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Carbohydrate polymer-supported metal and metal oxide nanoparticles for constructing electrochemical sensors

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Carbohydrate polymers have attracted significant attention due to their favorable characteristics, such as availability, non-toxicity, biocompatibility, and biodegradability, making them promising materials for many medical and industrial applications. Additionally, they can be reinforced with metal and metal oxide nanoparticles (NPs), resulting in the formation of nanocomposites (NCs), which can be incorporated in electrochemical sensors for enhancing their conductivity and catalytic activity. These NPs increase the catalytic activity of electrochemical sensors *via* redox cycling, while carbohydrate polymers are used to stabilize NPs against self-aggregation and act as matrix for them. The redox cycling process, which depends on NPs as redox mediators, facilitates the oxidation or reduction of the target analytes, leading to an optimized current signal. Carbohydrate polymers are more favorable than synthetic polymers given that they are readily available, cheap, and non-toxic materials. To date, various carbohydrate polymers, such as alginate, cellulose, chitosan, dextran, gums, locust bean gum, latex, mucilage, pectin, and starch, have been used for the preparation of electroactive metal/metal oxide–carbohydrate polymer NCs. Subsequently, these NCs have been employed for the detection of biological analytes, such as drugs, enzymes, hormones, aflatoxins, biomarkers, carbohydrates, and natural oxidants, and water pollutants, such as pesticides, dyes, metal ions, and phenolics. However, there are fewer studies regarding the use of carbohydrate polymers in electrochemical sensors compared with other applications. Overall, metal/metal oxide–carbohydrate polymers are considered promising materials for the detection of many target analytes with enhanced sensitivity, low detection limits, and optimized selectivity.

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Introduction

Nanomaterials are widely used in biomedical, environmental, and industrial applications.[1–3] Nowadays, a great attention has been focused on nanomaterials, especially with a size in the range of 1–100 nm, as electrode modifiers due to their high surface energy, specific surface area, reactivity, and superb catalytic activity compared to their bulk counterparts.[4] Additionally, they show superior chemical, physical, mechanical, and electronic characteristics.[5,6] Consequently, nanomaterials play a crucial role in the construction of high-performance electrochemical sensors.

Nanomaterial-based electrochemical sensors are robust analytical tools that show high sensitivity, selectivity, ease of miniaturization, and rapid response compared to conventional electrochemical sensors.[7] Thus, they have been extensively used for the detection of biological molecules, such as drugs, enzymes, biomarkers, hormones, and toxins.[8] Additionally, they have been used for the detection of water pollutants, such as organic pollutants[9–11] and heavy metals.[12]

A variety of nanomaterials, including zero-dimensional, one-dimensional, two-dimensional, and hybrid nanomaterials, has been used in chemical- and bio-sensing.[13] Zero-dimensional nanomaterials, including metal and metal oxide nanoparticles (NPs), are considered brilliant electrode modifiers due to their high surface area and catalytic activity.

Metal NPs and their oxides are broadly used in various applications, such as electronics, optics, information technologies, and batteries, because of their large specific surface area, adsorption activity, and high catalytic activity.[14] Additionally, they are extensively used in biomedicine and environmental applications due to their favorable optical, chemical, mechanical, electrical, and magnetic characteristics.[15–18] These NPs can be produced using a variety of physical, chemical, and biological methods.[19] Biological methods are regarded as a green route for the synthesis of metal and metal oxide NPs

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without requiring harmful chemicals and reagents.[20,21] They depend on the use of biological resources such as plants,[22] animals,[23] algae,[24] and fungi.[25] Plants represent a valuable source of carbohydrate polymers, which act as powerful reducing and capping agents for the synthesis of metal– and metal oxide–carbohydrate polymer nanocomposites (NCs). Alternatively, the as-synthesized NPs can be dispersed in carbohydrate polymers to form the NCs.

Carbohydrate polymers have attracted significant attention considering that they are bio-renewable and greener materials with diverse physical and chemical characteristics, making them good candidates for many medical and industrial applications.[26–30] The incorporation of metal NPs as nanofillers in carbohydrate polymers, such as chitin, chitosan, alginate, dextran, and gums, has significantly improved the features of carbohydrate polymers.[31] Consequently, metal NP–carbohydrate polymer composites have been used in many industrial and biological applications.[32] For example, the removal of metal ions and dyes from water.[33] Moreover, conducting polymers such as carbohydrate polymers reinforced with metal-based NPs have been used in electrochemical sensors.[34]

Recently, a review article was published on metal/metal oxide NPs-carbohydrate polymers as promising materials in industrial and biological applications.[32] Alternatively, the present review is focused on the use of reactive metal and metal oxide NPs, which are easily oxidized and reduced on the electrode surface, capped by carbohydrate polymers as an efficient strategy for the electrochemical detection of different analytes especially biological molecules and water pollutants for the first time.

Electrochemical sensors

Electrochemistry is a branch of science related to the oxidation and reduction of substances on the surface of electrodes. Generally, electrochemical approaches can be divided into potentiometric and potentiostatic methods. The potentiostatic method involves the use of a potentiostat, which is an instrument that forces a change in voltage away from the open-circuit potential to initiate redox reactions in an electrolytic cell, and is considered more favorable for chemical analysis.[35] The potentiostat is connected to an electrochemical cell, which contains three electrodes, *i.e.*, reference, auxiliary, and working electrodes. The electrochemical cell is filled with electrolyte, which is responsible for the ion transport between the electrodes. Different concentrations of the target analyte are dissolved in the electrolyte, which is subsequently oxidized or reduced on the electrode surface. The potential at which the oxidation or reduction peak appears depends on the chemistry of the analyte, types of electrodes, and electrolytic conditions such as the type of electrolyte and its pH. The produced current depends on the concentration of the target analyte in the electrolyte solution.[36]

Electrochemical sensors have been demonstrated to have greater applicability compared with other detection methods, such as spectrophotometry, gas chromatography, and high-performance liquid chromatography, in different fields ranging from healthcare to the environment due to their favorable features such as portability, cost-effectiveness, rapid analysis, and lower solvent consumption.[4,37,38] They have been extensively used for detecting different types of substances such as drugs, sweat ions, bioactive molecules, pesticides, dyes, mycotoxins, and heavy metals.[8,39–43] Basically, electrochemical sensors convert chemical reactions of the targeted substances into electrical impulses with variations in potential, current, impedance, and conductivity.[44] These variations are used as electrochemical signals to investigate the composition and/or concentration of the targeted substances.[45] Different electrochemical methods such as potentiometric, amperometric, chronoamperometric, voltammetric, and impedimetric or electrochemical impedance spectroscopy (EIS) can be used for monitoring the electrochemical signal (s) of the substance of interest.

Potentiometric sensors are based on the measurement of the variation in potential at different concentrations of the target analyte under the conditions of no current flow, while amperometric and chronoamperometric sensors are based on the measurement of the current produced from the oxidation or reduction of the target analyte.[46,47]

Voltammetric methods are extensively used for detecting target analytes, which include different techniques such as cyclic voltammetry (CV), differential pulse voltammetry (DPV), square wave voltammetry (SWV), differential pulse stripping voltammetry (DPSV), linear sweep voltammetry (LSV), and square wave anodic stripping voltammetry (SWASV).[8]

Impedimetric methods rely on receptors that result in an increase or decrease in resistance in the presence of the target analyte, while amperometric methods are based on the determination of the concentration of the target analyte at a constant potential.[8] Fig. 1 shows the electrochemical signal of the voltametric, EIS, amperometry, and chronoamperometry methods, which are mainly used in electroanalytical applications.

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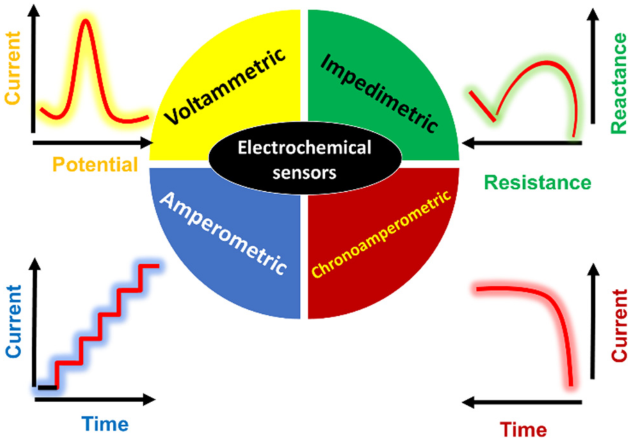

Fig. 1 Schematic representation of the electrochemical methods mainly used in sensing applications.

Among them, voltametric sensors are frequently used in the electrochemical detection of analytes given that they are simple, sensitive, and selective and possess desirable features such as fast response and lower detection limits.[48]

Electrochemical sensors have been developed to enhance their sensitivity, reproducibility, selectivity, affordability, and stability. This development can be achieved by modifying the electrode surface with recognition and redox probes such as biofilms, enzymes, metal–organic frameworks, and nanomaterials.[49–52] Electrode modification with nanomaterials has gained significant interest, given that it results in an enhancement in electrocatalytic activity, reduction in the peak-to-peak separation, improvement in the current response, and increase in the electrode surface area.[38] The modification of electrodes with nanomaterials can be achieved *via* dipping or sticking the electrode in a nanosuspension, electrodeposition, coating, spray coating, drop casting, spin coating, or carbon pasting.[8,53] Nanomaterials such as metallic nanoparticles (NPs) act as redox mediators, enabling the sensitive detection of the target analytes. For example, AgNPs were studied as redox mediators for enhancing the detection of bromocresol green dye. The SWV method was used for achieving redox mediation or redox cycling, where the oxidation of bromocresol green (forward pulse) was followed by its reduction (backward pulse). The backward current was enhanced in presence of AgNPs, leading to an increase in the net peak current, which is a combination of the forward and backward current.[54] Fig. 2 shows how the presence of AgNPs as a redox mediator enhances the oxidation of bromocresol green dye.

Polymer-based nanocomposites

A polymer is a macromolecule composed of repeating structural units connected by covalent chemical bonds. Polymers have become very popular due to their attractive features such as lightweight, tunable strength and elasticity, easy shaping and coloring, tunable transparency, and thermal and electric insulation.[55] Therefore, they have been extensively used in many applications such as photonics, optoelectronics, energy storage devices, and medical monitoring sensors.[56–59] Alternatively, they can be combined with other nanomaterials to form polymer NCs. Polymer NCs are composed of organic or inorganic nanomaterials (nanofillers) dispersed in a polymer matrix. These NCs combine the characteristics of the nanofillers and polymers, resulting in macroscopic features (strength, hardness, and toughness) in the NCs.[60] Accordingly, they have been utilized in various applications such as adhesives, anticorrosive coatings, drilling fluids, electronic devices, and electric circuits.[32,61–63]

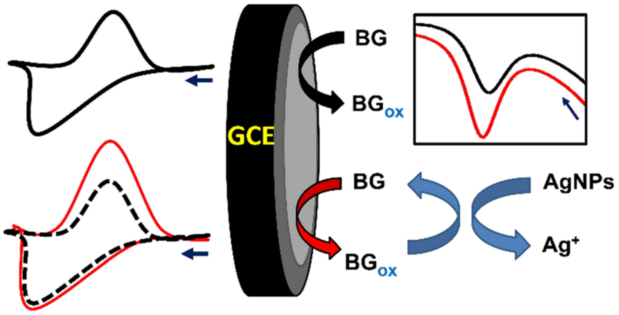

Fig. 2 Schematic representation of the detection of bromocresol green dye using AgNPs as a redox mediator.[54]

Metal-synthetic polymer NCs as electrode modifiers for sensing applications

The modification of the surface of electrodes with polymers results in the creation of functional materials, which can be used in sensing applications. The modification can be achieved *via* different approaches such as electro-grafting, self-assembly, and electrodeposition.[64] Additionally, the polymer can be processed using the molecular imprinting technique before its adsorption on the electrode surface. This technique creates molecular cavities in the polymeric matrix, which are produced in the presence of template molecules, forming artificial binding sites, which leads to an enhancement in the selectivity of the sensor.[65,66] Alternatively, the surface of electrodes can be modified using metal–polymer NCs *via* different pathways such as polymerization with subsequent metal ion reduction, metal ion reduction with subsequent polymerization, and direct adsorption (Fig. 3). Previously, metal NPs were incorporated in synthetic polymers to modify the surface of electrodes for the construction of electrochemical sensors.[67,68] Herein, the focus is on carbohydrate polymers mixed with metal and metal oxide NPs as efficient alternatives to synthetic polymer-based NCs.

Metal/metal oxide–carbohydrate polymer NCs for sensing applications

Carbohydrate polymers are biodegradable materials that can be broken down into smaller compounds by biological processes and organisms such as bacteria and fungi.[69] They can be derived from various resources such as plants, seafood, and

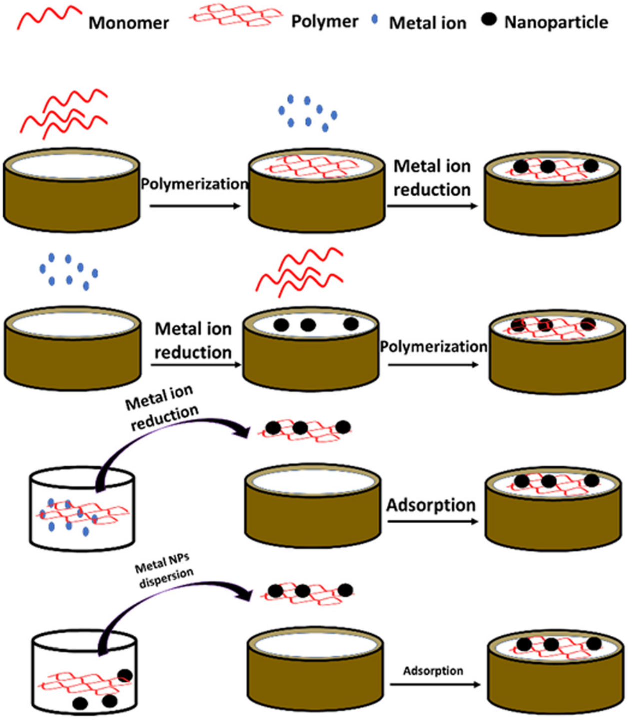

Fig. 3 Schematic representation of the different pathways used for electrode modification with metal–polymer NCs.

Fig. 4 Schematic representation of the different pathways used for the modification of electrodes with metal–polymer NCs.

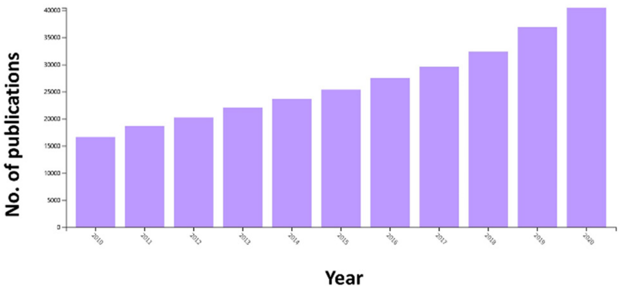

Fig. 5 Visualization of research impact of ''carbohydrate polymers'' and ''metal and metal oxide NPs'' in the field of ''electrochemical sensors'' in the period 2000 to 2022 according to the results of Web of Science Core Collection.

algae (Fig. 4). They are broadly utilized in many medical applications such as bone tissue engineering, tissue regeneration, drug delivery systems, and imaging.[70] Carbohydrate polymers as natural polymers are more favorable than synthetic polymers given that they are economical, readily available, non-toxic, biodegradable, biocompatible, and cost-effective materials. Consequently, they have been used in industrial applications such as binders, drug release modifiers, film coatings, viscosity enhancers, stabilizers, disintegrants, emulsifiers, gelling agents, bioadhesives, sensors, and water treatment.[71–74] Additionally, carbohydrate polymers and their NCs can be used as corrosion inhibitors[75] and adsorbents for the removal of heavy metals[76] and organic pollutants.[77] Recently, they have been receiving increasing attention as electrode modifiers for the detection of analytes.

Fig. 5 shows the key trend of ''carbohydrate polymers'' and ''metal NPs'' in the field of ''electrochemical sensors'' in the period of 2010–2020. Obviously, there was an exponential increase in publications annually.

Previously, carbohydrate polymers such as cellulose, chitin, chitosan, and pectin have been reported as electrode modifiers for the electrochemical detection of drugs and environmental pollutants.[78–81] Also, to realize superior catalytic activity, high sensitivity, and low detection limits, carbohydrate polymers have been incorporated with other natural polymers,[82] synthetic polymers,[83,84] carbon nanotubes,[81,83,85] graphene oxide,[86] organoclay,[87] and metal/metal oxide NPs for the fabrication of electrochemical sensors (Fig. 6).

For example, cellulose polymer was mixed with carbon nanotubes and copper ions for the selective detection of tryptophan enantiomers.[81] The sensor exhibited stronger complexation ability for L-Trp than D-Trp, leading to a difference in the oxidation peaks between the two enantiomers (Fig. 7). In this review, the focus is on NCs formed from carbohydrate polymers, such as alginate, cellulose, chitin, chitosan, dextran, pectin, and gums and metal/metal oxide NPs.

Fig. 4 shows the carbohydrate polymers and their sources that have been used for the preparation of metal/metal oxide–carbohydrate polymer NCs for subsequent immobilization on the surface of electrodes for electroanalytical applications. Additionally, the advantages and sensing properties of carbohydrate polymers are explained in Table 1.

These nanocomposites can be prepared using various techniques such as sonochemical, microwave, mechanochemical, evaporation, and electrochemical methods.[32] They combine the biodegradability, compatibility, and stability of carbohydrate polymers and conductivity of metal/metal oxide NPs, making them excellent candidates for electroanalytical applications. Next, these NCs are adsorbed on the electrode surface through coating, drop casting, dipping, electrodeposition, and carbon paste (Table 2).

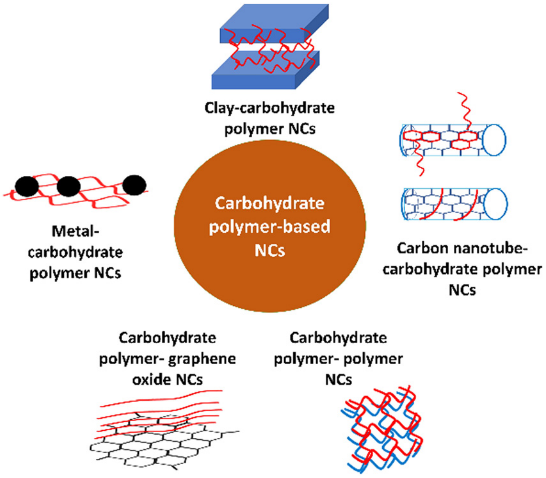

Fig. 6 Carbohydrate polymer-based NCs used in electroanalytical applications.

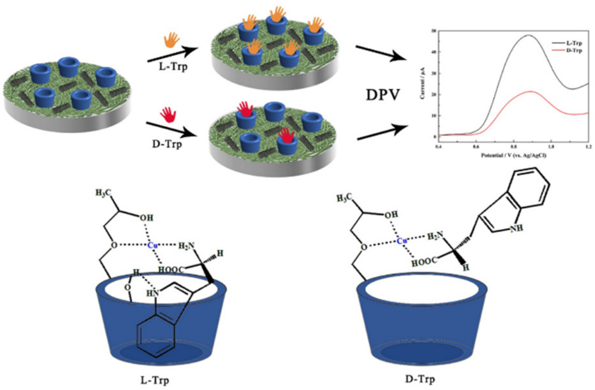

Fig. 7 Schematic representation the of electrochemical chiral recognition of tryptophan isomers (reprinted from ref. 81 with permission from Elsevier).

The previously studied analytes including biological molecules and water pollutants are shown in Fig. 8. The biological analytes include drugs, biomarkers, carbohydrates, enzymes, hormones, aflatoxins, and natural antioxidants, while the water pollutants include inorganic compounds, metal ions, pesticides, dyes, and phenolics. The composition of metal/metal oxide carbohydrate polymer NC-based modified electrodes, electrode modification methods, electrochemical techniques, sensing mechanisms, and their detection limits are presented in Table 2. The sensing mechanisms include direct oxidation/reduction of the analyte or inhibition/amplification of the electrochemical response of the modifier.

Alginate

Sodium alginate, a water-soluble anionic polyelectrolyte, is formed from two glycan monomers, *i.e.*, α-L-guluronic acid and β-D-mannuronic acid, linked in the (1 → 4) positions of the linear block copolymer structure.[96] Alginate-based polymers have attractive features such as biodegradability, high mechanical strength, and high adsorption capacity, making them desirable materials in many biomedical applications such as drug delivery, diagnosis, tissue engineering, microencapsulation, and wound healing.[97,98] Additionally, they have been used in industrial applications such as concrete.[99] Polyelectrolytes including alginate polymer have attracted significant attention due to their applications in various electrochemical devices such as batteries, supercapacitors, solar cells, and sensors.[100–104] Recently, a NC formed from sodium alginate polymer, CuO NPs, polyallylamine, and reduced graphene oxide was immobilized on a glassy carbon electrode for the electrochemical assessment of Cd^{2+} in river water using CV and chronoamperometry.[105]

Cellulose

Cellulose, a polymer obtained from animals and plants, is regarded as the most abundant material in nature.[106,107] It has been used for the preparation of materials possessing antimicrobial properties,[108] extracting chlorobenzenes from water,[109] producing components used in the automotive, packaging, and building materials sectors,[110] and preparing

Table 1 Advantages and sensing properties of carbohydrate polymers

Carbohydrate polymer	Properties/advantages	Sensing properties	Ref.
Alginate	It a high number of hydroxyl groups required for NP synthesis.	It is easily electropolymerized at the electrode surfaces providing functional groups for interaction with analytes.	87 and 88
Cellulose	It has increased surface area and superior dispersion of NPs.	It enhances the electrocatalysis.	89
Chitosan	It has good membrane-forming ability, high permeability, good adhesion, and high mechanical strength.	Its reactive amino and hydroxyl functional groups interact with the recognition elements.	90
Dextran	It stabilizes NPs against aggregation.	It provides steric hindrance, preventing the unspecific adsorption of interferences.	91
Gelatin	It is a good dispersing agent and excellent immobilization matrix.	It is used in biosensors due to the presence of amino acids.	92
Gum	It has high strength and good viscosity.	It forms highly sensitive NCs.	93
Pectin	It has hydroxyl and carboxyl groups required for the synthesis of NPs.	It presents good electrocatalytic capacity.	94
Starch	It is a good reducing agent required for the synthesis of NPs.	It provides more active sites to carry analyte and for oxidation/reduction.	95

Table 2 Metal and metal oxide-carbohydrate polymer NCs as electrode modifiers for the construction of electrochemical sensors

Carbohydrate Polymer	NP/NC	Electrode material	Modification method	Analyte	Method	Mechanism	LOD (nM)	Ref.
Alginate	CuO NP	Aodium alginate-*g*-polyallylamine/rGO/CuO GCE	Drop casting	Cd^{2+}	CV & CA		1.27	105
Cellulose	CuO NSs	CuO NSs/cellulose acetate butyrate/GCE	Coating	Hydrazine	LSV	Analyte oxidation	150	117
	Fe_3O_4 NPs	Cellulose nanofiber/Fe_3O_4 NC/GCE	Coating	Hydrazine	DPV	Analyte oxidation	0.5	89
		Cellulose nanofiber/Fe_3O_4 NC/CPE	Carbon paste	4-Chlorophenol	DPV	Analyte oxidation	0.5	118
		Methyl cellulose/graphene oxide/Fe_3O_4 NC/GCE	Drop casting	Uric acid	DPV	Analyte oxidation	170	119
	Au NPs	Au NPs/cellulose nanocrystals/SPCE	Drop casting	4,4′-Methylene diphenyl diamine	DPV	Analyte oxidation	57	114
	Ag NPs	AgNPs/cellulose nanofibers/graphite electrode	Drop casting	Ascorbic acid	DPV	Analyte reduction	29	115
				Dopamine			34	
				Paracetamol			19	
		Graphite/Ag NPs/TEMPO-oxidized cellulose nanofibers/GCE	Coating	Dopamine	A	Analyte oxidation	0. 5	113
		Ag/cellulose/GCE	Drop casting	DNA	DPSV	Modifier signal inhibition	0.023	116
		Cellulose–Ag NPs/CPE	Carbon paste	Ornidazole	SWV	Analyte reduction	758	112
	ZnO NPs	PANI–carboxymethyl cellulose/ZnO NC/GCE		Hydrogen peroxide	DPV	Analyte reduction	450	120
Chitosan	Au NPs	Au NPs/carbon nano-onions/SWCNT/chitosan/GCE		CEA	SWV	Modifier signal inhibition	100 fg mL^{-1}	90
	Nano-porous Au film electrode	Polypyrrole/chitosan/nano-porous Au film electrode		Metronidazole	DPV	Analyte oxidation	0.9	84
Dextran	Au NPs	Con A/Au NPs/phenoxy dextran/rGO/SPCE		Glucose	DPSV	Modifier signal inhibition	20 000	136
		Dextran–Au NPs/SPCE	Electro-deposition	Cr(VI) & Cr(III)	LSV	Analyte reduction	10	137
	Fe_3O_4 NPs	Abs–polyaldehyde–dextran–Fe_3O_4 NPs/SPCE		Peroxidase	A		0.44 ng mL^{-1}	91
Gums (almond gum)	Fe_2O_3 NPs	Almond gum/Mg–Fe_2O_3 NPs/graphite electrode		Paracetamol	CV			142
	Bi_2O_3/MgO/Fe_2O_3 NC	Almond gum/Bi_2O_3/MgO/Fe_2O_3 NC/graphite electrode		Paracetamol	CV			143
Gums (arabic gum)	Ag NPs	Arabic gum/Ag NPs/CPE	Carbon paste	Morin		Analyte oxidation	0.216	150
		Arabic gum/Ag NPs/GCE	Dipping	Methylene blue	SWASV	Analyte oxidation	64, 440 μg L^{-1}	151
						Modifier signal amplification	0.96 μg L^{-1}	
Gums (guar gum)	Ag–TiO_2 NPs	Guar gumAg–TiO_2 NPs/GCE	Drop casting	Hydroquinone	SWV	Analyte oxidation	195.2	156
				Catechol			161	
				Resorcinol			77.58	
				Nitrite			101	
Gums (locust bean gum)	Ag NPs	Ag NPs/copper-micro mesh grid electrode	Drop casting	Glucose	DPV	Analyte oxidation	1	93
Latex	Ag NPs	AgNPs–latex/GCE	Dipping	Eriochrome black T	SWV	Analyte oxidation	2.92 μg L^{-1}	166
						Modifier signal inhibition	7.01 μg L^{-1}	
Mucilage	Ag NPs	AgNPs–mucilage/GCE	Dipping	Chlorpyrifos	SWV	Modifier signal inhibition	17.2 ng L^{-1}	173
	Ag NPs &Au NPs	AgNPs–AuNPs–mucilage/GCE	Coating	Prostatic specific antigen	EIS	Modifier signal amplification	0.087 pg mL^{-1}	172

Table 2 *(continued)*

Carbohydrate Polymer	NP/NC	Electrode material	Modification method	Analyte	Method	Mechanism	LOD (nM)	Ref.
Pectin	CuO NPs	Graphene/pectin/CuO NPs/GCE	Drop casting	Glucose	A	Analyte oxidation	210	180
				Hydrogen peroxide	A	Analyte reduction	350	
	CuO NPs	CuO NPs/MWCNT/pectin/GCE	Electro-deposition	Glycerol	A	Analyte oxidation	5.8×10^{-6} g dm^{-3}	178
	Au NPs	Aptamer/pectin–Au NPs/GO/GCE	Electro-deposition	Aflatoxin M1	DPV	Inhibition of modifier signal	0.2 ng L^{-1}	94
Pectin–chitosan	CuO NPs	Lipase/magnetic NPs–chitosan/CuO NP/MWCNT/pectin/GCE	Drop casting	Glycerol	A	Analyte oxidation		179
Starch	Cu_2O	Cu_2O–starch/CPE	Carbon paste	Glucose	CV	Analyte oxidation	70 000	95
	Co	CoNPs/starch/CPE	Carbon paste	Paracetamol	DPV	Analyte oxidation	0.99	184

A: amperometry, Abs: antibodies, CA: chronoamperometry, Con A: Concanavalin A, CEA: carcinoembryonic antigen, CPE: carbon paste electrode, CV: cyclic voltammetry, DPSV: differential pulse stripping voltammetry, GCE: glassy carbon electrode, GO: graphene oxide, LSV: linear sweep voltammetry, LOD: limit of detection, MWCNT: multi-walled carbon nanotube, NC: nanocomposite, NP: nanoparticle, NS: nanosheet, PANI: polyaniline, PPY: polypyrrole, rGO: reduced graphene oxide, SPCE: screen-printed carbon electrode, SWASV: square wave anodic stripping voltammetry, SWCNT: single-walled carbon nanotube, SWV: square wave voltammetry, SWASV: square wave anodic stripping voltammetry, and TEMPO: 2,2,6,6 tetramethylpiperidine-1-oxyl.

materials for lithium-ion batteries.[111] Recently, it has been extensively utilized for the preparation of metal– and metal oxide–cellulose NCs as electrode modifiers for electroanalytical applications. Fig. 9 exhibits the synthesis of an Ag–cellulose NC and its subsequent adsorption on the electrode surface.[112] Metal–cellulose NCs such as Au– and Ag–cellulose NCs have been used for detecting organic molecules. An Au–cellulose NC/screen-printed electrode was studied as an electrochemical sensor for assessing 4,4′-methylene diphenyl diamine based on its oxidation using DPV *via* two-electron transfer, while an Ag–cellulose/carbon paste electrode and Ag–cellulose/glassy carbon electrode were utilized for the detection of ornidazole and dopamine *via* two-electron transfer, respectively.[112–114]

Additionally, an AgNP/cellulose nanofiber/graphite electrode was used for the sensitive detection of ascorbic acid, dopamine, and paracetamol based on their reduction.[115]

Ag–cellulose NCs were also used for the detection of DNA hybridization based on the inhibition of the AgNP signal.[116] Alternatively, metal oxide–cellulose NCs such as CuO–, Fe_3O_4–, and ZnO–cellulose NCs were used for detecting organic and inorganic analytes. For example, hydrazine was electrochemically detected *via* its LSV and DPV oxidation on CuO nanosheet–cellulose acetate butyrate- and Fe_3O_4–cellulose NC-modified glassy carbon electrodes, respectively.[89,117] Notably, the Fe_3O_4–cellulose NCs showed a lower detection limit than CuO nanosheet–cellulose acetate butyrate. The oxidation mechanism of hydrazine using CuO NSs/cellulose acetate butyrate was based on the transfer of four electrons, while the Fe_3O_4–cellulose NCs showed an electron transfer coefficient of 0.44 using the Tafel plot slope, confirming the irreversible oxidation of hydrazine. Also, an Fe_3O_4–cellulose NC was used as a carbon paste electrode modifier for the detection of 4-chlorophenol *via* its oxidation using DPV.[118] The value of the electron transfer coefficient, which was calculated using the Tafel plot slope, was 0.22, confirming the irreversible oxidation of 4-chlorophenol on the surface of the Fe_3O_4–cellulose NC-modified electrode. An Fe_3O_4–cellulose NC was also used for the detection of uric acid in urine.[119] Additionally, a ZnO–carboxymethyl cellulose NC was applied for the reduction of hydrogen peroxide for its detection *via* the DPV technique.[120]

Chitin and chitosan

Chitin, a linear homopolymer of *N*-acetyl-D-glucosamine, is the second most abundant polymeric polysaccharide after cellulose.[121] It is a white, hard, and non-elastic material, which can be obtained from shrimp and crab shells, while chitosan, a copolymer of α-(1 → 4) glucosamine, is derived from chitin by deacetylation.[122,123] The biocompatibility, biodegradability, and non-toxicity of chitin and chitosan polymers make them efficient for application in drug delivery.[124] Recently, water-soluble based chitosan composites have been used in sensing and biomedical engineering.[125] Additionally, chitosan polymers have been used for the preparation of hydrogels for application in tissue engineering and drug delivery.[126] Moreover, a chitin nanofiber hydrogel was studied as a conductive material for the construction of a wearable sensor.[127]

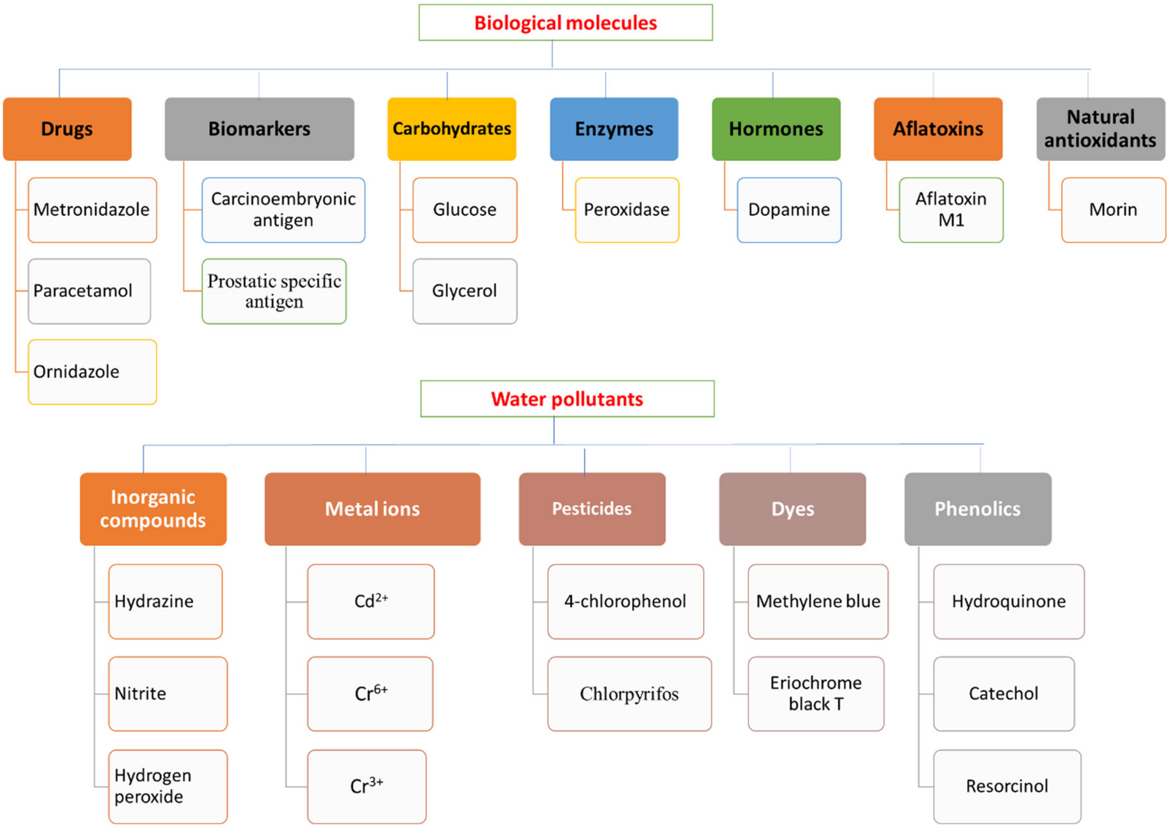

Fig. 8 Classification of the biological molecules and water pollutants electrochemically detected using metal–carbohydrate polymer NCs.

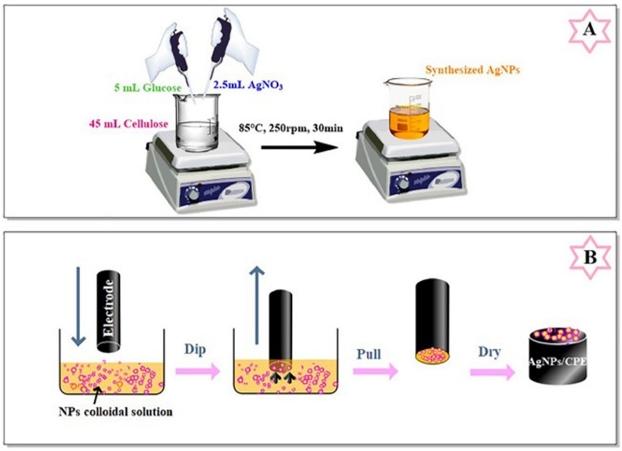

Fig. 9 Schematic representation of Ag–cellulose NC synthesis and subsequent adsorption on the electrode surface (reprinted from ref. 112 with permission from Elsevier).

Alternatively, chitin and chitosan have been extensively used in the construction of electrochemical sensors.[128] For example, potentiometric sensors based on a chitin-grafted polyaniline electrode and chitosan nanocomposite were used for the electrochemical sensing of copper ions[129] and monohydrogen phosphate ions,[130] respectively. Metal–chitosan NCs were prepared for used in the construction of electrochemical sensors. For example, Au NPs, carbon nano-onions, and single-walled carbon nanotubes were incorporated in chitosan to form an electroactive NC for the determination of a carcinoembryonic antigen.[90] The detection strategy was based on the inhibition of the modifier signal in presence of the carcinoembryonic antigen. Moreover, a chitosan/polypyrrole-modified nano-porous film Au electrode was applied for the assessment of metronidazole drug due to its high electrical conductivity and selectivity. The assessment of the drug was achieved using DPV through its oxidation.[84]

Dextran

Dextran, a neutral hydrophilic polymer produced from sucrose by *Leuconostoc mesenteroides*, has attracted significant attention in medical applications because of its nontoxicity, biodegradability, and biocompatibility.[131] Furthermore, is highly efficient for the preparation of drug delivery systems[132,133] and energy storage devices.[134,135] Its metal and metal oxide NCs can be used as efficient electrode modifiers for targeting analytes. For example, Au–dextran NC as a screen-printed carbon electrode modifier was used for the biological detection of glucose using DPSV. The mechanism of detection was based on the inhibition of the modifier signal in the presence of glucose.[136] Also, it was used as a non-enzymatic sensor for the detection of Cr(VI) and Cr(III) using LSV based on their electrochemical reduction. Furthermore, dextran was used as a sorbent for the extraction, separation, and the analysis of chromium ions.[137]

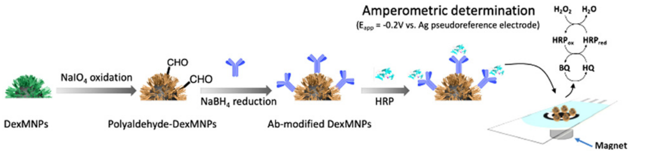

Fig. 10 Schematic representation of the amperometric determination of peroxidase using polyaldehyde–dextran metal NPs (reprinted from ref. 91 with permission from Elsevier).

Recently, a dextran–Fe_3O_4 NC immobilized on a screen-printed electrode was used as an immunosensor for the assessment of peroxidase using chronoamperometry, where hydroquinone was used as the redox mediator.[91] The mechanism for the chronoamperometric determination of peroxidase is shown in Fig. 10.

Gums

Gums are polysaccharides that contain sugar units such as glucose, galactose, arabinose, xylose, and mannose.[66] They include almond, Arabic, guar, and locust bean gums. Gums can form three-dimensional interconnected molecular networks called gels. The gel strength relies on the structure and concentration of the gum, as well as parameters such as ionic strength, pH, and temperature. These gums have been used for the preparation of NCs to be used in the construction of electrochemical sensors.

Almond gum

Almond gum, an exudate produced by the trunk, branches, and fruits of the *Prunus amygdalus* tree, is composed of polysaccharides such as arabinose, galactose, uronic acid, and protein.[138] It can be used as preservative, emulsifier, stabilizer, and food strengthener in the food industry.[139,140] Additionally, it has been applied in the pharmaceutical industry for improving the binding and emulsification features of drug formulations.[141] Recently, an almond gum/Mg–Fe_2O_3 NP/graphite electrode and almond gum/Bi_2O_3/MgO/Fe_2O_3 NC/graphite electrode were used for detecting paracetamol using the CV technique.[142,143]

Arabic gum

Arabic gum, a water-soluble polymer originating from the *Acacia Senegal* tree, is broadly used for food and drug production. It is composed of highly branched polysaccharides containing charged groups such as amine and carboxyl, which make it an efficient stabilizing agent for NPs.[144] Also, has been is applied in the food industry,[145] oil industry,[146] membrane technology,[147] and corrosion inhibition.[148] Additionally, it has been used for the preparation of metal–Arabic gum NCs for pharmaceutical and medical applications.[149] Recently, Ag–Arabic gum NCs have been used as electrode modifiers for the electrochemical detection of analytes. For example, Ag–Arabic gum NC incorporated in a modified carbon paste electrode was utilized for detecting morin based on its irreversible oxidation after its hydrogen bonding interaction with the modified electrode (Fig. 11).[150] Additionally, an Ag–Arabic gum NC/glassy carbon electrode was used for detecting methylene blue dye based on its oxidation and modifier signal amplification. The oxidation was achieved *via* two-electron and one-proton transfer (Fig. 12), while the signal amplification mechanism depends on the role of methylene blue analyte as the redox mediator, which catalyzes the oxidation of AgNPs.[151]

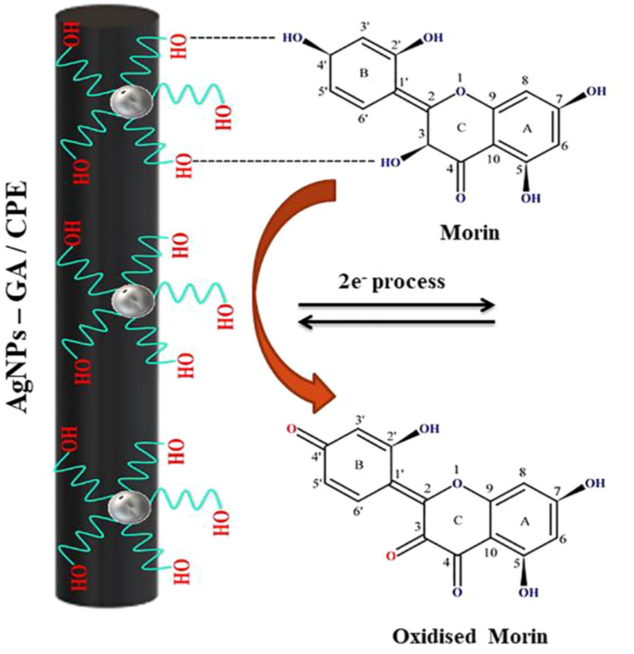

Fig. 11 Schematic representation of the mechanism of the electrochemical oxidation of morin at AgNP–gum Arabic (GA)/CPE (reprinted from ref. 150 with permission from Elsevier).

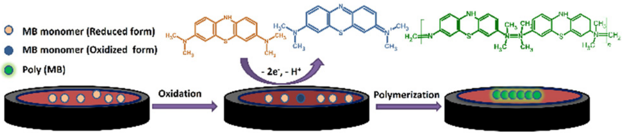

Fig. 12 Schematic representation of the oxidation and subsequent polymerization of methylene blue at gum Arabic-AgNPs/GCE (reprinted from ref. 151 with permission from Elsevier).

Guar gum

Guar gum, a water-soluble polysaccharide, is obtained from the seeds of *Cyamopsis tetragonolobus*.[152] It has been applied in drug delivery[153] and solar cell[154] systems. Additionally, it was mixed with Au nanoclusters for the preparation of a fluorescence sensor to screen anti-diabetic agents in plant extracts.[155]

Additionally, it has been used for the preparation of electroactive NCs. Recently, Ag–TiO_2 NPs mixed with guar gum were used as a glassy carbon electrode modifier for the electrochemical detection of hydroquinone, catechol, resorcinol, and nitrite using SWV based on their oxidation *via* one-electron transfer (Fig. 13).[156] Compared with the ZnO NP–carboxymethyl cellulose composite, the Ag–TiO_2 NP–guar gum composite can be used for the detection of hydroquinone with a lower detection limit (Table 2).

Locust bean gum

Locust bean gum, which can be extracted from the carob fruit, is composed of a mixture of components such as polysaccharides,

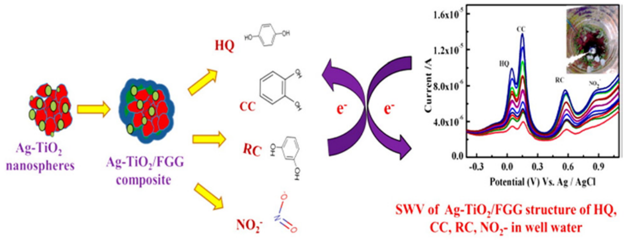

Fig. 13 Schematic representation of Ag–TiO$_2$/functionalized guar gum NC for the detection of hydroquinone, catechol, resorcinol, and nitrite (reprinted from ref. 156 with permission from Elsevier).

protein, fat, and fibers.[157] It was used in the formation of a network hydrogel for the preparation of 3D printing products.[158] Additionally, it has been used for drug delivery[159] and in the food industry.[160] Alternatively, it was mixed with Ag NPs for the preparation of an effective electrode modifier for sensing glucose, allowing the maximum accommodation of glucose enzyme before the sensing process.[93] The Ag NP–locust bean gum composite showed the highest sensitivity and lowest detection limit towards glucose compared to other carbohydrate polymer-based nanocomposites such as Au NP–dextran[136] and Cu$_2$O NP–starch NCs.[95]

Latex (natural rubber)

Natural latex is composed of micelles of rubber, lipids, amino acids, nucleic acids, and proteins.[161] It has been mixed with inorganic NPs for the construction of NCs, which can be used in applications such as catalysis, chromatography, ceramics, electronics, biotechnology, medicine, and drug delivery.[162–165] Additionally, latex has been incorporated with Ag NPs to form wound dressings.[161] Alternatively, an Ag–latex NC was studied as an electrochemical probe for detecting Eriochrome black T using the SWV technique. The sensing process was based on the oxidation of Eriochrome black T and the inhibition of the oxidation peak current of Ag NPs. The oxidation of Eriochrome black T was achieved through one-electron transfer (Fig. 14), while the inhibition of the AgNP signal was attributed to the displacement of the AgNPs by Eriochrome black T at the electrode surface (Fig. 15).[166]

Mucilage

Mucilage, a complex water-soluble polysaccharides, is composed of monosaccharides and uronic acids.[167] It has been utilized in numerous applications such as the food industry,[167] delivery of bioactive compounds,[168] emulsification,[169] catalysis,[170] and water treatment.[171] Recently, it has been used for the preparation of metal-mucilage NCs as electroactive materials. For example, an Ag/Au-mucilage NC was used as an immunosensor for the detection of the prostatic specific antigen using EIS. The presence of Au NPs and Ag NPs enhanced the conductivity of the mucilage, while the presence of the analyte resulted in a decrease in conductivity and an increase in impedance.[172] Additionally, an Ag-mucilage NC was used as a glassy carbon electrode modifier for the detection of chlorpyrifos based on the inhibition of the peak current of AgNP oxidation.[173]

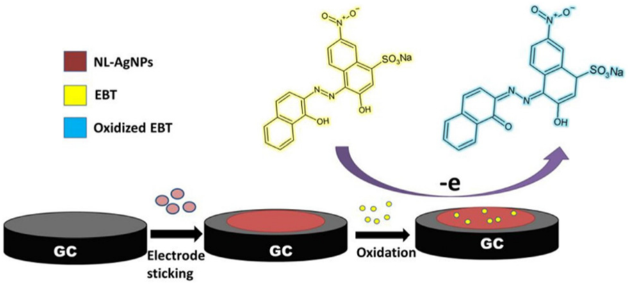

Fig. 14 Schematic representation of Eriochrome black T (EBT) oxidation at the natural latex–AgNPs/GCE (reprinted from ref. 166 with permission from Elsevier).

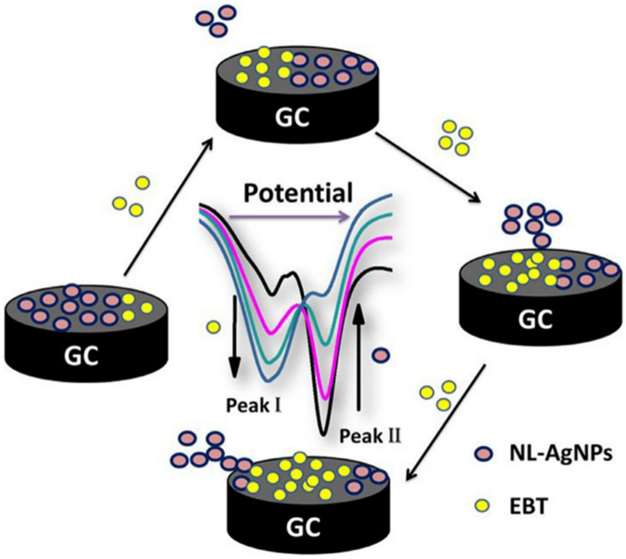

Fig. 15 Schematic representation of the electrochemical displacement of AgNPs by Eriochrome black T (EBT) (reprinted from ref. 166 with permission from Elsevier).

Pectin

Pectin, a heteropolysaccharide, is composed of galacturonic acid, rhamnose, arabinose, and xylose.[174] It has been used in many applications such as, drug delivery,[175] tissue engineering,[176] and the food industry.[177] It has also been used for the preparation of metal–pectin NCs for electroanalytical applications. For example, CuO–pectin NC was incorporated with multiwalled carbon nanotubes on the surface of a glassy carbon electrode for the detection of glycerol based on its oxidation using amperometry.[178] Similarly, CuO–pectin NC was immobilized with chitosan, lipase, multiwalled carbon nanotubes, and magnetic NPs on the surface of a glassy carbon electrode for sensing *glycerol* based on its oxidation using amperometry (Fig. 16).[179] Additionally, a graphene/pectin/CuO NP/GCE was used for the detection of glucose and hydrogen peroxide in human serum based on their amperometric oxidation and reduction respectively.[180] This sensor exhibited many advantages such as simplicity and high sensitivity, stability and reproducibility. Recently, an Au–pectin NC was studied as an aptameric sensor for the detection of aflatoxin M1 using DPV based on the inhibition of the modifier signal.[94]

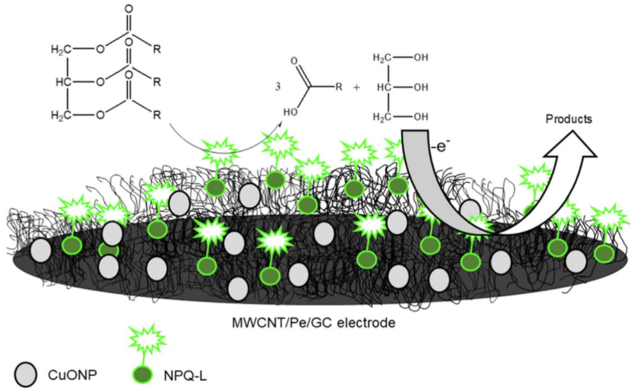

Fig. 16 Schematic representation of *glycerol* determination using copper oxide/multiwalled carbon nanotube/pectin/GCE (reprinted from ref. 179 with permission from Elsevier).

Starch

Starch is a high-molecular-weight carbohydrate that is produced by polymerizing glucose molecules. It has been utilized for developing conducting biofilms, fuel-cell coatings, supercapacitor electrodes, solar cells, and colorimetric and electrochemical sensors.[181–183] Cu_2O–starch NC as a modified carbon paste electrode has been used as an electrochemical sensor for the assessment of glucose using the CV technique based on its oxidation.[95] Additionally, a CoNP/starch/CPE was used for the detection of paracetamol based on its oxidation *via* two-electron and two-proton transfer.[184]

Conclusion

In summary, electrochemical sensors are considered promising tools for the detection of various analytes. Additionally, the efficiency of electrochemical sensors can be improved by using metal– and metal oxide–carbohydrate polymer NCs as electrode modifiers. Carbohydrate polymers act as efficient reducing and stabilizing agents for the synthesis of metal and metal oxide NPs. Additionally, they can be used for the homogenous distribution of NPs. Herein, metal– and metal oxide–carbohydrate polymer NCs represent a valuable tool for the electrochemical detection of biological molecules and water pollutants. Initially, these NCs can be incorporated in electrochemical sensors *via* polymerization with subsequent metal ion reduction, metal ion reduction with subsequent polymerization, or through direct adsorption. Next, the electrodes modified with metal– or metal oxide–carbohydrate polymer NCs can be used as electrochemical sensors for the detection of analytes using different electrochemical methods such as voltammetry, EIS, amperometry, and chronoamperometry. The sensing of the analytes depends on their oxidation/reduction on the surface of the modified electrodes or the amplification/inhibition of the electrochemical response of the modifier in the presence of the analyte of interest. The role of carbohydrate polymers in these electrochemical sensors is crucial given that they are responsible for the synthesis, stabilization, and distribution of NPs as well as for their interaction with the target analytes, facilitating the detection process. Overall, metal/metal oxide NP–carbohydrate polymer nanocomposites represent a promising tool for the electrochemical detection of different analytes. They may be useful for detecting numerous biological and environmental molecules. However, the selectivity of carbohydrate polymers is still poor compared to molecularly imprinted polymers, enzymes, and aptamers. Thus, the selectivity of carbohydrate polymers-based electrochemical sensors needs to be enhanced. In this case, it is recommended to enhance the selectivity of these electrochemical systems as the primary step in their commercialization.

Conflicts of interest

There are no conflicts to declare.

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