

REMARKABLE BREAKTHROUGH OF NANOMATERIAL BASED ELECTROCHEMICAL SENSORS AS SCREENING PLATFORMS FOR CHEMICAL CONTAMINATION IN FOOD

Abstract

Concern over security and safety of food has become a topic of public health concern around the globe. Throughout the perpetual food supply chain, food can get contaminated with a number of harmful substances, posing a variety of threats to human health. Each phase of the food supply chain gets impacted by the risks brought on by the omnipresence of pesticides, heavy metals, antibiotics, food additives, and other toxic chemicals. As a result, sensitive, selective, and realistic methods of analysis for different food safety concerns are highly valued. To ensure environmental safety, it is crucial to identify any food contaminants that are existing in ecosystems and eliminate them through detection and degradation. It is of utmost importance to remove these contaminants from sources of food and water which account for the potentially harmful consequences, and hence various approaches are attempted to degrade them.[1–7]In this chapter, we discuss the recent applications of nanomaterials as sensing materials for the detection of risk factors in food, such as residues of pesticides, heavy metals, food additives and other toxic contaminants.

Keywords: Electrochemical sensing, food safety, heavy metal ions, antibiotics, food additives

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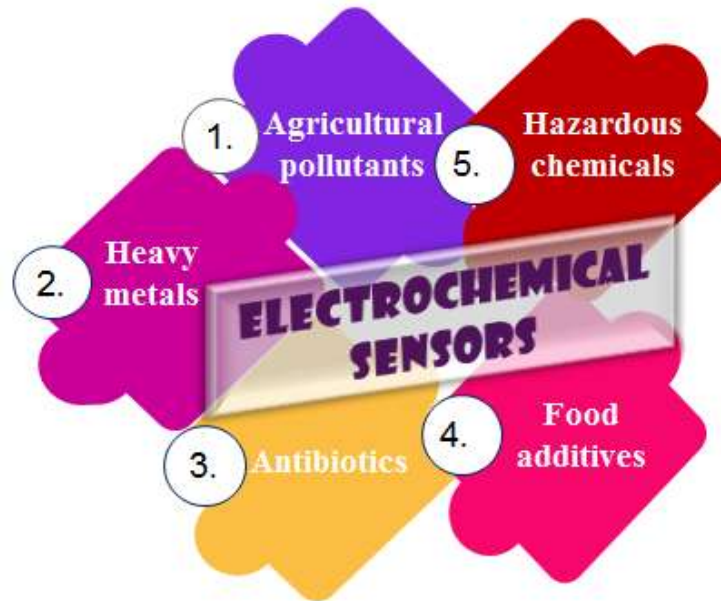
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I. INTRODUCTION

For maintaining healthy life and fostering good health having access to adequate supplies of safe and nourishing food is of pivotal importance. The inappropriate and unrestricted usage of pesticides, coloring agents, and antibiotics has resulted in food contamination. With the goal of guaranteeing the safety of the environment and nutrition in food, on-site detection of these residues in food items is highly valuable. For on-site or in-field detection of these contaminants, conventional detection methods are labor-intensive and ineffective. To avoid the food borne illness from being transmitted by food contaminants, the inspection of food is crucial. The augmentation of accurate, simple tests that can efficiently determine the association of any hazardous pollutants in food is crucial for managing and resolving the issues associated with food borne diseases. This will make it possible for the implementation of the remedial steps. The presence of food allergens, growth promoters, veterinary drugs, food adulterants has affected the food quality from the stage of harvesting to the storage. Profiteers, contrarily, seek out new ways to jeopardize the wellbeing of society in an effort to increase their profits by artificially lowering manufacturing costs.

Nano structured sensors have been considered as competent materials eventually in the past ten years with increased sensitivity and response times, and they have encountered a significant impact in the electrochemical detection discipline. Beyond the simple and inexpensive fabrication of these nanosensors, their popularity is unquestionably attributed to their numerous distinctive properties, which are used in endless applications. Due to their sensitive response, and straightforward operation, electrochemical sensing has recently attracted a lot of attention and holds a dominant position in various sectors like environmental monitoring, clinical diagnosis, agricultural analysis and pharmaceutical fields.[8–13]For the commercial applications as a sensor, the versatility, the device affordability, its miniaturization and credibility are critical. These technical considerations for the market together with the robustness, dependability, and response time including sensor fouling prevention constitute the essential requirements. The combined knowledge of electrochemists, electronic engineers, biochemical experts, synthetic and material chemists will be necessary to address the challenges related to electrochemical sensors. Nano material by the virtue of good optical properties, low toxicity, higher bleaching resistance, higher ease of functionalization, good biocompatibility chosen for the detection of food contaminants are discussed here. These distinctive and alluring qualities have paved the way for the development of electro analytical systems with alluring and promising analytical behaviors.

II. APPLICATIONS IN FOOD SAFETY ASSESSMENTS

- 1. Detection of Agricultural Pollutants:** Carbendazim which is considered as an extremely toxic insecticide by the WHO has the potential to cause cancer in human is a commonly used pesticide. It also interferes with the endocrine system.[14]Luiz R.G. Silva et al., fabricated an electrochemical sensor with the composite of Carbon black (CB) -PLA. The increased efficiency and the electron transfer process of sensor aroused by the ubeity of greater number of grooves due to the surface removal of PLA after electrochemical treatment. Since the CB has oxygenated groups, the interaction with water is favored resulting in increased hydrophilicity. The electrochemical detection of CBZ analysis produced satisfactory results with a low LOD (0.91 mol L^{-1}) that complies with the Brazilian legal requirements for analysis[15].Another pesticide cyromazine, is widely

exploited in the production of vegetables and fruits concomitant with its low mammalian toxicity. But its metabolite melamine formed after photo degradation causes acute renal failure. Therefore, a study focused on the fabrication of molecular imprinted sensors for the detection of cyromazine in cowpea, tomato and water samples. The sensor also exhibited outstanding repeatability, interference resistance and offered the lower limit of detection with 0.5 mol/L [16]. The excess usage of glyphosate has sparked concerns over the dangers it poses to the environment and human health. Glyphosate is electrically passive and hence it is challenging to directly detect it by sensing techniques. But, due to the presence of two donor groups, it can form a ring (five membered) with the Cu^{2+} . Hence Rui Jiang et al., synthesized a Cu-TCCP /AuNPs/CP having strong catalytic activity and wide surface area because the presence of these copper sites can react with GLY which in turn increase its sensitivity and aid the electrochemical detection. Thus, this built-in sensor, made of AuNPs, had high conductivity and successfully used applied to the samples of water, carrot, soybean and wheat. [17] Owing to more stability and less toxic nature of La_2S_3 , Umamaheswari Rajaji et al., fabricated a novel electrode made of $\text{Sr@La}_2\text{S}_3$. The structural alterations were brought about by the metal-to-metal sulphide doping and this improved the electrochemical performance. The increased surface area and conductivity along with layered structure promoted easy movement of electrons in the MTO's redox process.

The RSD values were below two percent and hence it indicated the excellent selective detection of MTO with respect to other species in spiked samples of fruit extracts, river and industrial wastewater. [18]. Li Ruiyi et al., described the synthesis of a nanohybrid of gold-graphene QD by functionalized with aspartic acid to detect acetamiprid and omethoate. By the formation of Schottky heterojunctions at the interface, the addition of Au nanocrystals to Arg/Asp-GQD promoted the Au atoms exposure to boost the catalytic efficiency of the compound. The structural robustness of Arg/Asp-GQD-Au was improved by the effective contact of several Au particles which greatly improve repeatability for the electrochemical detection of ACE and OME [19]. Abdullah Alsulami et al., developed a FeV/RGO nano composite by a less harmful DES-mediated solvo thermal methodology. The material acted as a dual applicant in pesticide detection and its total destruction. A clear current response was observed for Methyl parathion while detecting in real samples of green beans and river water. [20]

- 2. Detection of Heavy Metals:** Heavy metal ion contamination has a negative impact on the ecosystem effecting food safety and in turn human health. [21,22] Also, the potential applications of MOF composites are thought to encourage their use and synthesis. [23,24] The innovative sensing platform was developed by Xinxing Wang et al., where UiO-66 MOFs were used concurrently for the detection of heavy metal ions where the composite consisted of thermally reduced GO with UiO-66- NH_2 MOF functionalized with ferrocene carboxylic acid. Thus the amino-group in the UiO MOF and activated Fc carboxylate covalently bonded and led to the confined Fc throughout the MOF skeleton. The Fc incorporation played dual roles, firstly the redox active sites are created in the network expediting the composite's conductivity. Second, ratiometric detection can exploit the Fc signal as an internal reference. This strategy contributes to the reduction of signal and background fluctuations resulting in great improvement in the detection dependability. The sensing platform exhibits outstanding electrochemical performance and exceptional structural properties enabling the detection of Pb^{2+} , Cd^{2+} and Cu^{2+} with

high sensitivity and reliability[25]. An investigation was done by Xinai Zhang to develop a sensor to examine the ppt level of lead in leafy vegetables. For the amplification of signal, the electrochemical sensor of porph@MOF to mimic peroxidase was used for Hg^{2+} detection.

This sensor with pb dependent receptor (DNA-zyme) showed good recovery, anti-jamming ability, high sensitivity and reliability. Thus this sensor was used for the lead detection in green cabbage and spinach samples[26]. Shangshang Ma et al., developed a three dimensional composite made rGO and Ag to electrochemically evaluate Hg^{2+} in human blood and fish samples. The large active electrochemical area with multiple fold structures present in the composite facilitates the Hg^{2+} deposition and hence its sensing. Negligible interference was observed when selectivity tests were carried out with the fabricated sensor. The sensor was practically tested for Hg^{2+} tracing in human whole blood and fish which showed good selectivity in various Hg^{2+} concentrations.[27]. Graphdiyne based electrochemical sensor was developed by Ying Li et al. to detect the trace amounts of Cd^{2+} and Pb^{2+} in water samples. Due to abundance of π -electrons on GDY, the surface becomes negatively charged creating conducive environment for the binding of metal cations. The empty orbitals of Cd^{2+} or Pb^{2+} made it possible to accept the electrons of the carbon atoms of the GDY which are sp hybridized. The GDY's acetylenic bonds functioned as the sites of the adsorption and alleviated the necessity of extra functional groups. Also, comparison studies of GDY with rGO was performed which implied that compared to reduced graphene oxide (rGO), the interaction between $\text{Cd}^{2+}/\text{Pb}^{2+}$ and graphdiyne (GDY) was more robust. This serves as additional evidence of the essential impact that the alkynyl groups in GDY [28]. Mehwish Akhtar et al., devised an electrochemical sensor by synergistically integrating the chelating and electro-catalytic properties of aniline and polyaniline with the reduced graphene oxide having exceptional stability and chemo-electric property.

The sensing abilities were improved by the linkage of functional groups of nitrogen such as imines and amines and augmented the rapid charge exchange kinetics, increased surface sites and the conductivity. Thus, a sensor with high response for Cu^{2+} , Pb^{2+} , and Cd^{2+} was developed with improved recovery percentages of metal ions and was applied for real-time application[29]. The in-depth study of electrochemical behavior of $\text{UiO-66-NH}_2/\text{GaOOH}$ was studied by Jing Ru et al., where the composite combined the advantages of GaOOH which has distinct electronic features and geometric structures and led to accelerated electron transfer. The peak currents recorded for different ions were distinct and showed the absence of interference between them. This chelation ability and adsorption capacity of this modified electrode facilitated the anti-interference mechanism. The active oxygen and nitrogen sites which were evenly dispersed on the surface made it plausible the heavy metal ions coordination with ligand. Further, the comparison studies were carried out for the detection of single metal ions with that of multiple ions and it was concluded that the mixture of ions showed a broad linear range. Hg^{2+} showed a steeper slope among the ions, but Pb^{2+} , Cd^{2+} and Cu^{2+} showed comparatively higher limits of detection and this was explained by the intermetallic compound formation and competitive deposition.[30].

- 3. Detection of Antibiotics:** Mani Govindasamy et al., developed a core-shell nanostar from $\text{Bi}_2\text{S}_3@\text{GCN}$ to electrochemically determine the CPL in samples of shrimp, milk and

honey. The peak response obtained for the core-shell material was higher compared to the bare and composite. Both the electrical conductivity and electrochemical abilities were significantly enhanced by synergic contribution of both graphitic carbon nitride and bismuth sulfide. The mechanism followed nitro-reduction of CPL where conversion of nitrophenyl group to hydroxylamine took place.[31]Chelladurai Karuppiah et al., fabricated a reliable PDA-VGCF sensor for chloramphenicol (CAP) detection. The materials chosen were PDA and VGCF, because VGCF has cost effectiveness, immense surface area, faster ionic mobility, higher electrochemical and mechanical strength and also possess high porosities.

The integration of quinoline and amine groups present in the PDA coating can change the nature of the surface characteristics from hydrophobic to hydrophilic. The electrochemical mechanism explored that the adsorption of nitro group present in CAP was made easier by the active electron rich sites of the PDA-VGCF sensor and followed successive reduction. Another significant benefit of using this sensor for CAP sensing is the abundance of EDG (electron-donating groups) that primarily occurred on the electrode's surface. Also, in contrast to other nitrogen based interferants, CAP features a free and powerful EWG at the planar structure. This metal-free catalyst was able to detect CAP in milk, honey and apple juice samples with good stability, reproducibility and low LOD.[32]Thomas Abraham et al. developed a binary composite of $ZrFe_2O_5/Ag_3PO_4/GCE$ to electrochemically detect tetracycline in spiked samples of milk.

The fabricated sensor had superior conductivity, low resistance, good anti-interference activity and pronounced reproducibility. [33]Amit K. Yadav et al., tried to find a label-free immunosensing platform using $nMoS_2$ NPs and by linking amide. Further the spiked samples of orange juice, milk and tap water were examined with the fabricated sensor and the sensor possessed acceptable stability, great selectivity, a wide detection range, a considerable detection limit and repeatability for the detection of AMP.[34]ROX, a coccidiostat is a prominent feed additive and causes neurological, cardiovascular and endocrine disorders by releasing arsenic, hence Nikhil et al., developed a sensor to detect ROX from Activated Carbon material obtained from *Desmostachy bipinnata* because it contained various functional groups like carboxylic and phenolic. During the electro catalytic reduction of ROX, a good linear response, better electron transfer and good accuracy and anti-interference were observed. The good adsorption towards ROX due to different types of interactions between ROX and AC. The sensor was tested in real blood samples which showed good LOD and LOQ values along with excellent rates of recoverability.[35]

- 4. Detection of Food Additives:** The Majority of the food colors contain hazardous complex aromatic compounds and an azo bond. Therefore identification of synthetic dyes and its detection degradation is imperative in order to regulate and manage the addition of synthetic colors.[36–39]Ke Zhang et al., constructed a screen printed microchip with core-shell nanostructure of $Mn_3O_4@C$ to detect the quantities of allura red (AR). The sensor showed high electro catalysis, remarkable recoverability, good anti-interference and higher electron transfer ability.

The sensor was capable of detecting even the low quantities of AR within 30 minutes in real sports juices. It had a broad linear range and possessed excellent

reusability even after 30 days due to stability of core shell structure[40]. N. Hareesha et al., developed an electrochemical food sensor with Poly(GA)/(MWCNTs-GT)CPS to detect Vanillin(VL) This sensor showed amplified electrochemical surface area with more active sites, enhanced proton and electron transfer rates. Since the pKa value was determined to be 7.5, it was concluded that the oxidation took place at the phenolic group. The study of effect of temperature showed enhanced oxidation peak currents for the variation of temperature from 5 to 30 °C and showed lesser current sensitivity after 30°C. The 4 different sample solutions containing vanillin i.e. milkshake, cream cake, biscuits and vanilla extract were analyzed which showed low LOD, excellent sensitivity and storage stabilities[41]. Ritu Singh et al., fabricated an analytical method to determine the acesulfame target by providing electrochemical platform combined with MIP. Different interferents such as saccharine, sucralose, fructose, caffeine and glucose did not affect the Ace-K rebinding signal even when the amount of interferents concentration increased by 10 fold. In particular, the imprinting factor which was 10.8 which signified the extreme recognition sites are present on MIP which are absent in non-imprinted sensor.

The electrochemical analysis reports for acesulfame detection were obtained after examining real samples of candy, cola drink and tabletop sweetener and these showed excellent rates of recoverability[42]. Rajasree G. Krishnan et al., developed a pencil graphite electrode for the detection of coumarin, a hepatotoxin. Here the coumaric acid is formed by the lactone ring opening of coumarin under an alkaline environment during electrochemical process. The effectiveness of the sensor in samples of raw milk was investigated and the faradic peak for coumarin electrooxidation while additional interfering agents failed to provide current response in voltammogram. This developed sensor is highly accurate and is cost effective as it does not involve pre-treatment procedures during detection and high linear range[43]. Pemmatte A. Pushpanjali et al., used electrochemical technique to detect curcumin in real turmeric samples. The electrode made up of PARMCNTPS showed intensified catalytic activity towards curcumin which was attributable to the large electroactive surface area. The outcome of the electrochemical response at the surface of electrode supported the reversible nature of curcumin. This electrode was simultaneously able to detect low quantities of curcumin even with the simultaneous occurrence of riboflavin and ascorbic acid[44].

- 5. Detection of Hazardous Chemicals:** Since OTA produced by fungi is a carcinogenic product found in malt and beer, hence Chaonan Sun et al., developed an electrochemical sensor to detect OTA (ochratoxin A) by using Au/TGA/bovine serum albumin electrode. During the electrochemical studies, it was figured out that the electrostatic repulsion between the COOH group and $[\text{Fe}(\text{CN})_6]^{3-}$ became weak since the negatively charged COOH groups got activated by EDC/NHS, which strengthened the oxidation peak current.

The sensor performed with great precision and no interference. Further its dependability was confirmed in actual spiked malt samples with low LOD[45]. The hazardous effects linked to consuming fish and seafood is specifically brought on by the activity of biogenic amines. Among which histamine is major biogenic amine is a major lung irritant. Yuwen Xu et al., developed Ni@C material as a sensor that is excellently sensitive and has a large linear range as intended and was used effectively to measure HA

in real samples which demonstrated excellent practicability and dependability. It is therefore Ni@C material has significantly enhanced the electrochemical behaviour of the sensor and has enormous promise as an electrochemical reaction platform for the detection of HA.[46]BPA,one of the endocrine-disrupting chemicals, BPA induces cell abnormalities, hypertension, and other problems even at low doses. Therefore its detection and elimination is highly appreciated.[47]Palanisamy Karthika et al., developed MIP|ERGO|GCE and examined the sensitivity of BPA in water and milk samples. They studied the interaction between MIP and BPA using computational analyses. According to their findings, the composite showed good binding energies, good recovery and a low LOD.[48]Tert-butylhydroquinone (TBHQ) is a type of chemical-based phenolic antioxidant that has been used extensively as an addition for preserving food, cosmetics, oil, and lipids from oxidizing while being stored and processed. But they have detrimental effect on stomach and liver.Fei Yan used GCE modified by VMSF/ErGO film to account for TBHQ detection in edible oils and cosmetics.

Here the ErGO was produced by electrochemically reducing GO onto the GCE surface and it acts as the functional substrate for the EASA method's stable and quick growth of VMSF. The sensitive reactivity of TBHQ was promoted by favourable electroactivity of ErGO and the VMSF hydrogen bond.[49]The incredible ability of nitrite, a well-liked food additive, to stop the growth of deteriorating microbes and to enhance the color and flavor of processed meat, makes it a common ingredient in meat products. However, in biological systems, the nitrite ions have been shown to interact with amides and amines to produce N-nitrosamines, which increases the risk of carcinogenic forms [50].Hence, Sethupathi Velmurugan et al., developed an electrode by coating with SnS₂ hexagons to detect nitrite. The analytical findings towards nitrite sensing showed better results and accuracy in comparison to spectrophotometric method. The results obtained elucidated that the sensor was able to electro-oxidize the compound and sense the lower quantities of nitrite in real meat samples[51]

III. CONCLUSIONS

This book chapter highlighted the use of various electrodes for sensing of pesticides, hazardous chemicals, food additives, antibiotics and hazardous chemicals The present status of research on the sensing technology is discussed here in the context of how various nanomaterials can be used to construct outstanding electrochemical sensing systems Even though development of electrochemical sensors has advanced convincingly, breakthroughs in the analysis of real samples are still required to be prioritized. It is envisaged that unprecedented developments in the proliferation of nanomaterials-based sensing devices will be comprehended in the foreseeable future to effectively tackle the pervasive chemical intoxication of the environment and foods due to ongoing and swift progress across many facets of sensing.

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