



METAL NANOPARTICLES IN NANOSENSORS FOR FOOD QUALITY ASSURANCE

Renata Dobrucka

Poznan University of Economics and Business, Poznań, Poland

ABSTRACT. Background: Nanotechnology is applied in the food industry to ensure food safety, and it is used both in the processing of food and detection of contaminants. The assurance of quality and safety of food has become an important issue for authorities and food supply chain actors. In order to protect consumers from contamination, adulteration and spoilage, it is absolutely necessary to conduct analyses of food, as it is exposed to numerous chemical substances, which may be harmful to human beings and the environment.

Methods: This work presents an overview of the literature concerning nanosensors with metal nanoparticles, which are used to detect the presence of chemical contaminants, pathogens and toxins, as well as to monitor food quality status. Such solutions will undoubtedly contribute to maintaining the safety and quality of food.

Results and conclusion: At present, food supply chains are becoming more complex, environmental constraints are becoming stricter, and consumers are changing the way in which they select and consume food, and all those factors inspire modern societies to be more concerned about the harmful substances that could be present in food products. Application of nanoparticles in the food production industry are farreaching and more research in this space is warranted. As developments in the research and development of nanotechnologies continue, so will the opportunities for the food industry to benefit from nanoscience.

Key words: nanotechnology, nanosensor, safety food.

INTRODUCTION

At present, food industry is the largest one in the world and it is still undergoing dynamic development. Food safety is reflected by the ability to cater for the food needs of people and access food that is necessary to ensure a healthy living. Food safety is one of the major global concerns that human beings have to confront and are continuously fighting for. According to the World Health Organization [WHO, 2015], safe food should be nontoxic and innocuous. Due to the global increase in food trade, both developed and developing countries have become concerned about food safety, as this issue may lead to numerous consequences that extend beyond life and health. Foodborne diseases also affect

economy, trade and other industries, and they may require considerable outlays. Such outbreaks may cause medical and non-medical costs, productivity losses, as well as require additional expenditure of funds by the affected manufacturers, the relevant agencies, as well as public health and food safety authorities [Thomas et al., 2015]. In order to ensure the highest quality of food, the worldwide food industry extensively adopts food safety standards, such as BRC, FSSC 22000, IFS and HACCP [Aung, Chang, 2014, Chassy et al., 2004].

The presence of unwanted substances in food products may pose a threat to consumer health. One of the basic ways to ensure safe food quality is to constantly monitor food products for the presence of harmful

substances and pathogenic parasites, bacteria, viruses and prions. With the constant improvement of food testing methods and control programs, the threat to consumers is becoming significantly weaker. The control tests of chemical residues in food not only protect consumer health but also help to comply with the requirements of international food trade. Although traditional methods for identifying chemical residues in food are relatively sensitive and specific for the detection of microorganisms and tested analytes, most of these tests are laborious and time-consuming [Gracias and McKillip, 2004, Zhao et al., 2014], which makes them incompatible for point-of care testing.

According to King [2018], nanotechnology has emerged as a technological advancement to develop and transform the agrifood sector, with the potential to increase global food production, in addition to the nutritional value, quality and safety of food. Detection methods that employ nanotechnology have some advantages that can make them more beneficial than traditional laboratory methods. The use of nanoparticles combined with electrochemical or optical detection methods leads to the development of fast, sensitive and cost-effective procedures that allow for miniaturization and automation for point-of-care testing. Within the last ten years, we have witnessed some promising developments in modern nanotechnology and its application. Thanks to their unique characteristics, nanoparticles can be used in order to develop highly sensitive strategies for detecting contaminants [Krishna et al., 2018].

NANOSENSORS TO DETECT THE PRESENCE OF CHEMICAL CONTAMINANTS

Metal nanoparticles are applied in the production of nanosensors for detecting the presence of chemical compounds or pesticides. One example of the use of metal nanoparticles is the development of nanosensors for detecting melamine. Melamine is an aromatic compound that belongs to the amine group. It is a derivative of triazine and a trimer of cyanamide. It is used to produce melamine resins, which are applied in the manufacturing

of household items, decorative laminates, glues, paints and lacquers. Due to the high nitrogen content [66% of mass], it was used to obtain a falsely high protein content in the analyses of animal feed and food products. Since the mass poisoning of children in China due to the presence of melamine in powdered milk, there have been introduced strict controls of melamine content in food. Wu et al. [2015] proposed a nanosensor for detecting the presence of melamine on the basis of energetic transitions related to the fluorescence between gold nanoparticles.

A similar sensor was created by Kumar et al. [2014]. It contained gold nanoparticles stabilized with sodium citrate. The presence of melamine in the tested samples led to the aggregation of gold nanoparticles and, in turn, a visible change in color. Another group of scientists [Ai et al., 2009] proposed a nanosensor in which gold nanoparticles reacted with a derivative of cyanuric acid. That derivative selectively bonded with melamine by means of hydrogen bonds. After bonding with melamine, the aggregated gold nanoparticles changed their color from red to blue.

Metal nanoparticles undoubtedly make it easier to examine detergent residues in food products, whose presence is inadvisable due to the high food safety standards. Kumar et al. [2016] used gold nanoparticles to develop a m in milk for children. The sensor works in such a way that gold nanoparticles are stabilized due to electrostatic repulsion among negatively charged citrate ions on the surface, preventing them from aggregation. The addition of inducer to gold nanoparticles neutralizes the surface charge and causes aggregation, which is reflected in color change of the solution from red to purple. It was observed that the aggregation of nanoparticles was impeded in the presence of anionic detergents and HCl, so the solution remained red.

For example, Zheng et al. [2018] used graphene-Au nanoparticles to develop the sensor of 4-nonylphenol in milk and its packaging materials. The studies carried out by the scientists showed that 4-nonylphenol was found in many food products, including vegetables, fruit, grains and drinks, and its

main source was probably the packaging material. Therefore, it was very important to develop an effective and fast method for identifying 4-nonylphenol in the product and its packaging. Authors created the electrochemical sensor by depositing poly[p-aminothiophenol] film on an electrode modified with graphene-Au nanoparticles. The developed sensor was characterized by higher sensitivity and selectivity.

Another sensor has been developed by Shim et al. [2018]. The authors employed dendritic platinum nanoparticles to create a sensor designed for bisphenol A [BPA] detection, which may be used to assess the quality of packaged food and BPA migration from the packaging.

NANOSENSORS TO DETECT THE PRESENCE OF PATHOGENS AND TOXINS

The achievements in nanotechnology also offer technological solutions that make it possible to detect pathogens and toxins in food. Usually, they are based on the optical or electronic characteristics of nanomaterials [Valdes et al. 2009, Leonard et al. 2003]. Kalele et al. [2006] conjugated rabbit immunoglobulins G [IgG] with silver nanoparticles in order to quickly and selectively detect *E. coli* in the range of 5-109 by monitoring the shifts of the SPR band in the presence of *E. coli* cells. Wang et al. [2015] prepared an electrochemical immunosensor for *E. coli* 0157:H7 detection without any pretreatment. Proposed sensor was consisted of magnetic separation using antibody-functionalized MNPs and electrochemical reporters using lead sulfide nanoparticles linked to polyclonal antibody-functionalized Au nanoparticles. Dungchai et al. [2008] used gold nanoparticles to develop an effective immunological method for identifying *S. typhimurium*.

Moreover, nanosensors have been developed for the detection of a number of foodborne pathogens relevant to the poultry industry. Nanosensors have been designed to detect and quantify many types of analytes

relevant to the meat industry, including gasses, vapors and ions, small organic molecules, biomolecules, and a range of foodborne pathogens [King et al.2018]. Liu et al. [2015] described the application of nanosensors for the detection of biogenic amines (i.e. putrescine, cadaverine) in the monitoring of spoilage in raw chicken meat.

Joo research group [2012] developed an easy and sensitive method for detecting pathogenic bacteria in milk. Salmonella bacteria present in milk were captured by antibodies coupled with magnetic nanoparticles and separated from analyte samples by means of an external magnetic field. The complexes of nanoparticles and Salmonella were dispersed in the buffer solution and then immobilized with the use of TiO₂ nanoparticles, which absorbed UV light. As the intensity of light absorption was inversely proportional to the concentration of Salmonella, the test was highly sensitive to low concentrations of the bacteria. The discovered detection limit of the bacteria in milk was 100 cfu ml⁻¹. Yuan et al. [2014] developed a visible detection method for Salmonella Typhimurium based on AuNPs labeling and silver enhancement signal amplification.

Staphylococcus enterotoxins are a family of proteins produced by some strains of *S. aureus*. Those toxins are characterized by resistance to heat, resistance to enzymatic proteolysis as well as mitogenic properties. In order to detect staphylococcus enterotoxins in food, Yang et al. [2009] developed an immunological nanosensor with gold nanoparticles based on enhanced chemiluminescence [ECL]. Chudobova research group [2015] developed a 3D-printed chip for detection of methicillin-resistant Staphylococcus aureus by measuring the color change, caused by the non-crosslinking aggregation phenomenon of DNA-functionalized AuNPs when *mecA* gene reacted with the AuNP probes.

NANOSENSORS FOR MONITORING FOOD QUALITY STATUS

Nanomaterials are also applied to monitor the freshness of food. The literature presents numerous examples of fish, fruit or meat

freshness sensors. Chen et al. [2017] developed a visual sensor for monitoring the freshness of fish. The authors based the structure of the indicator on the presence of hypoxanthine, the end product of purine metabolism that is produced in the course of decay of animal meat. In their method, hypoxanthine reacted with dissolved oxygen in order to produce H_2O_2 in the presence of xanthine oxidase. Gold nanoparticles detected by H_2O_2 in the presence of Fe^{2+} caused a visible change in the indicator's color. Different concentrations of hypoxanthine caused the sensor to change its color.

Albelda et al. [2017] designed a sensor of meat freshness. The authors used a graphene– TiO_2 composite, which formed a beneficial microenvironment for the oxidation of xanthine oxidase. To develop a freshness sensor, the group of Zhang et al. [2008] used a SnO_2 – ZnO nanocomposite. The sensor was highly sensitive and it quickly reacted to trimethylamines present in the tested samples. As xanthines are the product of purine decomposition, the sensor may be used to predict the shelf life of meat and fish.

Another sensor was developed by Devi et al. [2012]. Their xanthine sensor was based on chitosan modified with ZnO nanoparticles on a multi-layer system of carbon nanotubes in a polyaniline matrix, on which xanthine oxidase was bonded by means of a covalent bond. The lower xanthine detection limit indicated by the sensor was 0.1 mM. In 2013, the same research group proposed a biosensor with xanthine oxidase immobilized with the use of silver nanoparticles. The authors proved that the presence of silver nanoparticles increased the stability of xanthine oxidase activity during storage at room temperature for about 60 days [Devi et al., 2013].

Zheng et al. [2010] used silver and gold nanoparticles to develop a vanillin sensor. The presence of nanoparticles increased the sensitivity of the sensor by five times. Another solution was proposed by Dridi et al. [2015] – they created a stable biosensor with gold nanoparticles for direct conductometric detection of ochratoxin A [OTA], i.e. mycotoxin, in olive oil samples. In the food industry, an electronic nose and tongue are

used to assess and classify raw materials and finished products. They help to assess the sensory properties of food, its durability, and changes that occur throughout storage. They are also used to monitor the respective stages of production, as well as to identify food preservation processes. Ghasemi Varnamkhistia et al. [2011] presented the possibility of using an electronic nose and tongue in the brewing industry in order to assess the quality of beer, especially during fermentation. An electronic nose was used to identify the contamination of grains with fungi, and to detect the presence of *Ganoderma boninense* on oil palm trunks [Abdullah et al., 2011]. Zhang et al. [2006] used an electronic nose to characterize 17 commercial vinegars. The nose contained nine sensors with ZnO nanoparticles doped with MnO_2 , TiO_2 , V_2O_5 , Bi_2O_3 , W and Ag, as well as fly ashes.

CONCLUSIONS

From the consumer's point of view, food safety is the most important feature of quality. The current legal conditions impose strict requirements on food manufacturers and all other entities in the food chain, thanks to which consumers can feel safe on the food product market. One of the greatest threats to food is contamination. Society's health and correct development depend on access to food that is not contaminated. Early and accurate detection of contamination is prerequisite for preventing, controlling and mitigating the impact of potential outbreaks. This work has presented nanosensors for detecting the presence of: a) chemical contamination, b) pathogens and toxins, and c) monitoring food quality status. The use of nanosensors will undoubtedly help to maintain food quality.

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NANOCZĄSTKI METALI W NANOSENSORACH ZAPEWNIĄCYCH JAKOŚĆ ŻYWNOŚCI

STRESZCZENIE. Wstęp: Nanotechnologia jest stosowana w przemyśle spożywczym w celu zapewnienia bezpieczeństwa żywności i jest wykorzystywana zarówno w przetwórstwie żywności, jak i wykrywaniu zanieczyszczeń. Zapewnienie jakości i bezpieczeństwa żywności jest ważną kwestią w łańcuchu dostaw żywności. Aby chronić konsumentów przed skażeniem, zafałszowaniem i psuciem, absolutnie konieczne jest przeprowadzenie oceny jakości żywności, ze względu na narażenie na substancje, które mogą być szkodliwe dla ludzi i środowiska.

Metody: W pracy przedstawiono przegląd literatury dotyczącej nanosensorów zawierających nanocząstki metali, które służą do wykrywania obecności zanieczyszczeń chemicznych, patogenów i toksyn, a także do monitorowania stanu jakości żywności. Takie rozwiązania niewątpliwie przyczynią się do utrzymania bezpieczeństwa i jakości żywności.

Wyniki i podsumowanie: Obecnie łańcuchy dostaw żywności stają się coraz bardziej złożone, ograniczenia środowiskowe stają się coraz surowsze, a konsumenci zmieniają sposób, w jaki wybierają i spożywają żywność. Wszystkie te czynniki powodują zainteresowanie i coraz większą dbałość o jakość i bezpieczeństwo żywności. Zastosowanie nanocząstek w przemyśle spożywczym daje szerokie perspektywy, w związku z tym uzasadnione są dalsze badania w tym obszarze. Wraz z rozwojem badań i rozwoju nanotechnologii będą również rosnąć możliwości, jakie przemysł spożywczy może czerpać z nanonauki.

Słowa kluczowe: nanotechnologia, nanosensor, bezpieczeństwo żywności

Renata Dobrucka ORCID ID: <https://orcid.org/0000-0003-1486-9412>
Department of Non-Food Products Quality and Packaging Development
Institute of Quality Science
Poznan University of Economics and Business
al. Niepodległości 10, 61-875 Poznan, **Poland**
e-mail: renata.dobrucka@ue.poznan.pl