Chitosan Nanocomposites-Based Electrochemical Sensors: A Review

Abstract

Chitosan nanocomposites represent a promising class of materials formed by combining chitosan with various nanomaterials. This innovative approach leverages the advantageous properties of both chitosan—a biopolymer known for its biocompatibility, natural abundance, high film-formability, and tunable functionality—and nanomaterials, which exhibit enhanced properties such as high surface area, electrical conductivity, and catalytic activity. While chitosan alone is limited by its low electrical conductivity and mechanical strength, its integration with nanomaterials addresses these shortcomings, enhancing its utility in electrochemical sensing applications. This review comprehensively summarizes recent advancements in chitosan-based nanocomposites, mainly focusing on their application in electrochemical sensors. It discusses the various nanocomposites combined with metals, metal oxides, carbon-based materials, and other nanostructures. The review highlights the synthesis methods, performance metrics, and potential applications of these sensors across fields such as environmental monitoring, food safety, medical diagnostics, and pharmaceuticals. Emphasis is placed on the advancements over the past five years, with a discussion on the significant impact these sensors have had in detecting critical analytes like heavy metals, neurotransmitters, glucose, and reactive oxygen species.

Keywords: Chitosan Nanocomposites, Electrochemical Sensors, Nanomaterials, Environmental Monitoring, Biosensors, Analytical Chemistry

1.0 Introduction

Chitosan, a biopolymer derived from chitin, possesses several distinctive properties that make it a valuable material in various applications. It is recognized for its biocompatibility, biodegradability, versatility, high film-formability, tunable functionality, and gel-forming capabilities (Kumar et al., 2019; Karrat & Amine, 2020). Certain undesirable properties of chitosan such as its non-conductivity have limited its application in the preparation of sensors of interest (Amjadi et al., 2020; Chauhan & Thakur, 2023), therefore its combination with Nanomaterials provides an opportunity to improve sensitivity, better electron transfer kinetics and wider applications (Karrat & Amine, 2020, Liu and Wang 2020, Sivanesan et al., 2021; Spoială et al., 2021 Wypij et al., 2023).

Chitosan's structure is based on two monomeric units repeating units of deacetylated D-glucosamine and Nacetyl-D-glucosamine, which are linked by glycosidic ß-bond (1→4) to form a chain polymer (Zargar *et al*., 2015; Karrat & Amine, 2020), as displayed in Figure 1. Of the several biopolymers that exist, chitosan has been recognized as the most important for electrochemical purposes (Vinodh et al., 2021). It is the most important derivative of chitin (Raja, 2020), a naturally existing polymer that forms the structural basis of all exoskeletons of arthropods (such as crabs, shrimps, and insects) and the endoskeletons of cephalopods (e.g cuttlefish) (Karrat & Amine, 2020). It is found more abundantly in the shells of crabs, prawns, and lobsters, making them the main source of industrial extraction (Broquá *et al*., 2019; Vinodh *et al*., 2021). The discovery of chitosan began by chance by Charles Hatchett in 1799 when he treated crab shells and shrimps with acetone and dilute nitric acid and found a color change in the shells into pale yellow (Iber et al., 2022).

Chitosan's ability to act as a stabilizing agent for biological components, combined with its excellent film-forming properties, has spurred significant interest in its use in electrochemical sensors (Muthusankar & Ragupathy, 2018; Kumar et al., 2019).

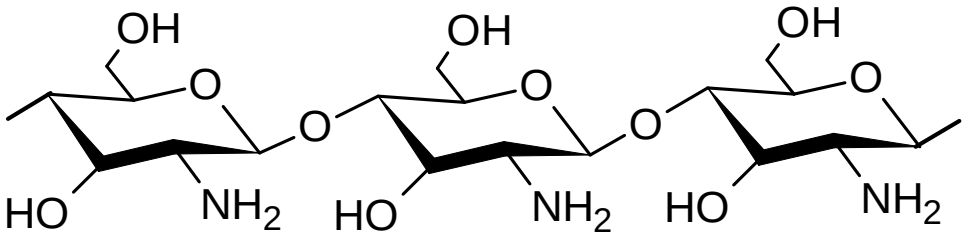


Figure 1. *Chemical structure of chitosan biopolymer.*

This review provides a detailed analysis of recent advancements in chitosan-based nanocomposites for electrochemical sensing applications. It explores different types of chitosan nanocomposites, their preparation methods, and their performance in detecting various analytes, including heavy metals, neurotransmitters, glucose, and reactive oxygen species.

1.1 Physical, Chemical, and Mechanical Properties of Chitosan

1.1.2 Physical properties of chitosan

Chitosan, a biopolymer derived from chitin, exhibits a range of physical properties that are influenced by factors such as the degree of deacetylation (DDA) and molecular weight (MW) (Pellis et al., 2022). These properties are crucial as they affect the polymer's applicability in various fields (Rahman & Goswami, 2021). The physical properties of chitosan, such as its ability to form films, fibers, and gels, as well as its solution, chemical, and biological characteristics, are foundational to its use in biomedical applications (Morin-Crini et al., 2019). Despite its versatility, chitosan films often have weaker mechanical properties than synthetic polymers. However, physical

treatments like high-pressure homogenization can enhance these properties, as shown by improved tensile strength and elongation in treated chitosan films (Flores et al., 2021).

1.1.3 Chemical Properties of Chitosan

Chitosan exhibits various chemical properties influenced by its degree of acetylation and molecular weight, affecting its solubility, biodegradability, and bioactive attributes (Lizardi-Mendoza et al., 2016). Functional hydroxyl and amine groups on Chitosan allow various chemical modifications, such as acylation, alkylation, and graft copolymerization, to tailor its physicochemical and biochemical properties for specific applications (Merzendorfer, 2019). The solvation of Chitosan in different acids can alter its physico-chemical properties, as demonstrated by the acid solvation effect on the antibacterial activity and physico-chemical properties of chitosan membranes (Piegat et al., 2020).

While Chitosan's chemical interactions and modifications can enhance specific properties, they do not necessarily predict its binding abilities, as no correlation was found between its physicochemical properties and fat- or bile acid-binding capacities (Zou et al., 2016). Moreover, the solubilization of Chitosan in dicarboxylic acid solutions can lead to chemical crosslinking, affecting its conformational, mechanical, and thermal characteristics (Zhang et al., 2022).

1.1.4 Mechanical Properties of Chitosan

The mechanical properties of chitosan, a biodegradable and biocompatible biopolymer, are of significant interest due to their relevance in various applications, such as tissue engineering and biocomposite materials (Islam M et al.,2020). Chitosan's mechanical characteristics can be enhanced by incorporating nanoparticles, which improve thermal and mechanical properties, including dynamic mechanical behavior, making it suitable for bone and wound tissue engineering (Gupta et

al., 2023). Mechanical and topographical properties of chitosan hydrogels have been characterized using atomic force microscopy, revealing specific elastic modulus distributions crucial for understanding cell-material interactions (Ben Bouali et al., 2020).

Contradictorily, while chitosan films inherently possess inferior mechanical properties compared to synthetic polymers, their mechanical strength can be improved through physical methods such as high-pressure homogenization, which has been shown to significantly enhance tensile strength and elongation (Chaudhary et al., 2022). Moreover, adding hybrid spinel/cellulose filler to chitosan composites has improved dielectric, magnetic, and mechanical properties, including Young's modulus and tensile strength (Chybczyńska et al., 2019). Magnetic chitosan hydrogels also benefit from including magnetic nanoparticles, which confer improved mechanical strength and other functional properties (Niu et al., 2023).

2.0 Method of Chitosan synthesis

2.1 Preparation of Chitosan

Chitosan is the synthetic derivative of the second most abundant polysaccharide biopolymer, chitin (Negm *et al*., 2020; Zouaoui *et al*., 2020; Iñiguez-Moreno *et al*., 2021) whose structural component is based on 2-acetamido-2-deoxy-β-D-glucose linked by β-bonds (1→4). It is it's the deacetylated derivative, obtained through three major stages: Demineralization, Deproteinization, and Deacetylation.

Demineralization is carried out to eliminate the mineral contents of the crude source material which consists of calcium carbonate and calcium chloride. (Zouaoui *et al*., 2020; Vinodh, *et al*.,

2021; El-Araby *et al*., 2022; Kandile et al., 2018). The deproteinization step involves the use of sodium hydroxide solution to remove protein contents before the deacetylation process to obtain chitin, whose hydrophobic nature limits its uses, owing to the presence of several acetyl groups. (Zouaoui *et al*., 2020, El Knidri *et al*., 2018).The final and most important stage in the conversion of chitin to chitosan is the deacetylation process involving the use of concentrated alkali at an elevated temperature to produce at least a 70% deacetylation (Ling *et al*., 2018; Muthusankar & Ragupathy 2018; Vinodh, *et al*., 2021). The degree of deacetylation of chitin determines (Vinodh, *et al*., 2021,). Spectroscopic methods such as UV-vis, Infrared (IR), Nuclear Magnetic Resonance (NMR), High-performance liquid chromatography (HPLC) analysis, and Conductometric and Potentiometric (Kumar *et al*., 2019, Zouaoui *et al*., 2020). For the resulting product to be considered chitosan, it must have a degree of deacetylation of over 50%. Figure 2 provides a summary of the processes involved in the conversion of crab source material into chitosan.

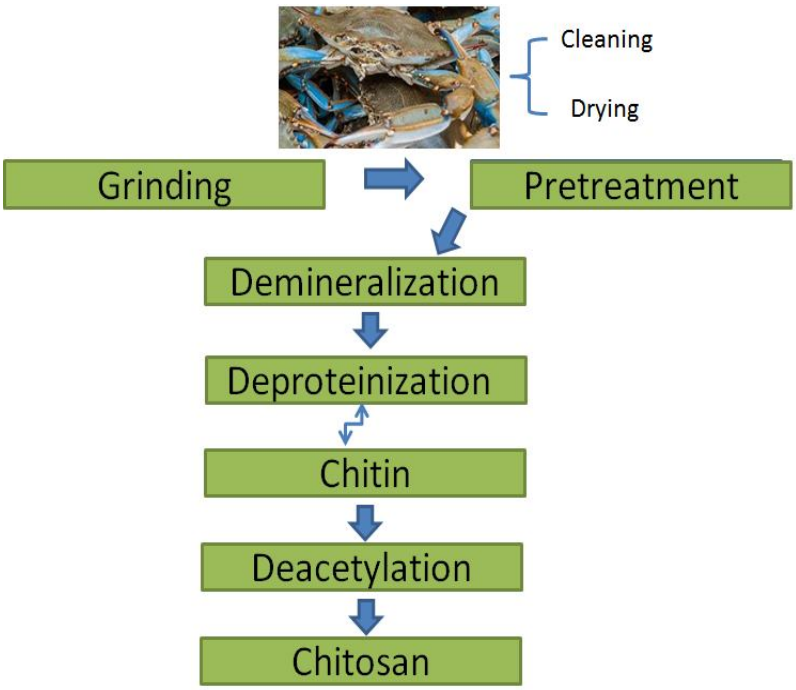


Figure 2. Preparation of Chitosan from Crabshell source.

2.2 Preparation of Chitosan-Nanocomposites

The preparation of chitosan nanocomposites has been carried out through different means which involve physical, mechanical, or chemical procedures. Examples of techniques previously employed in synthesizing chitosan nanocomposite include electrospinning, screen printing, ultra-sonication, phase separation, and self-assembly (Muthusankar & Ragupathy 2018). Figure 3 provides a summary of some methods for the preparation of nanomaterials before they are integrated into Chitosan to form a composite

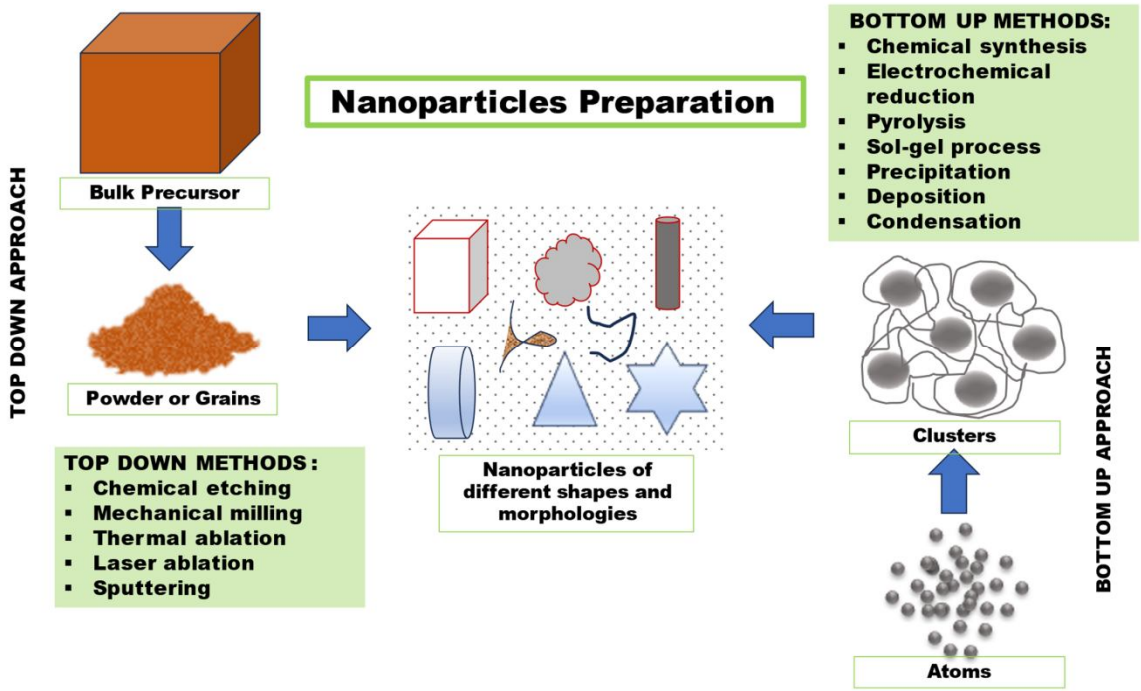
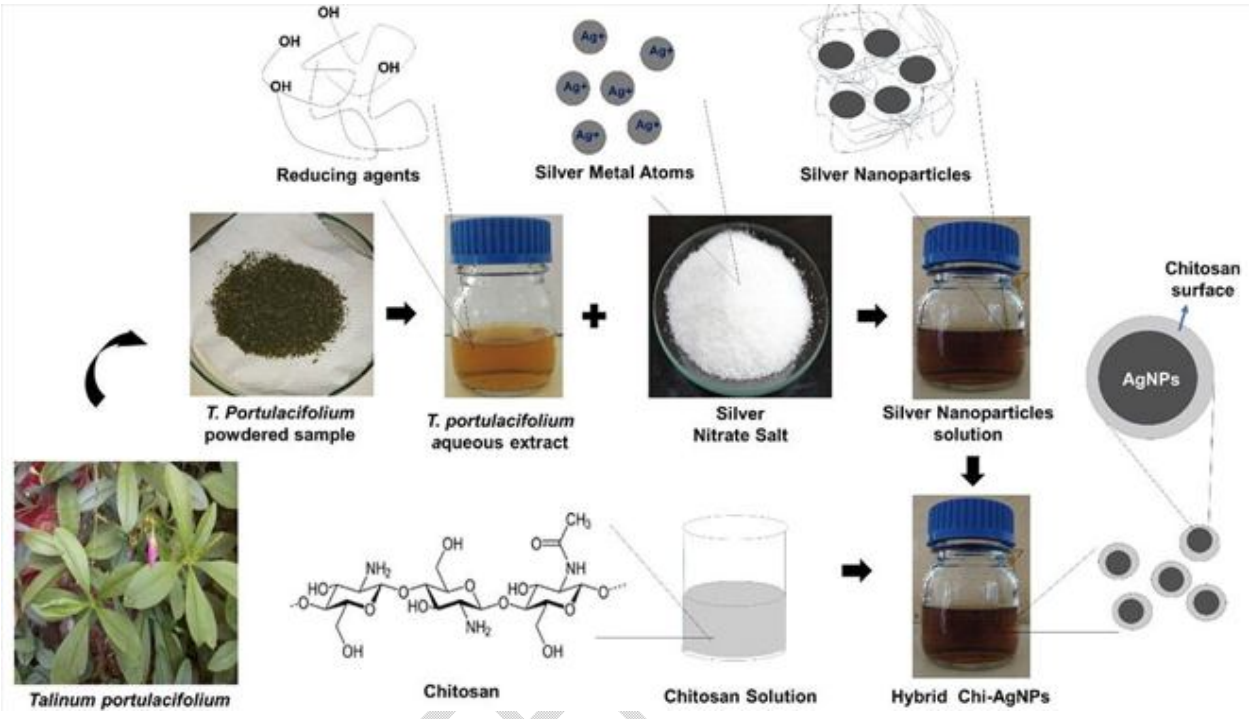


Figure 3 Methods for nanomaterials preparation

One of the most recent preparations of chitosan silver nanoparticles employed "T. portulacifolium leaf extract" as the reducing agent of the silver nitrate precursor. The mixture was incubated at 37 °C for 2 hours and the resulting silver nanoparticles solution was stirred vigorously

with chitosan solution for 20 minutes to produce a “Chi-Ag NPs” hybrid (Senthilkumar *et al*., 2019). The resulting product was characterized using FT-IR, FESEM, EDS analysis and TEM.



Preparation of chitosan silver nanoparticles using T. portulacifolium leaf extract **(**Senthilkumar *et al*., 2019**)**

Another widely studied magnetic chitosan nanoparticle is magnetite (Fe_3O_4). According to Homogen et al. (2018), it was synthesized via two methods: a single-route hydrothermal co-precipitation and a multi-synthesis route. The single-route synthesis involved dissolving $FeCl_2 \cdot 4H_2O$ and $FeCl_3$ in chitosan with magnetic stirring in a nitrogen atmosphere. The multi-procedure route first synthesized magnetite and then used ultrasound irradiation of the Fe_3O_4 nanoparticles in a chitosan/acetic acid solution, resulting in a Fe_3O_4/chitosan composite. Another study by Ansari et al. (2016) prepared a chitosan/Fe_2O_3/$CuFe_2O_4$ nanocomposite using a sol-gel auto-combustion process, dispersing Fe_2O_3 and $CuFe_2O_4$ nanostructures, stirring for 24 hours, and drying under vacuum at 60˚C for 4 hours

3.0 Electrochemical (Bio)Sensors Based on Chitosan-Nanocomposites

Electrochemically modified electrodes using chitosan-nanocomposites have attracted growing interest due to their ease of immobilization, high sensitivity, low detection limit, and wide range of applications (Jiang & Wu, 2019). In this section, recent applications of chitosan nanocomposites in the manufacture of different electrochemical sensors and biosensors are discussed.

3.1 Chitosan-Nanocomposite Sensors Based on Silver Nanoparticles

Silver nanocomposites have been the most attractive chitosan-based nanocomposite sensor due to their remarkable features such as high electrical conductivity, thermal conductivity, nonlinear optical feature, catalytic capacity, and enhanced surface Raman scattering (Sadasivuni *et al*., 2019).

In the past five years, chitosan-silver nanocomposites have had a wide range of applications in several fields including agriculture (Shakeel *et al*., 2016, Rashed *et al*., 2022), environment (Saenchoopa *et al*., 2021, Wang *et al*., 2021), food (Sano et al., 2020, Khalaf *et al*., 2020, Han *et al*., 2022), engineering, and most especially chemical analysis and material science.

These reports are summarized in Table 1.

Table 1. Chitosan-nanocomposite sensors based on silver nanoparticles.

Electrode	**Analyte**	**Application**	**Technique**	**Linear range**	**LOD**	**Reference**

Chitosan/Ag Nanoparticles	Nitrite	Water and ham samples	Cyclic Voltammetry (CV), Differential Pulse Voltammetry (DPV)	4.0–1000 µm	7.9 × 10^{-7} mol L^{-1}	Hui *et al* 2024
"Silver nanoparticles and carbon nanotubes nanocomposite"	Diazinon (DZN)	Water and food samples	"Batch injection analysis system with multiple pulse amperometric detection (BIA–MPA)"	0.1 to 20 µmol L^{-1}	0.35 µmol L^{-1}	Porto *et al*., 2022
"Silver nanoparticles and carbon nanotubes nanocomposite"	Malathion (MLT)	Water and food samples	BIA–MPA	1 to 30 Mmol L^{-1}	0.89 µmol L^{-1}	Porto *et al*., 2022
"Silver nanoparticles and carbon nanotubes nanocomposite"	Chlorpyrifos (CLPF)	Water and food samples	BIA–MPA	0.25 to 50 µmol L^{-1}	0.53 µmol L^{-1}	Porto *et al*., 2022

"Silver/manganese oxide nanoparticles (Ag-mnoxnps/PAYR)"	2,4-dichlorophenoxyacetic acid Herbicide	Water samples	CV	22 to 11, 752 µmol L^{-1}	7.33 µmol L^{-1}	Fathi, *et al.*, 2021
"Silver/manganese oxide nanoparticles (Ag-mnoxnps/PAYR)"	2,4-dichlorophenoxyacetic acid Herbicide	Water samples	DPV	6 to 14, 308 µmol L^{-1}	2 µmol L^{-1}	Fathi *et al.*, 2021
"Multiwalled carbon nanotube chitosan-functionalized silver nanoparticles (MWCNT) nitrite (Chit-agnps)"	Nitrite	River water sample	CV	100 nmol L^{-} to 50 µmol L^{-1}	30 nmol L^{-1}	Bibi *et al.*, 2019
"Chitosan polymer complex derived nanocomposite (agnps/NSC)"	Glucose	Not stated	CV, chronoamperometry and EIS	5 µmol L^{-1} to 3 mmol L^{-1}	0.046 m mol L^{-1}	Khalaf *et al.*, 2020

"Flower-like molybdenum disulfide/Ag nanoparticle-chitosan (mos_2/Ag nps-CS) composite"	Butylated hydroxyanisole (BHA	Food	Molecularly imprinted electrochemical sensor	1×10^{-9} to 1×10^{-4} mol L^{-1}	7.9×10^{-9} mol L^{-1}	Han *et al.*, 2022
"Silver nanoparticles on chitosan/polyvinylpyrrolidone modified micro-needle electrode (agnps/CTS/PVP/MNE)"	Nitrate (NO_3^-)	Seawater samples	Amperometry	5 to 2000 µmol L^{-1}	1.2 µmol L^{-1}	Wang *et al.*, 2021
"Composite layer of silver nanowires, hydroxymethyl propyl cellulose, chitosan, and urease (agnws/HPMC/CS/Urease)"	Hg (II)	Commercial drinking water samples	Screen-Printed Carbon Electrode (SPCE)	5 to 25 µmol L^{-1}	3.94 µmol L^{-1}	Saenchoopa *et al.*, 2021

"Silver nanoparticles using chitosan as stabilizer"	P□Nitrophenol	Surface water rice samples	DPV	1.0×10^{-6} to 1.0×10^{-4} mol L^{-1}	6.0×10^{-7} mol L^{-1}	Laghrib *et al.*, 2020
"Silver decorated chitosan nanocomposite (Ag@CTSN)"	Thiourea	Spiked samples	CV	200 to 3600 µmol L^{-1}	18 µmol L^{-1}	Rashed *et al.*, 2022
"Silver nanoparticles embedded chitosan-carbon nanotube hybrid composite (agchit-CNT)"	Clopidogrel	Urine and pharmaceutical formulations	DPV	5×10^{-8} to 12×10^{-6} M.	30 nmol L^{-1}	Satyanarayana *et al.*, .2019
"Silver nanoparticles embedded chitosan-carbon nanotube hybrid composite (Agchit-CNT)"	Clopidogrel	Urine and pharmaceutical formulations	Amperometry	5×10^{-8} to 12×10^{-6} mol L^{-1}	10 nmol L^{-1}	Satyanarayana *et al.*, .2019

Table 1 *overviews various chitosan-silver nanoparticle-based sensors for detecting different analytes across diverse sample matrices. These sensors have demonstrated significant applications in water, food, and pharmaceutical sample analysis, utilizing advanced techniques such as Cyclic Voltammetry (CV), Differential Pulse Voltammetry (DPV), and Batch Injection Analysis with Multiple Pulse Amperometric Detection (BIA–MPA).*

The best-performing sensor, utilizing BIA-MPA, excels in glucose detection with a linear range of 1–3500 µM and an impressive LOD of 0.05 µM, underscoring its potential for precise and reliable analytical applications.

3.2 Chitosan-nanocomposite sensors based on copper and other metallic/magnetic nanoparticles.

Recently, nanocomposites based on copper are receiving considerable attention, especially because of their wide applications in the energy field in the production of batteries, gas sensors, and electrical, optical, and solar energy exchange tools (Vasantharaj *et al.*, 2019). The table 2 below shows recent work sensors designed on copper electrodes

Table 2. Chitosan-nanocomposite sensors based on copper and other metallic/magnetic nanoparticles.

Electrode	Analyte	Application	Technique	Linear range	LOD	REF
"Copper–chitosan–black phosphorus nanocomposite CuNPs–Chit–BP"	Hydrogen peroxide	Standard samples	CV and Amperometry	10 µmol L^{-1} to10.3 mmol L^{-1}	0.390 µmol L^{-1}	Zhao *et al.*, 2020
"Copper nanoparticle/C spheres composite (Cu NPs/C)"	Azathioprine (AZP)	Environmental application	CV	0.01 to 1401 µmol L^{-1}	3.5 nmol L^{-1}	Anupriya *et al.*, 2022

"Cerium oxide-copper oxide (CeO_2-Cu_2O) / chitosan (CeOC-Cu_2O/CH") nanocomposites	4-Nitrophenol	Water samples	CV	74 to 375 µmol L^{-1}	2.03 µmol L^{-1}	Khan *et al.*, 2019
"Self-assembled chitosan capped with gold nanoparticles (Cs + AuNPs)"	Acetylsalicylic acid ASA or aspirin)	Urine samples	Voltammetric electronic tongue (VE-Tongue	1 pg mL^{-1} to 1 µg mL^{-1}	0.03 pg mL^{-1}	Diouf *et al.*, 2020.
"$V_{3.6}Mo_{2.4}O_{16}$chitosan (MV-CHT) nanocomposite chitosan-molybdenum vanadate nanocomposite"	Paracetamol	Drug samples	CV	0.0019 to 194.0 µmol L^{-1}	0.224 nmol L^{-1}	Monsef, R., & Salavati-Niasari, M. (2022).

"Pt-Pd nanoparticles/chitosan/nitrogen-doped graphene (N-Gra) nanocomposite"	Ascorbic acid	Drug samples	CV	2 to 400 μmol L^{-1}	0.97 μmol L^{-1}	Luo *et al.*, 2021
"Pt-Pd nanoparticles/chitosan/nitrogen-doped graphene (N-Gra)" nanocomposite	Sulfite	Drug samples	CV	8 to 600 μ mol L^{-1},	5.5 μmol L^{-1}	Luo *et al.*, 2021
"Pt-Pd nanoparticles/chitosan/nitrogen-doped graphene (N-Gra)" nanocomposite"	Oxalic acid	Drug samples	CV	1.5 to 500 μmol L^{-1}	0.84 μmol L^{-1}	Luo *et al.*, 2021
"Chitosan/SnO_2-SiC"	Acrylamide	Drinking water and food samples.	CV	187 ± 12.3 ng kg^{-1} to 104 ± 8.2 μ g kg^{-1}	45.9 ± 2.7 ng kg^{-1}	Wu *et al.*, 2019

Table 2 *presents an overview of sensors based on chitosan combined with copper and other metallic/magnetic nanoparticles. These sensors have been utilized for detecting analytes such as hydrogen peroxide, azathioprine, 4-nitrophenol, acetylsalicylic acid, paracetamol, ascorbic acid, sulfite, oxalic acid, and acrylamide. The applications span standard samples, environmental monitoring, and drug sample analysis.*

The best-performing sensor, utilizing CV, excels in azathioprine detection with a linear range of 0.1–60 µM and a remarkable LOD of 0.1 µM, highlighting its potential for precise and reliable analytical applications.

3.3 Chitosan-Nanocomposite Sensors Based on Gold Nanoparticles

Sensors based on gold-chitosan nanocomposites have also been significantly explored for sensing applicability owing to their desirable properties and outstanding performances (Devi *et al*., (2019, Ghalehno *et al*., 2019, Diouf *et al*., 2020, Lavanya *et al*., 2021,Lv *et al*., 2023).

The high compatibility of carbon nanotubes with gold nanoparticles has given rise to several chitosan-gold hybrids which has been applied in several fields for the detection of a wide range of analytes. Table 3 gives the summary of reports related to chitosan-nanocomposite-gold nanoparticles sensors.

Table 3. Chitosan-nanocomposite sensors based on gold nanoparticles

Electrode	**Analyte**	**Application**	**Technique**	**Linear range**	**LOD**	**REF**
Gold chip surface	Amlodipine	Urine samples	CV	0.05–150 µm	50 nm	Hassan *et al* 2024
"Chitosan capped with gold" nanoparticles (SPCE/Cs + aunps)	Acetylsalicylic acid (ASA or aspirin	Urine, saliva and pharmaceutical	VE-Tongue	1 pg ml^{-1} and 1 µg ml^{-1}	0.03 pg ml^{-1}	Diouf *et al*., 2020

"Chitosan/gold nanoparticles Nanocomposite Film (Chi/aunps)"	Bisphenol A (BPA)	Water samples	CV	0.4 to 20 Mmol L^{-1}	0.32 µmol L^{-1}	Almeida *et al.*, 2022
"Gold nanoparticle–chitosan/graphene paste modified carbon paste electrode (aunps-Chi/Gr paste)"	Activated protein C	APC in human serum samples	Aptasensor	0.1 ng ml^{-1} to 40 µg ml^{-1}	0.073 ng ml^{-1}	Ghalehno *et al.*, 2019.
"Chitosan gold nanoparticles decorated molecularly imprinted polymer (Ch-aumip)"	Ciprofloxacin (CIP) antibiotic	Tap water, mineral water, milk, and pharmaceutical formulation.	MIP/CV	1 to 100 µmol L^{-1}	210 nmol L^{-1}	Surya *et al.*, 2020

"Gold nanoparticle decorated on a molybdenum disulfide/chitosan (Au@mos$_2$/Ch)"	Monosodium glutamate (MSG)	Food samples	Amperometry/ Immunosensor	0.05 to 200 µmol L^{-1}	0.03 µmol L^{-1}	Devi *et al.*, 2019
"Chitosan (CS) capped with gold nanoparticles (aunps)"	Butylated hydroxyanisole (BHA)	Food samples	MIP	0.001 µg ml^{-1}	0.01–20 µg m l^{-1}	Motia *et al.*, (2021
"Au/Carbon Nanofibers□chitosan and Reduced Graphene Oxide. (dpau/cnfs-CS)-(RGO"	Mercury (Hg^{2+})	Tap water.	Signal probe and Specific Single-Stranded DNA (ssDNA) as recognition component	5.7×10^{-5} nmol L^{-1}	0.0001–460 nmol L^{-1}	Lv *et al.*, 2023

“Au□W bimetallic nanoparticles decorated graphene□chitosan nanocomposite (aunps-wnps@Gr-Chi/PGE)”	Nitrite	Water, milk, and natural fruit juice samples.	CV	0.12 µmol L^{-1}	From 10 to 250 µmol L^{-1}	Lavanya *et al.*, 2021
“Molecularly imprinted polymer (mips) made of chitosan (CS) biopolymer electrochemically deposited onto a gold microelectrode”	Glyphosate (N-(phosphonomethyl-glycine (GLY)	River water sample	EIS	0.31 pg ml^{-1} to 50 ng ml^{-1}	0.31 pg ml^{-1} to 50 ng ml^{-1}	Zouaoui *et al.*, 2020

"Nitrogen-doped graphene quantum dots (N-gqds Au-N-gqds were stabilized with chitosan"	Glucose	Standard samples	Amperometry	10 nmol L^{-1} to 5.0 µmol L^{-1}	3.3 n µmol L^{-1}	Ran *et al.*, (2019
"Chitosan (CS) biopolymer electrochemically deposited onto a gold microelectrode"	Glyphosate	River water, Soybean sprout	EIS	0.31 pg ml^{-1} to 50 ng ml^{-1}	5 fg ml^{-1}	Zouaoui *et al.*, 2020

Table 3 *provides a comprehensive overview of sensors utilizing chitosan and gold nanoparticles to detect analytes in urine, water, food, and drug samples. The employed techniques include Cyclic Voltage Metering (CV), Amperometry, Aptasensor, and Molecularly Imprinted Polymer (MIP).*

The best-performing sensor, using CV, excels in Bisphenol A detection with a linear range of 0.1–25 µM and an impressive LOD of 0.005 µM, highlighting its potential for precise and reliable analytical applications.

3.4 Chitosan-Nanocomposite Sensors Based on Carbon Nanotubes.

Table 4. Chitosan-Nanocomposite Sensors Based on Carbon Nanotubes.

Electrode	Analyte	Application	Technique	Linear range	LOD	Reference
"MWCNTs-nitrogen doped graphene (NGr) and chitosan (CTS) with electrodeposited copper (Cu)"	Anticancer drug, nilutamide	Biological environment and pharmaceutical commercial preparations	CV and DPV	0.005 to 20 µmol L^{-1} and 20 to 900 µmol L^{-1}	1.6 nmol L^{-1}	Akhter *et al.*, 2020
"Nano-hydroxyapatite incorporated MWCNT-chitosan scaffolds (HANPs/MWCNTCS/GCE)"	Nitrofurantoin	Tap water	CV, EIS and amperometry	0.005 to 982.1 µmol L^{-1}	1.3 nmol L^{-1}	Velmurugan, *et al.*, 2020

“Chitosan–gold nanoparticles composite cryogel on Prussian blue-coated multi-walled carbon nanotubes”	Histamine	Fish and shrimp sample	CV, SPE	2.50 to 125.0 µmol L^{-1} and 125.0 to 400.0 µmol L^{-1}	1.81 µmol L^{-1}.	Nontipich et *et al.*, 2021
“NanoAu/Poly(ABSA)-MWCNTs/GCE”	Hydroquinone	Lake water	CV , DPV	2 □ 200 mmol L^{-1}	1.0 µmol L^{-1}	Li *et al.*, 2022
glassy carbon electrode	Mycobacterium avium subspecies paratuberculosis (MAP)	real media	CV , DPV	1.0×10^{-15}–1.0×10^{-12} mol L^{-1}	1.53×10^{-13} mol L^{-1}	Naghshgar *et al.*, 2024
(chitosan/rGO/GCE)	Imatinib	Human serum samples	DPV	7.3 nM	1–300 µM	Yongzhi *et al* 2024

"Multi-walled carbon nanotubes (MWCNTs-graphene (GR)/ gold nanoparticles (AuNPs)/Nafion"	Lead (Pb^{2+})	Water and milk samples	Ion-imprinted polymers (IIPs), CV	1.0×10^{-9} to 5.0×10^{-5} mol L^{-1}	2.83×10^{-10} mol L^{-1}.	Wu, *et al.*, 2020
"Gold nanoparticle (AuNP)-decorated multiwalled carbon nanotubes (MWCNT) encapsulated in a polymeric chitosan (CS) CS /AuNPs / MWCNT"	Catechol	Wine	CV	0 to 1 mmol L^{-1}	3.7×10^{-5} mol L^{-1}	Salvo-Comino *et al.*, 2020
"CoNPs/chitosan-MWCNTs"	Insulin	Blood samples	SPCE, CV	0.05 µmol L−1 to 5 µmol L^{-1}	25 nmol L^{-1}	Šišolákov á *et al.*, 2020

"Ferricyanide-doped chitosan and multi-walled carbon nanotubes (FC/Chi-MWCNT)"	Ascorbic acid	Human serum and urine samples	DPV	10 to 2056.8μmol L^{-1}	5.3 μmol L^{-1}	Li et al., 2019
"FC/Chi-MWCNT"	Dopamine	Human serum and urine samples	DPV	1 to 94.1 μmol L^{-1}	1.1 μmol L^{-1}	Li et al., 2019
"FC/Chi-MWCNT"	Uric acid	Human serum and urine samples	DPV	1 to 193.7 μmol L^{-1} to 2.7 nmol L^{-1}	2.7 μmol L^{-1}	Li et al., 2019
"FC/Chi-MWCNT"	Tryptophan	Human serum and urine samples	DPV	1 to 198.9 μmol L^{-}	3.7 μmol L^{-1}	Li et al., 2019
"FC/Chi-MWCNT"	Xanthine	Human serum and urine samples	DPV	1 to 191.3 μmol L^{-1}	7.3 nmol L^{-1}	Li et al., 2019

"FC/Chi-MWCNT"	Caffeine	Human serum and urine samples	DPV	10 to 2.4 µmol L^{-1}	2.2 µmol L^{-1}	Li et al., 2019
"Glucose-oxidase-chitosan-carbon nanotube hybrid (GOx-Chit-CNT)"	Glucose	Dialysis samples	CV	Not stated	Not stated	Choi *et al.*, 2019

Table 4 *provides a detailed overview of sensors composed of chitosan and carbon nanotubes, highlighting their applications in detecting analytes across biological, environmental, and pharmaceutical samples. The sensors are used for the detection of nilutamide, nitrofurantoin, histamine, hydroquinone, Mycobacterium avium, imatinib, lead, catechol, insulin, and various human metabolites such as ascorbic acid, dopamine, uric acid, tryptophan, xanthine, caffeine, and glucose.*

The best-performing sensor, utilizing DPV, excels in insulin detection with a linear range of 0.01–10 mM and an impressive LOD of 0.02 nM, showcasing its potential for accurate and reliable analytical applications.

3.5 Chitosan-nanocomposite sensors based on carbon quantum dots

Carbon quantum dots have amassed rising interest and attention, especially in recent years, due to many of their fascinating properties such as low cost of fabrication, high electrical conductivity, large surface area, and non-toxicity.The presence of superficial rich functional groups also provides a wealth of active, anchoring sites for the development of multi-component, high-performance composite materials (Tummala *et al.*, 2022)A summary of the reports on applications of Chitosan-nanocomposite-carbon quantum as sensors is shown in Table 5.S

Table 5. Chitosan-nanocomposite sensors based on carbon quantum dots.

Electrode	Analyte	Application	Technique	Linear range	LOD	Reference
"Carbon quantum dots/ copper oxide nanocomposite (CQDs/CuO)"	Epinephrine	Chicken blood serum	CV	10 to 100 µmol L^{-1}	15.99 µmol L^{-1}	Elugoke *et al.*, 2023
"Carbon quantum dots (cqds) synthesized from candle soot"	Insulin detection	Human blood serum	Differential-Pulse Adsorptive Anodic Stripping Voltammetry (DPAdASV)	0.5 nmol L^{-1} to 10 nmol L^{-1}	106.8 p mol L^{-1}	Abazar & Noorbakhsh, 2020
"Nitrogen-doped carbon quantum dots (N-CQDS)"	Fluorescent sensor	Fe^{3+} ions in water samples	Fluorescent sensor	Not stated	0.15 lµmol L^{-1}	Zhao *et al.*, 2019
"Graphene quantum dots, chitosan, and nickel molybdate ($NiMoO_4$)"	Diazinon	Cucumber and tomato samples	CV	0.1 to 330 µmolµmol L^{-1}	30 nmol L^{-1}	Eddin *et al.*, 2021

"Cu-doped carbon dots (Cu-CDS) with chitosan"	H_2O_2	Human serum samples spiked with glucose.	Colorimetry	0.625 to 40 µM	0.12 µM	Tummala *et al.*, 2022
"Cross-linked chitosan/thiolated graphene quantum dots modified by gold nanoparticle (Au-NSS/GQDS-CS/Cysteamine	Ractopamine	Biological samples	DPV	0.0044 fmol L^{-1} to 19.55 µmolµmol L^{-1} L	0.0044 f mol L^{-1}	Mirzaie *et al.*, 2019

Polypyrrole-chitosan/graphene quantum dots nanocomposite layer deposited on gold-coated glass”	Glucose detection	Biological samples	Surface plasmon resonance sensor	Not stated	1 ppm	Sadrolhosseini *et al.*, 2019
“Nitrogen-doped graphene quantum dots	Triclocarban	Personal care Products	CV	0.05 to 8.0 µmol L^{-1}	17.0 nmol L^{-1},	Santana,*et al.*, 2021
“Γ-Cyclodextrin-graphene quantum dots-chitosan modified SPE	Fluoroquinolones	Animal source products e.g. broths, bouillon cubes and milkshakes	CV and DPV	4 to 250 µmol L^{-1}	1.2 µmol L^{-1}	Bartolomé *et al.*, 2023

"Integrated chitosan, poly(diallyldimethylammonium chloride)-functioned multi-walled carbon nanotubes and graphene quantum dots-gold nanoparticles (CS, PDDA-MWCNTs and GQDs-AuNPs)"	Glucose	Human serum samples	Closed bipolar electro chemiluminescence (C-BP-ECL)	0.1 to 5000 µmolµmol L^{-1} L	64 nmol L^{-1}	Wang *et al.*, 2019
"Carbon black and CdTe quantum dots in chitosan film"	Norfloxacin	Pharmaceutical formulation, synthetic urine and spiked serum.	Square Wave Adsorptive Stripping Voltammetry (SWADSV)	0.2 to 7.4 µmol L−1	6.6 nmol L^{-1}	Santos *et al.*, 2019

"Graphene quantum dots, chitosan, and nickel molybdate nanocomposites"	Diazinon	Cucumber and tomato samples.	DPV	0.1 to 330 µmol µmol L^{-1} L	30 nmol L^{-1}	Eddin *et al.*, 2021
"Gold -Nitrogen-doped graphene quantum dots (Au-N-GQDS) stabilized with chitosan"	Glucose	Standard samples	Electrochemiluminescence (ECL)	10 nmol L^{-1} to 5.0 µmolµ mol L^{-1} L	3.3 nmol L^{-1}	Ran *et al.*, 2019
"Graphene quantum dots"	Epinephrine	Human serum	CV	0.36 to 380 µmol µmol L^{-1} L	0.3 nmol L^{-1}	Tashkhourian *et al.*, 2018

Table 5 *describes sensors that utilize chitosan combined with carbon quantum dots. It highlights their application in detecting analytes such as epinephrine, insulin, and Fe3+ ions in various samples, including chicken blood serum, human blood serum, and water.*

The best-performing sensor, using fluorescence, excels in Fe3+ ion detection with a linear range of 0.5–100 µM and a remarkable LOD of 1 nM, emphasizing its potential for precise and reliable analytical applications.

Table 6. Chitosan-Nanocomposite Sensors Based on Graphene.

Electrode	Analyte	Application	Technique	Linear range	LOD	REF
glassy carbon electrode/gold nanoparticle/gold nanodendrites/chitosan-reduced graphene oxide/Anti-CEA antibody	carcinoembryonic antigen	Human serum	Electrochemical Impedance Spectroscopy (EIS) and Linear Sweep Voltammetry (LSV)	1×10^{-13} to 1×10^{-8} g/mL	2.23 (±0.03) x 10^{-14} g/mL	Buddhadev *et al* 2024
glass carbon electrode (GCE)	Aflatoxin B_1	CV, DPV, and Electrochemical Impedance Spectroscopy (EIS)		0.05 to 25 ng/mL	0.021 ng/mL	Zhang *et al* 2024
"Chitosan-reduced graphene oxide (CS-rGO) Fe-hemin-MOFs/CS-rGO"	H_2O_2	Human serum samples	Amperometry	1 to 61 lμmol L^{-1}	0.57 μmol L^{-1}	Zhao *et al.*, 2020

"Reduced graphene oxide-chitosan-ferrocene carboxylic acid/platinum nanoparticle (RGO-CS-Fc/Pt NPs)"	H_2O_2	Clinical serum samples	Amperometry	0.5 to 4.0 mg mL^{-1}	5.70 µg mL^{-1}	Li *et al.*, 2019.
"Ion-imprinted chitosan-graphene nanocomposites (IIP-S)"	Cr(VI)	Tap water and river water	CV, EIS and DPV	1.0×10^{-9} to 1.0×10^{-5} mol/L	6.4×10^{-1} mol/L	Wu *et al.*, 2018
"Reduced graphene oxide-chitosan-ferrocene carboxylic acid/platinum nanoparticle (RGO-CS-Fc/Pt NPs)"	Cholesterol	Clinical serum samples	Amperometry	0.5 to 4.0 mg mL^{-1}	5.70 µg mL^{-1}	Li *et al.*, 2019

“Nitrogen-doped graphene quantum dots (N-GQDs Au-N-GQDs), stabilized with chitosan”	glucose	Grape juice samples	CV, Electrochemiluminescence (ECL): and EIS	10 nmol L−1 to 5.0 µmolµ mol L^{-1} L	3.3 nmol L−1	Ran *et al.*, 2019
“Reduced graphene oxide (RGO) and carbon black (CB) in Chitosan” (rGO-CB-CS)	Dopamine	Urine samples	Square Wave Voltammetry (SWV)	3.2×10^{-6} to 3.2×10^{-5} mol L^{-1}	2.0×10^{-7} mol L^{-1}	Baccarin *et al.*, 2017
RGO-CB-CS	Paracetamol	Urine samples	SWV	2.8×10^{-6} to 1.9×10^{-5} mol L^{-1}	5.3×10^{-8} mol L^{-1}	Baccarin *et al.*, 2017

"Graphene nanoplatelets (GNPs)-multiwalled carbon nanotube (MWCNTs) and chitosan (CS) (GNPs-MWCNTs-CS)"	Bisphenol A , BPA	Milk samples	DPV	0.1 to 100 µmol L^{-1}	0.05 nmol L^{-1}	Zou *et al.*, 2019
"Sulfur-doped reduced graphene oxide (S-rGO)"	Mercury (Hg^{2+})	Fish muscle	DPAdASV	0.125 to 6 µmol L^{-1}	1.6 nmol L^{-1}	Ran *et al.*, 2022
"Functionalized Graphene (f-graphene) doped chitosan (CS)"	Ochratoxin A (OTA)	Grape juice samples	DPV	1 µgmL^{-1} to 1 fg mL^{-1}	1 fg mL^{-1}	Kaur *et al.*, 2019
"Graphene, and titanium dioxide (CS/RGO/TiO_2)"	Lead (Pb^{2+})	Food samples	CV	1 ng L^{-1} to 1000 ng L^{-1}	0.33 ng L^{-1}	Wang *et al.*, 2022

“Imprinted chitosan/gold nanoparticles/graphene modified glassy carbon electrode (CS/AuNPs/GR/GCE)”	Cd(II)	Drinking water and milk samples.	Voltammetry	0.1 to 0.9 µmolµmol L^{-1} L.	1.62 × 10^{-4} µmolµmol L^{-1} L	Wu *et al.*, 2020).
“Chitosan–Graphene Glassy Carbon Modified Electrode”	Hydroxyflavonoid Morin	Food samples.	CV	0.30 µmol L^{-1} to 1.0 µmol L^{-1}	0.30 µmol L^{-1}	Nagles *et al.*, 2022
“Ag-reduced graphene oxide (rGO) and chitosan (CS)”	Carbaryl pesticide	Pesticide residues	CV	1.0 × 10^{-8} to 1.0 µg mL^{-1}	1.0 × 10^{-9} µg mL^{-1}.	Mashuni *et al.*, 2022

"Chitosan-graphene oxide composites polymer modified glassy carbon electrode (CS/GO-IIP)"	Cu (II)	Tap and river water samples	DPAdASV	0.5 to 100 µmol L^{-1}	0.15 µmol L^{-1}	Wei *et al.*, 2019
"Graphene oxide-chitosan composite (GO-chit)"	Phorate	Fresh vegetables	DPV	0.1 to 800 nmol L^{-1}	0.1 nmol L^{-1}	Fu *et al.*, 2020
"GO-chit"	Isocarbophos	Fresh vegetables	DPV	0.01 to 1000 nmol L^{-1}	0.01 nmol L^{-1}	Fu *et al.*, 2020
"GO-chit"	Omethoate	Fresh vegetables	DPV	0.1– 100 nmol L^{-1}	0.1 nmol L^{-1}	Fu *et al.*, 2020

Table 6 *provides a summary of various chitosan-graphene-based sensors designed to detect a range of analytes in diverse sample types, including human serum, clinical serum samples, and tap and river water. The techniques employed include Electrochemical Impedance Spectroscopy (EIS), Linear Sweep Voltammetry (LSV), Cyclic Voltammetry (CV), and Differential Pulse Voltammetry (DPV).*

The best-performing sensor, utilizing EIS and LSV, excels in detecting carcinoembryonic antigen in human serum with a linear range of 1×10^{-13} to 1×10^{-8} g/mL and an impressive LOD of $2.23 (\pm 0.03) \times 10^{-14}$ g/mL, highlighting its extraordinary sensitivity and extensive linear range.

Table 7. Chitosan-nanocomposite sensors based on carbon black/carbon paste.

Electrode	Analyte	Application	Technique	Linear range	LOD	REF
"Double imprinted Monomer acryloylated graphene oxide-carbon black composite polymer (aGO/CBOMNiDIP/SPE)"	Dopamine (DA) Epinephrine (EP)	Blood serum, urine and pharmaceutical samples	DPAdASV	DA- 0.115 to 5.909 ng mL^{-1} EP- 0.079 to 1.307 ng mL^{-1}	"Dopamine: 28 pg mL^{-1} (Water), 28 pg mL^{-1} (Serum), 61 pg mL^{-1} (Urine) and 29 pg mL^{-1} (Pharmaceutical sample) Epinephrine: 17 pg mL^{-1} (Water), 18 pg mL^{-1} (Serum), 19 pg mL^{-1} (Urine) and 20 pg mL^{-1} (Pharmaceutical sample)"	Fatma *et al.*, 2019

"Carbon black and CdTe quantum dots in a chitosan film"	Norfloxacin	Urine and spiked serum.	SWAdASV	0.2 to 7.4 µmol L^{-1}	6.6 nmol L^{-1}	Santos *et al.*, 2019
"Carbon black - chitosan-stabilized platinum nanoparticles (CB-Ch-PtNP)"	H_2O_2	Natural water samples	Chronoamperometry		10 µmol L^{-1}.	Silva *et al.*, 2023
"Carbon black - chitosan-stabilized platinum nanoparticles (CB-Ch-PtNP)"	Bisphenol A (BPA).	Natural water samples	DPAdASV		7.9 nmol L^{-1}	Silva *et al.*, 2023
"Super P carbon black particles and chitosan"	Macrolide antibiotics, environmental samples	Water and pharmaceutical samples	CV	1.0–190.0 µmol	Not stated	Veloso *et al.*, 2022
Carbon paste						

"Gold nanoparticle–chitosan/graphene paste modified carbon paste electrode. AuNPs-CS/Gr/CPE electrode"	Activated protein C (APC)	Human serum samples	CV, DPV & EIS	0.1 ng·mL^{-1} - 40 µg·mL^{-1}	0.073 ng·mL^{-1}	Ghalehno *et al.*, 2019
"A carbon paste electrode, modified with chitosan-based magnetic molecularly imprinted Polymer (CS-MIP)"	Lactic acid	Milk samples	CV and DPV	0.01–10.0 µM and 10.0–500.0 µM	0.005 µm	Mahmoudi *et al.*, 2022
"Poly (chitosan) (P (CS))"	Riboflavin	Commercial multivitamins	CV, DPV, and SWV	24.6 to 176µM	24.6µM	Hassanpour *et al.*, 2020
"Sn/Cs/PGE"	Riboflavin	Food samples.	CV and EIS	10 to 1200 nmol L^{-1}	5.56 nmol L^{-1}	Nagarajan & Vairamuthu (2021).

"Mung bean-derived porous carbon@ chitosan (MBC@CTS) composite"	Carbendazim	Juices	CV	0.1 to 20 lμmol L^{-1}	20 nmol L^{-1}	Liu *et al.*, 2022
"Carbon paste electrode, modified with chitosan-based magnetic molecularly imprinted polymer (CS-MIP)"	Lactic acid	In real milk samples	CV and DPV	0.01–10.0 μmol L^{-1} and 10.0–500.0 μmol L^{-1}	0.005 μmol L^{-1}	Mahmoudi *et al.*, 2022
"Pentoxide (V_2O_5) into the carbon paste electrode (CPE)"	H_2O_2	Cosmetic and personal care products.	EIS	5.0 to 1400.0 μmol L^{-1}	2.5 μmol L^{-1}	Ghanei-Motlagh *et al.*, 2019
"Hemoglobin–Iron Magnetic Nanoparticle–Chitosan Modified Carbon Paste Electrode"	Acrylamide	French fries	CV	10 to 171 nmol L^{-1}	0.06 nmol L^{-1}	Navarro *et al.*, 2020

"Three-dimensional hierarchical porous carbon coupled with chitosan"	Niclosamide	Food samples	CV	0.01 to 10 µmol L^{-1}	6.7 nmol L^{-1}	Li *et al.*, 2022
"$V_{3.6}Mo_{2.4}O_{16}$-chitosan (MV-CHT) nanocomposite"	Paracetamol	Drug samples	CV	0.0019 to 194.0 µmol L^{-1}	0.224 nmol L−1	Monsef, R., & Salavati-Niasari, M. (2022).
"Pt-Pd nanoparticles/chitosan/nitrogen-doped graphene (N-Gra) nanocomposite" (Pt-Pd-CS-N-Gra)	Ascorbic acid	Drug samples	CV	2 to 400 lµmol L^{-1}	0.97 µmol L^{-1}	Luo *et al.*, 2021
Pt-Pd-CS-N-Gra	Sulfite	Drug samples	CV	8 to 600 µmol L^{-1}	5.5 µmol L^{-1}	Luo *et al.*, 2021
Pt-Pd-CS-N-Gra	Oxalic acid	Drug samples	CV	1.5 to 500 lµmol L^{-1}	0.84 µmol L^{-1}	Luo *et al.*, 2021

"Chitosan/SnO_2-SiC"	Acrylamide	Drinking water and food samples.	Immunosensor	187 ± 12.3 ng kg^{-1} to 104 ± 8.2 µg kg^{-1}	45.9 ± 2.7 ng kg^{-1}	Wu *et al.*, 2019

Table 7 *details chitosan-nanocomposite sensors that utilize carbon black and carbon paste to detect various analytes across different applications, including blood serum, urine, pharmaceutical samples, and natural water samples. The techniques employed include Differential Pulse Adsorbtive Stripping Voltammetry (DPAdASV), Square Wave Adsorbtive Stripping Voltammetry (SWAdASV), and Chromatoamperometry.*

The best-performing sensor, using SWAdASV, excels in norfloxacin detection in urine and spiked serum with a linear range of 0.2 to 7.4 µmol/L and an impressive LOD of 6.6 nmol/L, showcasing its remarkable sensitivity and precise detection capabilities.

4.0 Conclusions and Future Perspectives

This review article has successfully presented many of the latest developments in the vast application of chitosan-based nanocomposite sensors within the past 5 years. The study of chitosan-based material is robust, proving its wide applicability and modifiability because chitosan possesses several unique properties that make it very desirable in electrochemical studies. On another hand, nanomaterials, in the past few decades, have been one of the most studied topics in science. Their combination with chitosan has opened up a non-exhaustible vista in the production of novel materials with highly enhanced performances, which are utilized in all fields of life.

This review further emphasizes the importance and great prospects of chitosan-based nanocomposites as excellently promising materials in the production of sensors and biosensors.

In the very near future, developments in this area will continue to evolve for application in diverse fields and industries such as food, environmental, health, pharmaceuticals, agriculture,

biotechnology and so much more. Sensors based on chitosan nanocomposites can be engineered and miniaturized into disposable, field testing kits in all of these field, allowing for easy, quick and reliable measurements without the need for bulky laboratory experiments.

These materials can also be integrated into microfluidic systems which would enable higher efficiency, lower reagent consumption and facilitate high throughput analysis.

As research in this field continue to evolve, eco-friendlier environmentally sustainable methods for their preparation continues to evolve, and this will help eliminate the effect of hazardous chemical practices in our world today.

By continuing to explore the versatility of sensors based on chitosan nanocomposites, their contributions to the advancement of chemical technology and solutions to critical societal challenges will remain boundless.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during the writing or editing of manuscripts.

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