# Chapter 27
# Specific Applications of II–VI Semiconductor Nanomaterials-Based Biosensors for Food Analysis and Food Safety

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## 27.1 Introduction

Food quality and safety issue is the most important challenge in food processing industry. For instance, the regular occurrence of bacterial contamination in food supplies is a growing concern as it has recently led to multiple deaths in the USA and Europe. Rapid and noninvasive means of detecting bacterial contamination in food products are therefore highly desirable for monitoring the safety of the food supply at a reasonable cost [3, 12, 32, 83]. However, pathogenic bacterial are made of the same major constituents including amides, proteins, nucleic acids, polysaccharides, and phospholipids which complicates a highly selective identification

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between different strains based on simple chemical analysis [39]. Although much time and effort are spent on methods for this, more efficient sensing platforms are of great importance and urgency.

Traditional biosensors are widely used for this purpose as reported in the bibliography. The development of biosensors is an emergent area, in response to the demand for simple, reliable, and low-cost techniques against food residues [22]. However, major problems like low sensitivity, lack of practicality, and time-consuming response have limited their wide application in food hazard analysis. II–VI semiconducting nanomaterials, possessed different morphologies, semiconductors, and characterisation technologies, mainly included zinc oxide (ZnO) [68, 69, 73, 80, 82, 86], zinc sulphide (ZnS) [37, 44, 67, 75, 76, 87], cadmium sulphide (CdS) [59, 60, 62, 70, 71, 85], cadmium selenide (CdSe) [18, 29, 30, 48, 53, 59, 60], cadmium teluride (CdTe) [40, 46, 52, 54, 66, 75, 79], etc. They are attracting more and more attention from scientists for biosensor applications due to their advanced optical, catalytic, sensing and electrochemical properties [41, 55–57, 65, 70–72, 77].

These nanomaterials offered a large surface area for biomolecules recognition elements like antibody [19, 24], and nucleic acid aptamer [28, 42, 43, 55, 56, 84] to specific interaction with target analytes, and the improved sensitivity of biosensors was achieved. Compared to traditional biosensors, nanomaterials integrated biosensors have significant superiorities, including high sensitivity, rapid response, enhanced practicality and facile devices. The current research highlighted an increasing implementation of nanomaterials in biosensor development for both molecule recognition and signal transduction [1, 2, 7, 10, 47, 58]. Pathogens and food toxins are detected by optics coated with antibodies. Water-soluble vitamins, drug residues, or other small molecules can be detected and measured through a variety of immuno- and ligand-binding assays embedded on II–IV-based sensor systems. These sensors are widely used across the food industry. Nanosensors can advance the food sector by improving food processing, packaging, and quality monitoring [8]. More importantly, the advantages of nanobiosensors can lead to their use in the whole food industry: from raw material preparation, food processing (quality control), monitoring of storage conditions and use of these devices as cost-effective tools for quality and process controls as well as to ensure food safety.

This book chapter will provide a new view to the readers that II–VI semiconducting nanomaterials have been widely utilised by sensor construction for food analysis and food safety field (Fig. 27.1), and highlight the recent advances and future prospects. First of all, we introduce the characteristics and classification of II–VI semiconducting nanomaterials. Then a brief introduction of the application of II–VI semiconducting nanomaterials-based sensing platform for food quality and safety control was discussed. In addition, we comprehensively analyse and summarise the practical application of these nanomaterials in certain food samples.

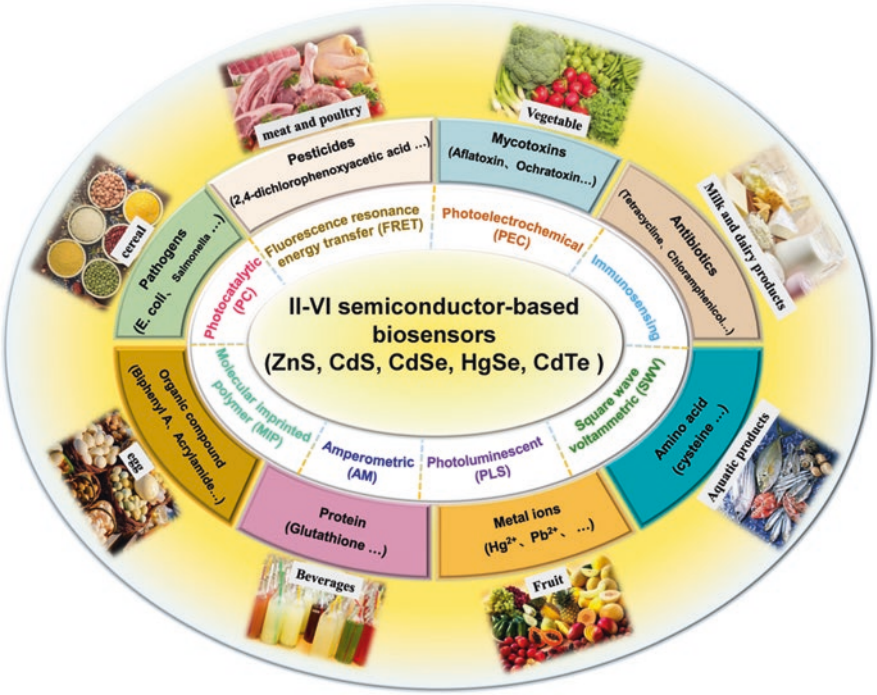


**Fig. 27.1** Scheme illustration of II–VI semiconducting nanomaterials-based biosensors for food analysis and food safety

## 27.2 II–VI Semiconducting Nanomaterials for Food Analysis

### *27.2.1 Detection of Pathogenic Bacteria*

Due to the growing concern of the risk that food- and water-borne pathogens pose to human health, there is an increasing demand from regulatory agencies to ensure a safe food supply. As shown in Fig. 27.2, II–VI semiconducting nanomaterials-based biosensing strategies for pathogens were illustrated. Xiong et al. reported the biosynthesis of CdSe QDs intracellularly and employed them as nanoprobes for the detection of bacteria (Fig. 27.2a). The bacteria detection involves a space-time-coupling strategy for converting the bacteria (*Staphylococcus aureus*) into fluorescent cells (cellular beacons) [61]. Typically, a low detection limit of 8.94 ng/mL was reported. The proposed scheme has many advantages like fluorescent probes being monodispersed with uniform size, high luminance with outstanding photostability. Also, the probes are highly accurate, reliable, and repeatable. By the suitable selection of the antibody conjugation, this kind of new bioprobe can be extended towards the sensitive detection of various other bacterial pathogens including pseudorabies virus, baculovirus, *Salmonella typhimurium*, and SKBR-3 cells [38]. CdSe was also

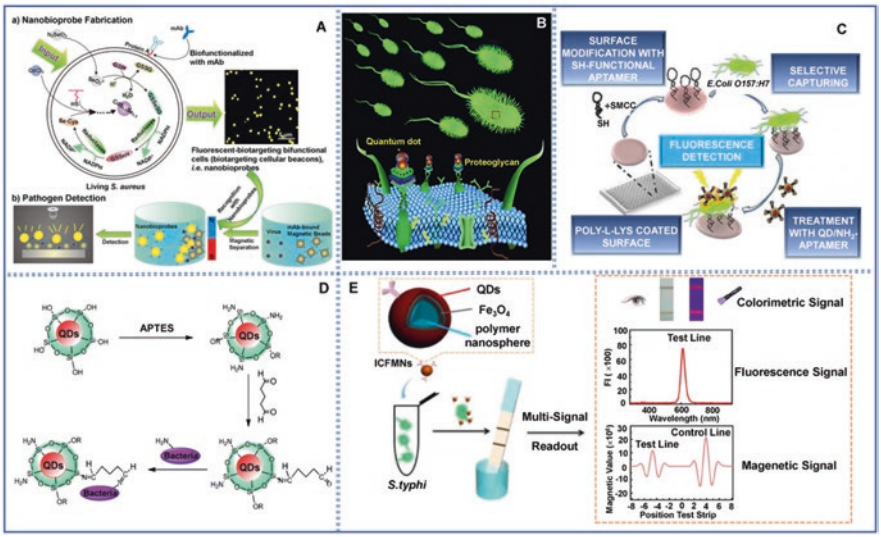


**Fig. 27.2** (**a**) Schematic representation of nanobioprobes fabrication for pathogen detection based on fluorescent CdSe QDs. (Reprinted with permission from Ref. [61]. Copyright 2014 American Chemical Society). (**b**) Schematic illustration of fluorescent detection of pathogenic bacteria *Vibrio harveyi* based on CdSe/ZnS QDs. (Reprinted with permission from Ref. [5]. Copyright 2016 Royal Society of Chemistry). (**c**) Schematic illustration of optical analysis of *E. coli* O157:H7 employing CdSe/ZnS QDs coupled with $NH_2$-aptamer. (Reprinted with permission from Ref. [11]. Copyright 2015: Taylor & Francis). (**d**) Schematic illustration of fluorescent sensing of *Salmonella typhi* based on the preparation and conjugation of CdSe/ZnS QDs. (Reprinted with permission from Ref. [51]. Copyright 2014: Royal Society of Chemistry). (**e**) Schematic representation of CdSe/ZnS QDs-based multimodal sensing of *S. typhi* in lateral flow immunoassay (LFIA). (Reprinted with permission from Ref. [14]. Copyright 2018: American Chemical Society)

employed for multi-QDs detection. For instance, Arshad et al. reported the use of CdSe/ZnS QDs for the detection of *Vibrio harveyi* in solution and in animal cells [5]. Techniques such as fluorescence microscopy, elastase assay, polyacrylamide gel electrophoresis (PAGE), and comet assay are used to evaluate the interactions of QDs with *V. harveyi*. The appearance of bright yellow fluorescence when different concentrations of QDs were applied confirms the perfect attachment of the QDs to the bacteria (Fig. 27.2b). It was also demonstrated that the toxicity level of CdSe/ZnS QDs is genetically and cytotoxically safe for labelling the bacteria allowing live imaging and tracking of the microorganisms.

*Escherichia coli*, a common pathogenic bacterium, is one of the main reason for food-borne diseases. Toxins can occur by *E. coli* strains and further affect human health. The development of high efficient method for detection of *E. coli* is of great importance. In a novel research, the stability of the sensors was significantly enhanced by using oligonucleotide microarray combined with CdSe/ZnS QDs as fluorescent labels. The bacterium was identified with PerkinElmer Gx microarray scanner displaying a sensitivity of 10 CFU $mL^{-1}$. Fluorescence detection of *E. Coli 0157: H7*bacteria was obtained by using CdSe/ZnS QDs with carboxylic functional

groups [11]. The 72-mer aptamer is used as the probe and sensing element where detection limit of $10^2$ CFU $mL^{-1}$ could be achieved (Fig. 27.2c). In addition, ZnO is an advanced nanomaterial, which is widely used for biosensors construction due to its unique optical and electrochemical characteristics. Azmy et al. introduced a ZnO coupled with reduce graphene oxides (ZnO-rGO) nanocomposite for high sensitive detection of *E. coli* [6]. More importantly, gamma radiation was applied to evaluate the analytic performance of the sensing strategy. Result demonstrated that the structure and morphology of the ZnO-rGO nanocomposite were improved by gamma radiation. Notably, the defects on the surface of ZnO allowed its adsorption towards various biomolecules.

Food-borne pathogens, commonly presented in food products, have a hazard impact on human health. Typically, of them, *Salmonella* is one of the most important food-borne pathogens. It was worth noting that the occurrence and mortality rate of *Salmonella* infection were obviously serious in numerous developing countries because of weak medical conditions. Taking the *Salmonella* infection risks into consideration, the rapid and sensitive detection methods are essential for *Salmonella* monitoring in food. Wang et al. first introduced a fluorescent sensing of *Salmonella typhimurium* based on CdSe/ZnS QDs (Fig. 27.2d). Notably, the $SiO_2$ spheres were embedded on CdSe/ZnS QDs for enhanced fluorescent signal [51]. The detection limit was calculated to be $3.3 \times 10^2$ CFU $mL^{-1}$. Based on similar mechanisms, the CdSe/ZnS QDs were synthesised and employed for multimodal sensing of *S. typhi* in lateral flow immunoassay (LFIA). In this study, colorimetric-fluorescent-magnetic multimodal signals were achieved by utilising the nanospheres for analyte separation and enrichment (Fig. 27.2e). The proposed sensing platform allowed ten-fold sensitivity improvement [14]. In particular, the colorimetric signal has exhibited a LOD of $1.88 \times 10^4$ CFU $mL^{-1}$, and that of $3.75 \times 10^3$ CFU $mL^{-1}$ was realised in magnetic signal. It was demonstrated that two to four orders of magnitude enhancement were detected over the conventional LFIAs. In addition, the multimodal sensing strategy was validated by successful application for *S. typhi* monitoring in milk analysis. In addition, Viter et al. reported the ZnO nanorods-based photoluminescence sensing of *Salmonella* for food pathogens. The Anti-*Salmonella* antibody was employed to interact with *Salmonella* as a result the surface charge changed. The achieved sensing performance was attributed to the photoluminescence signal quenching under the presence of *Salmonella* [50].

### *27.2.2 Detection of Pesticides*

In view of the great toxicity and hazards in food and agricultural product safety, it is urgent and essential to develop advanced nanomaterials for the degradation and removal of pesticides (Fig. 27.3). Inspired by this consideration, an example of biosensing based on the use of QDs/OPH bioconjugate for paraoxon detection has been first reported by Ji et al. The CdSe/ZnS core-shell QDs were modified with OPH using electrostatic interactions between negatively charged QDs surfaces and

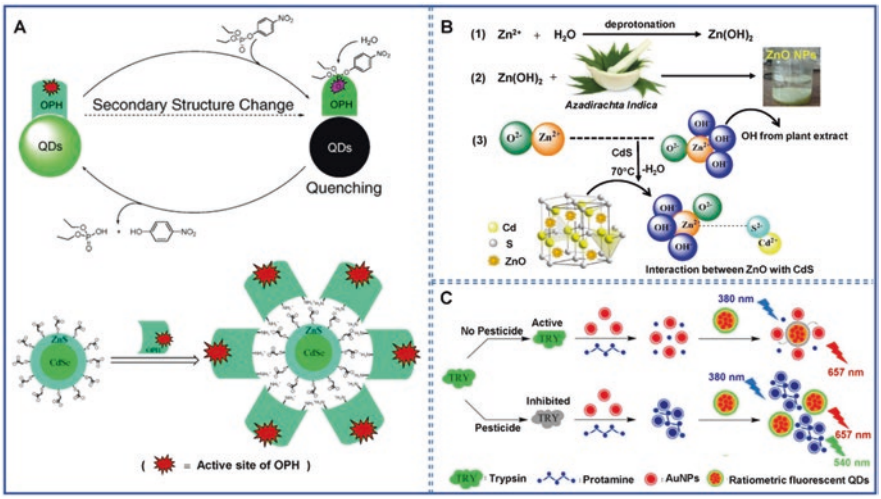


**Fig. 27.3** (**a**) Schematic illustration of photoluminescence sensing of paraoxon based on CdSe/ZnS QDs. (Reprinted with permission from Ref. [17]. Copyright 2005: American Chemical Society). (**b**) Schematic diagram of photodegradation of pesticides using ZnO@CdS nanoparticles. (Reprinted with permission from Ref. [36]. Copyright 2021: Elsevier). (**c**) Schematic illustration of optical sensor for detection of parathion-methyl (PM) based on two colored CdTe QDs. (Reprinted with permission from Ref. [64]. Copyright 2015: Elsevier)

the positively charged protein side chain and ending groups ($NH_2$). Photoluminescence (PL) intensity of the OPH/QDs bioconjugate was quenched in the presence of paraoxon (Fig. 27.3a). It was observed that the PL intensity of the OPH/QDs bioconjugate to different concentrations of paraoxon exhibited a decrease as the paraoxon concentration increased [17].

Furthermore, Vinayaka et al. [49] have developed a biosensor based on competitive fluoroimmunoassay for the analysis of the 2,4-dichlorophenoxyacetic acid using CdTe QD. This herbicide can cause human health problems even at low levels, hereby is very important to carry out a detection and quantification for applications in food analysis. The developed fluoroimmunoassay used an immunoreactor column which has been packed by immobilising anti-2,4-dichlorophenoxyacetic (2,4-D) antibodies; by this way it was possible to detect 2,4-D up to 250 pg $mL^{-1}$ in 50 mM phosphate buffer solution (pH 7.4).

Very recently, a novel and sustainable zinc oxide coupled with cadmium sulphide nanocomposite (ZnO@CdS) were prepared with the characteristic of green synthesis by plant leaf and high enriched product [36]. The photocatalytic activity of synthesized ZnO@CdS nanocomposite was highly enhanced compared to ZnO and CdS (Fig. 27.3b). In addition, the ZnO@CdS nanocomposite displayed optimised surface area (111 $m^2g^{-1}$), and reduced band energy (1.67 eV), resulting in great degradation efficiency towards pesticide residues in the range of 89–91%. In addition, two coloured CdTe QDs were synthesized and utilised in the fluorescent sensor for detection of parathion-methyl (PM). The red emissive QDs on silica sphere were

employed as the background signal, while the green emissive QDs on the surface of the silica acted as the measurement signal [64]. The fluorescent signal produced by the green emissive QDs were obviously quenched upon the utilisation of Au NPs. In the presence of protamine, the interaction between Au NPs and protamine were observed via the electrostatic attraction, which induced the aggregation of Au NPs, and further the recovery of the fluorescent signal (Fig. 27.3c). The proposed optical sensor allowed the sensitive detection of PM with a low LOD of 18 pg $mL^{-1}$. The successful application of this method was achieved for PM determination in milk and rice samples.

### *27.2.3 Detection of Amino Acids*

Cysteine is an essential member of glutathione (GSH), which poses an important role in functional foods field. There are great requirements for development of sensitive and selective detection technology against cysteine (Fig. 27.4). Photoelectrochemical biosensor was also utilised in the analysis of cysteine with

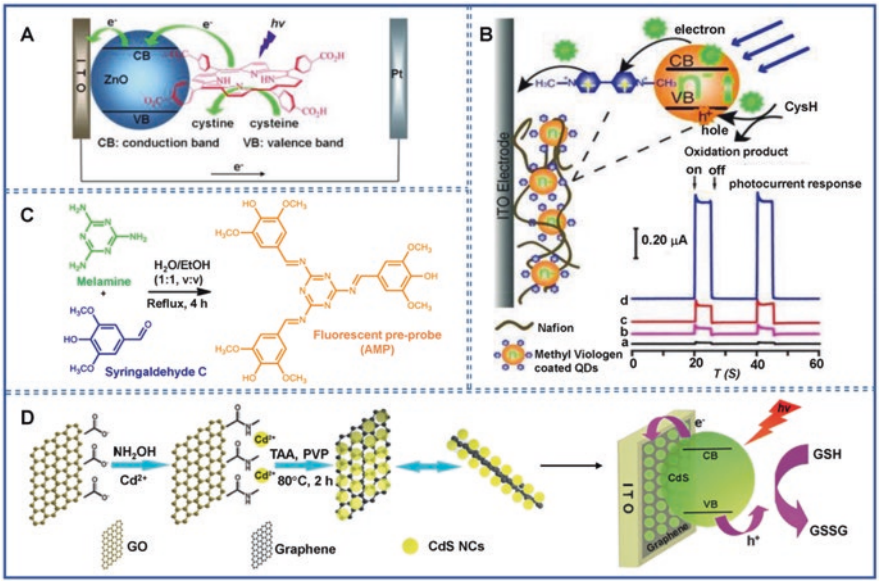


**Fig. 27.4** (**a**) Schematic representation of photoelectrochemical detection of cysteine at ZnO-coated ITO electrode. (Reprinted with permission from Ref. Tu et al. [45]. Copyright 2011: Wiley). (**b**) Schematic diagram of the photocurrent detection of cysteine at Nafion/CdS-MV decorated ITO electrode. (Reprinted with permission from Ref. Long et al. [26]. Copyright 2011: Wiley). (**c**) Diagram of fluorescent biosensing of cysteine based on ZnO QDs and fluorescent probe. (Reprinted with permission from Ref. [21]. Copyright 2021: Springer Nature). (**d**) Schematic illustration of photoelectrochemical detection of glutathione (GSH) at graphene-CdS decorated ITO electrode. (Reprinted with permission from Ref. [78]. Copyright 2012: Royal Society of Chemistry)

high sensitivity and specificity. A novel sensing platform was introduced for photoelectrochemical detection of cysteine based on free-base-porphyrin-functionalised ZnO NMs. In this design, ZnO NMs was employed to interact with functional nanohybrid, which was coated on an indium tin oxide (ITO) electrode (Fig. 27.4a). When cysteine existed, the photocurrent signal was significantly enhanced under irradiation. Achieved by this performance, the photoelectrochemical signal was a dynamic response versus target cysteine concentrations in the range of 0.6–157 μmol $L^{-1}$, and its detection of limit was 0.2 μmol $L^{-1}$. It has been demonstrated that ZnO-based semiconductor nanoparticles provided a potential application for biomolecules analysis [45]. Based on similar photoelectrochemical biosensing, methyl viologen was coated on CdS QDs, and the efficient electron was transported from cysteine to the QDs when cysteine existed (Fig. 27.4b). The electron transfer on the electrode was surveyed [26]. Upon light irradiation, electron transportation was performed from CdS QDs to methyl viologen, leading to efficient electron transportation to the indium tin oxide (ITO) electrode. The photocurrent signal was proportionally enhanced versus the levels of cysteine. A dynamic response was obtained ranging from 0.2 to 2.8 μM. Its detection limit was down to 0.1 μM. Very recently, ZnO QDs were first synthesized and characterised for fluorescent detection of cysteine with high sensitivity (LOD = 0.642 μM) (Fig. 27.4c) [21].

Glutathione (GSH) was not only used for drugs but also applied in functional foods for the improvement of immunosystem function. The detection of GSH levels was thus much in demand. The graphene/CdS nanomaterials were synthesized and employed to construct the photoelectrochemical sensing strategy for sensitive GSH determination [78]. It was confirmed that the current graphene/CdS nanomaterials improved the photoelectric properties like the great electron transport and the spatial separation, and further enhance the photocurrent signals (Fig. 27.4d). A good linear relationship was achieved between the photocurrent signals and concentrations of GSH. Its detection limit was calculated to be 0.003 mM. Results demonstrated that the graphene/CdS nanomaterials offer great potential in functional foods application due to their significantly enhanced photoelectric properties.

### *27.2.4 Detection of Organic Compounds*

Bisphenol A (BPA), a common contaminant in foods and water, was extensively used in food products and food package. Bisphenol A posed a great hazard to food safety. Thus, the detection and degradation of bisphenol A was attracted increasing interest from researches, especially in the exploration of low-cost and efficient methods. Rani et al. reported a novel ZnO doped with zinc-hexacyanoferrate (ZnO@ZnHCF) nanomaterials for high BPA degradation [35]. Through this synthesis and design, the surface area and band gap of ZnO@ZnHCF nanomaterials were obviously improved in comparison with ZnO or ZnHCF (Fig. 27.5a). Therefore, it was demonstrated that the proposed methods indicated the degradation pathway of BPA and the promising practicality of ZnO@ZnHCF nanomaterials.

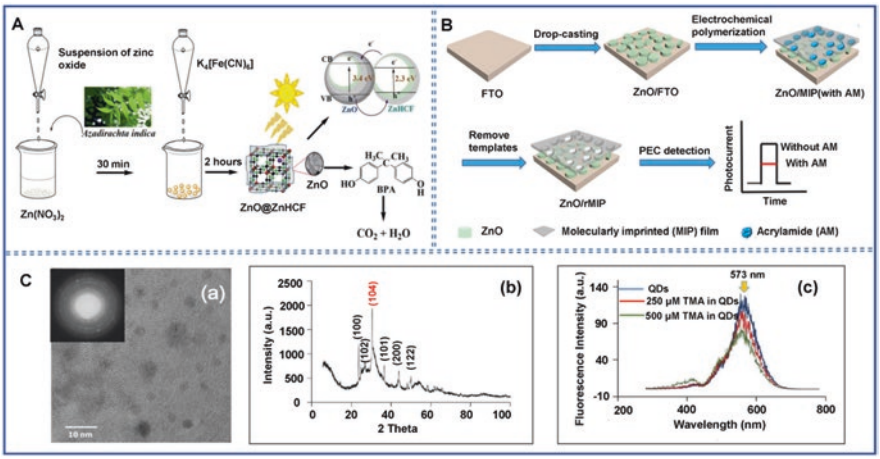


**Fig. 27.5** (**a**) Schematic diagram of photocatalytic degradation of bisphenol A using ZnO@ZnHCF nanocubes. (Reprinted with permission from Ref. [35]. Copyright 2018: Elsevier). (**b**) Schematic diagram of photoelectrochemical detection of acrylamide based on ZnO/polypyrrole nanocomposites. (Reprinted with permission from Ref. [81]. Copyright 2021: Elsevier). (**c**) Schematic illustration of electrochemiluminescence detection of trimethylamine (TMA) using thioglycolic acid-CdSe QDs. (Reprinted with permission from Ref. [33]. Copyright 2021: Elsevier)

Acrylamide (AM), a group 2A carcinogen classified by international regulation, was a common contaminant produced in potato chips and biscuits during the high-temperature operation. Given its severe hazards for food safety and human health, simple, sensitive and reliable detection approaches are much in demand. A ZnO nanocomposite-based molecular imprinting (MIP) platform for photoelectrochemical sensing of AM was introduced [81]. The ZnO nanocomposite was synthesized and employed as a special photoelectron material, and the polypyrrole (PPy) was modified on ZnO nanocomposites for specific recognition of target AM. When AM was presented, the adsorption of AM on PPy-ZnO caused the electron transport, and further led to the reduced photocurrent signal (Fig. 27.5b). A dynamic response was observed between the photocurrent signals and AM concentrations ranging from $10^{-1}$ to $2.5 \times 10^{-9}$ M. Its limit of detection was $2.147 \times 10^{-9}$ M. The developed PPy-ZnO-based photoelectrochemical sensing platform has a great potential to ensure food safety.

A paper-based electrochemiluminescence device (μPAD-ECL) for the estimation of trimethylamine (TMA) concentration in fish was developed using tris(2,2′-bipyridyl)ruthenium(II) complex coupled with water-soluble thioglycolic acid-capped CdSe quantum dots on the inkjet-printed paper-based device [33]. The quenching effect of tertiary amines on the ECL intensity was found to be sensitive and concentration-dependent. This effect allows the measurement of TMA at low concentrations (Fig. 27.5c). Under the optimal conditions, the linear concentration range was exhibited from $1 \times 10^{-12}$ to $1 \times 10^{-7}$ M and a detection limit of $2.09 \times 10^{-13}$ M, with a relative standard deviation of 1.97%. The applicability of

μPAD-ECL is demonstrated by the rapid estimation of trimethylamine concentration in fish tissue and could be used as a method for screening the total amount of tertiary amines in fishery products in remote communities. The results obtained using the paper-based devices agreed well with those obtained by applying high-performance liquid chromatography with benzoyl derivatisation, at a confidence level of 95%.

### *27.2.5 Detection of Small Molecules Mycotoxins*

Aflatoxin B1 (AFB1), one of the most common and toxic mycotoxins in foods, has been recognised as group 1 carcinogen by the International Agency for Research on Cancer (IARC). Therefore, rapid, reliable, and sensitive methods for AFB1 determination are of great importance and urgency. Li et al. first developed a lateral flow immunoassay (LFIA) for rapid analysis of AFB1 in cereal products based on CdSe/ZnS QDs (Fig. 27.6a). The anti-AFB1 was immobilised on CdSe/ZnS QDs modified with amino [23]. The enhanced sensitivity was thus achieved with a low LOD of 5 pg $mL^{-1}$. Inspired by this design, on the basis of CdSe/ZnS QDs, a novel iron oxide nanoparticle (IONP) was prepared and decorated by oleic acid. The CdSe/ZnS QDs were employed for the fluorescent signal amplification, while the IONPs were utilised to retain saturation magnetisation (Fig. 27.6b). The magnetic fluorescent beads (MFBs) were then synthesized with a highly fluorescent signal, and integrated into LFIA for AFB1 determination [13]. It was demonstrated that higher sensitivity was obtained with the LOD down to 3 pg $mL^{-1}$. Moreover, nucleic acid aptamers, considered as "chemical antibodies", possess high affinity and specificity that are similar to or even superior to antibodies. Accordingly, a novel ZnS QDs-based biosensor was established for the detection of AFB1 in peanuts via the specific aptamer recognition [55, 56]. In this work, ZnS-QDs were employed as the energy donors, while Ag nanocubes were used as the energy acceptors to produce fluorescence resonance energy transfer (FRET). When AFB1 was introduced, the conformational change of aptamer led to the release of the complementary strand DNA, which was modified on ZnS-QDs (Fig. 27.6c). The fluorescence signal was subsequently recovered. Compared to antibody-based immunoassay, enhanced analytical performance was achieved in this proposed aptasensor with high sensitivity (LOD = 2.67 pg $mL^{-1}$).

Based on a similar mechanism, CdTe QDs modified with the specific ochratoxin A (OTA) aptamer were utilised as the energy donors, and molybdenum disulphide ($MoS_2$) was conjugated to quench the fluorescent signal produced by QDs (Fig. 27.6d). This proposed aptasensor was demonstrated to be sensitive and successfully applied for OTA determination in red wine [27]. Very recently, Qileng et al. reported an immunosensor for detection of ochratoxins in millet and maize combining $MoS_2$-CdS with ZnS-$Ag_2S$ nanocages [34]. $MoS_2$-CdS was prepared to immobilise antigens, and ZnS-$Ag_2S$ nanocages were employed to capture the

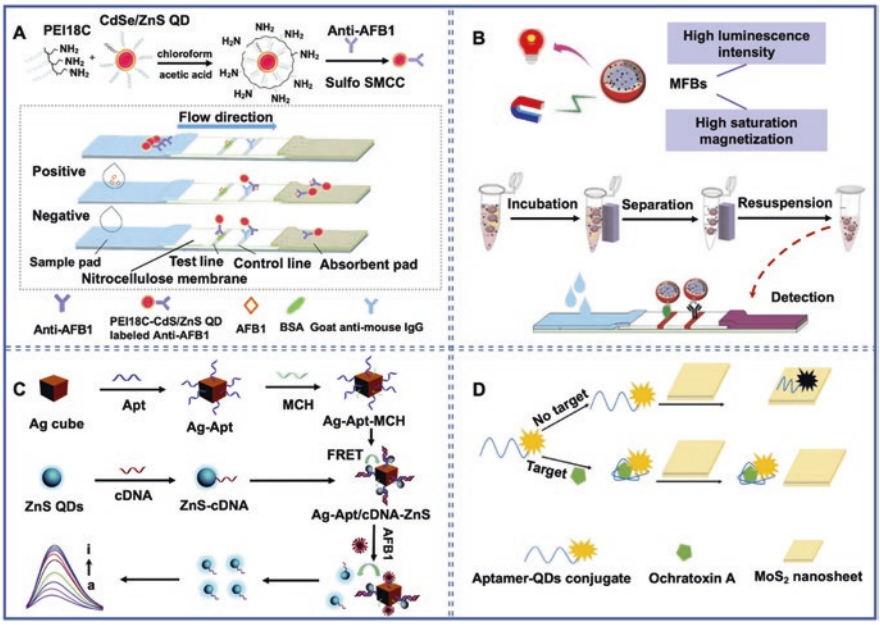


**Fig. 27.6** (**a**) Schematic illustration of fluorescent sensing of aflatoxin B1 based on CdSe/ZnS QDs and lateral flow immunoassay (LFIA). (Reprinted with permission from Ref. [23]. Copyright 2018: Royal Society of Chemistry). (**b**) Schematic diagram of fluorescent sensing of aflatoxin B1 based on CdSe/ZnS QDs and immunochromatographic assay (ICA). (Reprinted with permission from Ref. [13]. Copyright 2019: American Chemical Society). (**c**) Schematic illustration of FRET aptasensing of aflatoxin B1 based on ZnS QDs and Ag nanocubes. (Reprinted with permission from Ref. [55, 56]. Copyright 2021: Royal Society of Chemistry). (**d**) Schematic representation of fluorescent aptasensing of ochratoxin A using CdTe QDs and $MoS_2$ nanosheets. (Reprinted with permission from Ref. [27]. Copyright 2017: Elsevier)

antibody (Fig. 27.7a). The photoelectrochemical (PEC) signal and square wave voltammetric (SWV) signal were linear relationship with the levels of ochratoxins in the range of 1 ng $L^{-1}$ to 1 μg $L^{-1}$. Their limits of detection were calculated to be 0.1 ng $L^{-1}$, 0.5 ng $L^{-1}$ and 0.5 ng $L^{-1}$, for OTA, OTB and OTC, respectively. Notably, this novel sensing platform provided a promising route for the analysis of mixture molecules.

Zearalenone (ZEN), a common mycotoxin in cereals, poses great hazards to agricultural products and food safety. For rapid response, even trace levels of ZEN [9], a novel LFIA platform was introduced for fluorimetric detection of ZEN based on CdSe QDs (Fig. 27.7b). Unlike fluorescent microspheres, the CdSe QDs were employed for the fluorescent quenching LFIA mechanism, which exhibited a sensitive and specific detection towards ZEN (LOD = 0.58 ng $mL^{-1}$) in corn samples. For the improvement of detection sensitivity, the embedding of ZEN-labelled catalase in ELISA was used for $H_2O_2$ reduction, and CdTe QDs were sensitive to $H_2O_2$. A fluorescent ELISA was then established for high sensitive analysis of ZEN

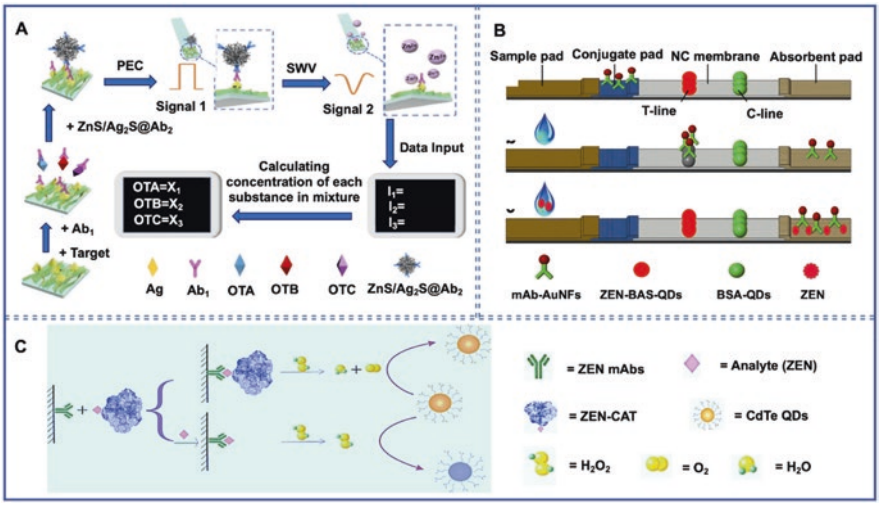


**Fig. 27.7** (**a**) Schematic diagram of the dual-signal immunosensing of ochratoxins based on ZnS/$Ag_2S$. (Reprinted with permission from Ref. [34]. Copyright 2020: Elsevier). (**b**) Schematic illustration of fluorescent sensing of zearalenone (ZEN) based on CdSe QDs and lateral flow immunoassay (LFIA). (Reprinted with permission from Ref. [9]. Copyright 2019: Springer Nature). (**c**) Schematic diagram of fluorescent sensing of ZEN based on CdTe QDs and enzyme-linked immunosorbent assay (ELISA). (Reprinted with permission from Ref. [74]. Copyright 2016: Elsevier)

(Fig. 27.7c). Its limit of detection was calculated down to 4.1 pg $mL^{-1}$, which was demonstrated nearly 140-fold improvement over the LFIA methods [74].

### *27.2.6 Detection of Other Analytes*

Hydrogen peroxide ($H_2O_2$), one of the most important indicators in food industry, is widely used in food processing such as sterilising, bottling, transporting and packing instruments. However, excess levels of $H_2O_2$ can cause the reduction of active components, and severe gastrointestinal disorders, as well as cellular damage, gene mutation, and even the cancer. Therefore, methods development for monitoring of $H_2O_2$ levels in food is much in demand. A PVP-capped $CoFe_2O_4$@CdSe QDs core-shell magnetic composite was synthesized by one-pot co-precipitation approach via modifying the glassy carbon electrode surface simply by drop casting of its suspension on electrode surface [31]. The resulting nanosensor ($CoFe_2O_4$@CdSeQDs/RIF/GCE) exhibited an excellent catalytic activity on the electroreduction of $H_2O_2$ attributed to the synergistic effect of $CoFe_2O_4$@CdSe QDs core-shell magnetic nanocomposite and RIF originating from the facile charge transfer between them. The proposed sensing platform was successfully applied to determine $H_2O_2$ in milk and juice samples. Tetracycline (TC), a widely used and common antibiotic, posed severe hazards to milk and food upon its excessive use. To ensure food safety,

sensitive and selective sensing strategy for TC monitoring was of importance and urgency. Herein, a novel molecularly imprinted polymer captivity ZnO nanorods (NRs) was designed and synthesized for fluorescent sensing of TC [25]. Great performance was achieved via the formation of shield to decline the toxicity of ZnO and the fluorescence quenching for the selective signal determination (Fig. 27.8a), as well as the high sensitivity of 1.02 μmol $L^{-1}$.

Heavy metal ion contamination in food was attracted more and more attention from scientists for decades owing to the great hazards towards humans. Notably, the occurrence of mercury (Hg) induced diverse toxic effects, including brain disease, kidney damage, as well as cognitive and physical disorders. In particular, $Hg^{2+}$, as the most common and stable mercury, was well studied since it possessed exciting water solubility. Accordingly, the Mn-doped CdS/ZnS QDs modified with single-stranded oligonucleotides (ssDNA) were prepared and employed as the fluorescent probe, while gold nanoparticles (Au NPs) decorated with complementary DNA were synthesized and used as the fluorescent quencher (Fig. 27.8c). In the absence of $Hg^{2+}$, the hybridisation of ssDNA into double-stranded DNA (ds DNA) caused that the fluorescent signal of CdS/ZnS QDs was quenched significantly. When $Hg^{2+}$ existed, the conformational change of ssDNA was generated to form T-$Hg^{2+}$-T structure, resulting in the release of complementary DNA and the recovery of the fluorescent signal [14]. The novel fluorescent sensing of $Hg^{2+}$ was achieved with a limit of detection of 0.18 nM. Moreover, the integration of long-lifetime Mn-doped CdS/ZnS QDs was obviously reduced the background signal.

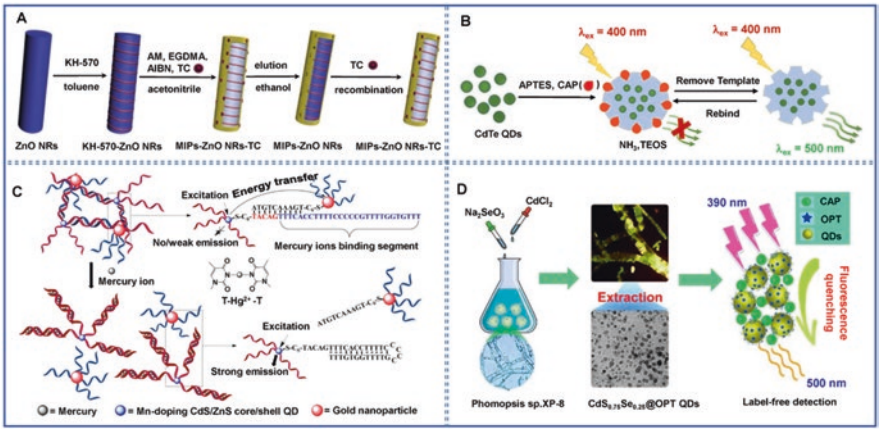


**Fig. 27.8** (**a**) Schematic representation of a novel molecularly imprinted polymer captivity ZnO nanorods (NRs) for fluorescent sensing of tetracycline (TC). (Reprinted with permission from Ref. [25]. Copyright 2020: Elsevier). (**b**) Schematic illustration of a fluorescent nanosensing for chloramphenicol (CAP) based on CdTe QDs and molecularly imprinted silica nanospheres. (Reprinted with permission from Ref. [4]. Copyright 2015: Wiley). (**c**) Schematic diagram of fluorescent sensing of $Hg^{2+}$, using Mn:CdS/ZnS QDs and Au NPs. (Reprinted with permission from Ref. [15]. Copyright 2012: American Chemical Society). (**d**) Schematic diagram of fluorescent sensing of CAP based on CdSSe QDs. (Reprinted with permission from Ref. [63]. Copyright 2020: American Chemical Society)

Chloramphenicol (CAP), one of the most broad-spectrum antibiotics, was extensively used for treating several infectious diseases. However, its severe side effects like aplastic anaemia and hypersensitivity in humans limit the wide applications. In particular, CAP was banned by European Commission in food-generating animals. Surprisingly, the utilisation of CAP was still well received in several countries due to its low cost, activity, as well as availability. Therefore, rapid, sensitive and selective analytical approaches for CAP monitoring in foods are of great importance and urgency. Owing to the excellent optical property, quantum dots (QDs) have attracted increasing interest in sensors and biosensors. Inspired by this knowledge, a fluorimetric sensing platform was established for detection of CAP in milk based on CdTe QDs (Fig. 27.8b). Notably, in this novel design [4], the molecularly imprinted silica nanospheres.

($SiO_2$@MIP) were integrated on CdTe QDs for preserving the fluorescence quantum yield. CAP, as a sensitive analyte probe, was observed to significantly quench the fluorescent signal produced by CdTe QDs via the electron transfer principle. The low limit of detection was measured to be 5.0 μg $L^{-1}$. On the basis of this protocol, an in-depth investigation was made for the biological assembly of $CdS_xSe_{1-x}$ QDs (Fig. 27.8d). It was found that the $CdS_{0.75}Se_{0.25}$ QDs with diameter of 3.22 ± 0.07 nm possessed great water solubility and exciting fluorescent characteristics. Enlightened by this advance, the proposed $CdS_{0.75}Se_{0.25}$ QDs were embedding to the fluorimetric sensor for the quantification of CAP in milk [63]. The detection sensitivity was improved over five-fold enhancement (LOD = 0.89 μg $L^{-1}$). Consequently, quantum dots-based fluorescent sensing offers a promising trend towards label-free monitoring of antibiotics for food safety.

## 27.3 Challenges and Limitations

II–VI semiconducting nanomaterials-based sensors and biosensors are continuously attracted increasing attention from scientists for food safety hazard detection. As indicated in Table 27.1, the recent advances in II–VI semiconducting nanomaterials-based sensors and biosensors for food safety hazards were introduced and summarised. Although the great performance was achieved for targets analysis like glucose, vitamin, pathogenic bacteria, pesticides, metal ions, as well as mycotoxins, etc. There are still following vital challenges and limitations: (i) The exploration of more advanced nanomaterials for the construction of biosensors and sensor devices with the properties of high sensitivity, low cost, ease of use, and long life, which relies on the materials size, morphology, surface area, semiconducting band gap, optical activity, and chemical properties. (ii) For real sample analysis, especially for complex matrix like food, when nanomaterials existed, the interference of other substances for biosensor performance should be taken into account due to their interaction with the nanomaterials. (iii) Given the toxicity reaction, potential risk and safety issues of nanomaterials, toxicity evaluation should be required related to the size, morphology, surface charge and area, and composition. By this, environment-friendly nanomaterials-based biosensors are preferable. (iv) Nanomaterials like CdS, CdSe, CdTe integrated biosensors

**Table 27.1** Summary of II–VI semiconducting nanomaterials (NMs) based biosensors for the detection of food hazards

| II–VI NMs composition | Detection methods | Transduction principle | Target | Dynamic Range | LOD | Samples | References |
|---|---|---|---|---|---|---|---|
| CdS | PEC | Graphene/CdS nanomaterials | GSH | 0.01–1.5 mM | 0.003 mM | Drug isethion | [78] |
| CdS | PEC | Methyl viologen-coated CdS QDs and light irradiation | Cysteine | 0.2–2.8 μM | 0.1 μM | NR | [26] |
| ZnO@CdS | EPCA | ZnO@CdS nanocomposite for degradation and removal of pesticides | Pesticides | NR | Quantitative removal of pesticides (89–91%) | NR | [36] |
| ZnO | PEC | Free-base-porphyrin-functionalised ZnO NMs and indium tin oxide (ITO) electrode | Cysteine | 0.6–157 μmol $L^{-1}$ | 0.2 μmol $L^{-1}$ | NR | [45] |
| ZnO | FL | ZnO QDs | Cysteine | 0.1–600 μM | 0.642 μM | Bovine serum albumin (BSA) and tap water | [21] |
| ZnO | ISABG | ZnO@ZnHCF nanomaterials for BPA degradation | BPA | NR | Half-life of BPA up to 2.8 h | NR | [35] |
| ZnO | FL | Molecularly imprinted polymer captivity ZnO nanorods (NRs) | TC | 5.0–120 μmol·$L^{-1}$ | 1.02 μmol $L^{-1}$ | Water | [25] |
| ZnO | PEC | ZnO nanocomposite-based molecular imprinting (MIP) | AM | $10^{-1}$ to $2.5 \times 10^{-9}$ M | $2.147 \times 10^{-9}$ M | Potato chips and biscuits | [80, 81] |
| $CdS_{0.75}Se_{0.25}$ | FL | $CdS_{0.75}Se_{0.25}$@oligopeptide transporter | CAP | 3.13–500 μg $L^{-1}$ | 0.89 μg $L^{-1}$ | Milk | [63] |

(continued)

**Table 27.1** (continued)

| II–VI NMs composition | Detection methods | Transduction principle | Target | Dynamic Range | LOD | Samples | References |
|---|---|---|---|---|---|---|---|
| CdSe | FL | CdSe QDs and fluorescent quenching lateral flow assay (LFIA) | ZEN | 0.78 to 25 ng $mL^{-1}$ | 0.58 ng $mL^{-1}$ | Corn | [9] |
| CdSe | FL | CdSe QDs and high luminance with photostability | *Staphylococcus aureus* | NR | 8.94 ng $mL^{-1}$ | NR | Xiong et al. (2020) |
| CdSe | EC | PVP-capped $CoFe_2O_4$@ CdSe QDs | $H_2O_2$ | 7–145 μM and 0.145–1.43 mM | 0.38 μM | Milk and juice samples | [31] |
| CdSe | ECL | Tris (2,2′-bipyridyl) ruthenium(II) complex coupled with CdSe QDs | TMA | $1 \times 10^{-12}$ to $1 \times 10^{-7}$ M | $2.09 \times 10^{-13}$ M | Fish | [33] |
| CdSe/ZnS | FL | CdSe/ZnS QDs combined with oligonucleotide microarray | *E. coli* | NR | 10 CFU $mL^{-1}$ | Mock-contaminated food samples | [16] |
| CdSe/ZnS | FL | CdSe/ZnS QDs combined with lateral flow immunoassay (LFIA) | AFB1 | 0.001–10 ng $mL^{-1}$ | 0.005 ng $mL^{-1}$ | Rice and peanuts | [23] |
| CdSe/ZnS | FL | CdSe/ZnS QDs and oleic acid-modified Iron oxide nanoparticles (OA-IONPs) | AFB1 | 5–150 pg $mL^{-1}$ | 3 pg $mL^{-1}$ | Sauce extract | [13] |
| CdSe/ZnS | FL | CdSe/ZnS@$SiO_2$ nanoparticles | *S. typhi* | $6.6 \times 10^2$ to $6.6 \times 10^4$ CFU $mL^{-1}$ | $3.3 \times 10^2$ CFU $mL^{-1}$ | Different stains | [51] |
| CdSe/ZnS | FL | CdSe/ZnS QDs and colorimetric-fluorescent-magnetic nanospheres (CFMNs) | *S. typhi* | $1.88 \times 10^4$ to $1.88 \times 10^7$ CFU $mL^{-1}$ | $3.5 \times 10^3$ CFU $mL^{-1}$ | Milk | [14] |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| ZnS | FL | ZnS-QDs-based fluorescence resonance energy transfer (FRET) | AFB1 | 5 pg $mL^{-1}$–300 ng $mL^{-1}$ | 2.67 pg $mL^{-1}$ | Peanut | [55, 56] |
| ZnS | PEC | $MoS_2$-CdS with ZnS-$Ag_2S$ nanocages | OTs | 1 ng $L^{-1}$ to 1 μg $L^{-1}$ | 0.1 ng $L^{-1}$, 0.5 ng $L^{-1}$, and 0.5 ng $L^{-1}$, for OTA, OTB, and OTC | Millet and maize | [34] |
| CdS/ZnS | FL | Mn:CdS/ZnS QDs and Au NPs | $Hg^{2+}$ | 0 to $1 \times 10^{-9}$ M | 0.18 nM | Water | [15] |
| CdTe | FL | CdTe QDs and Molybdenum disulphide ($MoS_2$) nanosheet | OTA | 1–1000 ng $mL^{-1}$ | 1 ng $mL^{-1}$ | Red wine | [27] |
| CdTe | FL | CdTe QDs and fluorescent enzyme-linked immunosorbent assay (ELISA) | ZEN | 2.4 pg $mL^{-1}$–1.25 ng $mL^{-1}$ | 4.1 pg $mL^{-1}$ | Corn | [74] |
| CdTe | FL | CdTe@$SiO_2$@MIP nanoparticles | CAP | 40–500 μg $L^{-1}$ | 5 μg $L^{-1}$ | Milk | [4] |
| CdTe | FL | Tb/CdTe QDs and smartphone colour recogniser | Norfloxacin (NFX) | 0–1200 nM | 6.03 nM | Honey/water | [20] |
| CdTe | FIA | CdTe QDs-based competitive fluoroimmunoassay | 2,4-D | 250–1000 pg $mL^{-1}$ | 250 pg $mL^{-1}$ | Phosphate-buffered solution | [49] |

*EC* electrochemical, *ECL* electrochemiluminescence, *EPCA* enhanced photocatalytic activity, *FL* fluorescent, *FIA* fluoroimmunoassay, *ISABG* improved surface area and band gap, *LOD* Limit of detection, *NR* not reported; *PEC* photoelectrochemical, *AFB1* aflatoxin B1, *OTA* ochratoxin A, *ZEN* zearalenone, *CAP* chloramphenicol, *2,4-D* 2,4-dichlorophenoxyacetic acid, *TMA* trimethylamine, *TC* Tetracycline, *AM* acrylamide, *BPA* Bisphenol A, *GSH* glutathione, *E. coli Escherichia coli*, *ELISA* enzyme-linked immunosorbent assay, *FRET* fluorescence resonance energy transfer, *CFMNs* colorimetric-fluorescent-magnetic nanospheres, *QDs* quantum dots

proved to be highly expensive, especially for large-scale application or clinical analysis. Therefore, the researchers should take the cost into consideration for nanobiosensing development. (v) Biosensor development for point-of-care (POC) testing devices is the future trend for portable, and high-throughput analysis of food safety hazards. For decades' efforts, the most successful examples like personal glucose metres (PGM) or smartphones have been widely used for food field. Therefore, focusing on these advanced nanomaterials for POC biosensing devices would open a new insights and transfer them to the market.

## 27.4 Conclusions and Future Trends

Food safety issue, a cause of global concern, imposed severe hazards on human health. Therefore, the establishment of simple, sensitive, and reliable sensing platform against analytes determination in food safety was much in demand. Biosensors coupled with II–VI semiconducting nanomaterials displayed unique advantages such as rapid response, improved sensitivity and selectivity, enhancing sensing performance, as well as the versatile platform for food analysis. This book chapter was systematically introduced and discussed the application of II–VI semiconducting nanomaterials-based sensors and biosensors for detection of food hazards targets in recent years. Furthermore, future research direction will focus on the advanced integrated nanocomposites for the practical application in food safety field and the transition of biosensors platform to the market.

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