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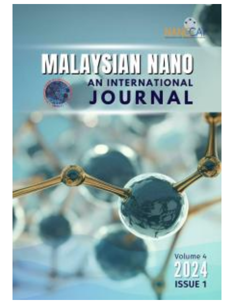

Review article

Role of nanomaterials in food authentication techniques: A mini-review

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Abstract

Food authentication is critical for ensuring food safety, quality, and compliance with regulatory standards. The growing complexity of food supply chains and increasing incidents of food fraud necessitate advanced and reliable methods for verifying food authenticity. Nanomaterials (NMs) have emerged as powerful tools in food authentication due to their unique physicochemical properties. This mini-review explores the application of various NMs, including metal nanoparticles (NPs), carbon-based NMs, and quantum dots, in the detection and identification of food adulteration and contamination. The review highlights recent advancements, practical applications, and future prospects of NMs in enhancing food authentication techniques. In this review, we explore the latest advancements in the application of NMs in food analysis. We summarize recent developments in NP usage for detecting contaminants in food and highlight the prospects and future directions for creating dependable devices for authentic analysis.

Keywords: Food authentication, nanomaterials, analytical method, food safety, sensors

1. Introduction

Food authentication involves verifying the origin, composition, and quality of food products to prevent fraud and ensure consumer safety. Verifying provenance is crucial for food safety, quality, and consumer protection, as well as for adhering to national laws, international standards, and guidelines [1]. Globalized food markets have heightened consumer interest in the geographical origin and quality of their food. Ensuring quality and authenticating foodstuffs is important for both commercial and legal reasons [2]. Since ancient times, authenticity has been a significant concern for consumers, regulators and manufacturers [3]. Traditional methods, such as chromatography, spectroscopy, enzyme-linked immunoassay (ELISA), PCR (polymerase chain reaction) etc. often require complex sample preparation and are time-consuming.

Over the past few decades, nanotechnology has emerged as an attractive and revolutionary force in the food sector. This technology operates on the nanometer scale, manipulating atoms, molecules, or macromolecules roughly 1–100 nm in size to develop materials with novel properties. These NMs feature one or more external dimensions, or an internal structure, within the 1 to 100 nm range, enabling the observation and manipulation of matter at this scale. Notably, these materials exhibit unique properties that differ from their macroscale counterparts due to their high surface-to-volume ratio and distinctive physicochemical characteristics, such as color, solubility, strength, diffusivity, toxicity, magnetic, optical, and thermodynamic properties, as well as their ability to interact with biological molecules at the nanoscale [4]. Therefore, NMs offer a promising alternative for developing authentic and reliable techniques for food product authentication. This review discusses the role of NMs in improving the sensitivity, specificity, and speed of food authentication techniques.

2. Nanomaterials in Food Authentication

NMs play a crucial role in food authentication by providing advanced methods for detecting adulteration, and contaminants, and verifying the origin of food products. Their unique properties, such as high sensitivity, large surface area, and tunable chemical characteristics, make them ideal for creating precise and reliable detection systems. These materials can be incorporated into sensors and other analytical devices to ensure the integrity and safety of food, protect consumers, and uphold the standards of food supply chains. Until now, researchers have developed numerous NMs to use in food authentication techniques such as gold NPs, silver NPs, graphene, carbon nanotubes, magnetic NPs, etc.

2.1 Metal Nanoparticles

Metal NPs, particularly gold (Au) and silver (Ag) NPs, play a significant role in food authentication due to their unique optical and chemical properties. Gold NPs are widely used for their strong localized surface plasmon resonance (LSPR) effect, which enhances the sensitivity and specificity of detection methods. These NPs can be functionalized with specific biomolecules, such as DNA biomarkers [5], antibodies [6] or aptamers [7], to detect food species, allergens, toxins, and pathogens with high precision. Silver NPs, known for their antimicrobial properties, are effective in detecting microbial contamination in food products [8, 9]. They can rapidly and sensitively identify bacterial DNA [10] and animal DNA [11], proteins [12], and other biomolecules, making them invaluable in preventing foodborne illnesses. The integration of metal NPs in sensor technologies not only improves the accuracy of food authentication but also offers the potential for developing portable and user-friendly devices for on-site testing [13].

2.1.1 Gold Nanoparticles (AuNPs)

Gold NPs are popular in biosensing applications because of their stability, biocompatibility, and strong LSPR effect. AuNPs possess remarkable properties like biocompatibility, conductivity, catalytic efficiency, density, and a high surface-to-volume ratio. Biomolecules such as DNA can be easily conjugated with AuNPs using thiol or amine groups without losing activity. These features enhance AuNPs' potential in biosensing and electrooxidation, offering improved conductivity for detecting substances at lower limits [5]. Hartati et al. [14] developed an electrochemical DNA biosensor using gold NP–DNA probe bioconjugates on a gold-modified screen-printed carbon electrode (SPCE-Gold) to detect Sus scrofa mitochondrial DNA (mtDNA). Optimal conditions included a 60-minute DNA hybridization time, with detection based on voltammetry using a methylene blue indicator signal at approximately −0.35 V. The biosensor achieved a detection limit of 0.58 μg/mL and 101.74% recovery, analyzing mtDNA in diverse meat samples. On the other hand, Ardhiyana et al. [15] developed a sensitive thiol-bond AuNP-Probe biosensor that changes color upon detecting pork DNA in the Cytochrome B region. The biosensor interacts with DNA samples, measured at 540 nm using a spectrophotometer. It was created by reducing gold with sodium citrate to produce gold NPs with a diameter of 39.05 nm. The biosensor achieved a limit of detection of 16.04 ng DNA/µl and a limit of quantification of 53.48 ng DNA/µl. Moreover, Dester et al. [16] developed a gold NP-based biosensor for visually distinguishing between the target (E. coli O157) and non-target DNA samples (Fig. 1). It demonstrated high specificity and sensitivity, detecting as little as 2.5 ng/μL of E. coli O157 DNA extracted from pure cultures.

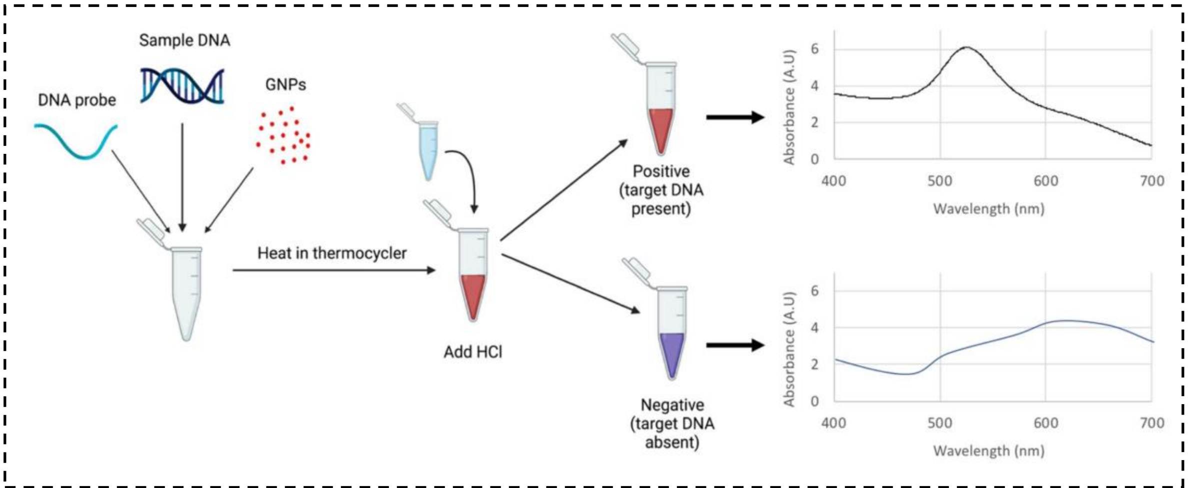

Figure 1: Basic procedure for gold NPs-based biosensor.

2.1.2 Silver Nanoparticles (AgNPs)

Silver NPs have antimicrobial properties and are used in detecting microbial contamination in food. Silver NPs (AgNPs) are highly sought after for their antimicrobial properties, driving research into effective delivery methods. Green synthesis of AgNPs is favored over chemical or physical methods due to its simplicity, cost-effectiveness, and safety. While both microbes and plants can be used, plants are preferred due to challenges in maintaining pure microbial cultures, making them ideal candidates for AgNP synthesis [17]. Recent studies underscore the broad-spectrum antibacterial efficacy of plant-based silver NPs (AgNPs) against both Gram-positive and Gram-negative bacteria [18, 19]. While the exact mechanism remains unclear, researchers propose that AgNPs interact with bacterial proteins' thiol groups [20] and DNA phosphorus moieties [21], disrupting cellular functions. Studies indicate that nano-silver is non-toxic to humans at low concentrations [22]. Consequently, efforts have focused on developing AgNP-coated systems for food preservation against harmful foodborne pathogens.

Tzeng et al. [23] developed a silver-based surface-enhanced Raman scattering (SERS) sensor with a remarkably low detection limit for adenine molecules. The sensor involved clusters of silver NPs deposited on discrete ball-like copper bumps partially covered with graphene, created via immersion in silver nitrate. Adenine molecules interacted with silver through electrostatic and functional groups, demonstrating low surface diffusivity and achieving a low detection limit of 10-11 M in aqueous solutions. Another study involved biosynthesis of silver NPs using Planomicrobium sp. and evaluated their antibacterial activity against foodborne pathogens including Bacillus subtilis, Klebsiella planticola, Klebsiella pneumoniae, Serratia nematodiphila, and Escherichia coli. Silver nitrate was added to the Planomicrobium sp. culture supernatant, and the NPs' bactericidal effects were assessed by measuring inhibition zone diameters. This research aims to enhance food packaging and safety through effective bacterial sensitivity testing [8].

2.2 Carbon-Based Nanomaterials

Carbon-based NMs, including fullerenes, carbon nanotubes, graphene, and graphene coils, have captivated scientific interest due to their distinct dimensional properties and unique chemical and electronic characteristics [24]. Recent research has focused on their preparation, modification, and diverse applications across fields like environmental monitoring and energy storage. These NMs exhibit small size, interface effects, high stability, and exceptional thermal and electronic conductivity [25, 26]. They are increasingly utilized in high-performance sensing devices for food safety, offering precise detection capabilities with minimal interference. Studies on newer carbon materials such as graphene and carbon dots have further bolstered the potential of carbon-based sensors, enhancing their utility in developing advanced food safety inspection devices characterized by accuracy and reliability in various environmental and biological applications [27].

2.2.1 Carbon Nanotubes (CNTs)

Carbon nanotubes (CNTs) are cylindrical carbon molecules with diameters ranging from nanometers to millimeters in length. They exist in two main types: single-walled (SWNTs) and multi-walled (MWNTs). Synthesized in 1991 [28], CNTs have gained widespread use and attention in various fields, including food authentication, due to their unique properties and nanostructure. These properties, such as large surface area, high aspect ratio, excellent electrical conductivity, chemical stability, and fluorescence, make CNTs ideal for chemical and biological sensing applications. However, effective utilization in biosensor development requires purification and functionalization with biorecognition elements. The critical challenge lies in optimizing the biosensing interface, balancing the immobilization of biorecognition elements for selective analyte recognition and transduction for rapid detection of analyte-induced changes. Successful biosensor design hinges on these optimizations to ensure sensitive and efficient detection capabilities, thereby advancing the use of CNTs in enhancing food authentication technologies. Functionalized CNTs with specific recognition elements, such as DNA or antibodies, improve the selectivity and sensitivity of these sensors.

Yang et al. [29] developed an optical CNT immunosensor to enhance ELISA assay sensitivity for detecting Staphylococcal Enterotoxin B (SEB) in food. Anti-SEB antibodies were immobilized on CNT surfaces, improving detection sensitivity by at least 6-fold. The CNT-based sensor successfully detected SEB in various foods, demonstrating the potential for enhancing optical-based immunological detection methods. Another research group developed an electrochemical sensor using multiwall carbon nanotubes (MWNT) to detect amaranth in food, emphasizing its potential health risks. The MWNT sensor, optimized for pH, MWNT amount, accumulation potential, and time, significantly enhanced amaranth oxidation, yielding a strong current signal. It detected amaranth in soft drinks across a linear range of 40 nM to 0.8 μM, with a low limit of detection of 35 nM, validated by high-performance liquid chromatography [30].

2.2.2 Graphene

Graphene, a single layer of carbon atoms arranged in a hexagonal lattice, has remarkable electron mobility, large surface area, and high functional capability [31]. Graphene NMs have emerged as powerful tools in the field of food authentication, offering innovative solutions for verifying the authenticity and quality of food products. These advanced materials possess exceptional electrical, thermal, and mechanical properties, making them ideal for developing sensitive and reliable detection systems. Graphene-based sensors can detect trace amounts of contaminants, adulterants, and other food fraud indicators with high precision [32]. Additionally, their large surface area and functionalization capabilities enable the selective recognition of specific target molecules, enhancing the accuracy of authentication processes [5]. By integrating graphene NMs into food authentication technologies, we can ensure the integrity of food supply chains, protect consumer health, and combat food fraud more effectively.

A novel electrochemical sensor using graphene (GN) and p-vinylbenzoic acid (VBA) in DMF solvent was developed for sensitive and selective detection of imidacloprid (IDP) residue. The sensor showed a linear response to IDP concentrations between 0.5–15 μM with a detection limit of 0.10 μM and was successfully applied to detect IDP in brown rice samples [33]. On the other hand, Peng et al. [34] developed a nanocomposite of 3D reduced graphene oxide (3D-rGO) and plasma-polymerized propargylamine (3D-rGO@PpPG) for a highly sensitive and selective DNA sensor to detect Hg2+. The sensor, leveraging strong electrostatic interactions and T–Hg2+–T coordination chemistry, detected Hg2+ in concentrations from 0.1 to 200 nM with a detection limit of 0.02 nM, showing high selectivity and stability. In addition, Parate et al. [35] used aerosol jet printing to create high-resolution interdigitated electrodes on flexible substrates, converting them into histamine sensors by linking monoclonal antibodies to oxygen moieties on graphene. The sensors exhibited a wide histamine sensing range (6.25-200 ppm) and a low detection limit (3.41 ppm) in actual tuna broth samples.

2.3 Magnetic nanoparticles

Magnetic NPs (MNPs) are highly applicable in biosensing systems due to their large surface area for biomolecule immobilization, ease of functionalization, and cost-effective synthesis [36]. They can be isolated using an external magnet, simplifying assay handling, concentrating analytes, and reducing analysis time [37]. However, their reactivity and sensitivity to air necessitate protection with an outer layer, such as a mussel-inspired polydopamine coating [38]. This layer, formed by dopamine auto-polymerization in an alkaline medium [39], provides stability and abundant reactive groups for the covalent immobilization of biomolecules. This versatile platform enables the attachment of various biomolecules to the MNP surface through Michael addition or Schiff base reactions, enhancing their functionality in biosensing applications [40].

Seddaoui et al. [41] developed a competitive assay using purified and porcine IgGs on magnetic NPs to bind a peroxidase-labelled antibody (Fig. 2). The colorimetric method detected pork in adulterated meat at a 0.01% concentration quickly. The immunoassay was highly specific for pork over lamb, turkey, chicken, and beef. Additionally, Yu et al. [42] synthesized magnetic NPs to extract Sudan dyes from chili powders, using magnetic ferroferric oxide NPs coated with polystyrene. Optimized extraction conditions included extraction/desorption time, solvent type/volume, and adsorbent mass. The method showed recovery rates of 80.2–115.8% with a relative standard deviation <3.8%, proving effective and efficient for extracting Sudan dyes.

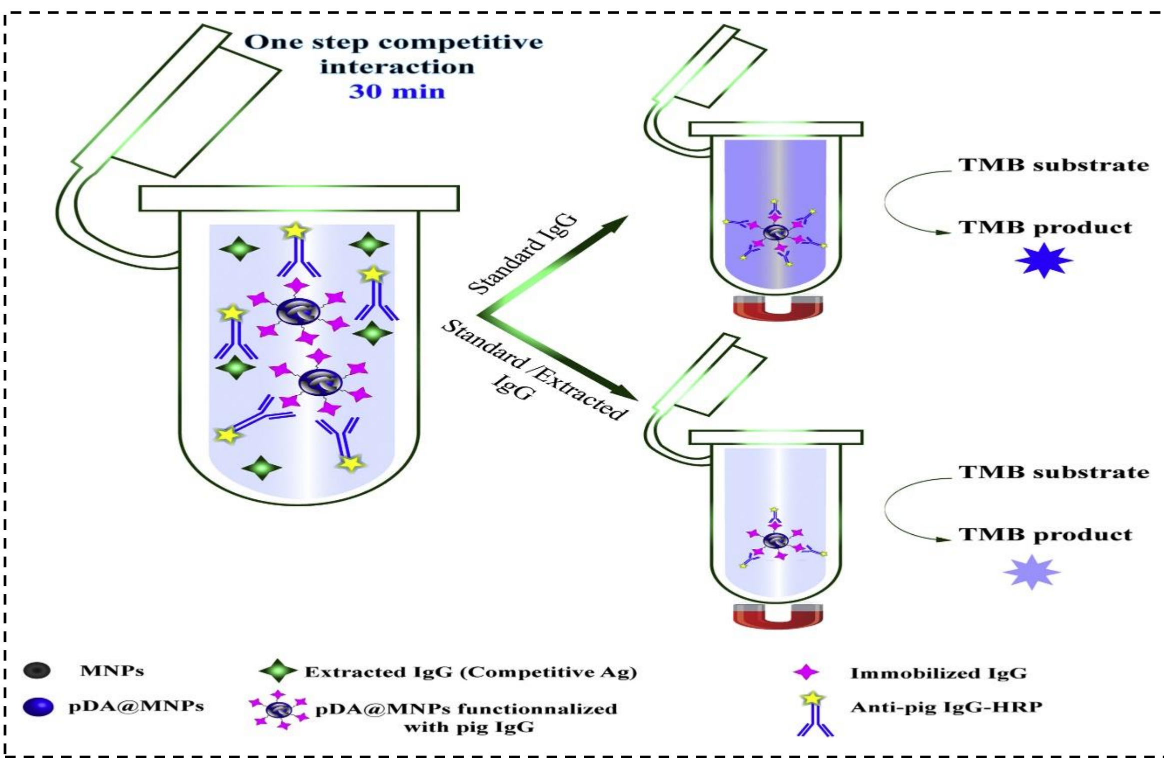

Figure 2: Schematic illustration of the colorimetric magneto-immunoassay devoted to the sensitive detection of pork in meat.

3. Future Prospects and Challenges

The integration of NMs with cutting-edge detection technologies, such as surface-enhanced Raman spectroscopy (SERS), nanoelectromechanical systems (NEMS), and DNA biosensors holds promise for highly sensitive and rapid food authentication methods, which could revolutionize food safety and traceability. Additionally, incorporating NMs into smart packaging can provide real-time monitoring of food quality and authenticity, as nanotechnology-enabled sensors and indicators detect spoilage, contamination, and fraudulent labeling, ensuring consumer safety and trust. Furthermore, combining NMs with blockchain technology can enhance the transparency and security of the food supply chain; NMs can serve as unique identifiers or markers, which, when recorded on a blockchain, provide an immutable record of a product's origin, processing, and distribution [43, 44]. The development of eco-friendly NMs derived from renewable sources can also address concerns regarding the environmental impact of nanotechnology, as biodegradable and non-toxic NMs ensure that food authentication technologies are both effective and sustainable. Lastly, establishing standardized protocols and regulatory frameworks for the use of NMs in food authentication is crucial, including defining safety guidelines, testing methodologies, and certification processes to facilitate global adoption and ensure consumer confidence.

The potential toxicity of certain NMs poses a significant challenge, necessitating comprehensive studies to assess the long-term effects of NM exposure on human health and the environment, which could lead to the development of safer alternatives. Additionally, the scalability and cost-effectiveness of NM-based authentication techniques remain hurdles, making it essential to develop manufacturing processes that can produce high-quality NMs at a commercial scale without compromising cost and efficiency for widespread adoption. Furthermore, integrating NMs with existing food authentication systems can be complex, requiring ongoing research and innovation to ensure compatibility with current infrastructure and technologies while overcoming technical challenges in the synthesis and functionalization of NMs. Public perception of nanotechnology in food applications can also be a barrier to adoption; therefore, transparent communication about the benefits and safety of NMs, coupled with educational initiatives, will be necessary to gain consumer trust and acceptance. Moreover, the lack of harmonized international regulations on NMs in food authentication can impede global trade and cooperation, necessitating collaborative efforts among regulatory bodies, industry stakeholders, and researchers to establish coherent and unified standards. Overall, while the role of

NMs in food authentication techniques presents promising opportunities, addressing these challenges through continued research, innovation, and collaboration will be vital for their successful implementation and acceptance in the food industry.

4. Conclusion

Ensuring the authenticity of food is essential for protecting public health, economic investments, and religious integrity. NMs play a pivotal role in advancing food authentication techniques, offering enhanced sensitivity, specificity, and rapid detection capabilities. The unique properties of metal NPs, carbon-based NMs, and quantum dots provide innovative solutions for detecting food adulteration, ensuring traceability, and monitoring food safety. Nanotechnology has found applications across various fields, including the detection of adulterants in food products, where advancements are still evolving. Electrochemical, piezoelectric, and optical sensors utilizing nanotechnology are primarily in the proof-of-concept stage. Nanosensors offer rapid, real-time, and cost-effective detection of pathogens and toxins in food, enhancing safety. These sensors can be automated for high throughput and portability, making them suitable for screening food and water samples for contaminants. Biosensor-based approaches are gaining traction due to their simplicity and affordability, catering to the demand for downsized analytical instruments. Combining multiple rapid detection methods is essential for ensuring comprehensive authenticity testing of food products, as no single method may suffice. Future research should focus on optimizing combinations of these methods to achieve the most accurate results. Ongoing advancements in NM exploration and process development promise to yield highly sensitive, selective, and economical nanosensors for evaluating food safety. This progress not only enhances detection capabilities but also facilitates broader adoption of biosensor technologies, which are user-friendly and require minimal training. Continued research efforts will be crucial in refining these technologies and establishing robust detection protocols for safeguarding food quality and consumer health. Continued research and development in this field will pave the way for more reliable and efficient food authentication methods, ultimately safeguarding consumer health and maintaining the integrity of the global food supply chain.

Conflicts of interest

The authors declare that they have no conflict of interest.

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