Recent Advances in (Bio)Chemical Sensors for Food Safety and Quality Based on Silver Nanomaterials

Irena Ivanišević, Stjepan Milardović and Petar Kassal*

Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, 10000 Zagreb, Croatia

Received: 24 July 2020
Accepted: 28 May 2021

SUMMARY

There is a continuing need for tools and devices which can simplify, quicken and reduce the cost of analyses of food safety and quality. Chemical sensors and biosensors are increasingly being developed for this purpose, reaping from the opportunities provided by nanotechnology. Due to the distinct electrical and optical properties of silver nanoparticles (AgNPs), this material plays a vital role in (bio)sensor development. This review is an analysis of chemical sensors and biosensors based on silver nanoparticles with application in food and beverage matrices. It consists of academic research published from 2015 to 2020. The paper is structured to separately explore the designs of two major (bio)sensor classes: electrochemical (including voltammetric and impedimetric sensors) and optical sensors (including colourimetric and luminescent), with special focus on the type of silver nanomaterial and its role in the sensor system. The review indicates that diverse nanosensors have been developed, capable of detecting analytes such as pesticides, mycotoxins, fertilisers, microorganisms, heavy metals, and various additives with exceptional analytical performance. Current trends in the design of such sensors are highlighted and challenges which need to be overcome in the future are discussed.

Key words: silver nanoparticles, nanosensors, chemical sensors, biosensors, food safety, food quality

INTRODUCTION

Today, the food industry is the largest manufacturing sector and, at the same time, causes major global concern (1). Adulteration of products with low quality ingredients, or spoilage during transport and storage periods can easily affect the condition and quality of food. Improper use of pesticides and fertilisers can lead to contamination and, along with natural toxins, drugs, foodborne pathogens and heavy metals, can have a direct negative impact on human health. Besides possible harmful pollutants in food products, there are numerous compounds whose concentrations are of interest for nutritional food quality and, hence, need to be analysed. Thus, ensuring food safety and quality is of global importance (2).

The high complexity of food matrices sets a large challenge before scientists to develop reliable analyses of chemical and/or biological substances in trace quantities, thereby commonly requiring a variety of analytical methods to be employed. Conventional methods, such as distinctive chromatographic techniques, often coupled with mass spectrometry or enzyme-linked immunosorbent assay (ELISA) technique, possess the merits of sensitivity and accuracy. However, they often require complex sample pretreatment, sophisticated equipment and long analysis time, making them impractical for in-the-field food-specific applications. Chemical sensors and biosensors, low-cost devices that allow facile and quick determination of target analytes, are therefore being increasingly leveraged in the food sector (3).

Nanotechnology has brought a revolution in modern science, opening new possibilities for much needed improved food sensor technologies (4,5). Conjunction of nanoparticles with electrochemical or optical transducers has created new opportunities in small molecule detection, enabling sensor miniaturisation and fabrication on an industrial scale.
Thus, nanotechnology offers cheaper, more reliable, quicker and highly sensitive nanocomposite architectures for application in the food industry. The immense leap in the application of nanotechnology is mainly attributable to advances in nanoparticle synthesis techniques during the last two decades, especially promoting silver nanomaterials (6).

Silver nanoparticles (AgNPs) are on the forefront of nanosensors, due to their distinctive localised surface plasmon resonance (LSPR) effect, combined with unique thermal and electrical properties. The colour change between dispersed and aggregated nanosilver grains can be associated with the concentration change of a target molecule in a suspension. This is a key feature in the fabrication of optical sensors (7). Furthermore, silver nanoparticles have been successfully paired with other nanomaterials in order to obtain novel hybrid architectures with enhanced electrochemical sensing performances. Nanosilver-based optical and electrochemical sensing arrays have found versatile application in the analysis of food and beverage matrices.

A large number of original scientific papers (8–13), as well as review articles (14–19) regarding food quality and/or food safety topics have been reported recently, providing a broad survey through the field of nanomaterial-based sensing platforms. In most of the publications, nanogold stands out above other metallic nanoparticles (20,21) and, although nanosilver-based devices are very abundant in the literature, a systematic review of food sensors based on silver nanoparticles has not been conducted (22–24). In the light of this, the authors considered the need to summarise selected examples of exclusively nanosilver-based (bio)chemical sensors for the detection of compounds concerning food safety and food quality. A literature survey using the Web of Science database revealed a large number of articles focused on these silver nanoparticle-based sensors for food matrices in the period of 2015–2020. The increasing number of publications in the selected period (Fig. 1) reinforces the importance of silver nanomaterial for food sensing purposes. The aim of this paper is to present the current state of knowledge and to give a critical review of the selected publications. This article is divided by transduction mechanism into two sections with the most frequent nanosilver-containing sensor categories – electrochemical and optical, preceded by a brief revision of nanosilver preparation approaches. In addition to electrochemical and optical sensors, our literature search has returned numerous examples of sensors based on surface-enhanced Raman scattering (SERS), exhibiting remarkable analytical performance (25–31). However, SERS sensors require highly sophisticated dedicated instruments and we have therefore omitted them from this review, focusing instead on sensors more appropriate for simple, rapid and on-site food analyses.

SYNTHESIS OF SILVER NANOMATERIALS

In general, synthetic routes of silver nanoparticles follow either bottom-up or top-down approaches. Top-down techniques are based on breaking down the bulk material by applying various physical forces; thereby allowing fabrication of small particles with a narrow size distribution without the involvement of hazardous chemicals. However, imperfections in the obtained surface structures and high energy consumption during the synthesis limit their broad application. The bottom-up approach uses silver atoms as elementary building blocks for controlled building-up assembly into a nanostructured material. In terms of particle synthesis for practical sensing application, applied bottom-up methods have the same denominator – reduction of a soluble silver(l) salt. The corresponding process can be conducted using appropriate chemical or biological reducing agent or aided by some external source such as electrical current (Fig. 2) (30–35). This is the basic principle of chemical, biological and electrochemical preparation methods (36). In the papers analysed in this review, synthesis of AgNPs was conducted exclusively through these bottom-up approaches. While the chemical reduction step was previously commonly performed using potentially hazardous agents (e.g. hydrazine (37) or hydroxylamine (38)), we have observed in this review a trend promoting green synthesis. The reduced silver nanomaterials are stabilised using a compulsory stabiliser molecule or capping agent; this is a key element that controls the particle size and shape. By modifying the reducing and capping agent and optimising the synthetic route, versatile silver nanostructures have been obtained and used in sensors (Fig. 2). As shown in this review, the type of silver nanostructure often has a large effect on the performance of the (bio)sensor in which it is employed. For the functional design of both electrochemical and optical sensors presented in this review, a powdered nanosilver product is often used. In these cases, the dried particles were either purchased (39,40), or isolated from the reaction suspension applying centrifugation (41,42), magnet separation (43), electrodeposition (34,44) or solution drying techniques (45,46). Furthermore, crystalline nanosilver...
Nano-engineered silver material has a great potential as a modifier due to excellent electrical conductivity and high catalytic activity. Furthermore, composites made of pure silver nanomaterial embedded into polymer matrices or core-shell bimetallic structures render a combination of useful properties, offering remarkable prospects in the construction of modified working electrodes. For this purpose, nanostructured silver is a material of great importance for the development of electrochemical sensors (53).

A current trend in the sensor field is directed towards solving analytical problems with the development of cost-effective, miniaturised and portable devices that could be operated in the field (54). A survey of the silver nanomaterial-based electrochemical sensors for food applications published in the last five years is listed in Table 1 (32, 34, 35, 39, 40, 44, 45, 47, 55–85). Selected examples of electrochemical sensors, both voltammetric and impedimetric, are shown in Fig. 3 (35).

**Voltammetric sensors**

Selective redox behaviour of an analyte of interest on the working electrode surface generates the current output, which is the basic principle of voltammetric sensor operation. During the measurement, the voltage of the working electrode can be changed linearly, in pulses or in cycles within a short time period, and the current produced by the system is measured. Detection established on the evaluation of current change at constant potential is also possible, which represents the basis of amperometric sensing. Operating in this mode, detected currents can be averaged over longer time periods, allowing more precise quantitative evaluation (86).

The reviewed voltammetric sensors for detection of small molecules and chemical pollutants in food samples rely on the nanosilver-enhanced electron transfer processes of the modified working electrodes.

Fertilisers, including nitrite and phosphate anions, are common inorganic pollutants found in drinking water, soil and food. Controlling nitrite concentration is of significant importance, because its presence in the human body can cause conversion of haemoglobin into its non-oxygen carrier form, methaemoglobin (41). Usage of amperometry as a transduction pathway is the common denominator in nitrite-sensing devices, where selective redox behaviour is achieved at a single operating potential. Synergistic effect of AgNPs and multi-walled carbon nanotubes (MWCNTs) magnifies a glassy carbon electrode (GCE) working area, rendering favourable analytical performance towards nitrite oxidation (55). AgNPs/MWCNTs/GCE successfully produced a rapid signal output with continuous nitrite additions, which makes the proposed method suitable for nitrite determination in tap water. Another sensor including glassy carbon as an electrode material was proposed by Shivakumar et al. (45). An eco-friendly synthetic approach, using paper industry waste material, was developed to fabricate particles with average crystallite size of 30 nm. Amperometric experiments, conducted in 0.1 M
### Table 1. Electrochemical sensors based on silver nanomaterials

| Analyte                  | Sample                        | Analytical method | Recognition element | Nanomaterial | AgNP synthesis | LOD         | Ref.       |
|--------------------------|-------------------------------|-------------------|---------------------|--------------|----------------|-------------|------------|
| Nitrite                  | Water                         | Amp               | Direct sensing      | AgNP/MWCNTs  | Electrodeposition | 0.095 µM (55) | (40)       |
| Nitrite                  | Tap water                     | Amp               | Direct sensing      | AgNS         | Green synthesis  | 0.031 µM (45) | (56)       |
| Nitrite                  | Milk, salami, mineral water   | Amp               | Direct sensing      | rGO/AgNPs    | Borohydride reduction | 0.012 µM (56) | (57)       |
| Phosphate                | Water                         | CV                | Direct sensing      | AMT/AgNW     | Aldehyde reduction | 3 µM        | (59)       |
| Monocrotophos, chlorpyrifos | Fruit samples              | DPV               | ACH enzyme          | AgNP-N-F-MoS2 nanosheets | In situ reduction | 0.2 pM(M) 3.0 pM(C) | (39)       |
| Paraoxon PCB28           | Garlic, cabbage               | Amp               | ACH enzyme          | AgNP/AChE   | Citrate reduction | –          | (59)       |
| Penidimethalin, Ethyl parathion | Mineral and tap water, lettuce, honey | SWV | Direct sensing      | AgNP        | Borohydride reduction | 36 nmol/L(PDM) 40 nmol/L(EPT) | (60)       |
| Paraoxon Methyl parathion | Onion                        | DPV               | Direct sensing      | AgNP        | Electrodeposition | 0.1 nM     | (61)       |
|                         | Cabbage, green beans, strawberry, nectarine | Amp | Direct sensing      | Ag@GNR      | In situ reduction | 0.5 nM     | (62)       |
| Thiodicarb               | Soya milk                     | SWAdSV            | Direct sensing      | Ag nanopowder | Purchased       | 7.2·10^{-4} M | (40)       |
| Vanillin                 | Cookie, pastry, jelly, chocolate | Amp         | Direct sensing      | Ag-Pd/GO     | In situ reduction | 5 nM       | (63)       |
| Sudan IV                 | Buffer                        | CV                | Direct sensing      | Au-Ag nanocomposite | Hydrothermal method | 4 µM      | (64)       |
| Sudan I                  | Ketchup, chilli powder        | Amp               | Direct sensing      | Ag-CuNP/rGO nanocomposite | Borohydride reduction | 0.4 nM     | (65)       |
| Orange II, Rhodamine B Amaranth | Water, fruit juice         | DPV               | Direct sensing      | Cbz-AgNP    | Borohydride reduction | 1.2 nM (OR II) 1.0 nM (RB) | (66)       |
|                         | Buffer                        | LSV               | Direct sensing      | graphene/TiO2-AgNP | Ascorbic acid reduction | 10^{-2} M     | (67)       |
| Sunset Yellow Chloramphenicol | Soft drinks                  | LSV               | MIPs                | GO/AgNP     | Citrate reduction | 0.02 µM    | (68)       |
|                         | Milk powder                   | LSSV              | Direct sensing      | Ag nanodendrites/Short-MWCNTs-COOH | Electrodeposition | 0.049 µM (34) | (69)       |
| S. aureus L. monocytogenes | Milk                         | Amp               | Anti-Lm             | Ag@[Ru(bpy)3]2+/chitosan | Borohydride reduction | 2 cell/mL | (70)       |
| Ascorbic acid            | Orange, kiwi and apple juice | SWV               | Direct sensing      | AgNP        | Green synthesis  | 0.1 µM     | (71)       |
| Ascorbic acid            | Pimento juice, orange juice   | SWV               | Direct sensing      | AgNP        | Green synthesis  | 0.02 µM    | (72)       |
| Vitamin C                | Fruit juice                   | CV                | Direct sensing      | AgNP        | Citrate reduction | 0.2 mM     | (73)       |
| Ascorbic acid            | Vitamin C tablet              | DPV               | Direct sensing      | Q-AgNPs+GNs | Electrodeposition | 0.39 mg/mL | (74)       |
| Hydrogen peroxide        | Apple juice                   | Amp               | Direct sensing      | rGO-Nf@Ag   | Hydrothermal method | 5.35·10^{-9} M | (75)       |
| Hydrogen peroxide        | Milk                          | Amp               | Direct sensing      | Pd@Ag/rGO-NH₃ | Borohydride reduction | 0.7 µM     | (76)       |
| Tyramine                 | Banana                        | Amp               | Direct sensing      | TiO₂-Ag/Ppy | –               | 2·10^{-8} M | (77)       |
| Urea                     | Milk, tap water               | CV                | Direct sensing      | Ag-N-SWCNTs | Thermal synthesis | 4.7 nM     | (78)       |
| Histamine                | Fish sauce                    | DPV               | Direct sensing      | Ag-Ag/D/MWCNTs | Electrodeposition | 0.18 µM    | (79)       |
| Ochraotoxin A             | Grape juice, wine             | DPV               | MIPs                | AgNP/POM/rGO | In situ reduction | 1.6·10^{-10} M | (80)       |
| Afliatoxin M1             | Milk                          | LSV               | Direct sensing      | GQD-α-CD-AgNP | Electrodeposition | 2 µM       | (81)       |
| Microcytin-LR             | Water                         | Amp               | Anti-MC-LR          | Ag@MSN      | One-step thermal treatment | 3.3·10^{-3} M | (82)       |
| Acetamiprid              | Cucumber, tomato, wastewater  | Impedance        | Aptamer             | Ag@MSN      | In situ via aptamer template | 0.0082 fg/mL | (47)       |
| Bleomycin                 | Milk                          | Impedance        | Aptamer             | AgNCs/Apt@CuFe/FeFe | Commercial ink | 10 µg/mL | (83)       |

(Ref.)
phosphate buffer solution at a constant potential of +0.86 V, confirmed remarkable electrocatalytic properties of silver nanospheres towards nitrite oxidation. Simplicity in device fabrication, along with the green synthetic approach and high analyte selectivity, highlights this sensor for practical in-field application in water samples. Successive application of vacuum filtration and electropolymerisation was carried out to prepare a graphene-based/silver nanoparticle/poly(pyronin Y) hybrid paper electrode. High absorption coefficient of poly(pyronin Y) (poly(PyY)) decreases the electrooxidation potential of nitrite and expands the active electrode surface area, while silver nanoparticles enhance low electrical conductivity of the reduced graphene oxide (rGO). Flexible and free-standing rGO/AgNPs/poly(PyY) paper is the first reported...
poses. Similar to pesticides, polychlorinated biphenyls (PCBs) approach, assert performance of this biosensor for practical pur-
as well as simplicity of fabrication through an eco-friendly ap-
tivity when using an electrode made of nano- than mi-
direct paraoxon detection, exhibited twofold better sensi-
(TCh) oxidation, as a product of the enzymatic reaction for-
determination in fruit samples. Zheng
The viability of this method was proven by selective pesticide-
tion, in accordance with the enzyme inhibition mechanism.

First stage monitoring of pesticides in food and beverage-
ates employed the usage of biosensors based on en-
zymes or antibodies as a recognition element. Acetylcholin-
esterase (AChE) is the most common enzyme used in electro-
chemical detection of organophosphorus and carbamate-
pesticides (89). These contaminants can cause irreversible es-
erase inhibition in the human central nervous system, lead-
ing to health issues. For selective electrochemical detection-
of monocrotophos and chlorpyrifos insecticides, a GCE mod-
ified with nitrogen-fluorine co-doped MoS₂ monolayer deco-
 rated with AgNPs was proposed (58). To construct an effective-
biosensor, amino-functionalised carbon nanotubes (CNTs-
-NH₃) were chosen for enzyme immobilisation onto the sens-
ing platform, ensuring a high enzyme-to-substrate affinity-
(low Michaelis-Menten constant of 42 μM). Both cyclic voltam-
metry (CV) and electrochemical impedance spectroscopy-
(EIS) evaluation confirmed that the introduction of AgNPs has-
improved electron transfer kinetics and expanded the active-
surface area tenfold compared to bare GCE. Differential pulse-
voltagmetry (DPV) responses of the AChE/CNTs-NH₃/AgNPs-
-N-F-MoS₂/GCE biosensor displayed linear decrement of the-
obxidation current with the increase of pesticide concentra-
tion, in accordance with the enzyme inhibition mechanism.
The viability of this method was proven by selective pesticide-
determination in fruit samples. Zheng et al. (39) designed an-
other AChE enzymatic sensor through chitosan layer-coated-
flexible nanosilver electrodes. The current of thiocholine-
(TCh) oxidation, as a product of the enzymatic reaction for ind-
direct paraoxon detection, exhibited twofold better sensi-
tivity when using an electrode made of nano- than mi-
croscaled silver powder. Feasibility of the proposed method-
in the analyses of vegetables, room temperature operation,
as well as simplicity of fabrication through an eco-friendly ap-
proach, assert performance of this biosensor for practical pur-
poses. Similar to pesticides, polychlorinated biphenyls (PCBs)
are persistent organic pollutants known by their toxic health-
effects, once widespread for industrial purposes (90). Anti-
bodies as a recognition element were successfully immobi-
ilised on the AgNPs/PANI/GCE via glutaraldehyde linker in a immuno-
sensor designed for PCB 28 detection (59). Square-
wave voltammetry (SWV) generated a linear electrochemical-
response to PCB 28, but also provided a signal for benzyl chlo-
ride and PCB 180 interfering agents. Another slight immuno-
sensor disadvantage is the antibody immobilisation period-
(30 min) and PCB 28 incubation period (2 h), which can be-
Further reduced by the usage of modified printed electrodes.

In response to enzyme instability and denaturation dur-
ing storage, the second stage of pesticide monitoring result-
ed in the development of non-enzymatic sensors based on-
ous silver-nanomaterial modifiers. Using chitosan-stabi-
ised AgNP-modified GCE, the sensitivity of CV and adsorptive-
SWV methods in sensing the ethyl parathion (EPT) and pen-
dimethalin (PDM) was compared by de Lima et al. (60). The aforesaid sensor was successfully applied for the de-
tection of these two distinctive contaminants in diverse ma-
tices – nitroaromatic herbicide (PDM) in mineral water, and-
typical organophosphate pesticide (EPT) in honey and let-
tuce samples. The accumulation step in voltammetric detec-
tion surpassed the problem of steep cathodic current decre-
ment observed after successive CV cycles, thus lowering the-
detection limit and broadening the linear range. Among elec-
rochemical detection methods, this modified electrode was-
the only one able to determine both pesticides. Moreover,-
the sensor has practical applications in various food matrices
without requirement for the sample pretreatment step. In an-
other study of paraoxon pesticide determination in onion-
 samples, a stearic acid/nanosilver composite decorated GCE-
was used (61). Unlike the aforementioned biosensor-based-
device (39), the combination of biocompatible stearic acid-
and the electrocatalytic behaviour of AgNPs have shown a synergetic effect, thus enabling the development of an en-
zyme-free sensor. Differential pulse voltammetry was proven-
a satisfactory measurement technique, achieving the lowest-
paraoxon LOD value (0.1 nM) presented in the literature.
Combining the AgNP electrocatalytic property with the oxygen-
rich edge chemistry of a graphene nanoribbon platform,
Ag@GNRs modified screen printed carbon electrode (SPCE)
sensor was designed for selective methyl parathion (MP) pes-
ticide determination (62). The lowest value of charge transfer-
resistance (71.4 Ω), obtained at the interface of Ag@GNRs/
SPCE and electrolyte, compared with unmodified SPCE (460.1
Ω), GNR/SPCE (223.6 Ω) and Ag/SPCE (189.0 Ω), indicates syn-
ergistic interaction between the highly conjugated graph-
ene-like material and AgNPs, which greatly reduces the overpotential and enhances the sensitivity towards MP.
Well-defined amperometric responses for MP determina-
tion in cabbage, green beans, strawberry and nectarine were-
oberved, with working range covering nano- and micromo-
lar regions for each real sample. A novel voltammetric sen-
sor, AgNP-supported solid amalgam electrode (SAE) for
thiodicarb insecticide detection, was presented for the first time by Lucca et al. (40). Despite the inclusion of mercury, due to miniscule amounts involved, amalgam electrodes (97) adhere to the green chemistry approach. A CV study, recorded with AgNPs–SAE in Britton–Robinson buffer solution (pH=6.0), along with SWAdS voltammograms, revealed irreversible thiodicarb behaviour with a pronounced cathodic current peak at a potential of −0.64 V (40). Furthermore, linear dependence on the thiodicarb concentration from 1.05×10⁻⁷ to 1.52×10⁻⁴ mol/L, with 7.2×10⁻⁹ limit of detection, surpassed the lowest achieved values among all reported methods. Taking into account that this is only the fourth scientific publication regarding electrochemical methods for the voltammetric determination of thiodicarb, it is inevitable to emphasise this work as an esteemed scientific contribution.

Additive is a term which refers to chemicals used as adulterants for enhancement of the visual appeal or taste of some food products. Due to the toxic impact of some additives on human health, sustainable methods for efficient and rapid detection of these contaminants are necessary (92). Vanillin is an aromatic compound extensively used as a flavouring and fragrance enhancer, but high exposure to vanillin can cause liver and kidney damage (93). Li et al. (63) synthesised bimetallic Ag-Pd nanoparticles utilising green and in situ chemical reduction strategy, and demonstrated that the electrochemical response to vanillin at the Ag-Pd/GO/GCE sensor takes place at a lower potential than GCE modified with monometallic counterparts (Ag or Pd). DPV revealed the outstanding catalytic ability of the 3D nanohybrid material, enabling quantitative detection of vanillin at a concentration range of 0.02 to 45 μM. Azo-dyes (e.g. Sudan class of molecules, Orange II, Sunset Yellow) account for 60–70% of all synthesised colourants in the food industry. These compounds, characterised with at least one –N=N– functional group, are classified as carcinogens (94). GCE is the most important working electrode for selective determination of these food adulterants, due to its efficiency, accuracy and ability to enlarge the active surface area with various modifiers. Pani et al. (64) compared the sensitivity of AuNP, AgNP and Au-Ag core–shell composite material–decorated GCE, as a rapid voltammetric sensor for Sudan IV dye. Joining a green synthetic approach with the autoclave technology, obtained nanostructures were of the same composition, structure and properties in all batches of production. Hence, all three electrodes were found to be applicable in Sudan IV sensing, with current peak proportional to dye concentration in practically the same linear range. GCE, modified with Ag-Cu nanoparticles anchored on reduced graphene oxide platform, was applied for determination of Sudan I in ketchup and chili powder (65). Amperometric current–time curves recorded in phosphate buffer solution (pH=6.5) at a constant potential of −0.112 V demonstrated the effective catalytic property of Ag-Cu/rGO/GCE reaching the lowest LOD value reported. Another food dye sensor was fabricated by drop-casting carbamazepine-functionalised silver nanoparticles (Cbz-AgNPs) onto the GCE (66). The bridging role of AgNPs leads to faster electron transfer between the donor (dye molecule) and acceptor (GCE), which is evident in the ability of the nanocomposite to boost the oxidation signals of Orange II and Rhodamine B dyes exceptionally, as compared to individual carbamazepine (Cbz)- or AgNPs-coated GCE (Fig. 3a). Achieved LOD values in the nanomolar range displayed high efficiency of this voltammetric sensor for the simultaneous detection of food dyes. Amaranth dye was chosen as an azo-dye model to study the electrochemical behaviour and degradation process utilising three graphene/TiO₂–Ag nanocomposite-coated gold electrodes (denoted Au/GTA-5/10/15, regarding mass fraction in % of TiO₂–AgNPs) (67). Linear sweep voltammetry (LSV) displayed the same obtained LOD value for all three electrodes (10⁻⁷ M), pointing out Au/GTA-10 in terms of considerably higher sensitivity towards the analyte. The same electrode exhibited first-order kinetics of amaranth degradation (2.10⁻⁵ M in 0.2 M KCl solution), tested by electrochemical polarization at +1.4 V vs Ag/AgCl. Molecularly imprinted polymers (MIPs) have been reported as excellent recognition elements for electrochemical sensors. An innovative sensor based on graphene oxide- and AgNPs-enhanced GCE was prepared using imprinting technology, with Sunset Yellow as the template molecule (68). Evaluated in the presence of Tartrazine, Amaranth, Brilliant Blue G and ascorbic acid as interfering agents, this sensor exhibited great selectivity towards the azo-dye, and was successfully applied for detection in soft drinks. GCE was also the working electrode of choice in the only example of chloramphenicol (CAP) detection in honey and milk powder samples (34). Decorated with Ag nanodendrites (immense specific surface area) anchored on carboxylic short-chain MWCNTs (fast electron transfer), the obtained sensor enabled ultrasensitive detection of CAP by linear sweep stripping voltammetry (LSSV) and CV techniques.

In the food safety sector, presence of pathogen bacteria needs to be strictly monitored. In order to detect S. aureus in water samples, bioassay system has been developed (69). Authors used two specific anti-S. aureus aptamer sequences. Primarily one, immobilised on streptavidin-coated magnetic beads, served as a capture probe, and the second one, conjugated to AgNPs, was the signalling probe. In the presence of target bacterium, a sandwich complex is formed which, after dissolution in 0.1 M HNO₃, during anodic stripping DPV measurement produces distinctive AgNPs signal, sufficient to detect only one colony forming unit (CFU) in mL sample. L. monocytogenes, Gram-positive rod-shaped foodborne bacteria, have been successfully captured via L. monocytogenes antibodies attached to silver-ruthenium bipyridine complex core–chitosan shell hybrid nanoparticles (HNPs), chemically deposited onto GO nanosheets (70). At the applied potential of +0.55 V oxidation of bimetallic complex occurs, with measured change in amperometric response being directly proportional to the bacterial concentration.
Ascorbic acid (AA) is one of a few permitted substances in food and beverages (95). Due to its instability in acidic media, and upon oxygen/light exposure, AA degrades, which distorts food quality control via a colour change (96). Voltammetry is an increasingly popular method carried out in the analysis of AA in food samples, due to its simplicity alongside little or no sample preparation requirement. Diverse modifications of carbon paste electrodes have shown to stand out among other presented sensing tools in electrochemical AA detection (97). Applying a green synthetic approach through onion (71) and fig (72) extracts, Khalilzadeh’s group prepared AgNPs modifiers for fabrication of silver-carbon paste working electrodes (AgNPs/CPE). A simple sensor design, combined with SWV detection, revealed good selectivity for AA analysis in fruit juices, covering micromolar concentration ranges. Another simple sensor preparation for quick in-field vitamin C quantification in commercial fruit juices was described by Jadav et al. (73). Alternately adding carbon and silver conductive layers, authors fabricated the AA sensing area of silver/carbon SPE. In another study, coupling the electrodeposition of AgNPs (8 cycles in continuous cycling intervals from −0.7 to 1.9 V in 1.0 mM AgNO₃, nitric acid solution), and quercetin from 0.5 mM solution in 0.1 M phosphate buffer (12 cycles of 0–40 mV potential scans), onto the graphene nanosheet-coated GCE, a new AA sensor was developed (74). DPV method provided three distinguished anodic peaks at the potentials of 10, 240 and 344 mV, corresponding to the simultaneous electrochemical oxidation responses to AA, uric acid and L-cysteine, respectively. Hydrogen peroxide is one of the most commonly used oxidising agents for the prevention of grocery spoilage. Thus, design of novel sensors for peroxide trace analysis is indispensable in the food quality sector. The rGO/AgNPs nanoarchitecture, coated onto the GCE via a Nafion layer, provided for the first enzymeless electrochemical selective detection of H₂O₂ (75). Using amperometry, the symbiotic effect of individual ternary hybrid nanostructure components significantly reinforced the sensor performance, enabling quantification of H₂O₂ in apple juice. A similar sensor, leaning on amperometry, GCE coated with a Nafion layer and reduced graphene oxide, this time modified with bimetallic Pd and Ag nanoparticles, was fabricated by Guler et al. (76). Due to the high loading and uniform dispersity of the prepared nanomaterial, the novel NF/Pd@Ag/rGO-NH₂ architecture showed noticeably improved catalytic properties towards H₂O₂. Unlike the previous reported sensor (LDR 1–10 μM), this sensor covers noticeably broader concentration ranges (2 to 19 500 μM).

In food quality analysis, freshness tests are based on detection of biogenic amines. In order to produce enzymatic or non-enzymatic amine sensors, adjustment of the GCE sensing surface with diverse nanostructured silver materials increases its practical analytical performance. Pioneering work in non-enzymatic sensing based on the TiO₂–Ag/PPy nanocomposite material for amperometric tyramine (TA) detection in banana samples was done by Erdogan et al. (77). Under the optimum conditions (0.1 M phosphate buffer solution and the potential of +0.6 V), linearity over the 10⁻⁶–10⁻⁴ M concentration range, and LOD value lower than other TA detecting devices (2·10⁻⁴ M) revealed this nanocomposite-gelatin-coated GCE as an exemplary amine sensor. In a report by Kumar and Sundaramoorthy (78), GCE coated with AgNPs-decorated nitrogen-doped SWCNT embedded in a Nafion layer (NF/Ag-N-SWCNT/GCE) served as a non-enzymatic sensor applicable for voltammetric urea detection in milk and water matrices. Butwong et al. (79) applied Ag–Ag₂O–decorated MWCNT-modified GCE for the detection of histamine (HIS) in fish sauce. Based on the oxidation of the –NH₂ group to the corresponding nitro compound during DPV measurements, the performance of the sensor was more stable and sensitive towards HIS (higher peak current shifted to a lower potential) than the CV data. As a result, determination of HIS, as a food spoilage indicator, at low concentration of 2 μg/L was achieved.

Mycotoxins are common food pollutants produced by organisms from the Fungi kingdom (98). Selective determination of mycotoxin in grape juice and wine samples was carried out applying MIPs (80). In this voltammetric sensor design, the GCE surface was coated with AgNPs, polyoxometalate (POM) and reduced graphene oxide layer, after which CV was used to imprint ochratoxin A (OCH). Synergistic effect between the AgNPs and POMs increased the rate of electrochemical reaction. Steep DPV troughs manifested ultra-high sensitivity of the MIP sensor towards OCH, with a detection limit of 1.6·10⁻¹⁰ M. For detection of aflatoxin M₁ (AFM₁) in milk samples, a modified GCE with long-term stability has been reported (44). The multilayered modifier film combines the advantages of α-cyclodextrin (excellent electrical conductivity), graphene quantum dots (as mediator), and AgNPs as electrocatalytical agent for selective LSV recognition of AFM₁. This sensor provided linearity from 0.015 to 25 mM concentration range. To develop a precise non-enzymatic immunosensor for electrochemical biosensing of cyanoxin microcystin-LR (MC-LR), Zhao et al. (81) introduced silver@mesoporous silica (Ag@MSN) nanoparticles as a horseradish peroxidase-mimicking enzyme. Such engineered nanomaterial catalyses the reduction of hydrogen peroxide to produce a current signal inversely proportional to the MC-LR concentration. The biosensor performance manifests in a three orders of magnitude linear range, with a remarkable LOD value obtained in water samples (0.2 ng/mL), which is much lower than the concentration of 1 μg/L in drinking water, submitted by the World Health Organization (99).

Impedimetric sensors

The application of electrochemical sensors based on impedance analysis has grown during the past decade owing to rapid response and the high sensitivity of such devices (down to picomolar range). The role of AgNPs is signal enhancement, which makes this technique extremely useful to detect the analyte of interest during interactions with
(bio)sensing platforms. Despite this fact, extensive sensor development has been limited mostly by the complexity of impedance analysis. Hence, in this article only a few impedimetric sensors have been reviewed regarding both quality and safety sectors.

As artificially synthesised oligonucleotide or peptide molecules, aptamers found their versatile purpose as highly selective recognition elements for target molecules in impedimetric sensors. An AgNP (large surface area)–nitrogen-doped graphene (excellent electrical properties)–aptamer system has shown to be an effective biosensing platform for impedimetric acetamiprid detection (82). Obtained impedimetric data displayed a linear picomolar concentration range, resulting in the lowest LOD value for pesticide sensing (3.3·10⁻¹⁴ M) among all presented electrochemical sensors.

Antibiotics are a broad family of chemically synthesised compounds used as a cure for bacterial infections. However, their intense usage in medicine, but also as feed additive, has led to negative effects on animal and human health. The omnipresence of antibiotics in meat and dairy products is a hot topic attracting the public attention nowadays. Therefore, the trace antibiotic levels in food products need to be strictly regulated (100). Combining Prussian blue (FeFe-PB) core with bimetallic CuFe shell, and coupling with silver nanoclusters via aptamer linkage in a one-step bio-inspired synthesis, an impedimetric aptasensor for bleomycin (BLM) antibiotic was developed (47). Owing to the formation of Fe(I)II-BLM complex, the AgNCs/Apt@CuFe@FeFe aptasensor outperformed the CuFe@FeFe-based one, giving an extremely low detection limit of 0.0082 fg/mL towards BLM. Rosati et al. (83) inkjet-printed an aptamer-functionalised sensor for ampicillin detection in milk samples. Although impedance data display a linear range over more than 2 orders of magnitude, the LOD value is not sufficient for prescribed EU standards. Nonetheless, this preliminary work presents a simple and cheap microelectrode fabrication method which can be easily subjected to further sensor improvement.

The combination of two distinctive silver nanomaterials with electrochemical impedance spectroscopy (EIS) detection technique have been shown as a rapid and efficient way for detection of E. coli in water and eggshell matrices. In the first report, bovine serum albumin templated 3D Ag nanoflower impedance immunosensor was fabricated (35). Pathogen capturing has been conducted via antibody binding and the charge transfer resistance (Rct) value increased proportionally to the logarithm of 3.0·10⁻¹⁻3.0·10⁰ CFU/mL concentration range (Fig. 3b). High specificity of the modified Au electrode was proven towards C. sakazaki, MRSA, S. albus, L. easei and S. flexneri. In the second report, encapsulation of negatively charged E. coli surface with positively charged poly(dimethylallylammonium chloride) (PDDA) enabled the connection between bacteria and nanogold particles (84). Silver enhancement reaction resulted in the formation of E. coli/PDDA/AuNP@Ag complex, which improved the performance of a novel microfluidic chip for the impedimetric detection of bacteria. The prepared complex increased the solution conductivity and the double layer capacitance around the microelectrodes, showing practical application in eggshell solution and tap water specimens.

A novel biosensor based on hybridisation chain reaction (HCR) as an enzymeless strategy for rapid bacteria detection in milk samples was proposed (85). In the presence of the biomarker (highly specific fragment of S. aureus 16S rRNA), and with the aid of hairpin-decorated gold nanoparticles, silver nanowire formation between the adjacent interdigitalised electrodes occurs. The switch from isolated AuNP nucleation sites to the conductive silver feature leads to the electrochemical signal transduction pathway. Despite the higher achieved LOD value (50 CFU/mL) than the previously presented S. aureus immunosensor analogue (only 1.0 CFU per mL sample) (69), the authors would like to highlight the benefit of the HCR method as a polymerase-free detection strategy, as well as the merits of high sensitivity and fast response (analysis accomplished in less than 100 min), which can be useful for point-of-care applications. Combining silk fibroin with silver nanowires, interesting biocompatible, wearable and optically transparent flexible bioelectronics were prepared (32). A single-use food sensor can be easily embedded into the vinyl or plastic food packaging. H₂S produced during chicken spoilage induces Ag surface corrosion, decreasing its electrical conductivity through the formation of sulfide film. This strategy can be also applied in colourimetric sensor design (see following chapter).

**OPTICAL SENSORS**

Optical chemical sensors are devices which measure changes in optical phenomena – absorbance, reflectance, luminescence, etc. – caused by an interaction of the analyte with the recognition element. Colloidal silver is coloured, with pronounced absorbance/LSPR maxima, and this is often the basis of colourimetric sensor development. Recently, silver nanoclusters (AgNCs) have found use as the fluorescent species in luminescent sensors. A summary of the silver nanomaterial-based optical sensors for food applications is presented in Table 2 (42,43,46,101–139). Selected examples of optical chemical sensors, both colourimetric and fluorescent, are shown in Fig. 4 (113,138).

**Colourimetric sensors**

Colourimetric sensors (measuring changes in the absorption or reflectance during analysis) are the single most represented group of sensors in this review, possibly owing to their simplicity of fabrication and use. As such, they have found use for determination of food quality as well as food safety. In the scope of food quality determination, colourimetric sensors have been developed for evaluation of food composition, but also for food freshness monitoring (e.g. through detection of decomposition products). Examples of the latter include AgNP solutions which change colour (from red or yellow to
Table 2. Optical chemical sensors based on silver nanomaterials

| Analyte                  | Sample                      | Analytical method         | Recognition element       | Nanomaterial                        | LOD     | Ref.  |
|--------------------------|-----------------------------|---------------------------|---------------------------|------------------------------------|---------|-------|
| VOC from decomposition   | Banana                      | Colourimetry              | Direct – AgNPs            | AgNPs                              | –       | (101) |
| VOC from decomposition   | Onion                       | Colourimetry              | Direct – AgNPs            | AgNPs (PEG stabilised)             | –       | (102) |
| Trimethylamine           | Buffer                      | Colourimetry/LSPR         | Resorcinol monoacetate    | Au@Ag nanorods (in situ) in agarose hydrogel | 8.6 nM  | (103) |
| Hydrogen sulfide         | Chicken, carp               | Colourimetry              | Direct – AgNPs            | AgNPs (gellan gum stabilised)      | 0.81 µM | (104) |
| Ammonia                  | Fish, carp                  | Colourimetry/LSPR         | Direct – AgNPs            | AgNPs in bacterial nanopaper       | 0.574·10^4 g/mL | (105) |
| Sugars                   | Soft drinks and apple       | Colourimetry              | Direct – AgNPs            | AgNPs (in situ, CTAC stabilised)   | 8.7 µM  | (106) |
| Flavonoids (4 types)     | Buffer                      | Colourimetry              | Direct – AgNPs            | AgNPs (in situ, PVP stabilised)    | 0.03–0.1 µg/mL | (107) |
| Lysozyme                 | Milk                        | Colourimetry/LSPR         | Direct – AgNPs            | AgNPs (glutamic acid stabilised)   | 1.5 nM  | (108) |
| Caffeine                 | Tea, Coca-Cola              | Colourimetry              | AgNPs (MMIP extraction)   | AgNPs                              | 1 µg/L  | (109) |
| γ-Aminobutyric acid      | Green tea                   | Second-order light scattering | AgNPs (Si pretreatment)   | AgNPs                              | 39.6 mg/L | (110) |
| Antioxidants (20 types)  | Tea, lemon                  | Colourimetry              | Direct – AgNPs/AuNPs      | AgNPs and AuNPs (multiple stabilisers) | 3.5–47 nM | (7 types) | (111) |
| Se(IV)                   | Mushroom garlic             | LSPR/colourimetry         | Direct – Ag nanoparticles | Ag nanoparticles                    | 1.2 µg/L | (112) |
| Chloride                 | Water                       | Colourimetry, distance based | AgNPs and H_2O_2 reaction | AgNPs                              | 2 mg/L  | (113) |
| Hg(II)                   | Buffer                      | Colourimetry              | Direct – AgNP reaction    | AgNPs (gelatin stabilised)         | 25 nM   | (114) |
| Hg(II)                   | Water, milk                 | LSPR/colourimetry         | Direct – Ag–AuNPs         | Ag–AuNPs                            | 5 nM    | (115) |
| Cu(II)                   | Water                       | Colourimetry/LSPR         | Cu(II) catalysed reaction | AgNPs (starch stabilised)          | 0.24 µg/L | (116) |
| Cu(II)                   | Water, tomato, rice         | Colourimetry              | Cu(II) catalysed reaction | AgNPs (CTAB stabilised)            | 0.3 µg/L | (117) |
| Fe(II)                   | Fe suppl.                   | Colourimetry              | Ag^+ reduction ABT        | AgNCs (PMAA stabilised)            | 76 nM   | (118) |
| Carbazim                 | Water, apple, carrot        | Colourimetry              | AgNPs (ABT stabilised)    | AgNCs (ABT stabilised)             | 1.04 µM | (119) |
| Triazophos               | Water, rice, apple          | Colourimetry              | MPA and GAA               | AgNPs (MPA and GAA stabilised)     | 0.08 µM | (110) |
| Thiophanate-methyl       | Water, tomato               | Colourimetry              | Direct – AgNPs            | AgNPs (citrate stabilised)         | 0.12 µM | (120) |
| Diazinon                 | Fruit, vegetable            | Colourimetry              | Direct – AgNPs            | AgNPs (borohydride stabilised)     | 7 µg/L  | (121) |
| Malathion                | Water, apple                | Colourimetry              | APTamer                    | AgNPs (citrate stabilised)         | 0.5 pM  | (122) |
| Methamidophos, malathion | Water                       | Colourimetry              | Enzyme (inhibition)       | Au@AgNPs                           | 0.17 nM | (123) |
| Melamine                 | Milk                        | Colourimetry/LSPR         | Direct – AgNPs            | AgNPs (green synthesised)          | 2 µM    | (124) |
| Hydrogen peroxide        | Chicken                     | LSPR/colourimetry         | Direct – AgNPs            | AgNPs                               | 3.2 µM  | (125) |
| L. monocytogenes         | Pork                        | Colourimetry              | Antibody, aptamer         | Antibody modified AgNCs             | 10 CFU/mL | (126) |
| Ochratoxin A             | Flour, beer                 | Fluorescence              | APTamer                    | AgNPs                              | 8.7 nM  | (127) |
| Ochratoxin A, aflatoxin  | Rice, corn, wheat           | Fluorescence              | APTamer                    | AgNCs (in situ)                    | 0.2 pg/mL OTA | (128) |
| T-2 mycotoxin            | Oat, corn                   | Fluorescence              | APTamer                    | AgNCs (in situ)                    | 0.03 pg/mL | (129) |
| T-2 mycotoxin (5 types)  | Wheat, maize                | Fluorescence              | APTamer                    | AgNCs                              | 0.93 pg/mL | (130) |
| Mycotoxins               | Wheat, nut, milk            | Colourimetry              | Direct – AgNP aggregation | AgNPs (caffeeic acid, PVP or dopamine stabilised) | 2.1 ng/mL to 7 ng/mL | (131) |
| E. coli                  | Milk, water                 | Fluorescence              | DNAzyme                    | DNA-templated AgNCs                 | 60 CFU/mL | (132) |
| S. typhimurium           | Chicken meat                | Fluorescence              | APTamer                    | AgNC (in situ)                     | 50 CFU/mL | (133) |
Table 2. Continued

| Analyte                | Sample          | Analytical method          | Recognition element | Nanomaterial                  | LOD     | Ref. |
|------------------------|-----------------|----------------------------|---------------------|--------------------------------|---------|------|
| *P. aeruginosa*        | Milk, juice     | Fluorescence               | Antibody            | AgNP (glucose stabilised)      | 1.5 CFU/mL | (133) |
| Carbamate              | Water, fruit    | Fluorescence/colourimetry  | Enzyme inhibition   | Rhodamine modified AgNPs       | 0.023 ng/L | (134) |
| Malathion              | Water, fruits,  | Fluorescence               | Enzyme inhibition   | AgNPs                          | 0.556 fM | (135) |
| vegetables             | Vegetables      |                            |                     |                                |         |      |
| Kanamycin              | Milk            | Fluorescence               | Aptamer             | AgNCs                          | 1 nM    | (136) |
| Fe(III), thiosulfate   | Fruits, yoghurt, rice | Fluorescence | Direct – AgNCs | AgNCs in PVA and borax hydrogel | 0.045 and 0.060 µM | (137) |
| Melamine               | Milk, formula,  | Fluorescence               | Direct – AgNCs      | AgNCs (PEI stabilized); in agaroose hydrogel | 30 nM | (138) |
| dog food               |                 |                            |                     |                                |         |      |
| Nitrite                | Water           | Fluorescence               | Direct – AgNCs      | AgNCs (PEI stabilised)         | 100 nM  | (139) |
| Nitrite                | Sausages        | Chemiluminescence          |                     | Ag@AgCl@GO@Fe$_2$O$_4$         | 25 nM   | (43)  |

LOD = limit of detection, VOC = volatile organic compound, AgNP = silver nanoparticle, PEG = polyethylene glycol, LSPR = localized surface plasmon resonance, CTAC = cetyltrimethylammonium chloride, PVP = polyvinylpyrrolidone, MMIP = magnetic molecularly imprinted polymeric microsphere, AuNP = gold nanoparticles, AgNPi = silver nanoplate, CTAB = cetyltrimethylammonium bromide, PMAA = polymethacrylic acid, ABT = 4-aminobenzenethiol, MPA = 3-mercaptopropionic acid, GAA = guanidine acetic acid, AgNR = silver nanorod, AgNC = silver nanocluster, PVA = polyvinyl alcohol, PEI = polyethyleneimine, GO = graphene oxide

I. IVANIŠEVIĆ et al.: Biochemical Sensors Based on Silver Nanomaterials

Fig. 4. Selected examples of optical chemical sensors for food safety: a) schematic design of the colourimetric distance-based paper sensor for chloride ions. Reproduced from Phoonsawat et al. (113) with permission from The Royal Society of Chemistry. b) fluorescent sensor for melamine. On the top are fluorescence spectra and corresponding photographs under UV light demonstrating solution-based sensing; on the bottom are AgNC-doped agarose hydrogels under UV light (1 Ag NCs, 2 Ag NCs-Hg$_2^{2+}$ system, and 3–6 Ag NCs-Hg$_2^{2+}$ system in the presence of melamine with concentrations 1, 2, 4 and 5 µM, respectively). Reproduced from Du et al. (138) with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry. NC = nanocluster

transparent) when AgNPs bind to volatile decomposition products of bananas (107) or onions (102). While these sensors were simple, specialised measurements were necessary and analytical performance was not evaluated. On the other hand, Lin et al. (103) have developed colourimetric sensors for biogenic amines (represented by trimethylamine), which are generated by bacterial decarboxylation of amino acids in protein-rich foods. The sensors were developed by immobilising Au nanorods, AgNO$_3$ and resorcinol monoacetate (RMA) within an agarose hydrogel. Biogenic amines cause hydrolysis of RMA; the product of this reaction reduces Ag$^+$ to form Au@Ag core-shell nanorods, and the colour change of the hydrogels can be evaluated by a smartphone. Agarose hydrogels loaded with AgNPs were also used to detect H$_2$S formed during chicken and carp spoilage (104). These sensors were based on a very stable Ag$_2$S formation and the resulting colour change of the hydrogels. Ammonia vapour is another by-product of fish/meat spoilage and its concentration was quantified using bacterial cellulose with embedded AgNPs (105). In this sensor, ammonia causes etching of the AgNPs, altering their population density, size distribution and interparticle distance; this in turn changes colour of the sensing paper.

The other important aspect of food quality control is assessment of the composition, i.e. contents of key ingredients. Some sensors exploit the reducing capabilities of these components and their potential to generate AgNPs in situ by reduction of Ag$^+$ ions; the colour of the formed AgNPs is usually measured with a spectrophotometer. Examples of this approach include a simple and quick sensor for sugar content determination (combined monosaccharides, disaccharides or polyols) (106), as well as a sensor for determination of four different reducing flavonoids (107). On the other hand, some analytes cause aggregation of the already prepared silver nanoparticles, which in turn causes changes in their absorption spectra – this was the basis for a sensor for lysozyme in milk (108). This sensor was optimised by selecting glutamic acid as the ideal capping agent which was not subject to interference from several common milk components and a very low LOD (1.5 nM) was achieved. Since aggregation can be caused by multiple substances found in complex food matrices, Deng et al. (109) have coupled AgNPs with magnetic molecularly imprinted polymeric microspheres (MMIPs) to improve the selectivity towards caffeine. Although a much lower LOD of caffeine than needed for tea and Coca-Cola samples was obtained (1 µg/L), this sensor does include a
previous extraction step. Sequential injection has also been used as pretreatment step, in a sensor for detecting γ-aminobutyric acid (GABA), a health-promoting substance found in certain foods (110). The positively charged GABA causes aggregation and a colour change of negatively charged AgNPs in solution. However, second-order light scattering was used for detection instead of colourimetry. Bordbar et al. (111) have developed a colourimetric array (an optoelectronic tongue), which can discriminate among 20 different antioxidants in food. Due to AgNPs, AuNPs and six different reducing/capping agents, the array provides a unique colourimetric response for each antioxidant: nanoparticle aggregation causes a red shift, while substitution of the capping agent with the antioxidant causes a change in the absorbance value. Very low LODs were thus achieved for seven antioxidants, while five antioxidants were detected simultaneously in tea and lemon juice. Different innovative approaches were used for the detection of selenium and chloride, two necessary elements which are undesirable at high concentrations. Selenite ions etch Ag nanoparticles and change their shape to nanodiscs, which causes an LSPR wavelength blue shift and colour change (112). Interestingly, this mechanism was confirmed by establishing that there was no effect on spherical AgNPs. The well-known oxidative etching of AgNPs by Cl⁻ in the presence of H₂O₂ was employed to develop a distance-based paper chloride sensor, Fig. 4a (113). In this simple and inexpensive sensor, the length of the white precipitate, as measured with a ruler, correlates with the concentration of chloride ions. Although coloured samples may present an issue, the naked eye LOD with water samples was 2 mg/L and no interference was observed from several ions (including halides).

Within the scope of food safety, colourimetric sensors have been developed for the detection of heavy metals, pesticides, bacteria and unwanted food additives. Heavy metals, ingested via food or water sources, pose a serious threat to human health. Mercury is one of the most toxic heavy metals and several sensors for its determination have been developed. In one example, gelatin-stabilised AgNPs were used for mercury sensing; these nanoparticles form an amalgam with Hg²⁺, which causes a change in the colour/spectrum (114). The nanoparticles were evaluated in three sensing forms: AgNPs in solution, in polyvinyl alcohol (PVA) hydrogels and on paper strips. While all sensors showed similar sensitivities, the response in the hydrogels and on paper was much slower, due to the heterogeneous reaction. Nevertheless, due to the simplicity, the paper strips were highlighted as having great potential for monitoring mercury in food samples. Tao et al. (115) achieved an improved LOD of Hg(II) by developing plasmonic sensors based on Ag–Au alloy nanoparticles (Ag–AuNPs). After the reaction with mercury, the amalgam shell caused a blue shift of the LSPR peak. Again, in addition to the colloid, heterogeneous sensors were developed: Ag–AuNPs were immobilised on an indium tin oxide glass surface using PDDA as a binder or embedded within a PVA film. Interestingly, the plasmonic sensor based on PVA demonstrated the best sensitivity and was used to detect mercury in drinking water and milk.

In the case of Cu(II) sensors, a different detection mechanism was used: catalytic etching of Ag by thiourea salt in the presence of Cu²⁺. This etching causes a colour change of a starch-stabilised AgNP suspension, correlated with Cu(II) concentration (116). Chaiyo et al. (117) went a step further and immobilised Ag nanoparticles (AgNPs) on paper substrates to form simple paper-based devices relying on the same mechanism. An LOD similar to suspension sensors (0.3 µg/L) was achieved with semi-quantitative image processing, but the number of samples was extended to include tomato and rice. The device holds great potential for portable, rapid, simple and low-cost field testing. Deficiency of iron is a common health problem, but the intake of this heavy metal via food or supplements should also be controlled. A colourimetric Fe(III) sensor was based on the growth of silver nanoclusters (AgNCs) upon reduction of excess Ag⁺ in the solution (46). While the fluorescence property of AgNCs is commonly exploited, this is a rare example of measurement of the size-dependent colour change of the clusters.

Pesticides represent a major group of toxins detected with colourimetric sensors. Non-covalent bonding between the pesticide and the nanoparticle stabiliser molecule is the basis of several sensors. In one example, 4-aminobenzene-thiol (ABT)-functionalised silver nanoparticles act as a colourimetric probe for the fungicide carbasazim (118). Due to strong ion-pair and π-π interactions between the stabiliser molecule and analyte, intense aggregation occurs (large conjugate network formation), which causes a visible red shift of the solution absorbance. The same group expanded on this sensing mechanism and developed AgNPs bifunctionalised with 3-mercaptopropionic acid (MPA) and guanidineacetic acid (GAA) (119). These nanoparticles can selectively bind triazophos (a broad spectrum organophosphorus pesticide) via hydrogen bonding; further aggregation via π-π interactions causes and even larger red shift than in their previous example and enables achieving low LODs (0.08 µM). Furthermore, the sensor did not react with several interferents and mixtures thereof (including cations, anions and other pesticides). In other examples, hydrogen bonding between citrate-stabilised AgNPs and thiophenate-methyl was exploited (120), as well as the non-covalent interaction between borohydride-stabilised AgNPs and diazinon pesticide (121). In addition to these non-covalent interactions, pesticides were detected with biosensors using biological recognition elements (aptamers and enzymes), which ensures high selectivity and, as demonstrated, superior LODs. The lowest LOD for pesticides (0.5 pM) was achieved by Bala et al. (122) with their aptasensor for malathion. In this solution-based sensor, the key components are AgNPs, a basic hexapeptide and malathion-specific aptamer. With no malathion present, the aptamer binds to the peptide and does not affect the optical properties of AgNPs. However, if the aptamer reacts with malathion in the
sample, then the free peptide interacts with negatively charged AgNPs, causing their aggregation and colour change. Enzyme inhibition was the basis for another biosensor for organophosphorus pesticides (methamidophos and malathion) (123). Alkaline phosphatase (ALP) catalyses the dephosphorylation of the added substrate p-aminophenyl phosphate (p-APP); the product reduces Ag(I) ion to Ag which is spontaneously deposited on the surface of the present AuNPs to form Au@AgNPs. Superiority of Au@AgNPs, compared to pure AgNPs or AuNPs, was demonstrated and sub-nanomolar LODs were obtained for both pesticides. A drawback may be the 2-hour enzyme inhibition period and an additional 30-minute period for Ag reduction and growth.

Colourimetric sensors were developed for several harmful food additives. Melamine, an illegal adulterant for presenting higher protein content of food, was detected with green-synthesised AgNPs, which aggregate upon analyte interaction and change colour (42). Since hydrogen peroxide is commonly used for oxidation and bleaching, a colourimetric sensor for its detection in food has also been developed (124). This sensor uses Au@Ag nanorods (Au@Ag NRs). In the presence of H₂O₂, silver atoms on the surface of the nanorods are oxidised to silver ions, thereby resulting in an LSPR red shift and colour change. Lastly, in an example of colourimetric bacteria detection, AgNCs play the role of an artificial enzyme (125). IgY antibody-coated AgNCs bind to Listeria monocytogenes, which is captured by aptamer-modified magnetic beads and then the whole sandwich-type immunocomplex is transferred to the reporting system. The reporting system contains AuNPs and α-phenylenediamine (OPD), which causes their aggregation. The AgNCs catalyse OPD oxidation and cause deaggregation of AuNCs with a pronounced effect on the UV-Vis spectrum. While the measurement procedure may seem complex, the assay takes 1 h and can specifically detect the target bacteria with a low detection limit (10 CFU/mL).

Luminescent sensors

Fluorescence measurements enable greater sensitivity and lower detection limits than obtainable with colourimetric sensors. As such, the fluorescent sensors found in this survey were developed exclusively for food safety monitoring – where detection of the smallest amounts of harmful agents is needed. This is best demonstrated in the case of sensors for mycotoxins, toxic fungal metabolites harmful to both humans and livestock. For example, a quick fluorescent method for detecting ochratoxin A (OCH) in flour and beer has been developed (126). This FRET ( Förster resonance energy transfer) sensor was based on nitrogen-doped carbon dots (CD) as energy donor and AgNP modified with aptamer and 6-mercaptop-1-hexanol (MCH) as energy acceptor. Upon interaction of OCH with the aptamer on AgNPs, FRET is inhibited and the resulting fluorescence intensity can be correlated with OCH concentration in the sample. The sensor has a wide concentration range (10–5000 nM) and can detect OCH in 30 min due to the use of MCH as stabiliser. Zhang et al. (127) developed another fluorescent aptasensor that further improved the sensitivity and provided detection limits of ochratoxin A and aflatoxin even lower than the voltammetric sensors previously described. Upon aptamer-mycotoxin interaction, signal probes are released into the supernatant and used as scaffolds for in situ fluorescent silver nanocluster (AgNC) synthesis. Fluorescence intensity of AgNCs was further increased with Zn²⁺ ions, achieving LODs of 0.2 pg/mL for OCH and 0.3 pg/mL for aflatoxin, respectively. A similar approach with fluorescent AgNCs has been adopted to develop aptasensors for another mycotoxin – T-2 mycotoxin. In one example, the DNA remaining after competitive binding of T-2 to the aptamer is amplified via exponential isothermal amplification reaction (EXPAR) (128). The produced DNA is used for in situ fluorescent AgNC formation and this provides a low concentration range (1 pg/mL to 100 ng/mL) and LOD (0.03 pg/mL). Alternatively, previously synthesised aptamer-functionalised AgNCs can be deposited on MoS₂ nanosheets, which causes quenching via FRET; presence of the T-2 mycotoxin causes recovery of the fluorescence signal which can be correlated with analyte concentration (129). Mycotoxins can also be detected with a colourimetric system, although with a tradeoff in sensitivity. Recently, a paper-based six-sensor array has been fabricated for the simultaneous detection and discrimination of five different mycotoxins (130). Caffeic acid, PVP and dopamine were used as stabilisers of AgNPs and AuNPs, which aggregate upon interaction with mycotoxins causing a colour change. For example, caffeic acid-capped AgNPs are mostly aggregated by aflatoxins and ochratoxin. Established LODs for the five mycotoxins were in the range from 2.1 to 7 ng/mL, which is unfortunately several orders of magnitude higher than the fluorescent sensors.

Fluorescence was also the most represented analytical method for detection of bacteria in food and beverage samples. In an improvement over their colourimetric sensor (140), Zheng and Zhang (131) developed a fluorescent turn-on E. coli sensor. In the presence of E. coli lysate, the free AChE is transferred into the DNA-AgNCs-containing system to catalyse the hydrolysis of acetylthiocholine (ATCh) to TCh. TCh significantly increases DNA-AgNCs fluorescence (via ligand-to-metal charge transfer (LMCT) or ligand-to-metal–metal charge transfer (LMMCT)), generating a 60 CFU/mL LOD. In a Salmonella typhimurium sensor, single-stranded sequences were released from an aptamer-sequence complex upon recognition, initiating a branch migration to release complementary scaffolds for AgNCs (132). This amplification was repeated thrice, producing highly fluorescent AgNCs in situ and achieving ultrasensitive (LOD=50 CFU/mL) and very linear bacterial detection. This lowest LOD (1.5 CFU/mL) was achieved with a Pseudomonas aeruginosa sensor based on a pyrimidine derivative probe tagged with glucose-stabilised AgNPs (133). The green-synthesised sensor was functional in several samples, including water, soil, milk, sugarcane and orange juices.

Among pesticides, fluorescent sensors for carbaryl (carbamate) (134) and malathion (organophosphorus) (135) were
developed. The carbaryl sensor relies on the fact that carbamate pesticides inhibit the activity of acetylcholinesterase (134). Adsorption of rhodamine on AgNP causes quenching of its fluorescence and this can be undone by thiouehine (along with aggregation-induced colour changes). With inhibited acetylcholinesterase, less thiouehine is produced, and the reduction in fluorescence intensity can be correlated with pesticide concentration. The fluorescent assay is more sensitive than the colourimetric one and produces LOD an order of magnitude lower. The same strategy, although without a fluorophore and instead relying on the fluorescence of AgNPs, was used for detecting the organophosphorus pesticide, malathion (135). DNA-templated AgNCs were also used as energy donor and AuNPs as energy acceptor in a surface plasmon-enhanced energy transfer (SPEET) sensor for the antibiotic kanamycin in milk samples (136). In an example of heterogeneous sensing, it was found that polyvinyl alcohol (PVA) and borax hydrogel can be used both as a reducing agent and immobilisation matrix for the formation of fluorescent AgNCs (137). This hydrogel acts as a dual on-off sensor for Fe(III) and thiosulfate. As Du et al. (138) demonstrated, fluorescence of AgNCs stabilised by polyethyleneimine (PEI) is quenched by Hg^{2+}, but recovered by melamine, Fig. 4b. This was the basis for the development of a fluorescent sensor for this harmful food additive. The AgNCs were further embedded within an agarose hydrogel to obtain simple devices for field testing. PEI-stabilised AgNCs were also used as a sensor for nitrite (139). In this sensor, the product of nitrite and added hydrogen peroxide reaction causes aggregation and quenching of AgNCs; a 100 nM LOD was achieved.

In the only example of a chemiluminescent sensor, nitrite was detected starting with Ag@AgCl nanoparticles grafted onto graphene oxide@Fe_{3}O_{4} nanocomposite (43). This composite causes light-initiated hydrogen peroxide generation and the peroxide reacts with nitrite in the sample. Decomposition of the product and uranine excitation causes chemiluminescence, the intensity of which is proportional to nitrite concentration. The obtained LOD surpassed other optical sensors found in this review.

CONCLUSIONS AND OUTLOOK

Silver nanoparticles have demonstrated the ability to significantly enhance detection capabilities of analytical devices and have accordingly been used in the development of electrochemical and optical chemical sensors. Among the papers analysed in this review, silver nanoparticles are commonly obtained by reduction of the silver nitrate precursor using borohydride, citrate or plant-derived reducing agents. A multitude of different stabilisers has been explored, as best evidenced from the previous chapters. The choice of stabiliser is of paramount importance, since it dictates the size and shape of the nanoparticles (which has an immense effect on the nanomaterial and sensor properties), but it is also in some sensors responsible for the analyte recognition itself.

We have analysed a total of 81 different sensors in this review. The majority of analytes were those related to food safety: most sensors were developed for detection of food additives and drugs (almost 24 %), pesticides (20 %), microorganisms (11 %), mycotoxins (10 %), and fertilisers and heavy metals with 7 % in each category. On the other hand, 10 % of all sensors were for food composition determination and 11 % were for freshness indicators, such as decomposition products. Regarding the transduction mechanism, we see that the sensors are almost evenly divided into electrochemical (39/81) and optical (42/81) sensors. Among both classes of sensors, generally simpler and quicker analytical methods are dominating the field: most electrochemical sensors relied on voltammetric techniques (32/39 electrochemical sensors), while colourimetry was most pronounced among optical sensors (28/42 optical sensors). Nevertheless, more complex techniques were used where achieving low limits of detection was of principal importance for food safety. Fluorescent sensors are generally much more sensitive than their colourimetric counterparts and femtomolar LODs were achieved for some mycotoxins and pesticides. Similarly, electrochemical impedance spectroscopy enabled detection of certain pesticides and drugs down to impressive femto- or even attomolar concentrations.

Regardless of the material used, in the development of electrochemical sensors, bare working electrodes are not the optimal choice due to their slow electron transfer kinetics. The oxidative peak of silver is about 100-fold more intense than the signal of colloidal gold with the same particle diameter and concentration. Thereby, the role of AgNPs in the fabrication of food sensors is directed towards amplification of sensitivity, while selectivity is improved by using aptamers or MIPs. To obtain faster electron transport, silver nanoparticles can be coated onto the working electrode surface: directly or via a polymeric layer. However, AgNPs are usually combined with other nanomaterials to form hybrid architectures. Hence, AgNPs are deposited onto SWCNTs, MWCNTs, MoS_{2} nanosheets, graphene, graphene oxide, reduced graphene oxide, etc. There are examples of silver nanomaterial-modified screen-printed electrodes, carbon paste electrodes, solid amalgam electrodes, disposable PVC electrodes and inkjet-printed flexible sensors. A major advantage of electrochemical sensors is the possibility of analysis of turbid samples, which most food samples are, without extensive sample pretreatment.

Optical (bio)chemical sensors are being thoroughly developed since they offer numerous advantages such as simplicity of fabrication and use, as well as lower cost. Optical sensing with AgNPs is commonly based on the following mechanisms: Ag(I) reduction by analyte for in situ generation of AgNPs/AgNCs with specific optical properties (colour, fluorescence, LSPR maxima); chemical reaction of the Ag nanomaterial causing change in optical properties due to shape/size transformation or formation of a coloured reaction product; interaction of the AgNP stabiliser molecule with the
analyte which causes aggregation/deaggregation of AgNPs and a subsequent colour change; catalytic effect of AgNCs on the detection reaction; fluorescent AgNCs formed in situ using (DNA) scaffolds released during a sensing event; and AgNCs acting as FRET or LMCT energy acceptors/quenchers (specifically in fluorescent sensors). However, most optical sensors detected in this survey were developed for homogeneous sensing in solutions, which makes reuse of the reagents (silver nanoparticles) difficult, driving the price up. Only several examples of optical sensors were found where the AgNPs were immobilised, usually in the following matrices: paper, bacterial nanocellulose, PVA and agarose hydrogels. Sensible immobilisation of the optical sensing chemistries into thin films or hydrogels would bring these sensors a step towards mobile, reusable and/or continuous food quality/safety monitoring and ultimately commercial products (141). Until then, electrochemical sensors have an advantage for this particular application.

We can see that nanosensing is still a growing field with many possibilities for both food safety and quality sectors, albeit with remaining challenges towards successful commercialisation. While green AgNP synthetic routes are already being promoted, future breakthroughs may come from leveraging greener, versatile and high-throughput technologies for fabrication of solid-state nanoparticle-based sensors, such as screen printing or inkjet printing (142). Together with the observed trends in miniaturisation and automation, smart sensors (and smart packaging) were labelled as the future of the food industry. Integration with low-cost mobile electronics or smartphones would enable simple portable on-site sensing, while incorporation of wireless communication would provide networking, improved connectivity and a higher degree of automation (143). Successful integration of these cutting-edge technologies, along with simultaneous advances in analytical performance of nanoparticle-based devices, will bring about this next generation of food safety and quality sensors.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

ORCID ID

I. IVANIŠEVIĆ @ https://orcid.org/0000-0001-5616-6315
S. Milardović @ https://orcid.org/0000-0002-0095-8441
P. Kassal @ https://orcid.org/0000-0001-7904-6439

REFERENCES

1. Deshmukh SP, Patil SM, Mullani SB, Delekar SD. Silver nanoparticles as an effective disinfectant: A review. Mater Sci Eng C Mater Biol Appl. 2019;97:954–65. https://doi.org/10.1016/j.msec.2018.12.102
2. Wang Y, Duncan TV. Nanoscale sensors for assuring the safety of food products. Curr Opin Biotechnol. 2017;44:74–86. https://doi.org/10.1016/j.copbio.2016.10.005
3. Cinti S. Novel paper-based electroanalytical tools for food surveillance. Anal Bioanal Chem. 2019;411:4303–11. https://doi.org/10.1007/s00216-019-01640-5
4. Krishna VD, Wu K, Su DQ, Cheean MCJ, Wang JP, Perez A. Nanotechnology: Review of concepts and potential application of sensing platforms in food safety. Food Microbiol. 2018;75:47–54. https://doi.org/10.1016/j.fm.2018.01.025
5. Lopes CM, Fernandes JR, Martins-Lopes P. Application of nanotechnology in the agro-food sector. Food Technol Biotechnol. 2013;51(2):183–97.
6. Pareek V, Gupta R, Panwar J. Do physico-chemical properties of silver nanoparticles decide their interaction with biological media and bactericidal action? A review. Mater Sci Eng C Mater Biol Appl. 2018;90:739–49. https://doi.org/10.1016/j.msec.2018.04.093
7. Carvalho F, George J, Sheikh HMA, Selvin R. Advances in screening, detection and enumeration of Escherichia coli using nanotechnology-based methods: A review. J Biomed Nanotechnol. 2018;14:829–46. https://doi.org/10.1166/jbn.2018.2549
8. Hu Y, Li YP, Liao YW, Jiang XH, Cheng ZJ. Poly(sodium-p-styrenesulfonate)-enhanced fluorescent silver nanoclusters for the assay of two food flavors and silicic acid. Food Chem. 2020;318:126502. https://doi.org/10.1016/j.foodchem.2020.126502
9. Tseng MH, Hu CC, Chiu TC. A fluorescence turn-on probe for sensing thiodicarb using rhodamine B functionalized gold nanoparticles. Dyes Pigment. 2019;171:7. https://doi.org/10.1016/j.dyepig.2019.107674
10. Teymoori N, Raoof JB, Khalilzadeh MA, Qjani R. An electrochemical sensor based on CuO nanoparticle for simultaneous determination of hydrazine and bisphenol A. J Iran Chem Soc. 2018;15:2271–9. https://doi.org/10.1007/s13738-018-1416-x
11. Gupta VK, Khalilzadeh MA, Rudbaraki A, Agarwal S, Yola ML, Atar N. Fabrication of highly sensitive nitrite electrochemical sensor in foodstuff using nanostructure sensor. Int J Electrochem Sci. 2017;12:3931–40. https://doi.org/10.20964/2017.05.72
12. Kannan P, Maiyalagan T, Marsili E, Ghosh S, Niedziolka-Jonsson J, Jonsson-Niedziolka M. Hierarchical 3-dimensional nickel-iron nanosheet arrays on carbon fiber paper as a novel electrode for non-enzymatic glucose sensing. Nanoscale. 2016;8:843–55. https://doi.org/10.1039/C5NR06802A
13. Raoof JB, Teymoori N, Khalilzadeh MA. ZnO nanoparticle ionic liquids carbon paste electrode as a voltammetric sensor for determination of Sudan III in the presence of vitamin B-6 in food samples. Food Anal Meth. 2015;8:885–92. https://doi.org/10.1007/s12161-014-9962-z
14. Nascimento CF, Santos PM, Pereira ER, Rocha FRP. Recent advances on determination of milk adulterants. Food Chem. 2017;221:1232–44. https://doi.org/10.1016/j.foodchem.2016.11.034

15. Bülbül G, Hayat A, Andreescu S. Portable nanoparticle-based sensors for food safety assessment. Sensors. 2015;15:30736–58. https://doi.org/10.3390/s151229826

16. Apak R, Çekić SD, Üzer A, Celik SE, Bener M, Bekdeşer B, et al. Novel spectroscopic and electrochemical sensors and nanoprobes for the characterization of food and biological antioxidants. Sensors. 2018;18(1):186. https://doi.org/10.3390/s18010186

17. Vinci G, Rapa M. Noble metal nanoparticles applications: Recent trends in food control. Bioengineering. 2019;6:10. https://doi.org/10.3390/bioengineering6010010

18. Galstyan V, Bhandari MP, Sberveglieri V, Sberveglieri G, Comini E. Metal oxide nanostructures in food applications: Quality control and packaging. Chemosensors. 2018;6(2):16. https://doi.org/10.3390/chemosensors6020016

19. Pan M, Yin ZJ, Liu KX, Du XL, Liu HL, Wang S. Carbon-based nanomaterials in sensors for food safety. Nanomaterials. 2019;9:23. https://doi.org/10.3390/nano9091330

20. López-Lorente AI, Valcárcel M. The third way in analytical nanoscience and nanotechnology: Involvement of nanotools and nananlytes in the same analytical process. TrAC Trends Anal Chem. 2016;75:1–9. https://doi.org/10.1016/j.trac.2015.06.011

21. Singh J, Vishwakarma K, Ramawat N, Rai P, Singh VK, Mishra RK, et al. Nanomaterials and microbes’ interactions: A contemporary overview. 3 Biotech. 2019;9:568. https://doi.org/10.1007/s13205-019-1576-0

22. Duan N, Wu S, Dai S, Gu H, Hao L, Ye H, Wang Z. Advances in aptasensors for the detection of food contaminants. Analyst. 2016;141(13):3942–61. https://doi.org/10.1039/C6AN00952B

23. Lim MC, Kim YR. Analytical Applications of nanomaterials in monitoring biological and chemical contaminants in food. J Microbiol Biotechnol. 2016;26:1505–16. https://doi.org/10.4014/jmjb.1605.05071

24. Manikandan VS, Adhikari B, Chen AC. Nanomaterial based electrochemical sensors for the safety and quality control of food and beverages. Analyst. 2018;143:4537–54. https://doi.org/10.1039/C8AN00497H

25. Yin W, Wu L, Ding F, Li Q, Wang P, Li J, et al. Surface-imprint-ed SiO@Ag nanoparticles for the selective detection of BPA using surface enhanced Raman scattering. Sens Actuators B Chem. 2018;258:566–73. https://doi.org/10.1016/j.snb.2017.11.141

26. Zhou H, Yang D, Mircescu NE, Ivleva NP, Schwarzeimer K, Wieser A, et al. Surface-enhanced Raman scattering detection of bacteria on microarrays at single cell levels using silver nanoparticles. Microchim Acta. 2015;182:2259–66. https://doi.org/10.1007/s00604-015-1570-0

27. Zeng Y, Wang L, Zeng L, Shen A, Hu J. A label-free SERS probe for highly sensitive detection of Hg based on functionalized Au@Ag nanoparticles. Talanta. 2017;162:374–9. https://doi.org/10.1016/j.talanta.2016.09.062

28. Shao B, Ma X, Zhao S, Lv Y, Hun X, Wang H, Wang Z. Nano-gapped Au@Ag core-shell nanoparticles coupled with FeO magnetic nanoparticles for the detection of ochratoxin A. Anal Chim Acta. 2018;1033:165–72. https://doi.org/10.1016/j.aca.2018.05.058

29. Zhu C, Wang XJ, Shi XF, Yang F, Meng GW, Xiong QH, et al. Detection of dithiocarbamate pesticides with a spongelike surface-enhanced Raman scattering substrate made of reduced graphene oxide-wrapped silver nanocubes. ACS Appl Mater Interfaces. 2017;9(45):39618–25. https://doi.org/10.1021/acsami.7b13479

30. Wang C, Gu B, Liu QQ, Pang YF, Xiao R, Wang SQ. Combined use of vancomycin-modified Ag-coated magnetic nanoparticles and secondary enhanced nanoparticles for rapid surface-enhanced Raman scattering detection of bacteria. Int J Nanomed. 2018;13:1159–78. https://doi.org/10.2147/IJN.S150336

31. Fu Q, Liu HWL, Wu Z, Liu A, Yao CZ, Li XQ, et al. Rough surface Au@Ag core-shell nanoparticles to fabricating high sensitivity SERS immunochromatographic sensors. J Nanobiotechnol. 2015;13:81. https://doi.org/10.1186/s12951-015-0142-0

32. Min K, Umar M, Seo H, Yim JH, Kam DG, Jeon H, et al. Bio-compatible, optically transparent, patterned, and flexible electrodes and radio-frequency antennas prepared from silk protein and silver nanowire networks. RSC Adv. 2017;7(1):574–80. https://doi.org/10.1039/C6RA25580A

33. Hasna K, Lakshmi K, Jayaraj MKE, Kumar KR, Matham MV. Development of high-sensitive, reproducible colloidal surface-enhanced Raman spectroscopy active substrate using silver nanocubes for potential biosensing applications. J Nanophotonics. 2016;10:9. https://doi.org/10.1117/1.JNP.10.026020

34. Zhang PP, Zhang NN, Jing LJ, Hu BB, Yang XD, Ma XL. Silver nanoparticles/carboxylic short-chain multi-wall carbon nanotubes as electrochemical sensor for ultrasensitive detection of chloramphenicol in food. Int J Electrochem Sci. 2019;14:9337–46. https://doi.org/10.2147/IJN.S150336

35. Huang H, Liu MH, Wang XS, Zhang WJ, Yang DP, Cui LH, Wang XS. Label-free 3D Ag nanoflower-based electrochemical immunosensor for the detection of Escherichia coli.}
obtained by green synthesis using pre-hydrolysed liquor. Electroanalysis. 2017;29:1434–42.
https://doi.org/10.1002/eila.201600775

46. Chaiendoo K, Tuntulani T, Ngeontae W. A highly selective colorimetric sensor for ferrous ion based on polymethylacrylic acid-templated silver nanoclusters. Sens Actuators B Chem. 2015;207:658–67.
https://doi.org/10.1016/j.snb.2014.10.062

47. Zhou N, Yang LY, Hu B, Song YP, He LH, Chen WZ, et al. Core-shell heterostructured CuFe2Fe Prussian blue analogue coupling with silver nanoclusters via a one-step bioinspired approach: Efficiently nonlabeled aptasensor for detection of bleomycin in various aqueous environments. Anal Chem. 2018;90(22):13624–31.
https://doi.org/10.1021/acs.analchem.8b03850

48. Ivanisević I, Rukavina V, Kassal P, Milardović S. Impact of weak organic acids on precipitation of poly(acrylic acid) stabilized silver nanoparticles; an electrochemical approach. Croat Chem Acta. 2018;91(4):491–9.
https://doi.org/10.5562/ccia445

49. Ivanisević I, Milardović S, Kassal P, Zlatar M. Electrochemical and spectroscopic characterization of AgNP suspension stability influenced by strong inorganic acids. Electrochim Acta. 2021;377:138126.
https://doi.org/10.1016/j.electacta.2021.138126

50. Thèvenot DR, Toth K, Durst RA, Wilson GS. Electrochemical biosensors: Recommended definitions and classification. Biosens Bioelectron. 2001;16:121–31.
https://doi.org/10.1016/S0956-5663(01)00115-4

51. Hulanicki A, Glab S, Ingman F. Chemical sensors definitions and classification. Pure Appl Chem. 1991;63:1247–50.
https://doi.org/10.1351/pac199163091247

52. Hanko M, Svorc L, Plankova A, Mikus P. Overview and recent advances in electrochemical sensing of glutathione – A review. Anal Chim Acta. 2019;1062:1–27.
https://doi.org/10.1016/j.talanta.2019.02.052

53. Ghaani M, Nasirizadeh N, Ardakani SAY, Mehrjardi FZ, Scampicchio M, Farris S. Development of an electrochemical approach. Croat Chem Acta. 2018;91(4):491–9.
https://doi.org/10.1021/acs.analchem.8b03850

54. Rotariu L, Lagarde F, Jaffrezic-Renault N, Bala C. Electrochemical biosensors for fast detection of food contaminants trends and perspective. TrAC Trends Anal Chem. 2016;79:80–70.
https://doi.org/10.1016/j.trac.2015.12.017

55. Wan Y, Zheng YF, Wan HT, Yin HY, Song XC. A novel electrochemical sensor based on Ag nanoparticles decorated multi-walled carbon nanotubes for applied determination of nitrite. Food Control. 2017;73:1507–13.
https://doi.org/10.1016/j.foodcont.2016.11.014
56. Daği K, Alanyalioglu M. Preparation of free-standing and flexible graphene/Ag nanoparticles/poly(pyronin Y) hybrid paper electrode for amperometric determination of nitrite. ACS Appl Mater Interfaces. 2016;8:2713–22. https://doi.org/10.1021/acsami.5b10973

57. Kabir MF, Rahman MT, Gurung A, Qiao QQ. Electrochemical phosphate sensors using silver nanowires treated screen printed electrodes. IEEE Sens J. 2018;18:3480–5. https://doi.org/10.1109/JSEN.2018.2808163

58. Song DD, Wang YZ, Lu X, Gao YK, Li Y, Gao FM. Ag nanoparticles-decorated nitrogen-fluorine co-doped monolayer MoS2 nanosheet for highly sensitive electrochemical sensing of organophosphorus pesticides. Sens Actuators B Chem. 2018;267:5–13. https://doi.org/10.1016/j.snb.2018.04.016

59. Khesuoe MP, Okumu FO, Matooteo MC. Development of a silver functionalised polyaniline electrochemical immunosensor for polychlorinated dibiphenyls. Anal Methods. 2016;8:7087–95. https://doi.org/10.1039/C6AY01733A

60. de Lima CA, Santana ER, Piovesan JV, Spinelli A. Silver nanoparticle-modified electrode for the determination of nitro compound-containing pesticides. Anal Bioanal Chem. 2016;408:2595–606. https://doi.org/10.1007/s00216-016-9367-5

61. Kumaravel A, Murugananthan M, Mangalam R, Jayakumar S. A novel, biocompatible and electrocatalytic stearic acid/nanosilver modified glassy carbon electrode for the sensing of paraaxon pesticide in food samples and commercial formulations. Food Chem. 2020;323:126814. https://doi.org/10.1016/j.foodchem.2020.126814

62. Govindasamy M, Mani V, Chen SM, Chen TW, Sundramoorthy AK. Methyl parathion detection in vegetables and fruits using silver/graphene nanoribbons nanocomposite modified screen printed electrode. Sci Rep. 2017;7:46471. https://doi.org/10.1038/srep46471

63. Li JH, Feng HB, Li J, Jiang JB, Feng YL, He LZ, Qian D. Bimetallic Ag-Pd nanoparticles-decorated graphene oxide: A fascinating three-dimensional nanohybrid as an efficient electrochemical sensing platform for vanillin determination. Electrochim Acta. 2015;176:827–35. https://doi.org/10.1016/j.electacta.2015.07.091

64. Pani A, Thanh TD, Kim NH, Lee JH, Yun SI. Peanut skin extract mediated synthesis of gold nanoparticles, silver nanoparticles and gold silver bionanocomposites for electrochemical Sudan IV sensing. IET Nanobiotechnol. 2016;10: 431–7. https://doi.org/10.1049/iet-nbt.2016.0017

65. Yao YZ, Liu YC, Yang ZS. Highly sensitive electrochemical sensor for the food toxicant Sudan I based on a glassy carbon electrode modified with reduced graphene oxide decorated with Ag-Cu nanoparticles. Microchim Acta. 2016;183:3275–83. https://doi.org/10.1007/s00604-016-1977-2

66. Shah A, Malik MS, Zahid A, Iftikhar FJ, Anwar A, Akhter MS, et al. Carbamazepine coated silver nanoparticles for the simultaneous electrochemical sensing of specific food toxins. Electrochim Acta. 2018;274:131–42. https://doi.org/10.1016/j.electacta.2018.04.096

67. Pogacean F, Rosu MC, Coros M, Mageruslan M, Moldovan M, Saroiu C, et al. Graphene/TiO2-Ag based composites used as sensitive electrode materials for amaranth electrochemical detection and degradation. J Electrochem Soc. 2018;165(8):B3054–9. https://doi.org/10.1149/2.0101808jes

68. Qin CC, Guo WL, Liu Y, Liu ZC, Qiu J, Peng JB. A novel electrochemical sensor based on graphene oxide decorated with silver nanoparticles–molecular imprinted polymers for determination of sunset yellow in soft drinks. Food Anal Meth. 2017;10:2293–301. https://doi.org/10.1007/s12161-016-0753-6

69. Abbaspour A, Norouz-Sarvestani F, Noon A, Soltani N. Aptamer-conjugated silver nanoparticles for electrochemical dual-aptamer-based sandwich detection of staphylococcus aureus. Biosens Bioelectron. 2015;68:149–55. https://doi.org/10.1016/j.bios.2014.12.040

70. Veerapandian M, Neethirajan S. Graphene oxide chemically-ly decorated with Ag-Ru/chitosan nanoparticles: Fabrication, electrode processing and immunosensing properties. RSC Adv. 2015;5:75015–24. https://doi.org/10.1039/C5RA15329H

71. Khalilzadeh MA, Borzoo M. Green synthesis of silver nanoparticles using onion extract and their application for the preparation of a modified electrode for determination of ascorbic acid. J Food Drug Anal. 2016;24:796–803. https://doi.org/10.1016/j.jfda.2016.05.004

72. Gheiibi S, Gharibi G, Khalilzadeh MA, Pourfarzad A. Electrochemical analysis of ascorbic acid in food and drug samples using a biosynthesized Ag nanoparticle as a mediator in carbon paste matrix. Anal Bioanal Electrochem. 2017;9:365–73.

73. Jadav JK, Umrania VV, Rathod KJ, Golakiya BA. Development of silver/carbon screen-printed electrode for rapid determination of vitamin C from fruit juices. LWT – Food Sci Technol. 2018;88:152–8. https://doi.org/10.1016/j.lwt.2017.10.005

74. Zare HR, Jahangiri-Dehaghi F, Shekari Z, Benvidi A. Electro-catalytic simultaneous determination of ascorbic acid, uric acid and l-cysteine in real samples using quercetin silver nanoparticles-graphene nanosheets modified glassy carbon electrode. Appl Surf Sci. 2016;375:169–78. https://doi.org/10.1016/j.apsusc.2016.03.098

75. Yusoff N, Rameshkumar P, Mehmood MS, Pandikumar A, Lee HW, Huang NM. Ternary nanohybrid of reduced graphene oxide-nafion@silver nanoparticles for boosting the sensor performance in non-enzymatic amperometric detection of paraoxon pesticide in food samples and commercial formulations. Food Chem. 2020;323:126814. https://doi.org/10.1016/j.foodchem.2020.126814
detection of hydrogen peroxide. Biosens Bioelectron. 2017; 87:1020–8. https://doi.org/10.1016/j.bios.2016.09.045

76. Guler M, Turkoglu V, Bulut A, Zahmakiran M. Electrochemical sensing of hydrogen peroxide using Pd@Ag bimetallic nanoparticles decorated functionalized reduced graphene oxide. Electrochim Acta. 2018;263:118–26. https://doi.org/10.1016/j.electacta.2018.01.048

77. Erdogan ZO, Akin I, Kucukkolbasi S. A new non-enzymatic sensor based on TiO2:Ag-polypyrrole for electrochemical detection of tyramine. Synth Met. 2018;246:96–100. https://doi.org/10.1016/j.synthmet.2018.10.006

78. Kumar THV, Sundaramoorthy AK. Non-enzymatic electrochemical detection of urea on silver nanoparticles anchored nitrogen-doped single-walled carbon nanotube modified electrode. J Electrochem Soc. 2018;165(8):B3006–16. https://doi.org/10.1149/2.0021808jes

79. Butwong N, Khajonklin J, Thongbor A, Luong JHT. Electrochemical sensing of histamine using a glassy carbon electrode modified with multilayered carbon nanotubes decorated with Ag–Ag2O nanoparticles. Microchim Acta. 2019; 186:714. https://doi.org/10.1007/s00604-019-3860-4

80. Yola ML, Gupta VK, Atar N. New molecular imprinted voltammetric sensor for determination of ochratoxin A. Mater Sci Eng C Mater Biol Appl. 2016;61:368–75. https://doi.org/10.1016/j.msec.2015.12.057

81. Zhao CL, Hu R, Liu TZ, Liu Y, Bai RY, Zhang KL, Yang YH. A non-enzymatic electrochemical immunosensor for microcystin-LR rapid detection based on Ag@MSN nanoparticles. Colloid Surf A Physicochem Eng Asp. 2016;490:336–42. https://doi.org/10.1016/j.colsurfa.2015.11.051

82. Jiang D, Du XJ, Liu Q, Zhou L, Dai LM, Qian J, Wang K. Silver nanoparticles anchored on nitrogen-doped graphene as a novel electrochemical biosensing platform with enhanced sensitivity for aptamer-based pesticide assay. Analyst. 2015;140(18):6404–11. https://doi.org/10.1039/C5AN01084E

83. Rosati G, Ravarotto M, Scaramuzza M, De Toni A, Paccagnella A. Silver nanoparticles inkjet-printed flexible biosensor for rapid label-free antibiotic detection in milk. Sens Actuators B Chem. 2019;280:280–9. https://doi.org/10.1016/j.snb.2018.09.084

84. Wang R, Xu Y, Sors T, Irudayaraj J, Ren W, Wang R. Impedimetric detection of bacteria by using a microfluidic chip and silver nanoparticle based signal enhancement. Microchim Acta. 2018;185:184. https://doi.org/10.1007/s00604-017-2645-x

85. Feng Y, Zhou D, Gao LJ, He FJ. Electrochemical biosensor for rapid detection of bacteria based on facile synthesis of silver wire across electrodes. Biosens Bioelectron. 2020; 168:112527. https://doi.org/10.1016/j.bios.2020.112527

86. Li Y, Wang ZX, Sun L, Liu LQ, Xu CL, Kuang H. Nanoparticle-based sensors for food contaminants. TrAC Trends Anal Chem. 2019;113:74–83. https://doi.org/10.1016/j.trac.2019.01.012

87. Zhao H, Hasi WLJ, Li N, Sha XY, Lin S, Han S. In situ analysis of pesticide residues on the surface of agricultural products via surface–enhanced Raman spectroscopy using a flexible Au@Ag-PDMS substrate. New J Chem. 2019;43: 13075–82. https://doi.org/10.1039/C9NJ01901D

88. Yang T, Huang HF, Zhu F, Lin QL, Zhang L, Liu JW. Recent progresses in nanobiosensing for food safety analysis. Sensors. 2016;16:19. https://doi.org/10.3390/s16071118

89. Paul IE, Kumar DN, Rajeshwari A, Alex SA, Karthiga D, Rai-chur AM, et al. Detection of food contaminants by gold and silver nanoparticles. In: Grumezescu AM, editor. Nanobiosensors. London, UK: Academic Press Elsevier Science Ltd; 2017. pp. 129–65. https://doi.org/10.1016/B978-0-12-804301-0.00004-7

90. Patrizi B, de Cumis MS, Viciani S, D’Amato F. Dioxin and related compound detection: Perspectives for optical monitoring. Int J Mol Sci. 2019;20:19. https://doi.org/10.3390/ijms2012671

91. Mikkelsen O, Schroder KH. Amalgam electrodes for electroanalysis. Electroanalysis. 2003;15:679–87. https://doi.org/10.1002/elan.200390085

92. Mog SR, Zang YJ. Safety assessment of food additives: Case example with myrcene, a synthetic flavoring agent. Toxicol Pathol. 2019;47:1035–37. https://doi.org/10.1177/019263319879634

93. Khalilzadeh MA, Arab Z. High sensitive nanostructure square wave voltammetric sensor for determination of vanillin in food samples. Curr Anal Chem. 2017;13:81–6. https://doi.org/10.2174/1573411012666160805145331

94. Zhang X, Zhang J, Li W, Yang Y, Qin P, Zhang X, Lu M. Magnetic graphene oxide nanocomposites as the adsorbent for extraction and pre-concentration of azo dyes in different food samples followed by high-performance liquid chromatography analysis. Food Addit Contam Part A Chem. 2018;35(11):2099–110. https://doi.org/10.1080/19440049.2018.1526415

95. Nasirizadeh N, Shekari Z, Dehghani M, Makarem S. Delphinidin immobilized on silver nanoparticles for the simultaneous determination of ascorbic acid, noradrenaline, uric acid, and tryptophan. J Food Drug Anal. 2016;24:406–16. https://doi.org/10.1016/j.jfda.2015.11.011

96. Gérard V, Ay E, Graff B, Morlet-Savary F, Galopin C, Mutliangwi W, Lalevée J. Ascorbic acid derivatives as potential substitutes for ascorbic acid to reduce color degradation of drinks containing ascorbic acid and anthocyanins from natural extracts. J Agric Food Chem. 2019;67(43):12061–71. https://doi.org/10.1021/acs.jafc.9b05049
117. Chaiyo S, Siangproh W, Apilux A, Chailapakul O. Highly selective and sensitive paper-based colorimetric sensor using thiosulfate catalytic etching of silver nanoparticles for trace determination of copper ions. Anal Chim Acta. 2015; 866:75–83. https://doi.org/10.1016/j.aca.2015.01.042.

118. Patel GM, Rohit JV, Singhal RK, Kailasa SK. Recognition of carbendazim fungicide in environmental samples by using 4-aminobenzenethiol functionalized silver nanoparticles as a colorimetric sensor. Sens Actuators B Chem. 2015;206:684–91. https://doi.org/10.1016/j.snb.2014.09.095.

119. Bhamore JR, Ganguly P, Kailasa SK. Molecular assembly of 3-mercaptopyrrolionic acid and guanidine acetic acid on silver nanoparticles for selective colorimetric detection of triazophos in water and food samples. Sens Actuators B Chem. 2016;233:486–95. https://doi.org/10.1016/j.snb.2016.04.111.

120. Zheng M, Wang Y, Wang C, Wei W, Ma S, Sun XH, He J. Silver nanoparticles-based colorimetric array for the detection of thiophanate-methyl. Spectrochim Acta A Mol Biomol Spectrosc. 2018;198:315–21. https://doi.org/10.1016/j.saa.2018.03.038.

121. Shrivas K, Sahu S, Sahu B, Kurrey R, Patle TK, Kant T, et al. Silver nanoparticles for selective detection of phosphorus pesticide containing N-conjugated pyrimidine nitrogen and sulfur moieties through non-covalent interactions. J Mol Liq. 2019;275:297–303. https://doi.org/10.1016/j.molliq.2018.11.071.

122. Bala R, Mittal S, Sharma RK, Wangoo N. A supersensitive silver nanoprobe based aptasensor for low cost detection of malathion residues in water and food samples. Spectrochim Acta A Mol Biomol Spectrosc. 2018;196:268–73. https://doi.org/10.1016/j.saa.2018.02.007.

123. Lv BJ, Wei M, Liu YJ, Liu X, Wei W, Liu SQ. Ultrasensitive photometric and visual determination of organophosphorus pesticides based on the inhibition of enzyme-triggered formation of core-shell gold-silver nanoparticles. Microchim Acta. 2016;183:2941–8. https://doi.org/10.1007/s00604-016-1939-8.

124. Chen QG, Lin TR, Huang JL, Chen Y, Guo LQ, Fu FF. Colorimetric detection of residual hydrogen peroxide in soaked food based on Au@Ag nanorods. Anal Methods. 2018;10:504–7. https://doi.org/10.1039/C7AY02819A.

125. Liu Y, Wang J, Song X, Xu K, Chen H, Zhao C, Li J. Colorimetric immunoassay for Listeria monocytogenes by using core gold nanoparticles, silver nanoclusters as oxidase mimetics, and aptamer-conjugated magnetic nanoparticles. Microchim Acta. 2018;185:360. https://doi.org/10.1007/s00604-018-2896-1.

126. Wang C, Tan R, Chen D. Fluorescence method for quickly detecting ochratoxin A in flour and beer using nitrogen doped carbon dots and silver nanoparticles. Talanta. 2018;182:363–70. https://doi.org/10.1016/j.talanta.2018.02.007.

127. Zhang J, Xia YK, Chen M, Wu DZ, Cai SX, Liu MM, et al. A fluorescent aptasensor based on DNA-scaffolded silver nanoclusters coupling with Zn(II)-ion signal-enhancement for simultaneous detection of OTA and AFB1. Sens Actuators B Chem. 2016;235:79–85. https://doi.org/10.1016/j.snb.2016.05.061.

128. Zhang M, Wang Y, Yuan S, Sun X, Huo BY, Bai JL, et al. Competitive fluorometric assay for the food toxin T-2 by using DNA-modified silver nanoclusters, aptamer-modified magnetic beads, and exponential isothermal amplification. Microchim Acta. 2019;186:219. https://doi.org/10.1007/s00604-019-3322-z.

129. Khan IM, Zhao S, Niazi S, Mohsin A, Shaob M, Duan N, et al. Silver nanoclusters based FRET aptasensor for sensitive and selective fluorescent detection of T-2 toxin. Sens Actuators B Chem. 2018;277:328–35. https://doi.org/10.1016/j.snb.2018.09.021.

130. Sheini A. Colorimetric aggregation assay based on array of gold and silver nanoparticles for simultaneous analysis of aflatoxins, ochratoxin and zearalenone by using chemometric analysis and paper based analytical devices. Microchim Acta. 2020;187:167. https://doi.org/10.1007/s00604-020-4147-5.

131. Zheng LB, Qi P, Zhang D. DNA-templated fluorescent silver nanoclusters for sensitive detection of pathogenic bacteria based on MNP-DNAzyme-ACHe complex. Sens Actuators B Chem. 2018;276:42–7. https://doi.org/10.1016/j.snb.2018.08.078.

132. Zhang P, Liu H, Li XC, Ma SZ, Men S, Wei H, et al. A label-free fluorescent direct detection of live Salmonella typhimurium using cascade triple trigger sequences-regenerated strand displacement amplification and hairpin template-generated-scaffolded silver nanoclusters. Biosens Bioelectron. 2017;87:1044–9. https://doi.org/10.1016/j.bios.2016.09.037.

133. Ellairaja S, Kirthiga N, Ponmariappan S, Vasantha VS. Novel pyrimidine tagged silver nanoparticle based fluorescent immunoassay for the detection of Pseudomonas aeruginosa. J Agric Food Chem. 2017;65:1802–12. https://doi.org/10.1021/acs.jafc.6b04790.

134. Luo QJ, Li YX, Zhang MQ, Qiu P, Deng YH. A highly sensitive, dual-signal assay based on rhodamine B covered silver nanoparticles for carbamate pesticides. Chin Chem Lett. 2017;28:345–9. https://doi.org/10.1016/j.cclet.2016.10.024.

135. Kumar DN, Alex SA, Kumar RSS, Chandrasekaran N, Mukherjee A. Acetylcholinesterase inhibition-based ultrasensitive fluorescent detection of malathion using unmodified...
silver nanoparticles. Colloid Surf A Physicochem Eng Asp. 2015;485:111–7.
https://doi.org/10.1016/j.colsurfa.2015.09.013

136. Ye T, Peng Y, Yuan M, Cao H, Yu JS, Li Y, Xu F. A “turn-on” fluorometric assay for kanamycin detection by using silver nanoclusters and surface plasmon enhanced energy transfer. Microchim Acta. 2019;186:40.
https://doi.org/10.1007/s00604-018-3161-3

137. Pourreza N, Ghomi M. In situ synthesized and embedded silver nanoclusters into poly vinyl alcohol-borax hydrogel as a novel dual mode “on and off” fluorescence sensor for Fe(III) and thiosulfate. Talanta. 2018;179:92–9.
https://doi.org/10.1016/j.talanta.2017.10.035

138. Du QQ, Qu F, Mao BB, Zhu SY, You JM. Turn-on fluorescent detection of melamine based on Ag nanoclusters-Hg²⁺ system. New J Chem. 2016;40:8459–64.
https://doi.org/10.1039/C6NJ01338D

139. Chen C, Yuan ZQ, Chang HT, Lu FN, Li ZH, Lu C. Silver nanoclusters as fluorescent nanosensors for selective and sensitive nitrite detection. Anal Methods. 2016;8:2628–33.
https://doi.org/10.1039/C6AY00214E

140. Zheng LB, Qi P, Zhang D. A simple, rapid and cost-effective colorimetric assay based on the 4-mercaptophenylboronic acid functionalized silver nanoparticles for bacteria monitoring. Sens Actuators B Chem. 2018;260:983–9.
https://doi.org/10.1016/j.snb.2018.01.115

141. Kassal P, Horak E, Sigurnjak M, Steinberg MD, Steinberg IM. Wireless and mobile optical chemical sensors and biosensors. Rev Anal Chem. 2018;37:27.
https://doi.org/10.1515/revac-2017-0024

142. Ivanišević I, Kassal P, Milinković A, Rogina A, Milardović S. Combined chemical and thermal sintering for high conductivity inkjet-printed silver nanoink on flexible substrates. Chem Biochem Eng Q. 2019;33:377–84.
https://doi.org/10.15255/CABEQ.2019.1585

143. Kassal P, Steinberg MD, Steinberg IM. Wireless chemical sensors and biosensors: A review. Sens Actuators B Chem. 2018;266:228–45.
https://doi.org/10.1016/j.snb.2018.03.074