10.1021/nl070708c.

[45] Schedin, F.; Geim, A. K.; Morozov, S. V.; Hill, E. W.; Blake, P.; Katsnelson, M. I.; Novoselov, K. S. Acute Toxic Effects of Drug Abuse: Diagnosis and Treatment. *J. Fla. Med. Assoc.* **1971**, *58*, 41–42.

[46] Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. Graphene-Based Composite Materials. *Nature* **2006**, *442*, 282–286. 10.1038/nature04969.

[47] Takamura, T.; Endo, K.; Fu, L.; Wu, Y.; Lee, K. J.; Matsumoto, T. Identification of Nano-Sized Holes by TEM in the Graphene Layer of Graphite and the High Rate Discharge Capability of Li-Ion Battery Anodes. *Electrochim. Acta* **2007**, *53*, 1055–1061. 10.1016/j.electacta.2007.03.052.

[48] Novoselov, K. S.; Jiang, D.; Schedin, F.; Booth, T. J.; Khotkevich, V. V.; Morozov, S. V.; Geim, A. K. Two-

Dimensional Atomic Crystals. *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 10451–10453. 10.1073/pnas.0502848102.

[49] Zhang, Y.; Park, M.; Kim, H. Y.; Ding, B.; Park, S. J. A Facile Ultrasonic-Assisted Fabrication of Nitrogen-Doped Carbon Dots/BiOBr up-Conversion Nanocomposites for Visible Light Photocatalytic Enhancements. *Sci. Rep.* **2017**, *7*, 1–12.10.1038/srep45086.

[50] Tarfaoui, M.; Lafdi, K.; El Moumen, A. Mechanical Properties of Carbon Nanotubes Based Polymer Composites. *Compos. B Eng.* **2016**, *103*, 113–121. 10.1016/j.compositesb.2016.08.016.

[51] Pant, B.; Park, M.; Kim, H. Y.; Park, S. J. Ag-ZnO Photocatalyst Anchored on Carbon Nanofibers: Synthesis, Characterization, and Photocatalytic Activities. *Synth. Met.* **2016**, *220*, 533–537. 10.1016/j.synthmet.2016.07.027.

[52] Raghubanshi, H.; Dikio, E. D.; Naidoo, E. B. The Properties and Applications of Helical Carbon Fibers and Related Materials: A Review. *J. Ind. Eng. Chem.* **2016**, *44*, 23–42. 10.1016/j.jiec.2016.08.023.

[53] Fang, H.; Zou, F.; Liu, W.; Wu, C.; Bai, Y.; Hui, D. Mechanical Performance of Concrete Pavement Reinforced by CFRP Grids for Bridge Deck Applications. *Compos. B Eng.* **2017**, *110*, 315–335. 10.1016/j.compositesb.2016.11.015.

[54] Zhang, Y.; Rhee, K. Y.; Hui, D.; Park, S. J. A Critical Review of Nanodiamond Based Nanocomposites: Synthesis, Properties and Applications. *Compos. B Eng.* **2018**, *143*, 19–27. 10.1016/j.compositesb.2018.01.028.

[55] Zambianco, N. A.; Silva, T. A.; Zanin, H.; Fatibello-Filho, O.; Janegitz, B. C. Novel Electrochemical Sensor Based on Nanodiamonds and Manioc Starch for Detection of Diquat in Environmental Samples. *Diam. Relat. Mater.* **2019**, *98*, 107512. 10.1016/j.diamond.2019.107512.

[56] Senthilkumar, S. T.; Vijaya Sankar, K.; Melo, J. S.; Gedanken, A.; Kalai Selvan, R. *Carbon-Based Hybrid Composites as Advanced Electrodes for Supercapacitors*. In *Advanced Functional Materials*; Wiley: New York, **2015**.10.1002/9781118998977.ch9.

[57] Laurila, T.; Sainio, S.; Caro, M. Hybrid Carbon Based Nanomaterials for Electrochemical Detection of Biomolecules. *Prog. Mater. Sci.* **2017**, *88*, 499–594. 10.1016/j.pmatsci.2017.04.012.

[58] Goodilin, E. A.; Xia, G.; Savilov, S.; Sillanpää mikaetapiosillanpaa, M.; Pavel Krivoshapkin, duytaneduvn, V.; Navrotskaya, A. G.; Aleksandrova, D. D.; Krivoshapkina, E. F.; Sillanpää, M.; Krivoshapkin, P. V. Hybrid Materials Based on Carbon Nanotubes and Nanofibers for Environmental Applications. *Front. Chem.* **2020**, *1*, 546.10.3389/fchem.2020.00546.

[59] Gowda, J. I.; Hanabaratti, R. M.; Tuwar, S. M. MWCNT Modified Glassy Carbon Electrode in Presence of Cationic Surfactant for the Electro-Analysis of Paclitaxel. *Res. Chem.* **2021**, *3*, 100243. 10.1016/j.rechem.2021.100243.

[60] Sharma, T. S. K.; Hwa, K. Y. Architecting Hierarchal $Zn_3V_2O_8$/P-RGO Nanostructure: Electrochemical Determination of Anti-Viral Drug Azithromycin in Biological Samples Using SPCE. *Chem. Eng. J.* **2022**, *439*, 135591. 10.1016/j.cej.2022.135591.

[61] Santhosh, A. S.; Sandeep, S.; James Bound, D.; Nandini, S.; Nalini, S.; Suresh, G. S.; Swamy, N. K.; Rajabathar, J. R.; Selvaraj, A. A Multianalyte Electrochemical Sensor Based on Cellulose Fibers with Silver Nanoparticles Composite as an Innovative Nano-Framework for the Simultaneous Determination of Ascorbic Acid, Dopamine and Paracetamol. *Surf. Interfaces* **2021**, *26*, 101377. 10.1016/j.surfin.2021.101377.

[62] Manjula, N.; Chen, T.-W.; Chen, S.-M.; Yu, J.; Hao, Q.; Lei, W. One Step Construction of Crystal Rod like Bi_2O_3/ZnO Nanocomposite for Voltammetry Determination of Isoprenaline in Pharmaceutical and Urine Sample. *Microchem. J.* **2022**, *172*, 106894. 10.1016/j.microc.2021.106894.

[63] Duan, D.; Lu, H.; Li, L.; Ding, Y.; Ma, G. A Molecularly Imprinted Electrochemical Sensors Based on Bamboo-like Carbon Nanotubes Loaded with Nickel Nanoclusters for Highly Selective Detection of Cortisol. *Microchem. J.* **2022**, *175*, 107231. 10.1016/j.microc.2022.107231.

[64] Ghalkhani, M.; Sohouli, E. Synthesis of the Decorated Carbon Nano Onions with Aminated MCM-41/Fe_3O_4 NPs: Morphology and Electrochemical Sensing Performance for Methotrexate Analysis. *Microporous Mesoporous Mater.* **2022**, *331*, 111658. 10.1016/j.micromeso.2021.111658.

[65] Mahmoudi-Moghaddam, H.; Garkani-Nejad, Z. Development of the Electrochemical Biosensor for Determination of Antibiotic Drug Isoniazid Using Ds-DNA/Carbon/La^{3+}/CuO/CPE. *Meas. J. Int. Meas. Confed.* **2022**, *189*, 110580. 10.1016/j.measurement.2021.110580.

[66] Yin, Z.; Ji, Z.; Bloom, B. P.; Jayapalan, A.; Liu, M.; Zeng, X.; Waldeck, D. H.; Wei, J. Manipulating Cobalt Oxide on N-Doped Aligned Electrospun Carbon Nanofibers towards Instant Electrochemical Detection of Dopamine Secreted by Living Cells. *Appl. Surf. Sci.* **2022**, *577*, 151912. 10.1016/j.apsusc.2021.151912.

[67] Foroughi, M. M.; Jahani, S.; Aramesh-Boroujeni, Z.; Vakili Fathabadi, M.; Hashemipour Rafsanjani, H.; Rostaminasab Dolatabad, M. Template-Free Synthesis of ZnO/Fe_3O_4/Carbon Magnetic Nanocomposite: Nanotubes with Hexagonal Cross Sections and Their Electrocatalytic Property for Simultaneous Determination of Oxymorphone and Heroin. *Microchem. J.* **2021**, *170*, 106679. 10.1016/j.microc.2021.106679.

[68] Materón, E. M.; Wong, A.; Freitas, T. A.; Faria, R. C.; Oliveira, O. N. A Sensitive Electrochemical Detection of Metronidazole in Synthetic Serum and Urine Samples Using Low-Cost Screen-Printed Electrodes Modified with Reduced Graphene Oxide and C60. *J. Pharm. Anal.* **2021**, *11*, 646–652. 10.1016/j.jpha.2021.03.004.

[69] Yang, J.; He, D.; Zhang, N.; Hu, C. Disposable Carbon Nanotube-Based Antifouling Electrochemical Sensors for Detection of Morphine in Unprocessed Coffee and Milk. *J. Electroanal. Chem.* **2022**, *905*, 115997. 10.1016/j.jelechem.2021.115997.

[70] Bavandpour, R.; Rajabi, M.; Asghari, A. Electrochemical Determination of Epirubicin in the Presence of Topotecan as Essential Anti-Cancer Compounds Using Paste Electrode Amplified with Pt/SWCNT Nanocomposite and a Deep Eutectic Solvent. *Chemosphere* **2022**, *289*, 133060. 10.1016/j.chemosphere.2021.133060.

[71] Sudha, K.; Elangovan, A.; Senthilkumar, S.; Jeevika, A.; Arivazhagan, G. Electrocatalytic Reduction of Nitrofurantoin in Biological Sample Based on Assembly of ScMo Anchored F-MCNNcs Modified GCE. *Microchem. J.* **2022**, *172*, 106943. 10.1016/j.microc.2021.106943.

[72] Monsef, R.; Salavati-Niasari, M. Electrochemical Sensor Based on a Chitosan-Molybdenum Vanadate Nanocomposite for Detection of Hydroxychloroquine in Biological Samples. *J. Colloid Interface Sci.* **2022**, *613*, 1–14. 10.1016/j.jcis.2022.01.039.

[73] Santos, B. G.; Gonçalves, J. M.; Rocha, D. P.; Higino, G. S.; Yadav, T. P.; Pedrotti, J. J.; Ajayan, P. M.; Angnes, L. Electrochemical Sensor for Isoniazid Detection by Using a WS_2/CNTs Nanocomposite. *Sens. Actuators Rep.* **2022**, *4*, 100073. 10.1016/j.snr.2021.100073.

[74] Bavandpour, R.; Rajabi, M.; Karimi-Maleh, H.; Asghari, A. Application of Deep Eutectic Solvent and SWCNT-ZrO_2 Nanocomposite as Conductive Mediators for the Fabrication of Simple and Rapid Electrochemical Sensor for Determination of Trace Anti-Migration Drugs. *Microchem. J.* **2021**, *165*, 106141. 10.1016/j.microc.2021.106141.

[75] Teglia, C. M.; Gutierrez, F. A.; Goicoechea, H. C. Natural Deep Eutectic Solvent: A Novelty Alternative as Multi-Walled Carbon Nanotubes Dispersing Agent for the Determination of Paracetamol in Urine. *Talanta* **2022**, *242*, 123290. 10.1016/j.talanta.2022.123290.

[76] Sravani, B.; Kiranmai, S.; Rajasekhara Reddy, G.; Park, J. P.; VeeraManohara Reddy, Y.; Madhavi, G. Highly Sensitive

Detection of Anti-Cancer Drug Based on Bimetallic Reduced Graphene Oxide Nanocomposite. *Chemosphere* **2022**, *287*, 132281. 10.1016/j.chemosphere.2021.132281.

[77] Guan, J.; He, K.; Gunasekaran, S. Self-Assembled Tetrahedral DNA Nanostructures-Based Ultrasensitive Label-Free Detection of Ampicillin. *Talanta* **2022**, *243*, 123292. 10.1016/j.talanta.2022.123292.

[78] Riahifar, V.; Haghnazari, N.; Keshavarzi, F.; Ahmadi, E. A Sensitive Voltammetric Sensor for Methamphetamine Determination Based on Modified Glassy Carbon Electrode Using Fe_3O_4@Poly Pyrrole Core-Shell and Graphene Oxide. *Microchem. J.* **2021**, *170*, 106748. 10.1016/j.microc.2021.106748.

[79] Mathad, A. S.; Seetharamappa, J.; Kalanur, S. S. *β*-Cyclodextrin Anchored Neem Carbon Dots for Enhanced Electrochemical Sensing Performance of an Anticancer Drug, Lapatinib via Host-Guest Inclusion. *J. Mol. Liq.* **2022**, *350*, 118582. 10.1016/j.molliq.2022.118582.

[80] Zhang, Z.; Yang, M.; Wu, X.; Dong, S.; Zhu, N.; Gyimah, E.; Wang, K.; Li, Y. A Competitive Immunosensor for Ultrasensitive Detection of Sulphonamides from Environmental Waters Using Silver Nanoparticles Decorated Single-Walled Carbon Nanohorns as Labels. *Chemosphere* **2019**, *225*, 282–287. 10.1016/j.chemosphere.2019.03.033.

[81] Saylakcı , R.; Incebay, H. An Electrochemical Platform of Tannic Acid and Carbon Nanotubes for the Sensitive Determination of the Antipsychotic Medication Clozapine in Pharmaceutical and Biological Samples. *J. Electroanal. Chem.* **2021**, *898*, 115638. 10.1016/j.jelechem.2021.115638.

[82] Li, Y.; Shen, Y.; Zhang, Y.; Zeng, T.; Wan, Q.; Lai, G.; Yang, N. A UiO-66-NH_2/Carbon Nanotube Nanocomposite for Simultaneous Sensing of Dopamine and Acetaminophen. *Anal. Chim. Acta* **2021**, *1158*, 338419. 10.1016/j.aca.2021.338419.

[83] Wong, A.; Riojas, A. C.; Baena-Moncada, A. M.; Sotomayor, M. D. P. T. A New Electrochemical Platform Based on Carbon Black Paste Electrode Modified with α-Cyclodextrin and Hierarchical Porous Carbon Used for the Simultaneous Determination of Dipyrone and Codeine. *Microchem. J.* **2021**, *164*, 106032. 10.1016/j.microc.2021.106032.

[84] Madej, M.; Fendrych, K.; Porada, R.; Flacha, M.; Kochana, J.; Baś, B. Application of Fe(III)-Exchanged Clinoptilolite/Graphite Nanocomposite for Electrochemical Sensing of Amitriptyline. *Microchem. J.* **2021**, *160*, 105648. 10.1016/j.microc.2020.105648.

[85] Scremin, J.; Olean-Oliveira, A.; Salamanca-Neto, C. A. R.; Ceravolo, G. S.; Dekker, R. F. H.; Barbosa-Dekker, A. M.; Banks, C. E.; Teixeira, M. F. S.; Sartori, E. R. Application of Botryosphaeran as a Carbon Black Adherent on a Glassy Carbon Electrode for the Electrochemical Determination of Cyclobenzaprine. *Electrochim. Acta* **2021**, *379*, 138176. 10.1016/j.electacta.2021.138176.

[86] Dash, S. R.; Bag, S. S.; Golder, A. K. Bio-Inspired PtNPs/Graphene Nanocomposite Based Electrocatalytic Sensing of Metabolites of Dipyrone. *Anal. Chim. Acta* **2021**, *1167*, 338562. 10.1016/j.aca.2021.338562.

[87] Rajaji, U.; Chinnapaiyan, S.; Chen, S. M.; Mani, G.; Alothman, A. A.; Alshgari, R. A. Bismuth Telluride Decorated on Graphitic Carbon Nitrides Based Binary Nanosheets: Its Application in Electrochemical Determination of Salbutamol (Feed Additive) in Meat Samples. *J. Hazard Mater.* **2021**, *413*, 125265. 10.1016/j.jhazmat.2021.125265.[PMC][33588330.

[88] Umesh, N. M.; Antolin Jesila, J.; Wang, S. F.; Govindasamy, M.; Alshgari, R. A.; Ouladsmane, M.; Asharani, I. V. Fabrication of Highly Sensitive Anticancer Drug Sensor Based on Heterostructured ZnO-Co_3O_4 Capped on Carbon Nitride Nanomaterials. *Microchem. J.* **2021**, *167*, 106244. 10.1016/j.microc.2021.106244.

[89] Duan, Y.; Wang, A.; Ding, Y.; Li, L.; Duan, D.; Lin, J.; Yu, C.; Liu, J. Fabrication of Poly-Sulfosalicylic Acid Film Decorated Pure Carbon Fiber as Electrochemical Sensing Platform for Detection of Theophylline. *J. Pharm. Biomed. Anal.* **2021**, *192*, 113663. 10.1016/j.jpba.2020.113663.[PMC][33053505.

[90] Khorablou, Z.; Shahdost-Fard, F.; Razmi, H. Voltammetric Determination of Pethidine in Biofluids at a Carbon Cloth Electrode Modified by Carbon Selenide Nanofilm. *Talanta* **2022**, *239*, 123131. 10.1016/j.talanta.2021.123131.

[91] Nataraj, N.; Chen, S. M. An Electrochemical Assay for the Detection of Nitrofurantoin Based on Bismuth Titanate Enclosed Carbon Nanofiber in Environmental and Biological Samples. *J. Electroanal. Chem.* **2021**, *887*, 115152. 10.1016/j.jelechem.2021.115152.

[92] Karuppiah, C.; Venkatesh, K.; Hsu, L. F.; Arunachalam, P.; Yang, C. C.; Ramaraj, S. K.; Ramalingam, R. J.; Arokiyaraj, S. A.; Al-Lohedan, H. An Improving Aqueous Dispersion of Polydopamine Functionalized Vapor Grown Carbon Fiber for the Effective Sensing Electrode Fabrication to Chloramphenicol Drug Detection in Food Samples. *Microchem. J.* **2021**, *170*, 106675. 10.1016/j.microc.2021.106675.

[93] Fan, L.; Xin, Y.; Xu, Y.; Zhang, X.; Cheng, X.; Liu, L.; Song, H.; Gao, S.; Huo, L. Carbon Nanospheres Modified with WO_2-Na_xWO_3 Nanoparticles for Highly Sensitive Electrochemical Detection of Dopamine. *Microchem. J.* **2021**, *170*, 106770. 10.1016/j.microc.2021.106770.

[94] Đurđić, S.; Stanković, V.; Vlahović, F.; Ognjanović, M.; Kalcher, K.; Manojlović, D.; Mutić, J.; Stanković, D. M. Carboxylated Single-Wall Carbon Nanotubes Decorated with SiO_2 Coated-Nd_2O_3 Nanoparticles as an Electrochemical Sensor for L-DOPA Detection. *Microchem. J.* **2021**, *168*, 106416. 10.1016/j.microc.2021.106416.

[95] Vinothkumar, V.; Kesavan, G.; Chen, S. M. Graphitic Carbon Nitride Nanosheets Incorporated with Polypyrrole Nanocomposite: A Sensitive Metal-Free Electrocatalyst for Determination of Antibiotic Drug Nitrofurantoin. *Colloids Surf. A Physicochem. Eng. Asp.* **2021**, *629*, 127433. 10.1016/j.colsurfa.2021.127433.

[96] Shanbhag, M. M.; Shetti, N. P.; Malode, S. J.; Veerapur, R. S.; Reddy, K. R. Cholesterol Intercalated 2D Graphene Oxide Sheets Fabricated Sensor for Voltammetric Analysis of Theophylline. *FlatChem* **2021**, *28*, 100255. 10.1016/j.flatc.2021.100255.

[97] Muthukutty, B.; Vivekanandan, A. K.; Chen, S. M.; Sivakumar, M.; Chen, S. H. Designing Hybrid Barium Tungstate on Functionalized Carbon Black as Electrode Modifier for Low Potential Detection of Antihistamine Drug Promethazine Hydrochloride. *Compos. B Eng.* **2021**, *215*, 108789. 10.1016/j.compositesb.2021.108789.

[98] Carvalho, C. L. C.; de Andrade Rodrigues, G.; Magalhães, J. L.; de Sousa Luz, R. A.; da Silva, E. T. S. G.; Cantanhêde, W. Effect of Ibuprofen on the Electrochemical Properties of Prussian Blue/Single-Walled Carbon Nanotubes Nanocomposite Modified Electrode. *Surf. Interfaces* **2021**, *25*, 101276. 10.1016/j.surfin.2021.101276.

[99] Chen, S.; Zhang, M.; Zhang, H.; Yan, X.; Xie, J.; Qi, J.; Sun, X.; Li, J. Dicyandiamide-Assisted HKUST-1 Derived Cu/N-Doped Porous Carbon Nanoarchitecture for Electrochemical Detection of Acetaminophen. *Environ. Res.* **2021**, *201*, 111500. 10.1016/j.envres.2021.111500.

[100] Liu, Y.; Yao, S.; Hu, G.; Ye, Y.; Wang, H. In-Situ Electrochemical Co-Deposition of Bimetallic CuCo Nanoparticles on Cubic Mesoporous Carbon for Ultrasensitive Electrochemical Sensing of Cyadox. *Electrochim. Acta* **2021**, *380*, 138128. 10.1016/j.electacta.2021.138128.

[101] Sudha, K.; Elangovan, A.; Jeevika, A.; Sharmila, C.; Arivazhagan, G.; Kalimuthu, P. Electroanalytical Detection of Amlodipine in Urine and Pharmaceutical Samples Using Ag-$Ce_2(WO_4)$3@CNF Nanocomposite-Modified Glassy Carbon Electrode. *Microchem. J.* **2021**, *165*, 106138. 10.1016/j.microc.2021.106138.

[102] Carvalho, J. H. S.; Gogola, J. L.; Bergamini, M. F.; Marcolino-Junior, L. H.; Janegitz, B. C. Disposable and Low-Cost Lab-Made Screen-Printed Electrodes for Voltammetric Determination of L-Dopa. *Sens. Actuators Rep.* **2021**, *3*, 100056. 10.1016/j.snr.2021.100056.

[103] Akbari Hasanjani, H. R.; Zarei, K. DNA/Au-Pt Bimetallic Nanoparticles/Graphene Oxide-Chitosan Composites Modified Pencil Graphite Electrode Used as an Electrochemical Biosensor for Sub-Picomolar Detection of Anti-HIV Drug Zidovudine. *Microchem. J.* **2021**, *164*, 106005. 10.1016/j.microc.2021.106005.

[104] Sriram, B.; Baby, J. N.; Hsu, Y. F.; Wang, S. F.; George, M.; Veerakumar, P.; Lin, K. C. Electrochemical Sensor-Based Barium Zirconate on Sulphur-Doped Graphitic Carbon Nitride for the Simultaneous Determination of Nitrofurantoin (Antibacterial Agent) and Nilutamide (Anticancer Drug). *J. Electroanal. Chem.* **2021**, *901*, 115782. 10.1016/j.jelechem.2021.115782.

[105] Hatamluyi, B.; Sadeghian, R.; Sany, S. B. T.; Alipourfard, I.; Rezayi, M. Dual-Signaling Electrochemical Ratiometric Strategy for Simultaneous Quantification of Anticancer Drugs. *Talanta* **2021**, *234*, 122662. 10.1016/j.talanta.2021.122662.

[106] Eldin, G. M. G.; Khalifa, M. E.; Munshi, A. M.; Aldawsari, A. M.; El-Metwaly, N. M. Determining Nadifloxacin in Pharmaceutical Formulations Using Novel Differential Pulse Voltammetric Approach. *Microchem. J.* **2021**, *163*, 105942. 10.1016/j.microc.2021.105942.

[107] Keerthana, S.; Rajapriya, A.; Amirthapandian, S.; Viswanathan, C.; Ponpandian, N. WS_2 Hierarchical Nanoflowers on RGO with Enhanced Electrochemical Performance for Sensitive and Selective Detection of Mesalazine in Real Sample Analysis. *Colloids Surf. A Physicochem. Eng. Asp.* **2021**, *618*, 126452. 10.1016/j.colsurfa.2021.126452.

[108] Wei, X.; Li, L.; Lian, H.; Cao, X.; Liu, B. Grain-like Chiral Metal-Organic Framework/Multi-Walled Carbon Nanotube Composited Electrosensing Interface for Enantiorecognition of Tryptophan. *J. Electroanal. Chem.* **2021**, *886*, 115108. 10.1016/j.jelechem.2021.115108.

[109] Singh, G.; Kushwaha, A.; Sharma, M. Electrochemistry of $Gd_2(MoO_4)$3-RGO Nanocomposite for Highly Sensitive and Selective Detection of Hazardous Hydroquinone and Chloramphenicol. *J. Environ. Chem. Eng.* **2021**, *9*, 106713. 10.1016/j.jece.2021.106713.

[110] Rajaji, U.; Chinnapaiyan, S.; Chen, T. W.; Chen, S. M.; Mani, G.; Mani, V.; Ali, M. A.; Al-Hemaid, F. M. A.; El-Shikh, M. S. Rational Construction of Novel Strontium Hexaferrite Decorated Graphitic Carbon Nitrides for Highly Sensitive Detection of Neurotoxic Organophosphate Pesticide in Fruits. *Electrochim. Acta* **2021**, *371*, 137756. 10.1016/j.electacta.2021.137756.

[111] Yang, X.; Zhao, P.; Xie, Z.; Ni, M.; Wang, C.; Yang, P.; Xie, Y.; Fei, J. Selective Determination of Epinephrine Using Electrochemical Sensor Based on Ordered Mesoporous Carbon/Nickel Oxide Nanocomposite. *Talanta* **2021**, *233*, 122545. 10.1016/j.talanta.2021.122545.

[112] Guo, L.; Hao, L.; Zhang, Y.; Yang, X.; Wang, Q.; Wang, Z.; Wang, C. Metal-Organic Framework Precursors Derived Ni-Doping Porous Carbon Spheres for Sensitive Electrochemical Detection of Acetaminophen. *Talanta* **2021**, *228*, 122228. 10.1016/j.talanta.2021.122228.

[113] Jamil, M.; Fatima, B.; Hussain, D.; Chohan, T. A.; Majeed, S.; Imran, M.; Khan, A. A.; Manzoor, S.; Nawaz, R.; Ashiq, M. N.; Najam-Ul-Haq, M. Quantitative Determination of Creatinine from Serum of Prostate Cancer Patients by N-Doped Porous Carbon Antimony (Sb/NPC) Nanoparticles. *Bioelectrochemistry* **2021**, *140*, 107815. 10.1016/j.bioelechem.2021.107815.

[114] Sharifi, J.; Fayazfar, H. Highly Sensitive Determination of Doxorubicin Hydrochloride Antitumor Agent via a Carbon Nanotube/Gold Nanoparticle Based Nanocomposite Biosensor. *Bioelectrochemistry* **2021**, *139*, 107741. 10.1016/j.bioelechem.2021.107741.

[115] Han, H.; Liu, C.; Sha, J.; Wang, Y.; Dong, C.; Li, M.; Jiao, T. Ferrocene-Reduced Graphene Oxide-Polyoxometalates Based Ternary Nanocomposites as Electrochemical Detection for Acetaminophen. *Talanta* **2021**, *235*, 122751. 10.1016/j.talanta.2021.122751.

[116] Luo, X.; Chen, L.; Yang, J.; Li, S.; Li, M.; Mo, Q.; Li, Y.; Li, X. Electrochemically Simultaneous Detection of Ascorbic Acid, Sulfite and Oxalic Acid on Pt-Pd Nanoparticles/Chitosan/Nitrogen Doped Graphene Modified Glassy Carbon Electrode: A Method for Drug Quality Control. *Microchem. J.* **2021**, *169*, 106623. 10.1016/j.microc.2021.106623.

[117] Babulal, S. M.; Venkatesh, K.; Chen, S. M.; Ramaraj, S. K.; Yang, C. C. Fe Doped NiO Incorporated Porous Carbon Hybrid Electrocatalyst: A State of the Art Analysis for the Selective Sensing of Acetaminophen in Biological and Pharmaceutical Samples. *J. Alloys Compd.* **2021**, *876*, 160215. 10.1016/j.jallcom.2021.160215.

[118] Sebastian, N.; Yu, W. C.; Hu, Y. C.; Balram, D.; Yu, Y. H. Morphological Evolution of Nanosheets-Stacked Spherical ZnO for Preparation of GO-Zn/ZnO Ternary Nanocomposite: A Novel Electrochemical Platform for Nanomolar Detection of Antihistamine Promethazine Hydrochloride. *J. Alloys Compd.* **2022**, *890*, 161768. 10.1016/j.jallcom.2021.161768.

[119] Agrawal, N.; Savalia, R.; Chatterjee, S. Nanostructured Zinc Oxide Film Amalgamated with Functionalized Carbon Nanotubes for Facile Electrochemical Determination of Nifedipine. *Colloids Surf. B Biointerfaces* **2021**, *201*, 111635. 10.1016/j.colsurfb.2021.111635.[PMC][33647712.

[120] Killedar, L. S.; Shanbhag, M. M.; Shetti, N. P.; Malode, S. J.; Veerapur, R. S.; Raghava Reddy, K. Novel Graphene-Nanoclay Hybrid Electrodes for Electrochemical Determination of Theophylline. *Microchem. J.* **2021**, *165*, 106115. 10.1016/j.microc.2021.106115.

[121] Bilge, S.; Dogan-Topal, B.; Atici, E. B.; Sınağ, A.; Ozkan, S. A. Rod-like CuO Nanoparticles/Waste Masks Carbon Modified Glassy Carbon Electrode as a Voltammetric Nanosensor for the Sensitive Determination of Anti-Cancer Drug Pazopanib in Biological and Pharmaceutical Samples. *Sens. Actuators B Chem.* **2021**, *343*, 130109. 10.1016/j.snb.2021.130109.

[122] Balram, D.; Lian, K. Y.; Sebastian, N.; Rasana, N. Surface Functionalization of CNTs with Amine Group and Decoration of Begonia-like ZnO for Detection of Antipyretic Drug Acetaminophen. *Appl. Surf. Sci.* **2021**, *559*, 149981. 10.1016/j.apsusc.2021.149981.

[123] Govindasamy, M.; Wang, S. F.; Almahri, A.; Rajaji, U. Effects of Sonochemical Approach and Induced Contraction of Core–Shell Bismuth Sulfide/Graphitic Carbon Nitride as an Efficient Electrode Materials for Electrocatalytic Detection of Antibiotic Drug in Foodstuffs. *Ultrason. Sonochem.* **2021**, *72*, 105445. 10.1016/j.ultsonch.2020.105445.

[124] Gadhari, N. S.; Gholave, J. V.; Patil, S. S.; Patil, V. R.; Upadhyay, S. S. Enantioselective High Performance New Solid Contact Ion-Selective Electrode Potentiometric Sensor Based on Sulphated γ-Cyclodextrin-Carbon Nanofiber Composite for Determination of Multichiral Drug Moxifloxacin. *J. Electroanal. Chem.* **2021**, *882*, 114981. 10.1016/j.jelechem.2021.114981.

[125] Lerdsri, J.; Upan, J.; Jakmunee, J. Nafion Mixed Carbon Nanotube Modified Screen-Printed Carbon Electrode as a Disposable Electrochemical Sensor for Quantification of Amitraz in Honey and Longan Samples. *Electrochim. Acta* **2022**, *410*, 140050. 10.1016/j.electacta.2022.140050.