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Functionalized Nanoparticles for Detection of Pesticides and Toxic Metal Ions: A Comprehensive Review

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Abstract

The emerging technology of nanotechnology has fundamentally changed the approach to environmental monitoring, especially in the process of pesticides and toxic metal ions detection in various environmental and biological samples. It is the functionalised nanoparticles (particularly gold and silver) which have emerged as a potent sensing surface, due to their unique physicochemical properties including large surface areas, surface plasmon resonance at the limit and tuneable optical results. This is a review of recent advances in the detection methodologies of substances in the nanoparticle-based detection of pesticides and toxic metal ions with emphasis on functionalisation strategies and sensing mechanisms along with practical applications. Conventional methods of analysis of pesticides and heavy metals, although accurate, are often time consuming, expensive and require use of advanced equipment and highly skilled employees. Compared to these, nanoparticle-based colourimetric sensors are fast, cost-efficient, and on-site applications with a visual output, which makes them highly applicable in the field and in environmentally limited conditions. The review critically analyzes a diversity of functionalised nanoparticles, such as carbon based, metal based, metal-oxide based and metal-organic framework based nanomaterials, with their synthesis protocols, characterisation mechanisms and detection mechanisms. Specific focus is made on the multimodal sensing strategies, a combination of colourimetric, fluorescent, electrochemical and surface enhanced Raman spectroscopies techniques, thus providing increased sensitivity and selectivity. The new developments in technology in nanozymes, aptamer-functionalised nanoparticles and portable sensors integrated into smartphones are mentioned. The current issues that have also been discussed in the review include matrix interference, reproducibility, standardisation and long-term stability of nanoparticle-based sensors. Future trends especially the incorporation of artificial intelligence, a microfluidic platform and point-of-care testing devices are addressed. This tedious examination is informative to the researcher involved in the manufacturing of next generation nanoparticles based sensors in environmental and food safety monitoring.

Keywords: Functionalized Gold & Silver nanoparticles; Pesticide detection; Heavy metal ions; Colorimetric sensing; Environmental monitoring

1. Introduction

One of the most urgent issues facing modern society is the environmental pollution by pesticides and toxic metal ions and its significant consequences on the health of people, the ecological sustainability and food safety [1][2]. The extensive use of pesticides in the farming methods has instilled their ubiquitous existence in the soil, water and the biotic food chains and industrial processes are introducing poisonous heavy metals into the environment[3]. These environmental pollutants are very dangerous to human health and they include carcinogenicity, endocrine disruption, neurotoxicity and reproductive disorders[4][5]. A science which deals with matter at the nano scale i.e. nanotechnology

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has become a revolutionary paradigm to solve the problem of environmental monitoring[6][7]. Nanoparticles exhibit distinctive physicochemical characteristics that are significantly different than those of their bulk counterparts including the quantum confinement effects, high surface-to-volume ratios and optical peculiarities[8]. Among the range of nanomaterials the noble metal nanoparticles have received significant interest based on their outstanding localised surface plasmon resonance characteristics which allow them to be visualised as changing colour when in contact with target analytes[9][10].

1.1. Pesticides as Environmental Pollutants

The agricultural agents include pesticides, especially the organophosphates, carbamates, organochlorines and pyrethroids which are a ubiquitous group of agricultural agents used to enhance crop productivity and reduce pest pressures [11]. Nevertheless, their extensive use has given rise to grave ecological and toxicological apprehensions since bioaccumulation and persistence of such compounds may cause adverse effects on non-target organisms and human being. Specifically, organophosphate pesticides block the action of acetylcholinesterase inducing the neurotoxic effects, including perspiration, vomiting, diarrhea, drowsiness, convulsions and in serious cases, coma [12][13]. The World Health Organization estimates the number of people dying in the developing areas due to organophosphate and carbamate poisoning is around 200,000 every year [14]. The fact that potent agrochemicals such as DDT, endosulfan, chlorpyrifos and malathion are long-lasting and persist in the environmental matrices makes it a requirement to maintain strict and continuous surveillance. Traditional quantitative methods like the gas chromatography, mass spectrometry and the high-performance liquid chromatography provide high quality quantitative data. however, they require complex equipment, costly consumables and highly trained personnel to operate[15][16]. The above limitations highlight the importance of quick, cost effective and field deployable detection systems that can easily be adopted by on-site staff.

1.2. Toxic Metal Ions and their impact on the environment

Non-biodegradable pollutants of heavy metals, including mercury, lead, cadmium, chromium and arsenic, accumulate in trophic webs and therefore cause severe toxicity in organisms[17][18]. The major sources of such contamination in aquatic and terrestrial systems are industrial discharges, mining by-products, agricultural runoff and improper waste disposal [19]. Even low levels of such metals are very dangerous to human health such as kidney damage, neurotoxicity, bone defects as well as carcinogenesis [20][21]. Heavy metals in drinking water and edibles have very strict limits set by regulations according to the World Health Organization. The highest concentrations that should be allowed in drinking water are 1 μg/L for mercury, 10 μg/L for cadmium, and 10 μg/L for lead [22]. Analysis of these low concentrations is necessitated by exceptionally sensitive analysis. Despite the popularity of atomic absorption spectroscopy and inductively coupled plasma mass spectrometry as gold standards, their cost and technological sophistication is prohibitive and restricts their common use in resource-limited areas [23].

1.3. Sensing Platforms Based on Nanoparticles

The introduction of nanoparticles based sensors has revolutionized environmental analytical chemistry and with its high sensitivity, versatility and portability the sensors are much better than their traditional counterparts [24][25]. Strong optical absorption properties of metallic nanoparticles are due to surface-plasmon resonance, which is extremely sensitive to particle size, shape, aggregation state and dielectric environment around the particle [26][27][28]. Therefore, alterations in these parameters are good indications of the presence of the analytes. These nanostructures are functionalized with custom recognition elements to increase their selectivity to particular targets. Some of the strategies include conjugation of organic ligands, biomolecules, aptamers, antibodies and polymeric shells to the nanoparticle surface [29][30]. Upon functionalization, nanoparticles are able to interact with pesticides or metal ions by means of electrostatic interactions, coordination bonds, hydrogen bonding and hydrophobic interactions, which allows them to selectively detect various contaminants[31][32].

1.4. Detection Mechanisms and Strategies

Detection based on nanoparticles mostly depends on the observation of change in optical properties when analyte is bound to the particle. There are four major modalities that are regularly used *colorimetric, fluorescence, surface-enhanced Raman spectroscopy and electrochemical sensing* [33][34]. The colorimetric method, which is based on hue variations caused by aggregation, provides naked-eye detection and eliminates the use of sophisticated equipment [35]. Fluorescence methods are sensitive by using quenching effects or enhancement effects [36]. The surface-enhanced Raman spectroscopy uses the amplification of electromagnetic fields at the surface of nanoparticles to enhance typical vibrational features [37]. The use of electrochemical sensors takes advantage of the catalytic qualities of nanoparticles to hasten the transfer of electrons, thus enhancing the limits of detection [38]. The future is predicted by multi-modal platforms that combine two or more sensing strategies to obtain synergistic analytical performance due to cross-validation of signals [39][40]. Combining these systems with smartphones, microfluidic systems and paper based systems has resulted in user friendly, portable instruments that can monitor in real time on site [41][42]. This is a general overview of the current state of the art of functionalized nanoparticles based sensors in detecting pesticides and toxic metal ions. It critically assesses synthesis pathways, functionalization strategies, sensing, analysis, practical applications and comments on the existing challenges and future research opportunities.

2. Materials and Methods

2.1. Synthetic Methods of Nanoparticle

Various methods of synthetic approaches have been developed to make nanoparticles of precisely controlled size, morphology and surface chemistry. The chosen synthetic pathway has a severe influence on the following physicochemical properties of the particles and hence, the selectivity and sensitivity of the resultant sensors.

2.1.1. Chemical Reduction Methods

The most common methodology of preparing metallic nanoparticles is chemical reduction. With gold, the Turkevich protocol, which eliminates chloroauric acid with sodium citrate at high temperatures, produces 10-20nm diameter monodisperse spheres[43]. The Brust Schiffrin method, which uses a biphasic system to stabilize the thiol is used to prepare smaller, highly stabilized particles[44]. In the case of silver nanoparticles, sodium borohydride along with the help of stabilizers (polyvinylpyrrolidone or citrate)[45][46], is regularly employed as an effective reducing agent. The degradation occurs through the reaction

$$AgNO_3 + NaBH_4 \rightarrow Ag^0 + \frac{1}{2}H_2 + \frac{1}{2}B_2H_6 + NaNO_3$$

in which the stoichiometry emphasizes the stoichiometric equilibrium between the reducing agent and the metal salt. Parameters of reaction such as concentration of reducing agent, temperature, pH and agitation rate play a critical role in determining the size distribution and morphology of the particles[47].

2.1.2. Green Synthesis Methods

Green synthetic pathways make use of sustainable reducing and stabilizing sources like plant extracts, microorganisms or biomolecules, thus providing a greener substitute to traditional chemical processes[48][49]. The intrinsic reducing agents are phytochemicals, such as flavonoids, terpenoids, and polyphenols[50]. It is worth noting that tea leaf extracts, neem extracts, and turmeric extracts have been effectively utilized in the production of nanoparticle[51][52]. Gold nanoparticle synthesis using silk fibroin has shown exceptional biocompatibility and stability and the random coil form of the protein has steric hindrance against uncontrolled aggregation[53]. The green methods usually produce nanoparticles at room temperature with reproducibility and increased biocompatibility.

2.1.3. Physical Methods

The physical fabrication methods, including laser ablation, thermal decomposition and electrochemical synthesis, provide detailed control of the properties of nanoparticles. Laser ablation produces ultrapurified particles by focused laser beams directed to metal targets immersed in liquid media thereby avoiding chemical contamination[54]. Electrochemical synthesis controls oxidation reduction cycles at electrode interfaces and allows the regulation of nanoparticle characteristics by fine control of current and potential [55].

2.2. Strategies of functionalization

Functionalization increases nanoparticle selectivity and stability by either covalently or noncovalently binding recognition moieties to the particle surface. The approach is specific to the analyte of interest and mechanism of detection.

2.2.1. Small Molecule Functionalization

This method allows functionalizing small molecules to overcome drug delivery and drug targeting issues. Metallic surfaces can be coordinated to small organic ligands thiols, amines, carboxylic acids, phosphates etc. by electrostatic or covalent interactions [56]. The most commonly used functionalizing agents are cysteamine, lipoic acid, mercaptopropionic acid and citrate [57]. p-sulfonatocalix 6 -arene-functionalized nanoparticles have shown better selectivity in pesticide detection [58]. Functionalization is commonly performed by combining the nanoparticles with a surplus of ligand at controlled pH and temperature whereby the ligand is used to remove capping agents that are loosely bound to the nanoparticles and creating strong bonds between the surface metal atoms and the ligand. The surface coverage and the orientation of the ligands have significant impacts on sensor performance [59].

2.2.2. Aptamer Functionalization

Aptamers are single-strand DNA or RNA oligonucleotides that exhibit an extraordinary specificity and affinity towards their targets [60]. This recognition efficiency is combined with the inherent optical properties of the nanomaterial using aptamer-functionalized nanoparticles [61]. Aptamers are commonly conjugated to gold or silver particles by modification at their ends with thiol or amine groups [62]. Recent studies have also reported aptamer-gold nanoparticle assemblies with a range of pesticides with nanomolar detection limits. A conformational change in the aptamer triggered by binding the target causes aggregation or dispersion of nanoparticles, producing a measurable colorimetric response [63][64].

2.2.3. Enzyme Functionalization

Enzyme-functionalized nanoparticles utilize the enzyme-catalysis and substrate-specificity of analyte recognition [65]. The acetylcholinesterase-decorated particles are used as some of the prominent platforms in the detection of organophosphate pesticides by inhibition mechanisms [66]. The enzyme can be attached onto the nanoparticle surface by physical adsorption, covalent conjugation or entrapment in polymer matrices [67]. Nanoenzymes are nanomaterials that possess natural enzyme-like catalytic properties, which have been introduced as alternatives to natural enzymes that are cost-effective and thermostable [68][69]. Carbon, metal-oxide and metal-organic framework nanozymes possess peroxidase, oxidase or catalase mimetic function, which makes them very appropriate in sensing applications [70][71].

3. Characterization Techniques

To truly understand the structural, optical and chemical properties of functionalized nanoparticles thorough characterization is necessary.

3.1. UV-Visible Spectroscopy

The primary technique to explain the optical characteristics of nanoparticles is UV visible spectroscopy. Silver nanoparticles show an absorption maximum around 400-420 nm, while gold nanoparticles show a distinctive surface plasmon resonance peak around 520-540 nm [72]. The size, concentration, and aggregation state of nanoparticles can be determined from the peak position, intensity, and width [73].

Colorimetric sensing depends on the red-shift of the plasmon band due to aggregation. Wavelength shift analysis or absorbance ratio measurements can be used to determine the spectral changes [74].

3.2. Transmission Electron Microscopy (TEM)

The structure, size distribution and aggregation behavior of nanoparticles can be observed directly through transmission electron microscopy [75]. Crystallographic analysis and atomic scale imaging can be made possible by high resolution TEM. Hydrodynamic diameter measurements in solution are comparable to dynamic light scattering [76].

3.3. Surface-Enhanced Raman Spectroscopy

Surface-enhanced Raman spectroscopy describes chemical interactions at nanoparticle surfaces by using amplified vibrational patterns [77]. The electromagnetic field enhancement near nanoparticle surfaces increases Raman scattering cross-sections by factors of 10^6 to 10^{14}, enabling single molecule detection [78].

3.4. Electrochemical Characterization

The electrochemical properties of the nanoparticles modified electrodes are characterized by cyclic voltammetry, differential pulse voltammetry and electrochemical impedance spectroscopy [79]. These methods are used to probe electron transfer kinetics, surface area as well as catalytic activity for electrochemical sensing purposes [80].

4. Results and Discussion

4.1. Gold Nanoparticle-Based Pesticide Detection

Gold nanoparticles have shown remarkable effectiveness in the detection of pesticides due to their unique optical characteristics and surface chemistry. Numerous research teams have created advanced sensors based on gold nanoparticles, employing various functionalization approaches and detection methods.

4.2. Citrate-Stabilized Gold Nanoparticles

Citrate-capped gold nanoparticles serve as a basic sensing platform for pesticide detection. Dar et al. devised a colorimetric sensor that utilized citric acid-coated gold nanoparticles to identify dimethoate and dicofol pesticides [81]. The detection mechanism relied on soft-soft interactions between the nanoparticles and sulfur groups present in dimethoate molecules. When dimethoate was introduced, the fluorescence intensity increased in a linear fashion relative to concentration, reaching detection limits in the parts-per-billion range.

The sensor displayed selectivity for organophosphate pesticides that contained sulfur or phosphorus functional groups, which can coordinate with gold surface atoms. In contrast, dicofol, which does not possess such coordinating groups, exhibited a negligible response. This highlights the significance of molecular structure in influencing the interactions between pesticides and nanoparticles [82].

4.3. Silk Fibroin-Gold Nanoparticle Conjugates

Mane et al. demonstrated a highly sensitive method for detecting chlorpyrifos using gold nanoparticles stabilized by silk fibroin [83]. The silk fibroin functioned in two ways: it acted as a reducing agent during the nanoparticle synthesis and as a stabilizing agent to prevent early aggregation. The biosynthesized nanoparticles showed a distinct surface plasmon resonance peak at 535 nm, suggesting a narrow size distribution.

When exposed to chlorpyrifos, the nanoparticles aggregated, causing a noticeable color shift from red to blue that could be seen with the naked eye. The mechanism for detection involved the binding of the organophosphate group to the gold surfaces via P=S bond interactions. Adding sodium chloride solution accelerated the aggregation process, thereby increasing sensitivity. The optimized sensor was capable of detecting chlorpyrifos in water samples at a limit of 27 ng/mL [84].

The random coil structure of silk fibroin was crucial for the stability of the nanoparticles while enabling controlled aggregation in the presence of the pesticide. This equilibrium between stability and responsiveness is essential for achieving sensitive and selective detection [85].

4.4. Aptamer-Functionalized Gold Nanoparticles

Recent developments have introduced aptamers as recognition elements to improve selectivity. An aptamer-gold nanoparticle sensor array designed for pesticide identification employed various aptamer sequences, each with unique binding affinities for different pesticides [86]. Upon exposure to different pesticides, the aptamer-stabilized nanoparticles exhibited distinct colorimetric response patterns.

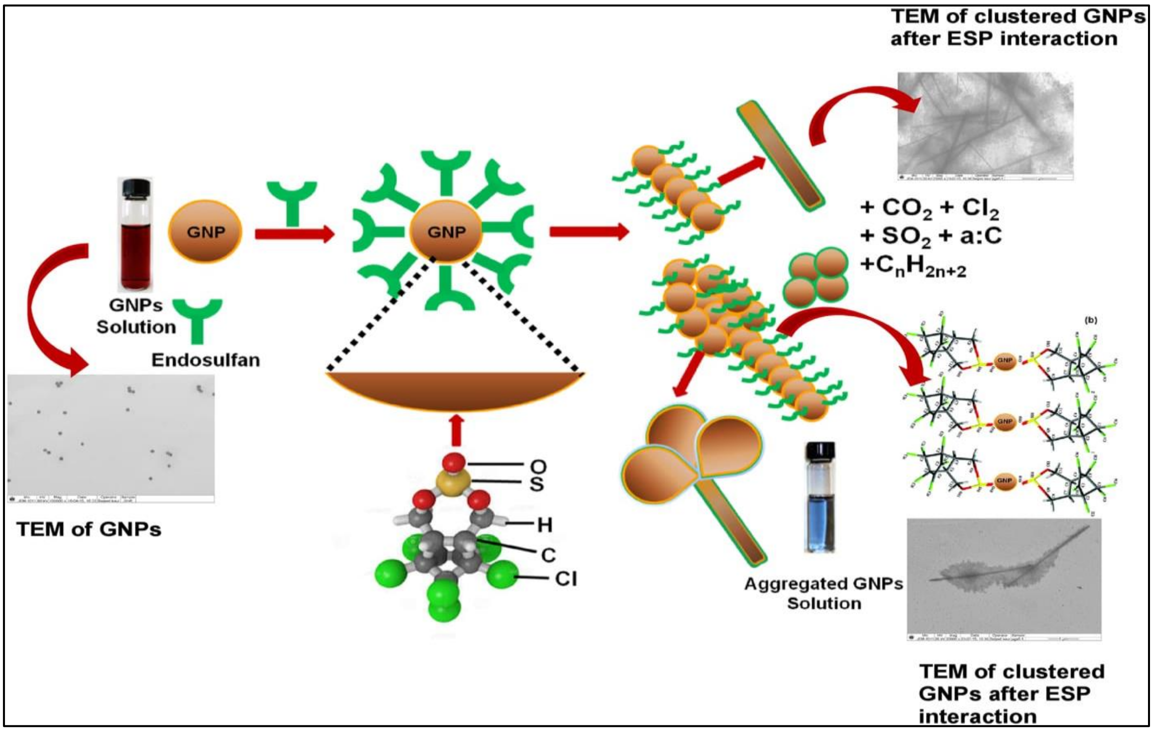

Figure 1 Schematic illustration of gold nanoparticle-based colorimetric detection mechanism for pesticides. The image shows the interaction between gold nanoparticles and pesticide molecules (Endosulfan) leading to aggregation and color change from red to blue, with TEM images showing nanoparticle morphology before and after pesticide interaction

By analyzing absorbance ratios at two key wavelengths and using multivariate statistical analysis, including linear discriminant analysis and hierarchical clustering, the sensor successfully identified and distinguished various pesticide types. This ability to detect multiple pesticides at once meets the need for simultaneous monitoring of different pesticide contaminants [87][88].

4.5. Nanozyme-Based Detection Systems

Nanozymes have changed pesticide detection by fusing catalytic activity with optical sensing. Carbon-based nanozymes that contain nitrogen and sulfur atoms show improved peroxidase-like activity. They catalyze chromogenic reactions of substrates like 3,3',5,5'-tetramethylbenzidine in the presence of hydrogen peroxide. Organophosphate pesticides inhibit nanozyme activity by blocking the active site or causing conformational changes, which provides an indirect detection method [90].

A recent study showed that single-atom copper-nitrogen-carbon nanozymes could detect organophosphate insecticides at levels as low as 0.60 ng/mL [91]. The arrangement of copper in nitrogen-doped carbon matrices created highly active CuN4 coordination sites with enzyme-like properties. This method combined the sensitivity of enzyme-based biosensors with the stability and cost-effectiveness of nanomaterials [92].

4.6. Silver Nanoparticle-Based Sensors

Silver nanoparticles have benefits that complement those of gold nanoparticles. They create stronger electromagnetic field enhancement for SERS applications and are cheaper for large-scale production.

4.7. Colorimetric Detection Using Silver Nanoparticles

Bhandari et al. created a paper-based flexible sensor using silver nanoparticles for on-site detection of paraquat pesticide [93]. The sensor was made by immobilizing silver nanoparticles on filter paper through simple drop-casting and drying. This paper-based platform has several benefits, including portability, disposability, low cost, and minimal sample volume needs.

The detection mechanism relied on the aggregation of silver nanoparticles caused by paraquat through electrostatic interactions. The sensor showed a clear color change from yellow to brown when exposed to paraquat, allowing for visual detection without instruments. Smartphone-based image analysis measured the color intensity, achieving detection limits similar to those of laboratory methods [94].

The sensor also showed excellent selectivity, with little interference from common agricultural chemicals and environmental factors. Field tests in actual water and soil samples confirmed its practical use [95].

4.8. Carbon Quantum Dot-Stabilized Silver Nanoparticles

Carbon Quantum Dot-Stabilized Silver Nanoparticles Murugesan et al. created carbon quantum dot-stabilized silver nanoparticles for pesticide detection [96]. The carbon quantum dots had two roles: they provided photoluminescent properties for fluorescence detection and stabilized silver nanoparticles against clumping. The hybrid nanocomposite showed multimodal detection abilities, combining colorimetric and fluorescence sensing. Detection efficiency varied by pesticide, following this order: imidacloprid, atrazine, and chlorpyrifos. This pattern matched the molecular structures and functional groups of the pesticides. The sensor achieved detection limits of 0.15 μg/mL for dimethoate in apple samples, showing its potential for food safety monitoring [97].

4.9. Alpha-Cyclodextrin Functionalized Silver Nanoparticles

Alpha-Cyclodextrin Functionalized Silver Nanoparticles Sahu et al. reported α-cyclodextrin-functionalized silver nanoparticles paired with micro-Soxhlet extraction for detecting chlorpyrifos in fruits and vegetables[98]. The cyclodextrin cavity offered selective binding sites for pesticide molecules using host-guest interactions. This mechanism improved selectivity compared to unfunctionalized nanoparticles. The integrated extraction-detection method increased sensitivity by pre-concentrating pesticides from complex food samples. UV-visible spectroscopy measured colorimetric changes caused by pesticide-induced nanoparticle aggregation. The approach was cost-effective and suitable for regular food testing applications [99].

4.10. Toxic Metal Ion Detection

Functionalized nanoparticles have shown excellent performance in detecting toxic heavy metal ions through colorimetric, fluorescence, and electrochemical methods.

4.11. DNA Probe-Based Lateral Flow Assays

DNA probe-based detection takes advantage of metal ion-dependent changes in specific DNA sequences [100]. Certain DNA sequences form stable secondary structures only in the presence of target metal ions. For instance, thymine-rich DNA sequences create T-T mismatches that selectively bind mercury ions [101].

Xie et al. developed lateral flow assays using DNA probes to detect mercury, cadmium, and lead ions [102]. The detection involved three steps: metal ion-induced DNA change, release of labeled reporters, and visual signal generation at the test line. This system reached detection limits at nanomolar levels and worked well for environmental and biological samples [103].

The visual readout, achievable within 10-30 minutes without needing power or complex instruments, made these sensors ideal for field use. Smartphone integration allowed for quantitative analysis through image processing algorithms [104].

4.12. Aptamer-Based Heavy Metal Detection

Aptamers have become strong recognition elements for heavy metal ions due to their high binding affinities and flexible structures[105]. Metal-specific aptamers change shape when they bind their targets, which can be turned into measurable signals using various methods.

A complex aptasensor using nitrogen-doped graphene-gold nanoparticle nanocomposites with chelating ligands detected lead ions with notable sensitivity[106]. The nanocomposite's structure provided many benefits: better electrical conductivity from graphene, improved charge transfer from gold nanoparticles, and specific binding from chelating ligands. These combined effects achieved detection limits of 4 x 10-13 mol/L for lead ions[107]. Similar methods have been developed for detecting cadmium, mercury, and chromium ions. Specificity comes from the unique ways different metal ions interact with the aptamer structures[108].

4.13. Magnetic Nanoparticle-Based Extraction and Detection

Functionalized magnetic nanoparticles allow for simultaneous extraction and detection of metal ions from complex samples[109]. Amino-functionalized $Fe_3O_4@SiO_2$ magnetic nanoparticles selectively absorbed cadmium, lead, and copper ions from water samples. Their magnetic properties made it easy to separate and concentrate target ions using external magnetic fields[110]. Thiol-functionalized magnetic nanoparticles showed a strong preference for binding soft metal ions, including mercury and lead, due to strong metal-sulfur coordination. The extraction efficiency exceeded 95% across a wide pH range, proving robustness for real sample analysis[111]. After extraction, various detection methods, such as inductively coupled plasma mass spectrometry, atomic absorption spectroscopy, or colorimetric techniques, quantified the absorbed metal ions. The pre-concentration step significantly improved detection limits and minimized matrix interference[112].

4.14. Electrochemical Sensors for Heavy Metals

Electrochemical sensors modified with nanoparticle-based materials have achieved highly sensitive detection of heavy metals through faster electron transfer and greater surface area[113]. Silver-graphene oxide nanocomposite-modified electrodes enabled portable microfluidic electrochemical sensing of lead ions with detection limits of 0.00464 μg/L[114].

The detection mechanism often uses anodic stripping voltammetry, where metal ions first concentrate on the electrode surface through electrochemical reduction, then strip off through oxidation while measuring the current response. The nanocomposite electrodes offer advantages like increased active surface area, better conductivity and enhanced electrocatalytic activity[115].

Table 1 The analytical performance of representative nanoparticle-based sensors for pesticide and heavy metal detection.

Nanoparticle Type	Target Analyte	Detection Limit	Detection Method
Au-Citrate	Dimethoate	5 ppb	Colorimetric
Au-Silk Fibroin	Chlorpyrifos	27 ng/mL	Colorimetric
Au-Aptamer	Multiple pesticides	1 nM	Colorimetric array
Cu-N-C Nanozyme	Organophosphates	0.60 ng/mL	Enzyme inhibition
Ag-Paper based	Paraquat	10 ppb	Visual/Smartphone
Ag-CQD	Imidacloprid	0.15 μg/mL	Fluorescence
DNA-AuNP-LFA	Mercury (Hg^{2+})	1 nM	Lateral flow
Aptamer-AuNP	Lead (Pb^{2+})	4×10^{-13} M	Electrochemical
Ag-GO	Lead (Pb^{2+})	0.00464 μg/L	Voltammetry

Au = Gold, Ag = Silver, CQD = Carbon quantum dots, GO = Graphene oxide, LFA = Lateral flow assay.

4.15. Multimodal Sensing Platforms

Combining multiple detection methods into single sensing platforms marks significant progress, allowing signal verification and improved reliability [116]. Multimodal sensors merge two or more techniques, often including colorimetric and fluorescence, fluorescence and photothermal, or electrochemical and colorimetric approaches.

4.16. Colorimetric-Fluorescence Dual-Mode Sensing

Carbon-based nanozymes doped with heteroatoms show both peroxidase-like activity and photoluminescent properties, enabling colorimetric and fluorescence detection at the same time[117]. This dual-mode output offers internal validation, reducing false-positive results and improving accuracy. A recent study demonstrated nitrogen-sulfur co-doped carbon nanozymes for simultaneous detection of five aromatic pesticides, with detection ranges from 5 to 500 μM [118]. The colorimetric signal came from catalytic oxidation, while fluorescence changes occurred from resonance energy transfer between carbon nanozymes and pesticide molecules. The two independent signals correlated well, increasing detection confidence[119].

4.17. Surface-Enhanced Raman Spectroscopy Integration

Surface-enhanced Raman spectroscopy combined with colorimetric detection offers molecular fingerprinting alongside visual sensing[120]. Gold nanoparticle arrays on dewdrop-structured surfaces achieved detection limits of 10^{-7} M for carbaryl and thiram pesticides due to SERS enhancement[121]. The SERS method provided detailed molecular information about pesticide structure and identity, while simultaneous colorimetric changes allowed for quick screening. This combination proved especially useful for analyzing complex mixtures of multiple pesticides[122].

4.18. Smartphone-Integrated Portable Sensors

The integration of smartphone technology has changed laboratory-based colorimetric sensors into portable, user-friendly devices suitable for on-site monitoring[123]. Smartphone cameras capture colorimetric signals, and specialized applications analyze data quantitatively through color space conversions and machine learning algorithms[124]. Paper-based sensors paired with smartphone analysis achieved detection performance similar to laboratory spectrophotometers while offering portability, affordability, and ease of use[125]. The RGB color intensity values extracted from smartphone images correlated linearly with analyte concentrations, enabling quantitative measurements. Cloud-based data systems allowed for remote monitoring and mapping of contamination patterns[126].

5. Challenges and Limitations

Despite notable progress, several challenges must be addressed to unlock the full potential of nanoparticle-based sensors for regular environmental monitoring.

5.1. Matrix Interference Effects

Complex environmental and food samples contain many substances that can impact nanoparticle stability and sensing ability [127]. Humic acids, proteins, lipids, and organic matter can adhere to nanoparticle surfaces, causing non-specific aggregation or blocking recognition sites [128]. High ionic strength in environmental samples might induce aggregation, generating false-positive signals [129].

Mitigation strategies include pre-treating samples, modifying surfaces with antifouling coatings, and adding internal standards. Machine learning algorithms trained on various sample matrices can also adjust for matrix effects through multivariate calibration [130].

5.2. Reproducibility and Standardization

Nanoparticle synthesis often results in batch variations in size, shape, and surface properties, affecting sensor reproducibility [131]. Standardizing synthesis protocols, quality control procedures, and evaluation metrics is crucial for commercialization and regulatory approval [132].

Recent efforts aim to develop automated synthesis systems, create reference materials, and define performance specifications for nanoparticle-based sensors. Standardization organizations are working on harmonizing testing protocols and validation guidelines [133].

5.3. Long-Term Stability

The stability of nanoparticles during storage and use continues to be a major concern. Metallic nanoparticles can oxidize, clump together, or dissolve over time, reducing sensing performance[134]. Functionalization ligands might desorb, affecting selectivity [135]. Stabilization strategies include encapsulation in protective materials, lyophilization for dry storage, and the use of antioxidants. Studies have shown that proper storage conditions can maintain sensor functionality for months to years [136].

5.4. Selectivity Limitations

Achieving selectivity in complex mixtures with multiple potential interferents remains tough. Many functionalized nanoparticles react to several analytes with similar chemical properties, limiting their application for specific detection [137].

Advanced methods like molecular imprinting, multiple recognition element arrays, and machine learning pattern recognition are being explored to improve selectivity. Sensor arrays that produce characteristic response patterns for different analytes can distinguish between similar compounds through analysis [138].

6. Conclusion

Functionalized nanoparticles have emerged as powerful tools for detecting pesticides and toxic metal ions, providing significant benefits over traditional methods in speed, cost-effectiveness and suitable field use. The unique optical, electronic, and catalytic properties of nanoparticles, combined with tailored functionalization strategies, enable sensitive and selective detection through colorimetric, fluorescence, SERS, and electrochemical techniques. Gold and silver nanoparticles are among the most thoroughly studied materials for environmental sensing, thanks to their excellent plasmon resonance properties and versatile surface chemistry. Recent progress in nanozymes, aptamer-functionalized systems, and multimodal sensing platforms has further improved detection performance. Their integration with smartphone technology, paper-based platforms, and microfluidic devices has moved research from laboratories to practical applications. While progress has been significant, several challenges need ongoing research. Addressing matrix interference, ensuring reproducibility, maintaining long-term stability, and overcoming selectivity limitations through advanced materials design, standardization, and innovative signal processing approaches is essential. Integrating artificial intelligence and machine learning holds promise for tackling these challenges through smart data analysis and pattern recognition. Future focuses include broadening the range of detectable analytes with new functionalization methods, enhancing multiplexing for simultaneous detection of various contaminants, improving quantification accuracy with better calibration techniques, developing biodegradable and eco-friendly nanomaterials, establishing regulatory frameworks and standardized testing processes, and creating integrated sensor networks for real-time environmental monitoring. The combination of nanotechnology, biotechnology, and information technology is pushing toward smart, connected sensor systems capable of providing in-depth environmental and food safety monitoring. As these technologies develop and overcome current limitations, nanoparticle-based sensors are set to play a vital role in protecting public health and environmental quality worldwide.

Compliance with ethical standards

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Disclosure of conflict of interest

The authors report no conflict of interest.

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