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# Insights into the Recent Advances in Nanomaterial Based Electrochemical Sensors for Pesticides in Food

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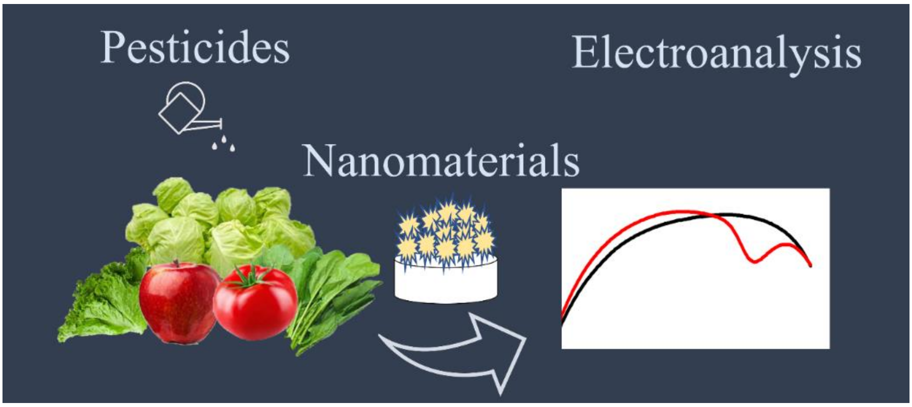
**Abstract.** Food safety is one of the rising concerns challenging all over the world and the analysis and determination of food contaminants to ensure the quality of food is highly inevitable. Electroanalytical sensors are a versatile tool for the accurate monitoring of food samples from the pollutants. Pesticides are one of the major sources of food pollutants and their impacts on human health is also very dangerous. This will trigger the researchers to develop more and more sensitive devices to monitor the level of various pesticides in various food samples, especially in agricultural products. Electrochemical sensors fabricated using nanocomposites offers more sensitive electrochemical response in the detection of these pesticides than traditional unmodified electrodes. This prompted us to write a mini review on the electrochemical sensors for pesticides in food using nanomaterials as modifiers from some of the previous reports. This review will motivate the experts working in this area to develop highly efficient sensing devices for pesticides, beneficial to the society as well.

Key words: Nanomaterials, electrochemical sensors, pesticides



Graphical Abstract

# 1. Introduction

Food safety is one of the serious predicaments that is facing all over the world in the present circumstances. It is an issue of major concern due to the increased health issues, mortality rates and huge economic responsibility associated with the usage of contaminated and low-quality food items [1]. Contamination of food may occur at various phases starting from their production to the processing and transportation stages [2]. The increased usage of pesticides in agriculture for economic interests is one main factor which contributes adverse effects in the food quality [3]. These pesticides are highly carcinogenic in nature and hence, its continuous exposure will cause serious health issues [4]. Thus, strict, and sensitive quantitative analytical techniques are required to monitor and control the misuse of these chemical species in food products.

Analytical techniques employing optical sensing [5], spectrophotometry [6], gas chromatography [7], ion -chromatography combined with fluorescence or UV detector [8], high performance liquid chromatography [9], etc. were reported for the quantification of different types of pesticides. However, compared to these analytical techniques, electrochemical detection offers advantages like easy miniaturization process, simpleness, rapid electrochemical reaction of target molecules etc. [10,11]. Also, electrochemical analysis renders high precision and reliability for the detection of analytes [12]. Owing to these excellences, a good deal of electrochemical sensors was reported for the direct electrochemical quantification of analytes for food safety [2]. In analytical and electrochemical applications, carbon- derived materials are highly significant due to their cost- effectiveness, extensive range of potential window, relative passivity towards various electrochemical reactions [13,14]. There are many reports for the electroanalytical determination of several analytes based on bare electrodes [15,16]. However, chemically modified electrodes exhibit more selectivity, sensitivity, and enhanced rate of electron transfer, thus making it suitable for the electrochemical sensing applications [17].

Nanomaterials are excellent class of materials to modify various electrodes to achieve properties appropriate for electrochemical sensors. Numerous electrochemical sensors were reported especially for the detection of pesticides using nanomaterials [18,19]. Nanocomposites of graphene oxide, CNTs, metals, polymers, Mxenes etc. were widely applied in the electrochemical sensors for various analytes [3,20]. Different nanomaterials utilized for the fabrication of electrochemical sensors for pesticides in food is given in figure 1. Considering the significance of these nanocomposites in fabricating highly selective and sensitive electrochemical sensing devices, we attempt to spotlight the nanocomposite modified electrochemical sensors for the detection of pesticides particularly in food. This review will help the researchers to explore the utility of nanocomposites in the far-reaching field of electrochemical analysis to enhance their research in future.

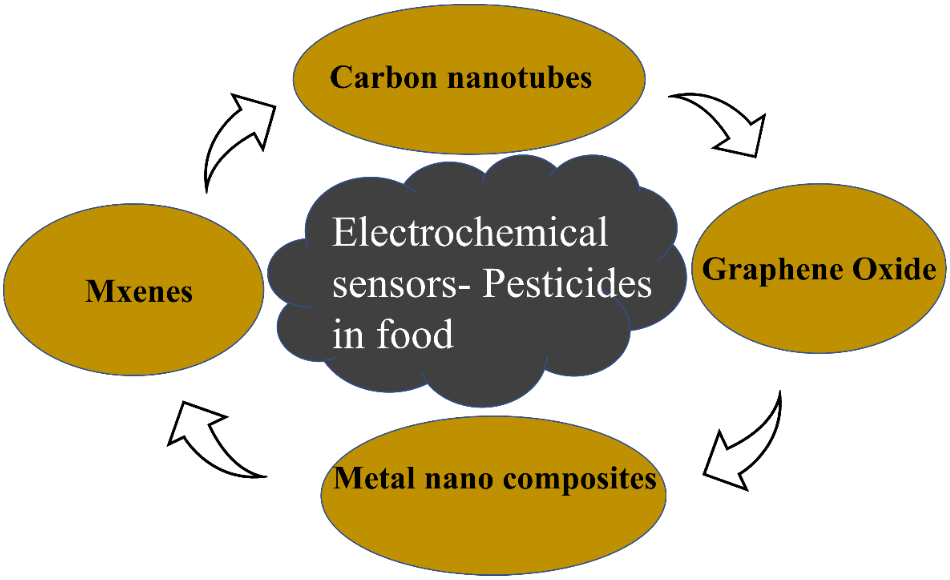


Figure1. Nanomaterials employed for the electrochemical detection of pesticides in food

### 1.1 Metal nanocomposites modified electrochemical sensors

Metal sulphides of transition metals are good choice for developing electrochemical sensors due to their environmentally benign nature, thermal and chemical stability, specific electronic structure etc. [21]. Among the various sulphides of transition metal series, nanomaterials of copper sulphides are fascinating biocompatible materials to be selected for electroanalytical research due to their simple preparation methods and good stability [22]. The bimetallic nanoparticles of copper and iron (CuFeS2) have high conductivity, electrocatalytic ability etc. and hence finds potential utilization in immunosensors, fuel cells, supercapacitors, dye-sensitized solar cells etc. [23–26]. Bimetallic nanoparticles (NPs) are more suitable for electrochemical sensors than single metallic nanoparticles due to their exceptional electrochemical properties [26]. However, the electrocatalytic properties of bimetallic nanoparticles can be further improved by incorporating these nanoparticles with graphene to form a nanocomposite [27]. A graphene oxide CuFeS2 nanocomposite on a screen-printed carbon electrode (SPE) was utilized for enhanced electrocatalytic determination of the pesticide methyl paraoxon (MP) in a non-enzymatic method [28]. MP is an active metabolite of the toxic pesticide methyl FT [29]. Electrochemical impedance spectroscopic (EIS) analysis of graphene oxide CuFeS2 nanocomposite modified SPE showed that conductivity of the electrode was increased to a great extent on the introduction of bimetallic NPs on the graphene. The highly conducting graphene oxide CuFeS2 nanocomposite enabled the electrochemical determination of MP by differential pulse voltametric (DPV) method. Cyclic voltammetry (CV) of MP on the modified SPE exhibited both oxidation and reduction peaks on phosphate buffer of pH 7. However, the peak current obtained due to the electro reduction was monitored for the quantification of MP. The reduction current increased linearly with amount of the analyte with a sensitivity of 17.97 μA/ μM/cm2. The highly selective, stable, and reproducible sensor was applied for the real time monitoring of MP in spiked extracts of vegetables with good recovery. Also, the proposed method was validated with standard HPLC method and proved its efficacy in the successful determination of the hazardous pesticide MP in real samples.

In another work, a nanocomposite of niobium carbide (NbC) and molybdenum was employed for the electroanalysis of fenitrothion (FT), an OP pesticide [30]. FT is a toxic chemical species added in agricultural fields to control the attack by insects, flies etc. on vegetables, fruits, grains etc [31][18]. FT is an endocrine disrupting compound that will impede the activity of acetylcholinesterase in human beings and leads to various neurological problems [32]. Due to the high conductivity and electrocatalytic nature, NbC nanocomposite was utilized in hydrogen evolution reactions [33]. Due to the enhanced surface area and distinctive optical, mechanical, and catalytic properties, Mo NPs is one of the widely studied material of interest in electrochemical research [34]. The combined effect of NbC and Mo in the nanocomposite was successful for the electrochemical detection of FT using DPV method. The fall off in the charge transfer resistance of the NbC-Mo/SPE compared to NbC/SPE, and Mo/SPE in the EIS analysis suggested the higher conductivity of the NbC-Mo/SPE. CV studies of FT on the modified SPE in PBS pH 7 showed both oxidation and reduction peaks. Nevertheless, the reduction peak at -0.58 V was selected for the quantitative determination of FT compared to anodic peak at 0.05 V. A very large decrease in the cathodic overpotential and improvement in the cathodic peak current was obtained on the NbC-Mo/SPE in comparison to other modified and bare SPE. This might be due to the substantial surface area of the nanocomposite comprising a 3-dimensional network of Mo and NbC nanofilms. A broad linear range of concentration was obtained towards the electroreduction of FT in DPV analysis and the sensor exhibited a sensitivity of 0.355 µA/ µM/cm2. Individual calibration plots were constructed for FT in the same experimental procedure with real samples of cranberry and grapes with very good results. This corroborated the effectiveness of NbC-Mo/SPE sensor in the real time monitoring of FT in fruit samples.

Mani Govidasamy et al. synthesised graphene nanoribbons (GNRs) backed with Ag nano particles on SPE for the electrochemical detection of methyl parathion (MPT) [35]. MPT is a highly toxic OP pesticide, which awfully affects our environment and food security systems [36]. Graphene based nanomaterials are one of the exemplary materials used in the electroanalytical research due to their unique properties [37][2][38]. GNRs are biocompatible and stable strips of quasi one-dimensional graphene nanosheets [39]. Several interesting properties like large surface area, higher electronic conductivity, robust mechanical properties etc. accelerates the dissemination of GNRs in the areas of drug delivery, bioimaging, sensors etc. [40]. Ag nanoparticles also holds certain properties like easily modifiable size, high surface area, catalytic activity, specific optical and chemical properties that paved the way for its applications in electrochemical sensors [41]. From the EIS analysis, a very large decrease in the charge transfer resistance for the GNRs-Ag/SPE compared to Ag/SPE and bare SPE. This makes the GNRs-Ag/SPE more relevant in electrochemical sensing strategies. In PBS pH 7, redox peaks of MPT were obtained for CV measurements. Howbeit, the reduction peak was suitable for electrochemical determination of MPT. The cathodic reduction potentials got a substantial decrease for GNRs-Ag/SPE from Ag/SPE and GNRs-Ag/SPE. This significant decrease of overpotential on GNRs-Ag/SPE may be due to the enhanced electrocatalytic ability of Ag nanoparticles [42]. The π-π interaction of the aromatic groups of MPT and GNRs along with the electrostatic interaction between the MPT and GNRs-Ag/SPE hastens the reduction process. The cathodic peak current of MPT increased linearly with increase in the concentration of MPT using amperometry with a sensitivity of 0.5940 µA/µM/ cm2. The GNRs-Ag/SPE validated its proficiency in the determination of MPT in vegetables such as cabbage, green beans and fruits like strawberry and nectarine fruit with high selectivity and reproducibility.

Another electrochemical sensor was reported for MPT based on cobalt bipyridyl complex (Co-BiPy) nanocomposite on a reduced graphene oxide (RGO) platform [43]. A Co-BiPy-RGO composite was modified on a glassy carbon electrode (GCE) for the real time monitoring of MPT in fruits and vegetable samples. An environmentally benign reduction method was adopted for the synthesis of RGO. RGO produced by the reduction process of GO are more conductive in nature compared to GO and graphene [44]. The properties of RGO can be tailored using different reduction techniques and can be applied in variety of applications [45]. Thus, RGO overshadowed graphene and GO in developing electrochemical sensors and biosensors [46]. Studies showed that, nanocomplexes are very effective in accelerating the electrochemical oxidation or reduction of the analytes at very low overpotentials with enhanced peak currents due to their active functional sites [47]. Several electrochemical sensors have been reported on grounds of metal organic nanocomplexes supported by carbon derived nanomaterials by virtue of its cost-effectiveness, excellent conductivity, high catalytic activity, and stability [48]. The Co-BiPy-RGO/GCE showed excellent electrocatalytic activity towards the electroreduction of MPT in PBS pH 7. EIS results of the modified and control electrodes displayed that, the introduction of cobalt bipyridyl complex on RGO significantly increased the conductivity of Co-BiPy-RGO/GCE than RGO/GCE and bare GCE. The electrocatalytic approach of the Co-BiPy-RGO/GCE towards electroreduction of MPT could be described due to the π-π interaction between the aromatic moieties of MPT and RGO. Also, some electrostatic interaction between the analyte and the modified electrode enhanced the electrocatalysis thereby reduction overpotential of MPT decreased to large extent compared to the control electrodes. Amperometry was used to determine the MPT and good linearity in a wide range was obtained for MPT detection 1.8197 µA/µM/ cm2. Satisfactory results were obtained for the important analytical characteristics of a sensor like stability, reproducibility, repeatability, and selectivity. The practical utility of the Co-BiPy- RGO/GCE sensor was done for the quantification of MPT in apple and tomato samples.

### 1.2 Electrochemical sensing devices based on nanocomposites of graphene oxide and carbon nanotubes

The use of nanoribbon forms of graphene oxide (GONRs) for the electrochemical determination of MPT on a SPE was introduced in another work by Mani Govidasamy et al. [49]. GONRs emerging class of one-dimensional nanomaterials obtained by the oxidative unzipping of carbon nanotubes (CNTs) [39][50]. GONRs are emerging carbon-based nanomaterials in electrochemical sensors due to the presence of several swinging bonds on the edges of the GONRs providing many reactive functional sites for electrochemical reactions [51]. Also, the large surface area of the GONRs provides a favourable route for these materials in electrochemical sensing applications [52]. The electrochemical performance of GONRs/SPE towards the reduction of MPT showed a very high reduction in overpotential compared to CNT/SPE and bare SPE. However, the GONRs/SPE was found be poorly conducting compared to the control electrodes such as CNT/SPE and bare SPE in EIS measurements due to the sp3 hybridised carbon along with the cluttered delocalised network of sp2 carbon atoms. This result agreed with GONRs-MWCNT /SPE for the analytical detection of the drug nimesulide [53]. The synergistic effect of GONRs and MWCNT influenced the electrochemical quantification of MPT on the developed sensor with highly stable and precise analytical performance. The sensor was fruitfully applied for the real time monitoring of MPT in fruits and vegetables.

Another graphene based electrochemical sensor for the determination of MPT was reported by Mani Govidasamy et al. in 2016 [54]. A GCE modified with a nanocomposite of graphene and molybdenum disulphide (MoS2) nanosheets were fabricated for the electrochemical sensing of MPT using amperometric method. MoS2 is one of the important lamellar-structured dichalcogenides of transition metals that offers a representative part in the fabrication of sensors, batteries, solar cells etc. [55]. The specific structural and electronic properties attracted MoS2 in the development of various electroanalytical sensing devices

[56]. MoS2 -GR nanocomposite was excellent for the electrochemical detection of MPT in limelight of their high surface area, good conductivity, and greater mechanical strength. The electrocatalytic ability of the MoS2 -GR/GCE towards the reduction of MPT enhanced the cathodic peak current to a large extent in 0.1M PBS pH 7. The π-π synergy between the aromatic groups of MPT and GR also greatly increased the electrocatalytic reduction of MPT on the nanocomposite modified GCE with a sensitivity of 0.457 (±0.008) μA/μM/ cm2. The amperometric sensing of MPT was done in fruits and vegetable samples with very low limit of detection (LOD).

Carbendazim (CZ) is a class of benzimidazole fungicide, used to wipe out various types of pathogens attacking the agricultural crops [57]. CZ is a barely degradable in soil due to its low solubility and the extensive use of highly toxic CZ will cause serious threats to human beings and the ecosystem [58]. An electrochemical sensor for the quantification of CZ was reported in 2020 utilizing the receptiveness of nanocomposites in the electroanalysis [59]. A CPE modified with a nanocomposite of fumed silica (FS) and Ag nanoparticles was used as an electroanalytical device for CZ monitoring. FS is having nano porous structure with high surface area, and it outperforms as a modifier in biosensors, electrochemical sensors, catalysis, adsorption etc. [60][61]. The combined effect of FS and Ag nanoparticles facilitated the electrooxidation of CZ on the electrode surface with a very high peak current. The DPV analysis of the electrode showed a linear variation in the current with the increase in the concentration of CZ with a slope 194 times higher than the unmodified CPE. This signifies the higher sensitivity of FS-Ag/CPE towards the electrochemical oxidation of CZ under the optimized analytical parameters. The FS-Ag/CPE acceded the electrochemical determination of CZ in spiked fruit juices and water samples with copacetic recovery.

Hexagonal boron nitrogen quantum dots (BNQDs), otherwise called ‘white graphene’ are biocompatible nanomaterials with prodigious properties such as better dispersibility, low toxicity and facile synthesis methods [62]. Hexagonal BNQDs are highly stable and have been applied in various areas of research like electrochemical sensors, catalysis, optoelectronics, semiconducting devices etc. [63]. A nanocomposite of BNQDs and GO were prepared and modified on a GCE for the simultaneous electrochemical detection of MP, diazinon (DZ) and chlorpyrifos (CPS) in water samples as well as apple juices [64]. GO has poor conductivity due to the disruption pf sp2 bonds and the formation of large number of surface functional groups during the synthesis of GO from graphene. However, the BNQDs-GO nanocomposite surmounted such limitations of GO and it is an assured scaffold for the electrocatalytic determination of MP, DZ and CPS in real samples. This improved electron transfer property is due to the synergistic effect of GO and BNQDs in the nanocomposite. The BNQDs- GO/GCE sensor displayed high selectivity for the determination of MP, DZ and CPS in picomolar levels.

CPEs modified with a biochar and RGO nanocomposite were investigated for the electrochemical oxidation of CZ in real samples using DPV analysis [65]. The association between biochar and RGO on CPE was proven selective and was practically implemented for the determination of CZ in spiked orange juice, lettuce leaves and water samples. The sensor enhanced the electrocatalytic oxidation of CZ with a higher anodic peak current due to the combined effect of biochar and RGO. The electrostatic as well as π- π interaction of the CZ and biochar coupled with the less resistance of the RGO strengthened the electrochemical response of CZ on the modified electrode with very low LOD [66][67].

Recently, an electrochemical detection device for the monitoring of toxic OP pesticide dicapthon (DN) was introduced by Lei Wang et al. based on a nanocomposite of multiwalled carbon nanotubes (MWCNT) and Au nanoparticles [68]. The MWCNT- Au nanoparticle modified GCE showed enhanced peak currents towards the electrochemical reduction of DN than the bare GCE and MWCNT-GCE in DPV measurements. This may be credited to the superior characteristics like colossal large surface area and huge conductivity of Au nanoparticles [69]. The sensor was successfully utilized for the selective determination of DN from food samples.

The MWCNT- Au nanoparticle on GCE was successfully applied for the electrochemical detection of another pesticide dichlorvos (DV) by Yi Chen et al. in 2021 [70]. DV is also a toxic OP pesticide used to flies, bugs etc. and it shows many adverse effects to human beings [71]. Under the optimized experimental parameters, the modified electrode showed high selectivity for the determination of DV in real vegetable samples.

The use of MWCNT in the modification of a CPE for the non-enzymatic electrochemical detection of DZ was reported in 2019 [72]. The sensor showed excellent electrocatalytic performance than bare CPE for the electrooxidation of DZ due to the exceptional properties of MWCNTs. Also, MWCNT-CPE showed its efficiency in the detection of toxic pesticide, DZ in vegetable and food samples with no significant interference.

Joan chepkoech kilele and co-workers fabricated an electrochemical sensor for the detection of FT using different types of nano materials such as ionic liquid (IL), carbon nanotube and metal oxide [73]. The IL/CoFe2O4NPs/MWCNTs/GCE exhibited improved electrochemical response for the electrooxidation of FT on GCE. IL acts as a good modifier for the development of electrochemical devices due to their high conductivity [74]. Also, Ils can be easily functionalized with CNTs due to the $\pi - \pi$ electronic interactions and moreover the CNT-metal oxide-IL modified electrode possessed high ionic and electrical conductivity [75]. The practicality of the sensor was tested in orange and grape samples with much selectivity.

A graphene and ZnO nanocomposite were employed for the electrochemical detection of MP from food and water samples in another work [76]. The metal oxides supported graphene oxide alters the properties of appropriate for electrochemical sensing applications [77]. The synergistic effect was fruitfully used for the detection of MP in cabbage and tomato samples with good recovery.

### 1.3 Electrochemical sensors based on MXene nanocomposites

A novel and sensitive electrochemical sensor for CZ was developed by Yu Xie te al. using electrochemically reduced graphene oxide (ERGO) and MXenes nanocomposites [78]. MXenes are 2-dimensional transition metal carbides that unveils great promise in the field of electroanalytical sensing and was reported by Michael Naguib et al. in 2011 [79][80]. MXenes provides intriguing characteristics like rich and tunable surface properties, higher electrical conductivity, biocompatibility, hydrophilicity, and easy preparation methods [81]. Thus, MXenes are good support for modifying the transducers in the electrochemical sensing of target molecules. Carbides of titanium (Ti3C2Tx) is one of the prominent and widely studied member of MXene family [82]. Tx in Ti3C2Tx represents the various functional groups on their surface and is responsible for the variable surface properties of Mxenes [83][84]. Albeit pristine Ti3C2Tx sheets encounters some bottleneck in electroanalytical applications due to the restacking of Ti3C2Tx layers [85]. The best suitable choice to overcome this limitation is to include carbon-based nanomaterials like CNTs and GRs in the 2- dimensional sheets of MXenes [86]. DPV was used for the electrochemical quantification of CZ in real samples like vegetable and fruit juices with high selectivity. The MXene – ERGO modified electrode showed higher current towards the redox behaviour of CZ compared to other control electrodes like bare GCE and ERGO-GCE. This revealed that the combined effect of MXene and ERGO showed a noteworthy role in the determination of CZ by voltammetric method.

Another electrochemical sensor based on bimetallic nanoparticle and MXene was developed by Wei Zhong et al. for the determination of CZ in vegetable samples [87]. A GCE was modified with a nanocomposite of amino- functionalized MWCNT, Au nanoparticles and Mxenes was utilized for the selective determination of CZ using DPV analysis. The amino- functionalized MWCNT-Au nanoparticles- Mxenes nanocomposite/GCE was proved to be highly efficient in the electrochemical detection of CZ, as it showed enhanced response for the electrooxidation of CZ compared to other control electrodes. Under the optimized conditions, the sensor showed excellent selectivity for CZ in vegetable samples with LOD in nanomolar concentrations. The comparison of the analytical performance of some of the electrochemical sensors for pesticides in food using nanomaterials is given in table 1.

TABLE 1. Comparison table

| **Electrode** | **Analyte** | **Electrochemical technique** | **Linear range (µM)** | **LOD (nM)** |
|---|---|---|---|---|
| **GO/CuFeS$_2$/SPE** | MP | DPV | 0.073– 801.5 | 4.5 |
| **NbC-Mo/SPE** | FT | DPV | 0.01-1889 | 0.15 |
| **GNRs-Ag/SPE** | MPT | Amperometry | 0.005 –2780 | 0.5 |
| **Co-BiPy- RGO/GCE** | MPT | Amperometry | 0.05-1700 | 2.9 |
| **GONRs/SPE** | MPT | Amperometry | 0.1 - 2500 | 0.5 |
| **GR-MoS$_2$/GCE** | MPT | Amperometry | 0.01–1905 | 3.23 (±0.82) |
| **FS-Ag/CPE** | CZ | DPV | 0.05 - 10 | 94 |
| **BNQDs- GO/GCE** | MP, DZ, CPS | DPV | $1\times10^{-6}$ -$1\times10^{-3}$ | $3.1\times10^{-4}$, $6.7\times10^{-5}$, $3.3\times10^{-5}$ |
| **Biochar-RGO/CPE** | CZ | DPV | 0.03 - 0.9 | 7.7 |
| **IL/CoFe2O4NPs/MWCNTs/GCE** | FT | DPV | 0.02–160 | 0.0135 |
| **MWCNT-Au/ GCE** | DN | DPV | 0 - 80.63 | $3.026\times10^{-4}$ |
| **MXene-Ag-NH2-MWCNTs/GCE** | CZ | DPV | $0.3\times10^{-3}$ 10 | $0.1\times10^{-3}$ |
| **Mxene-ERGO/GCE** | CZ | DPV | 0.002- 10 | 0.00067 |
| **MWCNT-Au/ GCE** | DV | DPV | 1-120 | 0.005 |
| **MWCNT/ CPE** | DZ | SWV | $1\times10^{-4}$ - $6\times10^{-2}$ | $4.5\times10^{-4}$ |
| **ZnO/GR/GCE** | MP | DPV | $8\times10^{-3}$ - $161\times10^{-3}$ and $242\times10^{-3}$ - $404\times10^{-2}$ | $6.47\times10^{-3}$ |

## Conclusion

Monitoring of food quality is one of the challenging areas of research, as the demand for food is increasing all over the world. Pesticides are the major class of chemical species which cause contamination to the food. These pesticides will cause severe side effects to humans even leads to serious health problems to future generation also. So, to assure the proper safety and quality of food, more and more advanced analytical techniques are required. Among the several analytical techniques, electrochemical techniques are more beneficial as it requires more simple instrumentation and even low concentration of analyte can be determined from the real samples. Detection of pesticides from food samples using highly efficient electrochemical sensors has been reported for many years. The electrochemical sensors utilizing the benefits of nanomaterials have also been reported. Nanomaterials and nanocomposites are very interesting class of materials in electrochemical sensing due to their extraordinary properties suitable for the electrocatalytic detection of pesticides. Owing to the importance of nanomaterials in the pesticide sensors, we focussed to write a mini review electrochemical sensors for pesticides in food employing the exceptional properties of nanomaterials. We also emphasised the performance of various electrochemical sensors in the analytical point of view. This review will aid the researchers to intrigue the features of nanomaterials in this area of research and will enlighten the future research to be more productive and beneficial to the society.

## References

[1] G. Bülbül, A. Hayat, S. Andreescu, Sensors (Switzerland). **15** 30736–30758 (2015)
[2] X. Hou, H. Xu, T. Zhen, W. Wu, Trends in Food Science and Technology. **105** 76–92 (2020)
[3] S. Viswanathan, P. Manisankar, Journal of Nanoscience and Nanotechnology. **15** 6914–6923 (2015)
[4] D.R. Wallace, A.B. Djordjevic, Current Opinion in Toxicology. (2020) https://doi.org/10.1016/j.cotox.2020.01.001.
[5] F.F. Talari, A. Bozorg, F. Faridbod, M. Vossoughi, Journal of Environmental Chemical Engineering. **9** 104878 (2021)
[6] M. Soylak, M. Agirbas, E. Yilmaz, Food Chemistry. **338** 128068 (2021)
[7] M.D. Hernando, A. Agüera, A.R. Fernández-Alba, L. Piedra, M. Contreras, Analyst. **126** 46–51 (2001)
[8] N. Muhammad, M. Zia-ul-Haq, A. Ali, S. Naeem, A. Intisar, D. Han, H. Cui, Y. Zhu, J.L. Zhong, A. Rahman, B. Wei, Arabian Journal of Chemistry. **14** 102972 (2021)
[9] H. Chen, X. Wang, P. Liu, Q. Jia, H. Han, C. Jiang, J. Qiu, Foods. **10** (2021). https://doi.org/10.3390/foods10010189.
[10] A. Santhy, B. Saraswathyamma, A. Parvathy Krishnan, L. Luscious, Materials Today: Proceedings. **46** 2998–3004 (2020)
[11] S. Antherjanam, B. Saraswathyamma, Mater Chem Phys. **275** 125223 (2021)
[12] A. Vadivaambigai, P.A. Senthilvasan, N. Kothurkar, M. Rangarajan, Nanoscience and Nanotechnology Letters. **7** 140–146 (2015)
[13] A. Qureshi, W.P. Kang, J.L. Davidson, Y. Gurbuz, Diamond and Related Materials. **18** 1401–1420 (2009)
[14] A.A. Lahcen, S. Rauf, T. Beduk, C. Durmus, A. Aljedaibi, S. Timur, H.N. Alshareef, A. Amine, O.S. Wolfbeis, K.N. Salama, Biosensors and Bioelectronics. **168** 112565 (2020)
[15] D. Kuzmanović, M. Khan, E. Mehmeti, R. Nazir, N.R.R. Amaizah, D.M. Stanković, Diamond and Related Materials. **64** 184–189 (2016)

[16] A. Santhy, S. Beena, G. Krishnan Rajasree, S. Greeshma, IOP Conference Series: Materials Science and Engineering. **872** 012127 (2020)
[17] M. Sajid, M.K. Nazal, M. Mansha, A. Alsharaa, S. Muhammad, S. Jillani, C. Basheer, Trends in Analytical Chemistry. **76** 15–29 (2015)
[18] A.A. Ensafi, R. Noroozi, N. Zandi–-Atashbar, B. Rezaei, Sensors and Actuators, B: Chemical. **245** 980–987 (2017)
[19] G. Aragay, F. Pino, A. Merkoçi, Chemical Reviews. **112** 5317–5338 (2012)
[20] F. Zhao, Y. Yao, C. Jiang, Y. Shao, D. Barceló, Y. Ying, J. Ping, Journal of Hazardous Materials. **384** 121358 (2020)
[21] Y. Li, L. Liu, X. Liu, Y. Ren, K. Xu, N. Zhang, X. Sun, X. Yang, X. Ren, Q. Wei, Biosensors and Bioelectronics. **163** 112280 (2020)
[22] Z.T. Liu, S.K. Li, R.T. Wei, A.Y. Chen, Y.Q. Chai, R. Yuan, Y. Zhuo, Sensors and Actuators, B: Chemical. **274** 110–115 (2018)
[23] A. Yang, X. Huangfu, L. Liu, W. Luo, W. Zhao, J. Yin, Journal of Electroanalytical Chemistry. **871** 114269 (2020)
[24] M. Zhang, W. Hong, R. Xue, L. Li, G. Huang, X. Xu, J. Gao, J. Yan, New Journal of Chemistry. **42** 2081–2088 (2018)
[25] A. Mohammadi Zardkhoshoui, S.S. Hosseiny Davarani, Dalton Transactions. **49** 3353–3364 (2020)
[26] M. Guler, V. Turkoglu, A. Bulut, M. Zahmakiran, Electrochimica Acta. **263** 118–126 (2018)
[27] D. Lu, Y. Zhang, S. Lin, L. Wang, C. Wang, Talanta. **112** 111–116 (2013)
[28] U. Rajaji, K. Murugan, S.M. Chen, M. Govindasamy, T.W. Chen, P.H. Lin, P. Lakshmi prabha, Compos B Eng. **160** 268–276 (2019)
[29] H. Parham, N. Rahbar, Journal of Hazardous Materials. **177** 1077–1084 (2010)
[30] M. Govindasamy, U. Rajaji, S.M. Chen, S. Kumaravel, T.W. Chen, F.M.A. Al-Hemaid, M.A. Ali, M.S. Elshikh, Anal Chim Acta. **1030** 52–60 (2018)
[31] N. Shams, H.N. Lim, R. Hajian, N.A. Yusof, J. Abdullah, Y. Sulaiman, I. Ibrahim, N.M. Huang, RSC Advances. **6** 89430–89439 (2016)
[32] J. Nebu, J.S. Anjali Devi, R.S. Aparna, B. Aswathy, G.M. Lekha, G. Sony, Sensors and Actuators, B: Chemical. **277** 271–280 (2018)
[33] E. Coy, L. Yate, D.P. Valencia, W. Aperador, K. Siuzdak, P. Torruella, E. Azanza, S. Estrade, I. Iatsunskyi, F. Peiro, X. Zhang, J. Tejada, R.F. Ziolo, ACS Applied Materials and Interfaces. **9** 30872–30879 (2017)
[34] M. Keerthi, G. Boopathy, S.M. Chen, T.W. Chen, B.S. Lou, Scientific Reports. **9** 1–12 (2019)
[35] M. Govindasamy, V. Mani, S.M. Chen, T.W. Chen, A.K. Sundramoorthy, Sci Rep. **7** 1–11 (2017)
[36] D. Pan, S. Ma, X. Bo, L. Guo, Microchimica Acta. **173** 215–221 (2011)
[37] T.Di. Bharathi, S. Prem Anandh, M. Rangarajan, in: INDICON 2018 - 15th IEEE India Council International Conference, 2018. https://doi.org/10.1109/INDICON45594.2018.8986994.

[38] S. Ramakrishnan, K.R. Pradeep, A. Raghul, R. Senthilkumar, M. Rangarajan, N.K. Kothurkar, Analytical Methods. **7** 779–786 (2015)

[39] F. Valentini, M. Carbone, G. Palleschi, Anal Bioanal Chem. **405** 3449–3474 (2013)

[40] P. Shende, S. Augustine, B. Prabhakar, Carbon Letters. **30** 465–475 (2020)

[41] A. Yu, Q. Wang, J. Yong, P.J. Mahon, F. Malherbe, F. Wang, H. Zhang, J. Wang, Electrochimica Acta. **74** 111–116 (2012)

[42] A. Kumaravel, M. Chandrasekaran, Journal of Electroanalytical Chemistry. **638** 231–235 (2010)

[43] M. Govindasamy, S. Sakthinathan, S.M. Chen, T.W. Chiu, A. Sathiyan, J.P. Merlin, Electroanalysis. **29** 1950–1960 (2017)

[44] R. Tarcan, O. Todor-Boer, I. Petrovai, C. Leordean, S. Astilean, I. Botiz, Journal of Materials Chemistry C. **8** 1198–1224 (2020)

[45] A.T. Smith, A.M. LaChance, S. Zeng, B. Liu, L. Sun, Nano Materials Science. **1** 31–47 (2019)

[46] B. Amanulla, S. Palanisamy, S.M. Chen, V. Velusamy, T.W. Chiu, T.W. Chen, S.K. Ramaraj, Journal of Colloid and Interface Science. **487** 370–377 (2017)

[47] T. Kondori, S. Tajik, N. Akbarzadeh-T, H. Beitollahi, C. Graiff, H.W. Jang, M. Shokouhimehr, RSC Advances. **11** 3049–3057 (2021)

[48] P. Gayathri, Sakshi, K. Ramanujam, Journal of The Electrochemical Society. **165** B603–B609 (2018)

[49] M. Govindasamy, R. Umamaheswari, S.-M. Chen, V. Mani, C. Su, J Electrochem Soc. **164** B403–B408 (2017)

[50] J. Kusuma, R.G. Balakrishna, S. Patil, M.S. Jyothi, H.R. Chandan, R. Shwetharani, Solar Energy Materials and Solar Cells. **183** 211–219 (2018)

[51] C.L. Sun, C.T. Chang, H.H. Lee, J. Zhou, J. Wang, T.K. Sham, W.F. Pong, ACS Nano. **5** 7788–7795 (2011)

[52] Y.X. Huang, X.W. Liu, J.F. Xie, G.P. Sheng, G.Y. Wang, Y.Y. Zhang, A.W. Xu, H.Q. Yu, Chemical Communications. **47** 5795–5797 (2011)

[53] M. Govindasamy, V. Mani, S.M. Chen, T. Maiyalagan, S. Selvaraj, T.W. Chen, S.Y. Lee, W.H. Chang, RSC Advances. **7** 33043–33051 (2017)

[54] M. Govindasamy, S.M. Chen, V. Mani, M. Akilarasan, S. Kogularasu, B. Subramani, Microchimica Acta. **184** 725–733 (2017)

[55] X. Li, X. Du, Sensors and Actuators, B: Chemical. **239** 536–543 (2017)

[56] T. Wang, K. Du, W. Liu, J. Zhang, M. Li, Electroanalysis. **27** 2091–2097 (2015)

[57] Y. Guo, S. Guo, J. Li, E. Wang, S. Dong, Talanta. **84** 60–64 (2011)

[58] T. Huang, T. Ding, D. Liu, J. Li, Journal of Agricultural and Food Chemistry. **68** 3703–3710 (2020)

[59] A. Özcan, F. Hamid, A.A. Özcan, Talanta. **222** (2021). https://doi.org/10.1016/j.talanta.2020.121591

[60] A. Kaushik, P.R. Solanki, K.N. Sood, S. Ahmad, B.D. Malhotra, Electrochemistry Communications. **11** 1919–1923 (2009)
[61] A. Özcan, M. Gürbüz, A. Özbal, Sensors and Actuators, B: Chemical. **255** 1517–1524 (2018)
[62] B. Huo, B. Liu, T. Chen, L. Cui, G. Xu, M. Liu, J. Liu, Langmuir. **33** 10673–10678 (2017)
[63] R. Jerome, A.K. Sundramoorthy, Journal of The Electrochemical Society. **166** B3017–B3024 (2019)
[64] M.L. Yola, J Mol Liq. **277** 50–57 (2019)
[65] M.V.S. Sant'Anna, S.W.M.M. Carvalho, A. Gevaerd, J.O.S. Silva, E. Santos, I.S.C. Carregosa, A. Wisniewski, L.H. Marcolino-Junior, M.F. Bergamini, E.M. Sussuchi, Talanta. **220** 1–8 (2020)
[66] P.R. de Oliveira, C. Kalinke, J.L. Gogola, A.S. Mangrich, L.H.M. Junior, M.F. Bergamini, Journal of Electroanalytical Chemistry. **799** 602–608 (2017)
[67] H. Shamkhalichenar, J.-W. Choi, Journal of The Electrochemical Society. **167** 037531 (2020)
[68] L. Wang, Y. Liu, Y. Chen, Int J Electrochem Sci. **16** 1–13 (2021)
[69] F. Wang, Y. Wang, K. Lu, X. Wei, B. Ye, Journal of Electroanalytical Chemistry. **674** 83–89 (2012)
[70] Y. Chen, K. He, F. Sun, D. Wei, H. Li, Int J Electrochem Sci. **16** 1–12 (2021)
[71] H.U. Okoroiwu, I.A. Iwara, Interdisciplinary Toxicology. **11** 129–137 (2018)
[72] F. zahirifar, M. Rahimnejad, R.A. Abdulkareem, G. Najafpour, Biocatal Agric Biotechnol. **20** 101245 (2019)
[73] J.C. Kilele, R. Chokkareddy, G.G. Redhi, Microchemical Journal. **164** 106012 (2021)
[74] Hadi Beitollahi, Fariba Garkani Nejad, Russian Journal of Electrochemistry. **55** 1162–1170 (2019)
[75] N.F. Atta, S.A. Abdel Gawad, E.H. El-Ads, A.R.M. El-Gohary, A. Galal, Sensors and Actuators, B: Chemical. **251** 65–73 (2017)
[76] A.E. Parab, K. Mohanapriya, N. Jha, Materials Today: Proceedings. **42** 710–717 (2020)
[77] G. Mathew, P. Dey, R. Das, S.D. Chowdhury, M. Paul Das, P. Veluswamy, B. Neppolian, J. Das, Biosens Bioelectron. **115** 53–60 (2018)
[78] Y. Xie, F. Gao, X. Tu, X. Ma, Q. Xu, R. Dai, X. Huang, Y. Yu, L. Lu, J Electrochem Soc. **166** B1673–B1680 (2019)
[79] D. Wu, M. Wu, J. Yang, H. Zhang, K. Xie, C. Te Lin, A. Yu, J. Yu, L. Fu, Materials Letters. **236** 412–415 (2019)
[80] M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi, M.W. Barsoum, Advanced Materials. **23** 4248–4253 (2011)

[81] F. Shahzad, S.A. Zaidi, R.A. Naqvi, Critical Reviews in Analytical Chemistry. **0** 1–18 (2020)
[82] M.R. Nateghi, Russian Journal of Electrochemistry. **55** 52–59 (2019)
[83] Y. Gogotsi, B. Anasori, ACS Nano. **13** 8491–8494 (2019)
[84] A. Szuplewska, D. Kulpińska, A. Dybko, M. Chudy, A.M. Jastrzębska, A. Olszyna, Z. Brzózka, Trends in Biotechnology. **38** 264–279 (2020)
[85] D. Xiong, X. Li, Z. Bai, S. Lu, Small. **14** 1–29 (2018)
[86] M.Q. Zhao, C.E. Ren, Z. Ling, M.R. Lukatskaya, C. Zhang, K.L. Van Aken, M.W. Barsoum, Y. Gogotsi, Advanced Materials. **27** 339–345 (2015)
[87] W. Zhong, F. Gao, J. Zou, S. Liu, M. Li, Y. Gao, Y. Yu, X. Wang, L. Lu, Food Chem. **360** 130006 (2021)