Biosensors and Bioelectronics 127 (2019) 72–84

Contents lists available at ScienceDirect

Biosensors and Bioelectronics

journal homepage: www.elsevier.com/locate/bios

Nanomaterials based surface plasmon resonance signal enhancement for detection of environmental pollutions

Mansour Mahmoudpour[a,b,c], Jafar Ezzati Nazhad Dolatabadi[d,*], Mohammadali Torbati[b,*], Aziz Homayouni-Rad[b]

[a] *Immunology Research Center, Tabriz University of Medical Sciences, Tabriz, Iran*
[b] *Department of Food Science and Technology, Faculty of Nutrition and Food Sciences, Nutrition Research Center, Tabriz University of Medical Sciences, Tabriz, Iran*
[c] *Student Research Committee, Tabriz University of Medical Sciences, Tabriz, Iran*
[d] *Research Center for Pharmaceutical Nanotechnology, Tabriz University of Medical Sciences, Tabriz, Iran*

ARTICLE INFO

Keywords:
Environmental pollution
Surface plasmon resonance (SPR)
Signal enhancement
Nanomaterials
Surface modification

ABSTRACT

Due to the nearby relationship between human health, socioeconomic development and environmental pollution, the detection and identification of environmental pollutants need more attention. Therefore, the development of suitable analytical devices that are sensitive, specific, precise, quick, and easy-to-use are required to resolve the increased request for legislative action on environmental pollution control and early detection of rising pollutants. Currently, the development of biosensing instruments attracted important attention because of their high selectivity, sensitivity, simplicity, reliability, low-cost and real-time response. Surface plasmon resonance (SPR) sensor as an example of portable, rapid, and smart biosensing devices widely used for qualitative and quantitative detection of multiplexed pollutant in real-time. Thus, SPR principles, assay formats, surface modification methods and signal enhancement are summarized in this review. Moreover, applications of SPR in the detection of pesticide, polycyclic aromatic hydrocarbons (PAHs), heavy metals and polychlorinated biphenyls (PCBs) over the past decade is discussed.

1. Introduction

As a consequence of human activity and industrial development, a wide range of potentially harmful man-made by-products and chemicals formed in combustion or industrial processes and still are widespread in the environment (Palchetti and Mascini, 2008). Some of these materials like polycyclic aromatic hydrocarbons (PAHs), heavy metals, pesticides and polychlorinated biphenyls (PCBs) are well-recognized pollutants that have harmful effects on the quality of the natural world (Kampa and Castanas, 2008). Thereby, determination of pollutant in the water, air and soil is an crucial step in management of human health and the environment hazards.

Chemical analysis of environmental samples has been conventionally accomplished by employing chromatographic methods as well as gas chromatography (GC), mass spectrometry (MS), and high-performance liquid chromatography (HPLC). Even though these techniques have been known as powerful trace analyzer with highest accuracy and excellent reproducibility but many disadvantage, such as tedious sample preparation, time consuming and sophisticated equipment noticeably limited their real-time and on-site application, especially in emergency cases (Rodriguez-Mozaz et al., 2004). Therefore, the development of novel analytical biosensors for effective evaluation and monitoring of risk assessment in food products and environment that able to provide fast, reliable, and sensitive measurements with lower cost has gathered much more attention nowadays (Arora et al., 2011).

The main advantages of the use of biosensors in comparison with traditional analytical methods are the portability, and the ability to determination of target analytes with minimal sample preparation in complex matrices (Dolatabadi and de la Guardia, 2014; Jamali et al., 2014). Although some of the systems developed such as biosensor cannot compete with conventional chromatographic methods in terms of reproducibility and accuracy but they can be utilized by industry and regulatory authorities to provide sufficient information for screening of samples and routine tests.

Surface plasmon resonance (SPR) sensor is an affinity optical sensor that provide a real-time and highly sensitive response to the binding of molecules of interest to the sensor's surface without the use of molecular labels. Therefore, it has attracted attention due to the high specific detection of target analytes in complex matrices with very low

---

* Corresponding authors.
E-mail addresses: ezzatij@tbzmed.ac.ir (J. Ezzati Nazhad Dolatabadi), torbatim@tbzmed.ac.ir (M. Torbati).

https://doi.org/10.1016/j.bios.2018.12.023
Received 4 October 2018; Received in revised form 27 November 2018; Accepted 10 December 2018

detection limits (Fathi et al., 2018; Sharifi et al., 2017a, 2017b). Since, most of the analytes in food, environmental and biomedical fields have low-molecular weight usually less than about 1000 Da, their detection is possible with SPR biosensor owing to its high sensitivity for mass change. Thus, due to the growing demand for detection of environment pollutants using SPR biosensors, the basic principle of SPR, the existing detection technique based on signal enhancement using nanomaterials and the advance on environment pollutants monitoring with SPR technique has been overviewed in more details in this article.

2. General principle of SPR

In several review articles, operation and basic principle of SPR has been illustrated (Mohammadzadeh-Asl et al., 2018; Olaru et al., 2015). Basic principle of SPR relies on a physical optics phenomenon, which observed when light wave passes through a high refractive index prism under total reflection conditions and strikes the surface of a metal that is located on the base of the prism. A thin layer of biomolecular (dielectric medium) that immobilized on the sensor surface can be used for detection of its coupled analyte in mobile phase solution. At certain incident light angle or wavelength, the surface plasmons (SP) generated by free electrons on the thin metal surface result in evanescent waves resonation and absorption of incident light energy by SP lead to a narrow dip in the spectrum of reflected light. This SP is exceedingly sensitive to the changes in refractive index of biomolecular layer. Consequently, change in the reflected light beam characteristics (phase, wavelength and angle) has been known as refractive index change, which in turn lead to SPR angle shift. The angle at which the reflectivity is minimum known as a SPR angle or resonance angle (Fig. 1). The SPR angle not only is very sensitive to the refractive index of the analytes contacting with the sensor surface but also can be affected by the amount of biomolecular layer immobilized on the sensor surface (Fathi et al., 2018; Mohammadzadeh-Asl et al., 2018; Taghipour et al., 2018).

3. SPR as an affinity biosensor

For evaluation of affinity in SPR biosensors, first step is immobilization of biomolecular recognition elements (probe) on the sensor surface then the capture analyte molecules (target) in solution is flow over it and a probe-target binding through affinity interaction occurs that results in the refractive index enhancement at the sensor surface, which is optically measured (Fathi et al., 2018; Taghipour et al., 2018).

The change in refractive index Δnd arising within a layer of thickness h can be demonstrated via Eq. (1):

$$\Delta n_{\mathrm{d}} = (\mathrm{dn/dc})_{\mathrm{vol}}\Delta\Gamma/\mathrm{h} \tag{1}$$

Where $(\mathrm{dn/dc})_{\mathrm{vol}}$ is the enhancement of refractive index n with the volume concentration of target analyte c, and ΔΓ is the target concentration that bound onto the chip surface (De Feijter et al., 1978; Tumolo et al., 2004). The refractive index alteration produced a real time change in the coupling of incident light into a propagating surface plasmon (PSP) on a chip surface.

Kinetic details can be determined by following the characteristics of light and interaction between probes immobilized and the target in solution on the sensor surface. Moreover, the parameter related to the refractive index may apply to recognize the target analyte and quantify their concentrations. Sensitivity of SPR sensors can be evaluated by limit of detection (LOD), which is the lowest surface concentration of target molecule generating the sensor response equivalent to three standard deviations of the response to the blank sample. LOD depends on optical property, molecular weight and target-probe binding via affinity on the sensor surface. LOD in terms of surface concentration can be estimated and expressed via the following Eq. (2)

$$\mathrm{C} = \rho \Delta d \tag{2}$$

Where ρ and Δd indicate density and changes in thickness of adsorbed layer, respectively (Kolomenskii et al., 1997).

4. SPR assay formats

In SPR assay, various measurement formats have been developed to ensure that the monitored target-probe binding event generate a measurable sensor response. The direct detection (Nakamura et al., 2003)

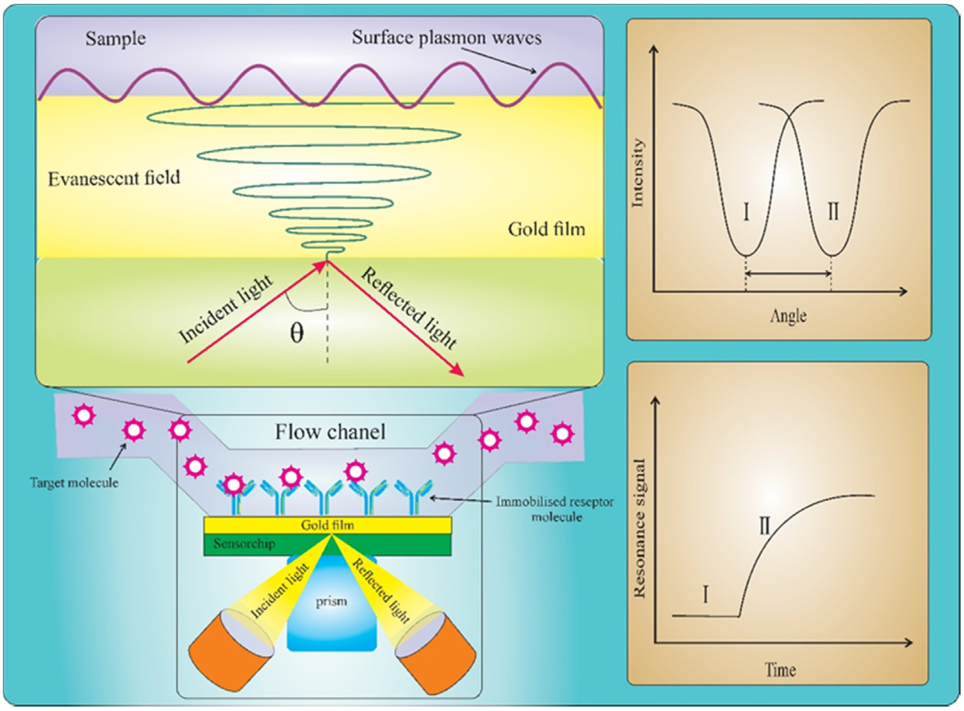

Fig. 1. A schematic illustration of the conventional Kretschmann optical configuration for SPR biosensing and the associated angle shift and sensorgram plot of resonance signal change with time.

sandwich (Severs et al., 1993; Wei et al., 2003) and competitive (Gobi et al., 2004) assays are examples of the most frequently detection formats that are used in SPR technique.

Direct detection assay can only be suitable for analyte detection with molecular weight greater than 5000 Da that is necessary to increase a refractive index change and resulting in detectable response. While for low-molecular-weight analytes, it does not always show sufficient signal but this defect can be improved through the competitive and sandwich assays. Enhancement of SPR signal in the sandwich assay can be done in two-step: First, sample containing target molecule is flow on ligand immobilized chip surface and after the analyte-ligand interaction occurring, in second step, this surface is incubated with amplification-signal molecules, which can bind specifically to the analytes and lead to the SPR signal enhancement.

In competitive assay, a constant concentration of respective antibodies is mixed with different amount of analyte molecule in solution, and then these combinations are flowed onto the sensor surface in reducing order of the analyte concentration during the test. Whenever the analyte concentrations are decreased in the mixtures, the amount of antibodies that interact with the chip surface rises that in turn results in improved SPR signal. The principle of these SPR assays has been shown in Fig. 2.

5. Surface modification methods for the ligand immobilization

Immobilization of ligand on a sensor surface is usually required to identify a specific receptor, such as a cell or macromolecule. The typical strategies for modification of chip surface will be explained in more details in this section and this process has been illustrated in Fig. 3.

5.1. Physical adsorption

In physical adsorption method, the ligand attached on a chip surface via non-covalent interactions such as hydrogen bonding, van der Waals, hydrophobic interactions and electrostatic forces. The hydrophobic head groups or thin layer modification can be applied for hydrophobic ligands immobilization on the chip surface. Ligand molecules bonded via adsorption tend to slowly leach from the sensor surface. It is noted that because of this attachment, layer formed in a randomly orient order may lead to reduced activity and weakly bound. Besides, the density of surface is not always very high (Kong and Hu, 2012).

5.2. Thiol binding

Thiol coupling can be used if thiol groups are available on the ligand. Ligand with a thiol group (R–SH) can strongly immobilize onto the gold chip surface via Au–S bond that result in a homogeneous ligand orientation. For generation of thiol group in ligands that lack the thiol group, protein engineering and chemical synthesis can be carried out (Lin et al., 2011).

5.3. Covalent immobilization

The most studied technique for covalent immobilization is formation of self-assembled monolayer (SAM) onto a chip surface that provides a powerful tool for attachment of biological molecules and creation of monomolecular films in dilute solution (Ulman, 1996). Thiolate monolayers on gold surface are the most extensively applied SAMs on SPR sensor. SAM with several surface properties such as the wettability, morphology and surface charge can be simply created by thiolates with different terminal functional groups.

Most macromolecules contain amine groups that can be coupled with amine coupling method. In this approach, covalent binding between the primary amine of a ligand and terminal carboxyl groups of monolayers on chip surface occurred through activation of the carboxyl group with N-hydroxysuccinimide (NHS) and 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC).

For immobilization of carbohydrate component, SAMs method with terminal carboxyl groups can be modified and activated with carbohydrazide or hydrazine and NaCNBH4, respectively that result in the aldehyde group production (Stefan et al., 1995). However, the nonspecific binding of ligand onto the chip surface can envelope the reactive functional groups and decrease the efficiency of immobilization methods based on the covalent coupling. Therefore, for prevention ligand from interaction with samples after their immobilization, blocking and deactivation agents, such as ethanolamine and bovine serum

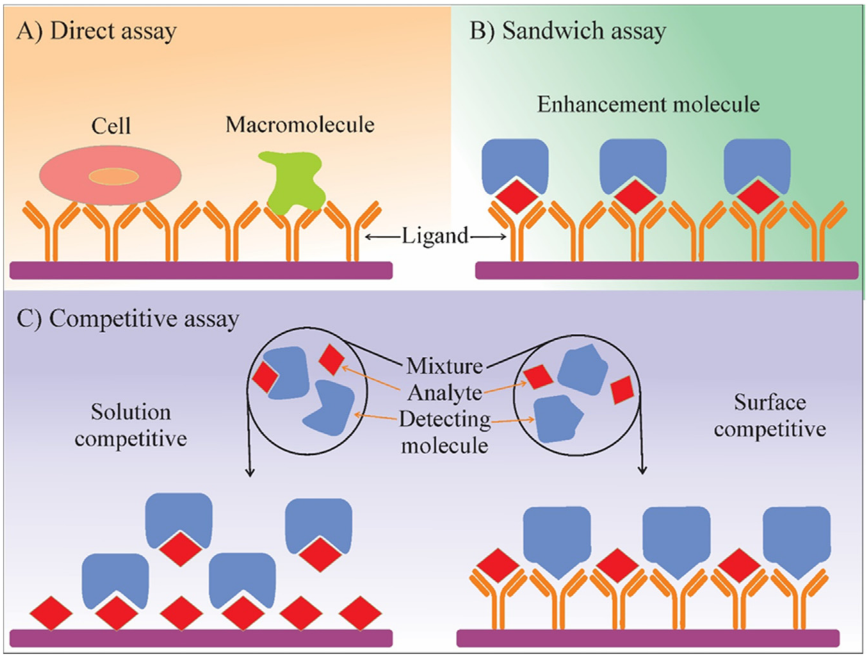

Fig. 2. Principle and procedure of SPR assay formats. (a) Direct assay; (b) Sandwich assay; (c) Competitive assay (left, solution competitive; right, surface competitive).

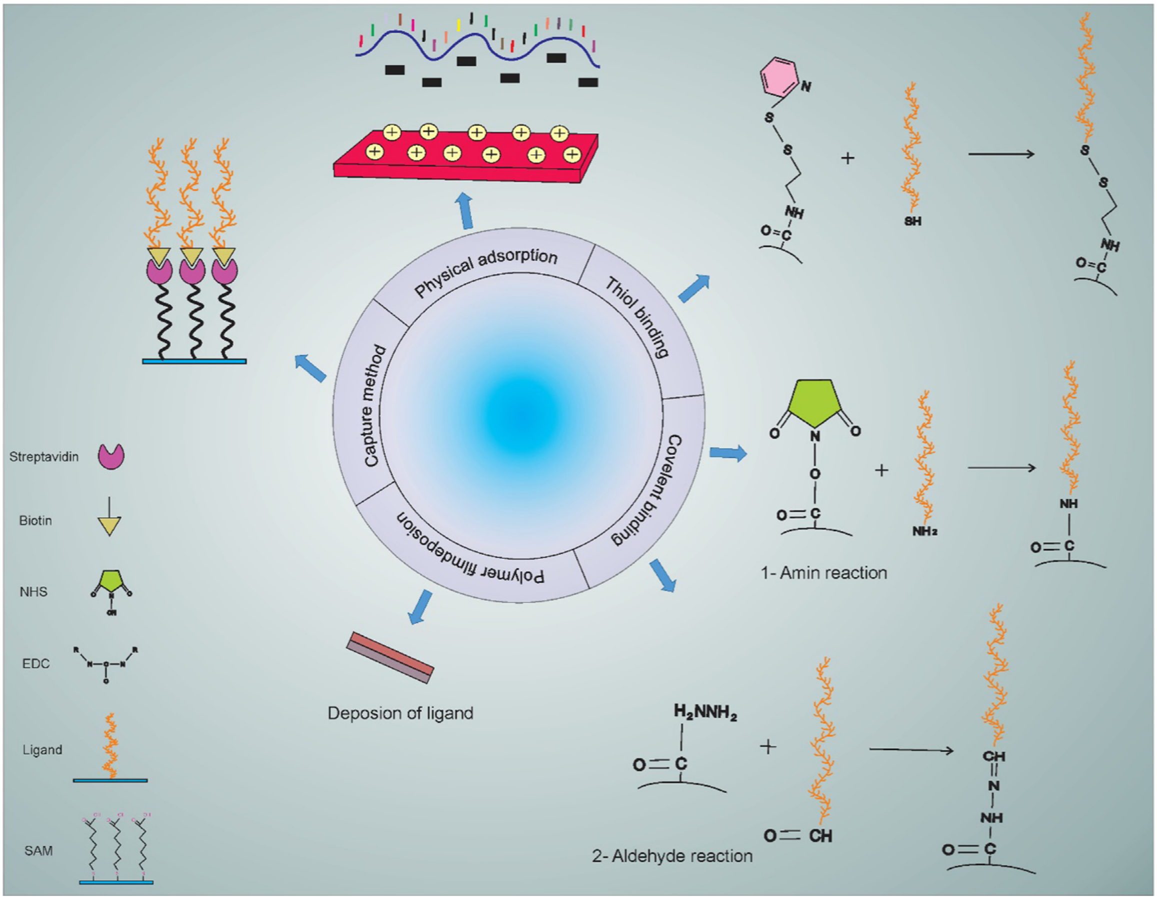

Fig. 3. Common strategies for preparation of modified surface including: (a) Physical adsorption, (b) Covalent immobilization (thiol-based and SAMs-based), (c) Capture, and (d) Polymer film deposition methods.

albumin (BSA) is used to cover unreacted remaining carboxylic groups on the sensor surface (Sharifi et al., 2017a, 2017b).

5.4. Capture method

Whenever, sufficient results from covalent immobilization processes did not be attained, we can use capturing method. In this technique, a capture molecule that has a sufficient affinity to the ligand is covalently immobilized onto the sensor surface and can be used for capturing of ligand. Antibody-antigen and streptavidin-biotin are the commonly used capture molecules in previous studies. For example, in Streptavidin-biotin capture, streptavidin can be immobilized in the sensor surface and it can capture biotinylated ligands. Since biotin affinity to streptavidin is very high, this method can be used for ligand permanent attachment onto the surface. Nucleic acids, polysaccharides and glycoconjugates are relatively easily biotinylated macromolecules. However, chip regeneration process can remove both analyte and ligand from the capturing molecule and for re-immobilization of ligand; we will need more new ligand, which results in excess utilization of it (Bergström and Mandenius, 2011; Wang et al., 2008).

5.5. Polymer film deposition

A nanolayer of polymer fabricate on the sensor surface chip in this method, which result in a highly sensitive SPR signal can be obtained. The thin film of polymer can be coated on chip surface via immersion of chip in a polymer solution using various protocols such as Langmuir-Blodgett (LB) technique and a spin-coating. Unlike the stable covalent bonding, the thin polymer films are weakly bound to the sensor chip by physisorption through non-covalent forces such as hydrophobic interactions, hydrogen bonding, and dipole interactions.

6. SPR signal enhancement

Detection and determination of small molecules at very low concentrations of analytes is an important issue in various field from food control and risk assessment to biological, therapeutical and pharmaceutical applications. For detection of this molecules based on changes in the thickness of the test medium or the effective refractive index in proximity of the Au surface, SPR sensors can be a suitable choice (J. Wang et al., 2010). However, the sensitivity of the system to measure analytes with low molecular weight (less than 8 kDa) or at extremely dilute concentrations (less than 1 pM) is very low (Kabashin et al., 2009; Law et al., 2011). To overcome this challenge, various methods for enhancement of SPR signal have been proposed (Fig. 4). Typically, two major approaches are considered for SPR signal enhancement: (1) sensor surface modification via application of nanoparticles (which increase the reflected light index). Different types of nanomaterials have been used in biosensors and biomedicine because of their intrinsic advantages over conventional materials. Exclusive advantages of nanoparticles such as simple and easy synthesis methods, high surface to volume ratio, very-small sizes, high specify, high biocompatibility, photostability and miscibility made them suitable candidate for various bioassays (Dolatabadi and de la Guardia, 2014; Dolatabadi and Omidi, 2016; Ezzati Nazhad Dolatabadi et al., 2018; Mokhtarzadeh et al., 2016). Simultaneous application of nanoparticles with SPR device increased mass concentration at the Au sensor surface, which results in sensitivity improvement. Gold and silver nanoparticles (Gao et al., 2012; Riskin et al., 2009), magnetic nanoparticles (Jia et al., 2018), quantum dots (Anfossi et al., 2018; Ghrera et al., 2016) and carbon

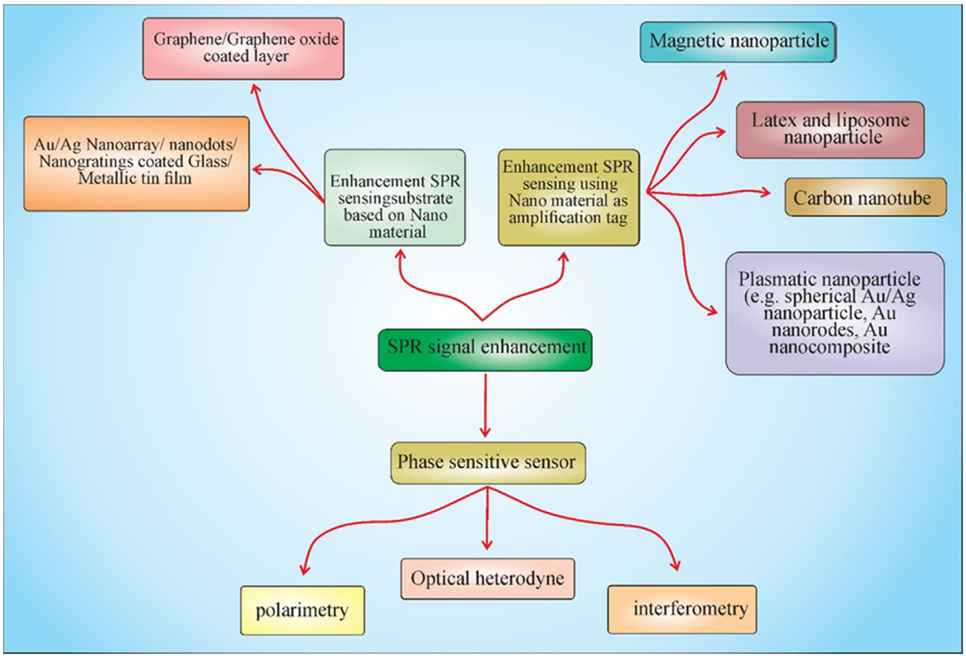

Fig. 4. Illustration of SPR signal amplification methods.

based nanocomponent (Lee et al., 2011; Wu et al., 2010) have attained more attention owing to facility in fabrication, suitable size and shape. (2) Phase-sensitive based SPR signal enhancement can detect tiny alteration in external properties of target, whereas the traditional SPR type cannot detect these changes (Mohammadzadeh-Asl et al., 2018).

Based on monitoring of amplitude characteristics, conventional SPR sensors lacks of sensitivity for the detection of target analytes having small molecular weight. Recently, phase-sensitive SPR has emerged as an upgrade of this technology, which enables to solve the sensitivity problem (Huang et al., 2012). In general, phase property of a system shows remarkably different behavior for exceptionally close changes of external parameters (for instance optical thickness in SPR sensor). This phenomenon is due to the topological nature of the phase of a system. Because of SPR sensor application in detection of bio and chemical interactions, using phase information of the reflected light would be beneficial for SPR sensitivity improvement (Mohammadzadeh-Asl et al., 2018). Nabok et al. developed a more sensitive SPR sensor based on the phase detection. The aim was to detect molecules that have molecular weight under 500. Electrostatic self-assembly method as a technique to immobilized polyclonal antibody specific to T2 mycotoxin and anti-serums specific to simazine, atrazine herbicide via polyallylamine hydrochloride layer onto the gold surface (Nabok et al., 2007). In-situ study of these analytics were performed by both phase-based and amplitude SPR sensors that phase detection was more sensitive and accurate compared to the amplitude-based SPR (Nabok et al., 2005). In other study, SPR interferometric technique is proposed for determination of 2, 4-d pesticides. However, only qualitative results were presented (Nikitin et al., 1997).

7. Detection of environmental pollution using SPR

7.1. Pesticide

The use of pesticides (e.g., fungicides, herbicides, insecticides) has increased significantly during the last decades. In modern agricultural industry pesticides are widely utilized to control, prevent or eliminate weeds and pests from products (Pundir and Chauhan, 2012; Songa and Okonkwo, 2016). The use of pesticides save almost one-third of crop production from weeds and pests globally. However, the presence of this components in soil, water and food has become a main issue due to environmental problems and their side effects on food consumers (Aspelin et al., 1992). Therefore, contamination with pesticides has attracted more attention and become one of the main problems in food safety. For appropriate control and management of pesticide, some organization, such as the World Health Organization (WHO) and the European Union (EU), have adopted some policies for permitting pesticide use and have established maximum residue level (MRLs) on agricultural products and food industry (Handford et al., 2015). Since some pesticides are mutagenic and carcinogenic and some can cause disorder in the nervous, reproductive and immune systems, at lower concentrations than it was expected, they can be extremely harmful to human health (Bird et al., 2008). Thus, for protection of human health from possible food hazards, determination of pesticide residues is highly demanded.

Traditional chromatographic methods like capillary electrophoresis, HPLC and GC-MS are effective tools for determination of pesticides residue in food and agriculture products but they have certain limitations such as requirement of skilled operator, time consuming, complex sample preparation, and expensive apparatus (Zeng et al., 2007). Therefore, alternative approaches for detection of pesticide residue in a speedy, facile, selective, sensitive and accurate way have been evaluated. In recent years, main attention has been attracted for pesticide analysis via fabrication and developing of optical biosensors such as SPR. There have been some reports about detection of various pesticide by SPR that have been discussed in details in this section.

For determination of thiabendazole in orange sample, Estevez et al. developed a highly specific and sensitive SPR via indirect competitive immunoassay. Under the optimal conditions, SPR-based immunosensor was able to the detect this pesticide with LOD of 0.16 μgL^{-1} and dynamic range between 0.24 and 1.7 $\mu g\,L^{-1}$ by monitoring mass variation (Estevez et al., 2012). SPR based non-competitive direct immunosensor as special sensitive technique for detection of triazophos pesticide in agricultural and environmental samples was developed by Guo et al. (Guo et al., 2018). In this work, antibody kinetics and immunoaffinity characterized via immobilization of two anti-triazophos monoclonal antibodies (mAbs) on the sensor surface (Fig. 5). The biosensor assay indicated an excellent specificity with the LOD of 0.096 $ng\,mL^{-1}$ at linear range of 0.98–8.29 $ng\,mL^{-1}$ for triazophos pesticide.

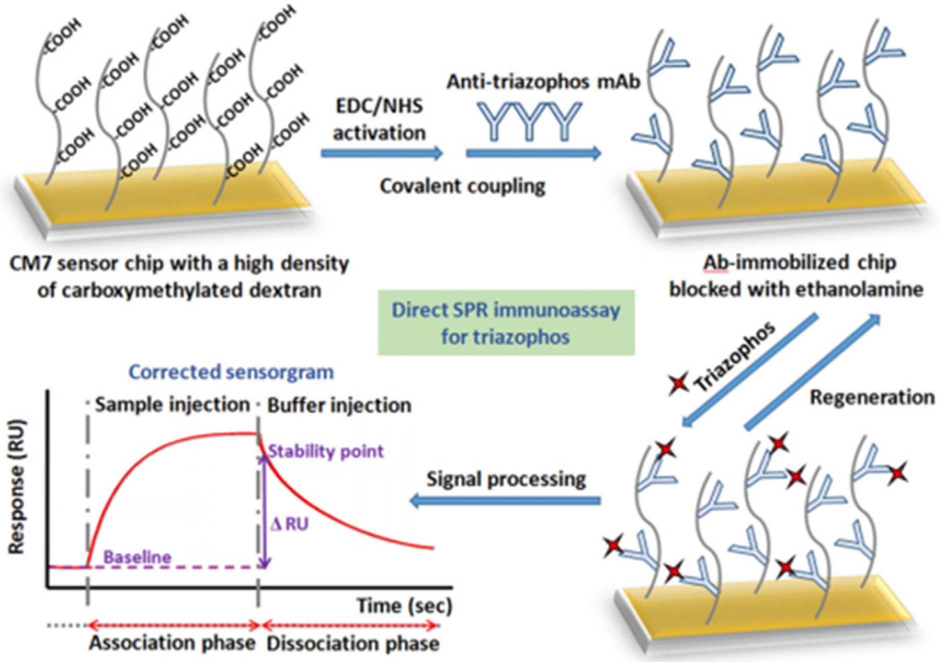

Fig. 5. Schematic illustration of preparation of mAb-immobilized sensor chip CM7 with high density of conjugation amount for direct detection of triazophos by SPR sensorgram for association and dissociation of the immunocomplex. Republished with permission from Guo et al. (2018).

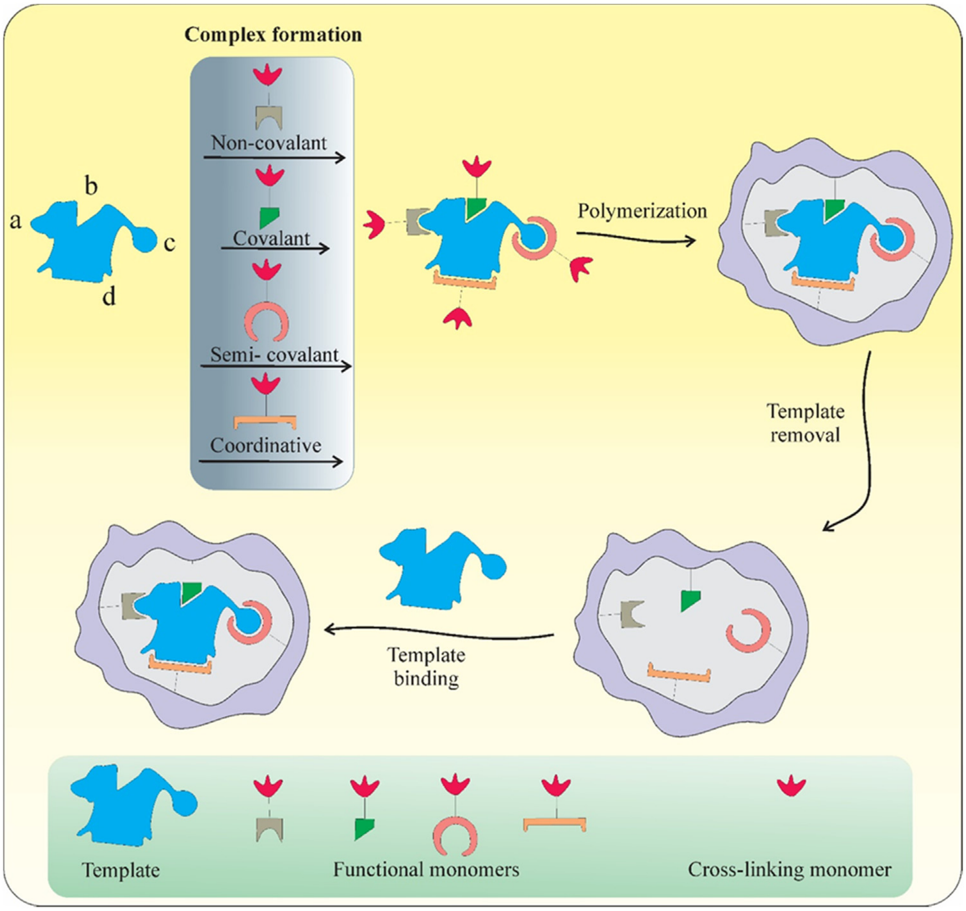

Fig. 6. Highly schematic representation of the molecular imprinting process.

Recently, significant attention has been dedicated to exchange biological receptors with synthetic counterpart as a recognition component in chemo-biosensors for the quick, simple, selective and sensitive detection of pesticides (Llorent-Martínez et al., 2011). Molecularly imprinted polymer (MIP) represents a new type of materials with outstanding mechanical properties that hold high stability and can be extensively utilized to enhance sensitivity and improve the separation efficacy in biosensing field. MIPs as a simple technique to design artificial receptors with specific recognition ability are easily fabricated by in situ polymerization of functional monomer and cross-linker around a template molecule (Fig. 6). SPR biosensor that uses MIPs ultrathin film as sensing material was developed for detection of profenofos in tap water by Dong et al. (Dong et al., 2012). They modified and synthesized SPR chips with MIP ultrathin films via using surface-initiated thermal polymerization, which used as sensing material for enhancing sensitivity. According to target-induced mass change, the MIP-SPR sensing method showed high selectivity, sensitivity and good stability with LOD of 3 0.6×10^{-4} μg mL-1 and recoveries range of 89.81–100.99%.

To solve the MIP sensors relatively low specificity and sensitivity, Yao et al. introduced a methodology for the synthesis of modified SPR sensor chip via integrating of magnetic nanoparticle and MIPs with high density and available recognition sites property for sensitive detection of chlorpyrifos (CPF) (Yao et al., 2013). The magnetic imprinted were fabricated by a facile methodology based on self-polymerization of dopamine on the Fe_3O_4 nanoparticles surface sensor in the presence of template CPF in solution as showed in Fig. 7. The obtained magnetic MIPs nanosphere not only provided direct capture and easy condensation but also detected target analyte in mixture samples in present of external magnetic field as result of significant magnetic properties of Fe_3O_4 core. Therefore, in sensing approach, integrating template-imprinting sites with the magnetic MIPs nanoparticles on the sensor chip via the particular interactions between the stabilized chlorpyrifos and acetylcholinesterase that rebound in the recognition cavities, results in a considerable signal enhancing due to excellent imprinted effect, the high refractive indixes and high molecular weights. The designed sensor showed an acceptable selectivity and specific sensitivity for chlorpyrifos with a dynamic linear range from 0.001 to 10 $\mu molL^{-1}$, satisfactory recoveries ranging from 93% to 104% and the LOD of 0.76 nmol L^{-1} (Yao et al., 2013).

7.2. Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) or polyarenes constitutes are compounds that consist from several aromatic rings and can be characterized by a structure made up of hydrogen and carbon atoms (Kamankesh et al., 2015). These component may be formed and released during the pyrolysis processes and incomplete combustion from natural sources and anthropogenic activity (Šimko, 2002). Significant amount of PAHs are produced by processing coal via burning of petroleum fuel and organic substances such as oil, coal, gas (Simon et al., 2008). These compounds are ubiquitous environmental contaminants and are widespread in atmosphere, soil and water. They have low biodegradability, high lipophilicity, and are potentially highly carcinogenic, genotoxic and mutagenic (Heemken et al., 1997; Wong and Wang, 2001).

Benzo[a]pyrene (BaP) was an example of PAHs that received the most attention due to its carcinogenic effect. It has been identified as an indicator for the determination and occurrence of carcinogenic PAHs in food chain (Purcaro et al., 2013) and maximum levels in a range of foodstuffs are now specified and identified by the International Programme on Chemical Safety (IPCS), Scientific Committee on Food (SCF) and the Joint FAO/WHO Expert Committee on Food Additives (JECFA).

Thereby, the isolation and determination of PAHs in food products are important analytical issues owing to their hazard properties. Analytical approaches for determining these compounds should be sensitive, selective and accurate in order to create a reliable proportion between intake and effects on human health.

Although traditional analytical techniques that developed for the measurement of BaP are precise and sensitive at sub-ppb levels but these techniques have certain limitations involving time-consuming in sample preparation or purification steps and/or tedious radio-labeling processes. Therefore, there is a urgent need for instrumentation that will allow the quick and sensitive in situ determination of PAHs, specifically BaP and other compounds, in various samples at low cost. In 2002, Miura et al. detected BaP by SPR technique for the first time (Miura et al., 2002). The principle of their work was based on SPR immunosensor with indirect inhibition method. These component have a low molecular weight and should conjugate with BSA, thereby, they immobilized the conjugated compound on gold surface of sensor chip. When a complex samples with specified concentration of antibody against BaP were injected through the sensor chip, the intensity of the reflected light changed. This SPR angle shift was equivalent to the concentration of BaP. The sensitivity of incident angle shift to BaP

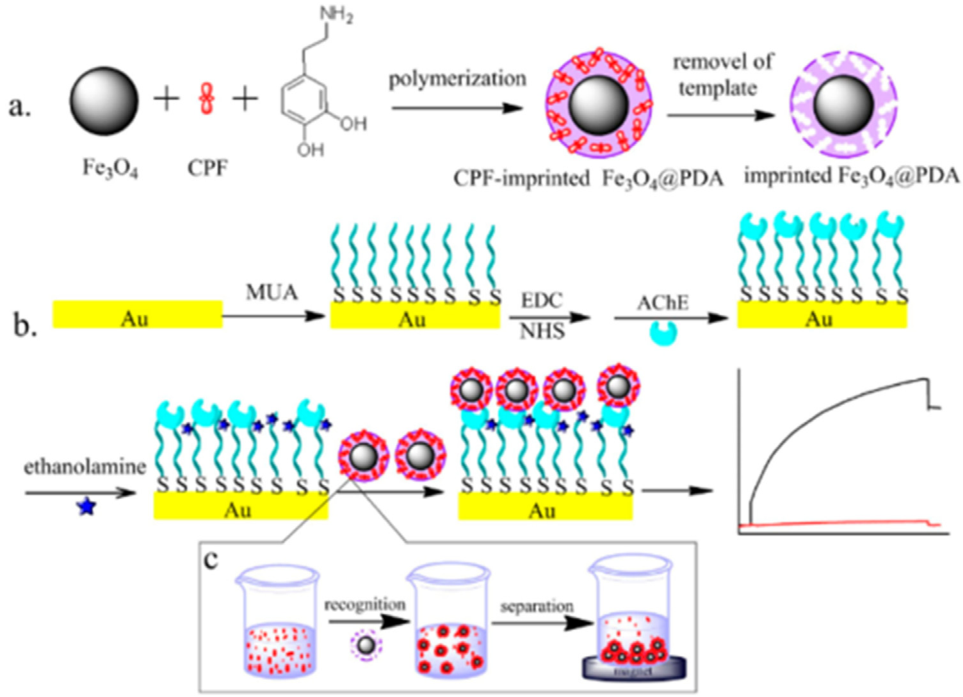

Fig. 7. (a) Preparation of magnetic imprinted Fe_3O_4 @polydopamine nanoparticles (Fe_3O_4 @ PDA) for chlorpyrifos (CPF) recognition, (b) illustration of the stepwise preparation process of the Au surface for CPF detection, and (c) Schematic illustration of recognition and separation of CPF with imprinted Fe_3O_4 @PDA. Republished with permission from Yao et al. (2013).

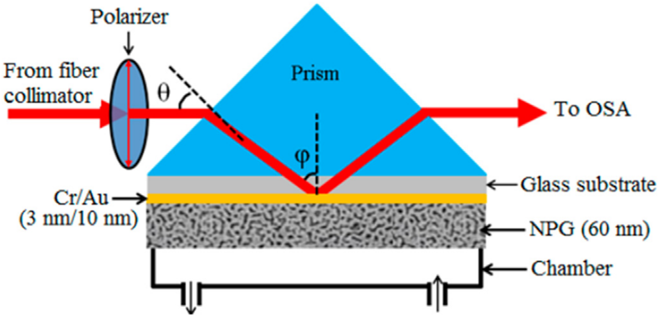

Fig. 8. Schematic diagram of the NPG-film-based wavelength-interrogated SPR sensor platform.
Republished with permission from ref (Wang et al., 2017).

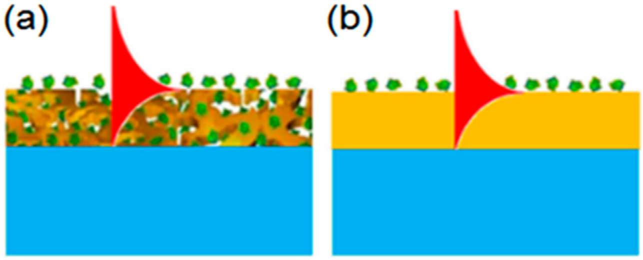

Fig. 9. Schematic diagram illustration of the difference in evanescent wave interaction with adsorbed molecules between (a) the NPG film and (b) the dense gold film. Republished with permission from Wang et al. (2017).

concentration was in the range of 0. 1–300 ppb with LOD of 0.1 ppb. A similar methodology for the determination of 2-hydroxybiphenyl with the same research group were applied (Gobi et al., 2004). In another study, the authors proposed the multiplexing detection method for simultaneous measurement of 2-hydroxybiphenyl (10 ppt - 1000 ppb) and BaP (10ppt - 300ppb) with SPR technique (Gobi and Miura, 2004).

The conventional SPR with a naked gold sensor can determine large biomolecules, and direct detection of small molecules is not possible due to its low sensitivity. This problem is because of formation of only a monolayer of analyte molecules on surface of bare gold film that restrict the depth of interaction between the plasmon field and analyte molecules to the monolayer thickness (Wang et al., 2017). To overcome this problem, Wang et al. proposed nanoporous gold (NPG) films as an alternative technique in SPR sensor for trace detection of BaP (Fig. 8). Application of the NPG film in SPR sensor not only enhanced sensitivity as result of supporting surface plasmon wave and analyte enrichment but also maintained the simple structure of SPR sensors. The NPG film is capable of absorbing a large amount of analyte molecules throughout the entire film thickness, which results in spatial overlap between the adsorbed analyte molecules and the evanescent field. Consequently, the interaction depth for the SPR based NPG-film is much more sensitive than conventional SPR with a naked gold sensor (Fig. 9). The LOD of the SPR sensor with the hydrophobic and functionalized NPG film with antibody were 1 nmol L^{-1} and 5 pmol L^{-1}, respectively. While, the conventional SPR sensor with dense gold film can give a response at BaP concertation of 100 pmolL^{-1}. The sensitivity of the SPR based NPG film is about 20 times larger than that of the conventional SPR sensors with dense gold film. The suggested technique in SPR sensor demonstrated excessive potential for the trace detection and measurement of small-molecule substances in the environment (Wang et al., 2017).

7.3. Heavy metals detection

Due to the increasing and development of industrial activities, contamination of natural environments with heavy metal is a major issue. Usually, heavy metal ions can be categorized into two groups: essential and nonessential. Lead (Pb), cadmium (Cd), arsenic (As) and mercury (Hg) as nonessential metal ions at trace amount exposure can cause a number of harmful effects on the health (Aragay et al., 2011; Zuo et al., 2009). Essential metals like zinc (Zn) and copper (Cu) are necessary to support biological activities (Fox, 2003; G. G. Georgopoulos, 2001). However, in excessive amounts even these essential metals ions can be changed to toxic agents. Numerous environmental organizations including WHO, US Environmental Protection Agency (EPA) and European Medical Agency (EMA) have been standardized permissible levels at ppt to ppm levels for different heavy metal ions based on the literature (Mehta et al., 2016). Most of these components may have a serious threat to human health due to their accumulation and non–biodegradable nature (Verma and Gupta, 2015). Therefore, monitoring the concentration of heavy metal at the trace level has become important issue in food chain, environments and drinking water, etc. Traditional quantitative techniques, such as atomic absorption/emission spectroscopy (Acar, 2005), inductively coupled plasma mass spectrometry (ICPMS) (Pourreza et al., 2009), anodic stripping voltammetry (ASV) (Baldo et al., 2004), and microprobes (Arai et al., 2003) have been comprehensively applied to detect metal ions. These techniques have one or more shortcomings as mentioned in Table 1 compared to SPR method (Kaur et al., 2015).

The principles and schematic illustrations of biorecognition elements for biosensing of heavy metal by SPR with different modification strategies are summarized in Table 2.

7.3.1. Alkanethiol SAM modified chips for heavy metals detection

By modification of SPR sensor chip with an appropriate alkanethiol

Table 1
A comparison of the conventional analytical techniques with SPR for detection of heavy metal ions.

Analytical technique	Detection range	Advantages	Disadvantages
ICPMS	pM to nM	High accuracy and precision; Very high sensitivity; high sample throughput	complicated sample pretreatment; Very high cost of instrumentation; destructive method
AAS	nM	High sensitivity; good accuracy and precision; high sample throughput	Destructive method; High cost of instrumentation; long measuring period; narrow dynamic range
INAA	Sub- nM to µM	High sensitivity and selectivity; good accuracy and precision; large dynamic range non-destructive	Long measuring period (long cooling periods for reduction of short-lived radioactivity); The necessity of nuclear facility for irradiation
XRF	nM to µM	Easy operation; Good selectivity; non-destructive; high sample throughput	Dependence on particle size and homogeneity; High self-absorption of emitted radiation limiting the analysis of thin films or surface layers; strong matrix effects
ASV	nM to µM	Simple and portable; low cost; non-destructive	Interferences problem; only can detect amalgam-forming metals
SPR	pM to µM	Very high sensitivity; able to monitor kinetic behavior; simple sample preparation; label-free detection; low cost; fast measurement capability; no necessity of reference solution; high reproducibility; non destructive	Relatively low selectivity (it can be improved)

can be directly identified some heavy metal ions. Chah et al. developed SPR technique via modification of Au surface with 1, 6 hexanedithiol (HDT) and used as a smart optical sensor for determination of mercuric ion, Hg^{2+}, aqueous solution (Chah et al., 2004). In this study for improvement of the adsorption of Hg^{2+} and enhancing changes in the SPR signals, Au substrate treated with HDT (HDT-Au) to produce SAMs. Enhancement of the SPR signal not only permitted quantification of the concentration of Hg^{2+} from 1.0 nM to 1.0 mM in solution but also could selectively detect Hg^{2+} in the presence of mixtures of heavy metal ions, i.e. Pb^{2+}, Ni^{2+}, Zn^{2+} and Cu^{2+} at the extensive range of concentrations (Chah et al., 2004).

Kang et al. designed a reusable SPR sensor surface via SAMs with the amino-terminated as a molecular recognition element for Cu^{2+} detection (Kang et al., 2005). The Au substrate treated with SAM of 2-aminoethane thiol hydrochloride and thereby the zwitterion-like species on the sensor surface was neutralized with 1 mM NaOH solution. The modified chip can be used to effectively detect and quantified the concentration of Cu^{2+} in the range of 1.0 µM to 1.0 mM. In a similar study, Hong et al. modified sensor chip with two types of SAMs for quantification of Cu^{2+} in solution: 6-aminohexane thiolhydrochloride (AHT) and 2-aminoethane thiolhydrochloride (AET). When the Cu^{2+} concentration was above 1.0 mM, SPR signal change with 6-aminohexane thiolhydrochloride modified chip was much more than that of 2-aminoethane thiolhydrochloride one and thereby the sensitivity becomes higher (Hong et al., 2007).

7.3.2. Biomacromolecule modified chip for heavy metals detection

The detection methods in Alkanethiol SAM relied on the electrostatic binding as a non-specific interaction between the carboxylic acid groups at the termini of preformed alkanethiol SAMs and metal cations. As a result, selective analysis of metal ion can not be completely achieved. Therefore, one of the approaches for attaining selectivity is utilization of biomolecular recognition in SPR sensing technique. There are extensive studies about modification of SPR sensor chip with biomolecular as a recognition element. Forzani et al. modified a high-resolution differential sensor chip with some peptide for determination of Ni^{2+} and Cu^{2+} in the ppt-ppb range. In their work, the NH_2-(His)6-COOH and NH_2-Gly-Gly-His-COOH peptides were coated onto the sensing chip surface for specific-detection of Ni^{2+} and Cu^{2+}, respectively. When metal ions containing solution flow over the sensor chip, due to specific binding between metal ions and properly selected peptides, the differential signal changes obtained, which provides a quantification and accurate real-time measurement of the metal ions. After regeneration by dipping sensor chip in 0.1 M perchloric acid, the designed surface gave a similar response, which showed a good reproducibility of designed sensor (Forzani et al., 2005).

Wu and Lin (2004) developed SPR sensor chip based on immobilization of metallothionein (MT) molecules onto carboxymethylated dextran via covalently interaction for the detection of several Cd, Zn and Ni ions. The binding affinity between the immobilized MT and the metal ions followed the order of Cd > Zn > Ni that shows MT chip good selectively to Cd ion from mixtures of heavy metal ions (Wu and Lin, 2004). Although the chip surface modification with dextran is efficient for non-specific protein adsorption elimination but since metal ions are usually non-discriminately absorbed on the sensor chips, using this component as a film for analysis of trace metal has no inherent advantage (Zhang et al., 2007). Besides, compared to preformed SAMs the dextran film is non-uniform and relatively thick. As a result, this issue could cause incorporation between MT molecules and the metal ions measured at distances further away from the metal film where the evanescent field is weak. For this reason, Zhang et al. modified a sensor chip based on immobilization of MT molecules onto preformed SAMs and they blocked chip surface with glycine-HCl buffer before heavy metal ion analysis. Due to the creation of compacts MT films with a uniform surface orientation, these MT chips have specific sensitivity for Cd^{2+} (0.1 µM or 15 ppb) and Hg^{2+} (5 µM or 1 ppm)

Table 2
Types of biorecognition elements for biosensing of heavy metal by SPR with different modification strategies.

Nanomaterial	Metal selectivity	Probe anchored	Strategies of surface modification	Detection range	References
Au	$Hg^{2.}$	Alkanethiol SAMs	Au substrate treated with 1,6-hexanedithiol to produce self-assembled monolayer (SAMs).	1.0 nM to 1.0 mM	(Chah et al., 2004)
Au	Cu^{2+}	Alkanethiol SAMs	Au substrate treated with of 2-aminoethane thiol hydrochloride and then the zwitterion-like species on the chip surface was neutralized using 1 mM NaOH solution.	1.0 µM to1.0 mM	(Kang et al., 2005)
Au	Cu^{2+}	Alkanethiol SAMs	Au substrate treated with of 6-aminohexane thiolhydrochloride	> 10 µM	(Hong et al., 2007)
Au	Ni^{2+} /Cu^{2+}	Modified biomacromolecule	NH_2-Gly-Gly-His-COOH and NH_2-(His)6-COOH immobilized by amino coupling	–	(Forzani et al., 2005)
Au	Cd^{2+}	Modified biomacromolecule	Mammalian metallothionein immobilized by amino coupling	2–10 µM 20–100 µM 200–1000 µM	(Wu and Lin, 2004)
Au	Cd^{2+}/ Hg^{2+}	Modified biomacromolecule	Apo-metallothioneins attached onto preformed self-assembled monolayers using amino coupling	0.13–200 µM	(Zhang et al., 2007)
Au	Pb^{2+}	Modified biomacromolecule	Immobilized p-*tert*-butylcalix [4] arene-tetrakis (BCAT) in chitosan thin films as an active layer	30 ppb to 5 ppm	(Fen et al., 2012)
Au	Pb^{2+}	Modified biomacromolecule	Chitosan/grapheneoxide nanostructure thin films	0.14–24 µM	(Lokman et al., 2014)
Ag and indium tin oxide (ITO)	Cd^{2+}	Modified biomacromolecule	Metal/metal oxide coated surface modified with pyrrole and chitosan	–	(Verma and Gupta, 2015)
Au	Cu^{2+}	Modified biomacromolecule	Albumin is denatured by heavy metal ions through the disruption of ionic interactions and disulfide bonds and these samples were pre-adsorbed on the surface(Vroman effect)	below 0.1 mg/L	(Wang et al., 2014)
Au	Hg^{2+}	Enhancemet with Nanomaterial	Mercury-specific oligonucleotide SAMs and amplified by gold nanoparticles	5–375 nM	(Wang et al., 2010b)
Au	Ni^{2+}	Enhancemet with Nanomaterial	NTA immobilization and amplification by polyhistidine-functionalized quasispherical Au nanoparticles	0.2–1 nM	(Kim et al., 2012)

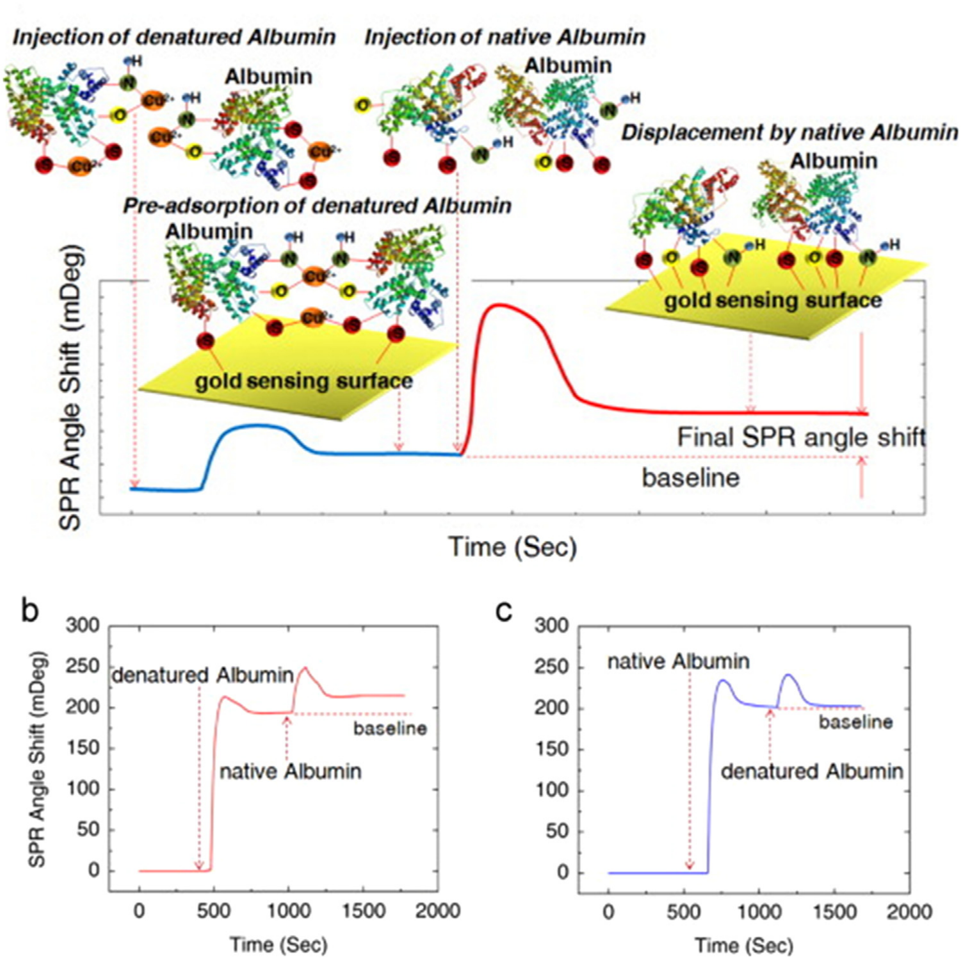

Fig. 10. The SPR angle profile describes the competitive adsorption of albumins. (a) Albumin is denatured by Cu^{2+} through the disruption of ionic interactions and disulfide bonds. Due to the weaker affinity, the pre-adsorbed denatured albumin is displaced by native albumin. Consequently, the conformation change adjacent to the gold sensing surface generates the change of SPR angle shift. (b) Consistent with a, the denatured proteins are replaced by native ones, which generates the increase of SPR angle shift. (c) However, the reverse sequence does not occur, and change of SPR angle shift is negligible. Republished with permission from Wang et al. (2014).

detection (Zhang et al., 2007).

In recent years, chitosan films because of the chelating property have been widely used in modification of SPR sensor chips for quantification of various analytic targets such as heavy metal ions. Fen et al. developed sensor chips based on chitosan thin film. In this study, p-*tert*-butylcalix [4] arene-tetrakis (BCAT) as active layer immobilized on chitosan thin film. Thereby, via spin coating technique; the BCAT immobilized chitosan thin film was coated on a gold layer and utilized for measurement of Pb^{2+} in mixed metal ions (Fen et al., 2012).

Lokman et al. synthesized chitosan/grapheneoxide compound nanostructure thin films for enhancement of sensitivity to detect Pb^{2+} ions at very low concentrations (below -ppb) (Lokman et al., 2014). Verma et al. (Verma and Gupta, 2015) designed and developed an optical fiber based SPR sensor for the quantification of heavy metal ions in the drinking water. For the fabrication of the sensor probe, they utilized silver (Ag) and indium tin oxide (ITO) metal (metal/metal oxide) which is further modified with the coating of pyrrole and chitosan composite. This modified probe was sensitive for all the heavy metal ions and is highly selective and specific sensitive for the Cd^{2+} rather than the other heavy metal ions.

Raghunandhan et al. synthesized fiber optics interferometric sensors based on functionalization with chitosan/polyacrylic acid bilayer for quantification of Ni^{2+} with sensitivity about 0.05 nM/μM (Raghunandhan et al., 2016). In another study, to enhance the sensitivity and selectivity of sensor, Sadrolhosseini et al. demonstrated the electro-deposition technique via immobilization of polypyrrole chitosan/nickel-ferrite thin layer on chip surface (Sadrolhosseini et al., 2017).

To determine copper ions in drinking water, Wang et al. utilized Vroman effect (competitive adsorption of proteins) and combined it with SPR sensor surface. In this work, after denaturation of albumin by heavy metal ions via disruption of disulfide bonds and ionic interactions, this combination were pre-adsorbed onto the sensor probe. After that, the native albumin samples flowed over the modified chip with stronger affinity passed through the pre-adsorbed surface and due to the weaker affinity, denatured albumin is replaced by native albumin, which led to a change in the SPR angle. By using this technique LOD for copper ions reached below 0.1 mg L^{-1} (Fig. 10) (Wang et al., 2014).

7.3.3. Nanomaterial based enhancement for heavy metals detection

Designing and modification in SPR chip probe with nanomaterials can improve and enhance measurements of heavy metal. Wang et al. proposed a technique for quantification of Hg^{2+} in aqueous solution with a low detection level and high sensitivity. In these study; firstly, mercury-specific oligonucleotide (MSO) probe immobilized on gold film via interaction of Au–S bond between gold film and DNA (L. Wang et al., 2010). Then sample containing Hg^{2+} flow over the modified chip surface, which results in free Hg^{2+} capturing by MSO probe with initial LOD of 0.3 μM. Finally, the detection level of this Hg^{2+} sensor significantly enhanced under amplifying of SPR signals based Au nanoparticle, which led to a LOD of 5 nM. In another work, Kim et al. demonstrated nanoparticle based SPR signal enhancement for detection of Ni(II) ions. Briefly, they immobilized Maleimido-modified N-[5-(3′-maleimidopropylamido)-carboxypentyl] iminodiacetic acid (NTA) onto 1,6-hexanedithiol-modified Au SPR chip and then used it for adsorption of Ni(II) ions in absence and presence of polyhistidine-functionalized quasispherical Au nanoparticles. They showed that signal enhancement with Au nanoparticles led to detect Ni(II) ions as low as 50 parts per trillion (ppt) (Kim et al., 2012).

7.4. Polychlorinated biphenyls

Polychlorinated biphenyls (PCBs) are ubiquitous environmental contaminants that extensively utilized in various industry as well as capacitors, condensers and transformers (Pascall et al., 2005). These organic chlorine compounds are composed of biphenyl ring that linked to 1–10 chlorine atoms. PCBs as a most dangerous synthetic chemicals have a destructive effect on immune functions and endogenous hormones and stimulate the formation of malignancies (Bender and Sadik, 1998; Renner, 1999). Therefore, regarding to their environmental and biological significance, a number of protocols and techniques have been established to identify or monitor PCBs. Several biosensors have been developed for quantification of PCBs in various environmental and industrial samples. DNA biosensor based on chronopotentiometric detection (Marrazza et al., 1999), fluorescence based immunosensors (Zhao et al., 1995), SPR (Shimomura et al., 2001), and electrochemical detection (Del Carlo et al., 1997) are examples of various techniques that has been used for PCBs detection. Among the different sensing methodology, SPR based sensor is a good candidate for measurement of PCBs. Yi et al. reported SPR based sensor as a high sensitive technique for quantification of PCB in an aqueous solution through evaluation of conformational change of Cytochrome c (Cyt c) that induced by PCB. The detection mechanism was based on the immobilization of Cyt c as a recognition element onto the Au thin film and monitoring of signal changes in smart sensing layer by SPR at a concentration of 0.1–8.0 ppb (Hong et al., 2008).

8. Conclusion and future trends

Herein, promising feature and basic concepts of the SPR based sensor, together with the monitoring and measurement of important environmental pollutants via different assay formats such as competitive inhibition assay, sandwich assay and Au nanoparticle-based assay have been highlighted. SPR as a potent analysis technique offers high selectivity and sensitivity, label-free detection in real-time with minimal sample preparation. Recently, SPR effectively utilized in determination of environmental pollutants in foodstuff and significant progress has been made on the detection of various pollutants including pesticide, PAHs, heavy metals and polychlorinated biphenyls via appropriate surface modification. It is strongly believed that with the increasing interest in smart sensing SPR and the further progresses of other fields such as microelectronics, material sciences, molecular biology, and engineering, this technique has great capability to be used in various chemicals evaluation and sensing.

Acknowledgment

The authors gratefully acknowledge the financial support of this study by the Tabriz University of Medical Sciences, which was a part of Ph.D thesis, Tabriz, Iran.

Conflict of interests

The authors declare that they have no conflict of interests.

Declarations of interest

None.

References

Acar, O., 2005. Determination of cadmium, copper and lead in soils, sediments and sea water samples by ETAAS using a Sc+ Pd+ NH4NO3 chemical modifier. Talanta 65 (3), 672–677.

Anfossi, L., Di Nardo, F., Cavalera, S., Giovannoli, C., Spano, G., Speranskaya, E.S., Goryacheva, I.Y., Baggiani, C., 2018. A lateral flow immunoassay for straightforward determination of fumonisin mycotoxins based on the quenching of the fluorescence of CdSe/ZnS quantum dots by gold and silver nanoparticles. Microchim. Acta 185 (2), 94.

Aragay, G., Pons, J., Merkoçi, A., 2011. Recent trends in macro-, micro-, and nanomaterial-based tools and strategies for heavy-metal detection. Chem. Rev. 111 (5), 3433–3458.

Arai, Y., Lanzirotti, A., Sutton, S., Davis, J., Sparks, D., 2003. Arsenic speciation and reactivity in poultry litter. Environ. Sci. Technol. 37 (18), 4083–4090.

Arora, P., Sindhu, A., Dilbaghi, N., Chaudhury, A., 2011. Biosensors as innovative tools for the detection of food borne pathogens. Biosens. Bioelectron. 28 (1), 1–12.

Aspelin, A.L., Grube, A.H., Torla, R., 1992. Pesticides Industry Sales and Usage: 1990 and 1991 Marked Estimates. EPA, Washington, US.

Baldo, M.A., Daniele, S., Ciani, I., Bragato, C., Wang, J., 2004. Remote stripping analysis of lead and copper by a mercury-coated platinum microelectrode. Electroanal.: Int. J. Devoted Fundam. Pract. Asp. Electroanal. 16 (5), 360–366.

Bender, S., Sadik, O.A., 1998. Direct electrochemical immunosensor for polychlorinated biphenyls. Environ. Sci. Technol. 32 (6), 788–797.

Bergström, G., Mandenius, C.-F., 2011. Orientation and capturing of antibody affinity ligands: applications to surface plasmon resonance biochips. Sens. Actuators B: Chem. 158 (1), 265–270.

Bird, S.B., Sutherland, T.D., Gresham, C., Oakeshott, J., Scott, C., Eddleston, M., 2008. OpdA, a bacterial organophosphorus hydrolase, prevents lethality in rats after poisoning with highly toxic organophosphorus pesticides. Toxicology 247 (2–3), 88–92.

Chah, S., Yi, J., Zare, R.N., 2004. Surface plasmon resonance analysis of aqueous mercuric ions. Sens. Actuators B: Chem. 99 (2–3), 216–222.

De Feijter, J., Benjamins, dJ., Veer, F., 1978. Ellipsometry as a tool to study the adsorption behavior of synthetic and biopolymers at the air–water interface. Biopolym.: Original Res. Biomol. 1759–1772.

Del Carlo, M., Lionti, I., Taccini, M., Cagnini, A., Mascini, M., 1997. Disposable screen-printed electrodes for the immunochemical detection of polychlorinated biphenyls. Anal. Chim. Acta 342 (2–3), 189–197.

Dolatabadi, J.E.N., de la Guardia, M., 2014. Nanomaterial-based electrochemical immunosensors as advanced diagnostic tools. Anal. Methods 6 (12), 3891–3900.

Dolatabadi, J.E.N., Omidi, Y., 2016. Solid lipid-based nanocarriers as efficient targeted drug and gene delivery systems. TrAC Trends Anal. Chem. 77, 100–108.

Dong, J., Gao, N., Peng, Y., Guo, C., Lv, Z., Wang, Y., Zhou, C., Ning, B., Liu, M., Gao, Z., 2012. Surface plasmon resonance sensor for profenofos detection using molecularly imprinted thin film as recognition element. Food Control 25 (2), 543–549.

Estevez, M.-C., Belenguer, J., Gomez-Montes, S., Miralles, J., Escuela, A.M., Montoya, A., Lechuga, L.M., 2012. Indirect competitive immunoassay for the detection of fungicide Thiabendazole in whole orange samples by surface plasmon resonance. Analyst 137 (23), 5659–5665.

Ezzati Nazhad Dolatabadi, J., Azami, A., Mohammadi, A., Hamishehkar, H., Panahi-Azar, V., Rahbar Saadat, Y., Saei, A.A, 2018. Formulation, characterization and cytotoxicity evaluation of ketotifen-loaded nanostructured lipid carriers. J. Drug Deliv. Sci. Technol. 46, 268–273.

Fathi, F., Mohammadzadeh-Aghdash, H., Sohrabi, Y., Dehghan, P., Ezzati Nazhad Dolatabadi, J., 2018. Kinetic and thermodynamic studies of bovine serum albumin interaction with ascorbyl palmitate and ascorbyl stearate food additives using surface plasmon resonance. Food Chem. 246, 228–232.

Fen, Y.W., Yunus, W.M.M., Yusof, N.A., 2012. Surface plasmon resonance optical sensor for detection of Pb2+ based on immobilized p-tert-butylcalix [4] arene-tetrakis in chitosan thin film as an active layer. Sens. Actuators B: Chem. 171, 287–293.

Forzani, E.S., Zhang, H., Chen, W., Tao, N., 2005. Detection of heavy metal ions in drinking water using a high-resolution differential surface plasmon resonance sensor. Environ. Sci. Technol. 39 (5), 1257–1262.

Fox, P.L., 2003. The copper-iron chronicles: the story of an intimate relationship. Biometals 16 (1), 9–40.

G. Georgopoulos, A.R., Yonone-Lioy, M.J., Opiekun, R.E., PJ Lioy, P., 2001. Environmental copper: its dynamics and human exposure issues. J. Toxicol. Environ. Health Part B: Crit. Rev. 4 (4), 341–394.

Gao, C., Lu, Z., Liu, Y., Zhang, Q., Chi, M., Cheng, Q., Yin, Y., 2012. Highly stable silver nanoplates for surface plasmon resonance biosensing. Angew. Chem. Int. Ed. 51 (23), 5629–5633.

Ghrera, A.S., Pandey, M.K., Malhotra, B.D., 2016. Quantum dot monolayer for surface plasmon resonance signal enhancement and DNA hybridization detection. Biosens. Bioelectron. 80, 477–482.

Gobi, K.V., Miura, N., 2004. Highly sensitive and interference-free simultaneous detection of two polycyclic aromatic hydrocarbons at parts-per-trillion levels using a surface plasmon resonance immunosensor. Sens. Actuators B: Chem. 103 (1–2), 265–271.

Gobi, K.V., Tanaka, H., Shoyama, Y., Miura, N., 2004. Continuous flow immunosensor for highly selective and real-time detection of sub-ppb levels of 2-hydroxybiphenyl by using surface plasmon resonance imaging. Biosens. Bioelectron. 20 (2), 350–357.

Guo, Y., Liu, R., Liu, Y., Xiang, D., Liu, Y., Gui, W., Li, M., Zhu, G., 2018. A non-competitive surface plasmon resonance immunosensor for rapid detection of triazophos residue in environmental and agricultural samples. Sci. Total Environ. 613, 783–791.

Handford, C.E., Elliott, C.T., Campbell, K., 2015. A review of the global pesticide legislation and the scale of challenge in reaching the global harmonization of food safety standards. Integr. Environ. Assess. Manag. 11 (4), 525–536.

Heemken, O.P., Theobald, N., Wenclawiak, B.W., 1997. Comparison of ASE and SFE with soxhlet, sonication, and methanolic saponification extractions for the determination of organic micropollutants in marine particulate matter. Anal. Chem. 69 (11), 2171–2180.

Hong, S., Kang, T., Moon, J., Oh, S., Yi, J., 2007. Surface plasmon resonance analysis of aqueous copper ions with amino-terminated self-assembled monolayers. Colloids Surf. A: Physicochem. Eng. Asp. 292 (2–3), 264–270.

Hong, S., Kang, T., Oh, S., Moon, J., Choi, I., Choi, K., Yi, J., 2008. Label-free sensitive optical detection of polychlorinated biphenyl (PCB) in an aqueous solution based on surface plasmon resonance measurements. Sens. Actuators B: Chem. 134 (1), 300–306.

Huang, Y.H., Ho, H.P., Kong, S.K., Kabashin, A.V., 2012. Phase-sensitive surface plasmon resonance biosensors: methodology, instrumentation and applications. Ann. Phys. 524 (11), 637–662.

Jamali, A.A., Pourhassan-Moghaddam, M., Dolatabadi, J.E.N., Omidi, Y., 2014. Nanomaterials on the road to microRNA detection with optical and electrochemical nanobiosensors. TrAC Trends Anal. Chem. 55, 24–42.

Jia, Y., Peng, Y., Bai, J., Zhang, X., Cui, Y., Ning, B., Cui, J., Gao, Z., 2018. Magnetic nanoparticle enhanced surface plasmon resonance sensor for estradiol analysis. Sens. Actuators B: Chem. 254, 629–635.

Kabashin, A., Evans, P., Pastkovsky, S., Hendren, W., Wurtz, G., Atkinson, R., Pollard, R., Podolskiy, V., Zayats, A., 2009. Plasmonic nanorod metamaterials for biosensing. Nat. Mater. 8 (11), 867.

Kamankesh, M., Mohammadi, A., Hosseini, H., Tehrani, Z.M., 2015. Rapid determination of polycyclic aromatic hydrocarbons in grilled meat using microwave-assisted extraction and dispersive liquid–liquid microextraction coupled to gas chromatography–mass spectrometry. Meat Sci. 103, 61–67.

Kampa, M., Castanas, E., 2008. Human health effects of air pollution. Environ. Pollut. 151 (2), 362–367.

Kang, T., Hong, S., Moon, J., Oh, S., Yi, J., 2005. Fabrication of reusable sensor for detection of Cu 2+ in an aqueous solution using a self-assembled monolayer with surface plasmon resonance spectroscopy. Chem. Commun. 29, 3721–3723.

Kaur, B., Srivastava, R., Satpati, B., 2015. Ultratrace detection of toxic heavy metal ions found in water bodies using hydroxyapatite supported nanocrystalline ZSM-5 modified electrodes. New J. Chem. 39 (7), 5137–5149.

Kim, E.J., Chung, B.H., Lee, H.J., 2012. Parts per trillion detection of Ni (II) ions by nanoparticle-enhanced surface plasmon resonance. Anal. Chem. 84 (22), 10091–10096.

Kolomenskii, A.A., Gershon, P., Schuessler, H., 1997. Sensitivity and detection limit of concentration and adsorption measurements by laser-induced surface-plasmon resonance. Appl. Opt. 36 (25), 6539–6547.

Kong, F., Hu, Y.F., 2012. Biomolecule immobilization techniques for bioactive paper fabrication. Anal. Bioanal. Chem. 403 (1), 7–13.

Law, W.-C., Yong, K.-T., Baev, A., Prasad, P.N., 2011. Sensitivity improved surface plasmon resonance biosensor for cancer biomarker detection based on plasmonic enhancement. ACS Nano 5 (6), 4858–4864.

Lee, E.G., Park, K.M., Jeong, J.Y., Lee, S.H., Baek, J.E., Lee, H.W., Jung, J.K., Chung, B.H., 2011. Carbon nanotube-assisted enhancement of surface plasmon resonance signal. Anal. Biochem. 408 (2), 206–211.

Lin, S., Zhang, B., Skoumal, M.J., Ramunno, B., Li, X., Wesdemiotis, C., Liu, L., Jia, L., 2011. Antifouling poly (β-peptoid) s. Biomacromolecules 12 (7), 2573–2582.

Llorent-Martínez, E., Ortega-Barrales, P., Fernández-de Córdova, M., Ruiz-Medina, A., 2011. Trends in flow-based analytical methods applied to pesticide detection: a review. Anal. Chim. Acta 684 (1–2), 30–39.

Lokman, N.F., Bakar, A.A.A., Suja, F., Abdullah, H., Ab Rahman, W.B.W., Huang, N.-M., Yaacob, M.H., 2014. Highly sensitive SPR response of Au/chitosan/graphene oxide nanostructured thin films toward Pb (II) ions. Sens. Actuators B: Chem. 195, 459–466.

Marrazza, G., Chianella, I., Mascini, M., 1999. Disposable DNA electrochemical biosensors for environmental monitoring. Anal. Chim. Acta 387 (3), 297–307.

Mehta, J., Bhardwaj, S.K., Bhardwaj, N., Paul, A., Kumar, P., Kim, K.-H., Deep, A., 2016. Progress in the biosensing techniques for trace-level heavy metals. Biotechnol. Adv. 34 (1), 47–60.

Miura, N., Sasaki, M., Sakai, G., Gobi, K.V., 2002. Regenerable surface plasmon resonance (SPR)-based immunosensor for highly sensitive measurement of sub-ppb levels of benzo (a) pyrene. Chem. Lett. 31 (3), 342–343.

Mohammadzadeh-Asl, S., Keshtkar, A., Dolatabadi, J.E.N., de la Guardia, M., 2018. Nanomaterials and phase sensitive based signal enhancment in surface plasmon resonance. Biosens. Bioelectron.

Mokhtarzadeh, A., Alibakhshi, A., Hejazi, M., Omidi, Y., Dolatabadi, J.E.N., 2016. Bacterial-derived biopolymers: advanced natural nanomaterials for drug delivery and tissue engineering. TrAC Trends Anal. Chem. 82, 367–384.

Nabok, A.V., Tsargorodskaya, A., Hassan, A.K., Starodub, N.F., 2005. Total internal reflection ellipsometry and SPR detection of low molecular weight environmental toxins. Appl. Surf. Sci. 246 (4), 381–386.

Nabok, A.V., Tsargorodskaya, A., Holloway, A., Starodub, N.F., Gojster, O., 2007. Registration of T-2 mycotoxin with total internal reflection ellipsometry and QCM impedance methods. Biosens. Bioelectron. 22 (6), 885–890.

Nakamura, C., Hasegawa, M., Nakamura, N., Miyake, J., 2003. Rapid and specific detection of herbicides using a self-assembled photosynthetic reaction center from purple bacterium on an SPR chip. Biosens. Bioelectron. 18 (5–6), 599–603.

Nikitin, P., Kabashin, A., Ksenevich, T., Kalabina, N., 1997. Bio-optoelectronical "tongue" for detection of pesticide contamination of water, In: Proceedings of International Solid State Sensors and Actuators Conference (Transducers '97), pp. 495–497 vol.491.

Olaru, A., Bala, C., Jaffrezic-Renault, N., Aboul-Enein, H.Y., 2015. Surface plasmon resonance (SPR) biosensors in pharmaceutical analysis. Crit. Rev. Anal. Chem. 45 (2), 97–105.

Palchetti, I., Mascini, M., 2008. Electroanalytical biosensors and their potential for food pathogen and toxin detection. Anal. Bioanal. Chem. 391 (2), 455–471.

Pascall, M.A., Zabik, M.E., Zabik, M.J., Hernandez, R.J., 2005. Uptake of polychlorinated biphenyls (PCBs) from an aqueous medium by polyethylene, polyvinyl chloride, and polystyrene films. J. Agric. Food Chem. 53 (1), 164–169.

Pourreza, N., Parham, H., Kiasat, A., Ghanemi, K., Abdollahi, N., 2009. Solid phase extraction of mercury on sulfur loaded with N-(2-chloro benzoyl)-N′-phenylthiourea as a new adsorbent and determination by cold vapor atomic absorption spectrometry. Talanta 78 (4–5), 1293–1297.

Pundir, C.S., Chauhan, N., 2012. Acetylcholinesterase inhibition-based biosensors for pesticide determination: a review. Anal. Biochem. 429 (1), 19–31.

Purcaro, G., Moret, S., Conte, L.S., 2013. Overview on polycyclic aromatic hydrocarbons: occurrence, legislation and innovative determination in foods. Talanta 105, 292–305.

Raghunandhan, R., Chen, L., Long, H., Leam, L., So, P., Ning, X., Chan, C., 2016. Chitosan/PAA based fiber-optic interferometric sensor for heavy metal ions detection. Sens. Actuators B: Chem. 233, 31–38.

Renner, R., 1999. Researchers question statistical power of PCB cancer study. Environ. Sci. Technol. 33 (9) (187A-187A).

Riskin, M., Tel-Vered, R., Lioubashevski, O., Willner, I., 2009. Ultrasensitive surface plasmon resonance detection of trinitrotoluene by a bis-aniline-cross-linked Au nanoparticles composite. J. Am. Chem. Soc. 131 (21), 7368–7378.

Rodriguez-Mozaz, S., Marco, M.-P., De Alda, M.L., Barceló, D., 2004. Biosensors for environmental applications: future development trends. Pure Appl. Chem. 76 (4), 723–752.

Sadrolhosseini, A.R., Naseri, M., Rashid, S.A., 2017. Polypyrrole-chitosan/nickel-ferrite nanoparticle composite layer for detecting heavy metal ions using surface plasmon resonance technique. Opt. Laser Technol. 93, 216–223.

Severs, A., Schasfoort, R., Salden, M., 1993. An immunosensor for syphilis screening based on surface plasmon resonance. Biosens. Bioelectron. 8 (3–4), 185–189.

Sharifi, M., Dolatabadi, J.E.N., Fathi, F., Rashidi, M., Jafari, B., Tajalli, H., Rashidi, M.-R., 2017a. Kinetic and thermodynamic study of bovine serum albumin interaction with rifampicin using surface plasmon resonance and molecular docking methods. J. Biomed. Opt. 22 (3), 037002.

Sharifi, M., Dolatabadi, J.E.N., Fathi, F., Zakariazadeh, M., Barzegar, A., Rashidi, M., Tajalli, H., Rashidi, M.-R., 2017b. Surface plasmon resonance and molecular docking studies of bovine serum albumin interaction with neomycin: kinetic and thermodynamic analysis. BioImpacts: BI 7 (2), 91.

Shimomura, M., Nomura, Y., Zhang, W., Sakino, M., Lee, K.-H., Ikebukuro, K., Karube, I., 2001. Simple and rapid detection method using surface plasmon resonance for dioxins, polychlorinated biphenylx and atrazine. Anal. Chim. Acta 434 (2), 223–230.

Šimko, P., 2002. Determination of polycyclic aromatic hydrocarbons in smoked meat products and smoke flavouring food additives. J. Chromatogr. B 770 (1–2), 3–18.

Simon, R., Ruiz, J.A.G., von Holst, C., Wenzl, T., Anklam, E., 2008. Results of a European inter-laboratory comparison study on the determination of EU priority polycyclic aromatic hydrocarbons (PAHs) in edible vegetable oils. Anal. Bioanal. Chem. 391 (4), 1397–1408.

Songa, E.A., Okonkwo, J.O., 2016. Recent approaches to improving selectivity and sensitivity of enzyme-based biosensors for organophosphorus pesticides: a review. Talanta 155, 289–304.

Stefan, L., Johnsson, B., Edström, Å., Hansson, A., Lindquist, G., Hillgren, R.-M.M., Stigh, L., 1995. Methods for site controlled coupling to carboxymethyldextran surfaces in surface plasmon resonance sensors. Biosens. Bioelectron. 10 (9–10), 813–822.

Taghipour, P., Zakariazadeh, M., Sharifi, M., Ezzati Nazhad Dolatabadi, J., Barzegar, A., 2018. Bovine serum albumin binding study to erlotinib using surface plasmon resonance and molecular docking methods. J. Photochem. Photobiol. B: Biol. 183, 11–15.

Tumolo, T., Angnes, L., Baptista, M.S., 2004. Determination of the refractive index increment (dn/dc) of molecule and macromolecule solutions by surface plasmon resonance. Anal. Biochem. 333 (2), 273–279.

Ulman, A., 1996. Formation and structure of self-assembled monolayers. Chem. Rev. 96 (4), 1533–1554.

Verma, R., Gupta, B.D., 2015. Detection of heavy metal ions in contaminated water by surface plasmon resonance based optical fibre sensor using conducting polymer and chitosan. Food Chem. 166, 568–575.

Wang, J., Lv, R., Xu, J., Xu, D., Chen, H., 2008. Characterizing the interaction between aptamers and human IgE by use of surface plasmon resonance. Anal. Bioanal. Chem. 390 (4), 1059–1065.

Wang, J., Munir, A., Zhu, Z., Zhou, H.S., 2010a. Magnetic nanoparticle enhanced surface plasmon resonance sensing and its application for the ultrasensitive detection of magnetic nanoparticle-enriched small molecules. Anal. Chem. 82 (16), 6782–6789.

Wang, L., Li, T., Du, Y., Chen, C., Li, B., Zhou, M., Dong, S., 2010b. Au NPs-enhanced surface plasmon resonance for sensitive detection of mercury (II) ions. Biosens. Bioelectron. 25 (12), 2622–2626.

Wang, L., Wan, X.-M., Gao, R., Lu, D.-F., Qi, Z.-M., 2017. Nanoporous gold films prepared by a combination of sputtering and dealloying for trace detection of benzo [a] pyrene based on surface plasmon resonance spectroscopy. Sensors 17 (6), 1255.

Wang, R., Wang, W., Ren, H., Chae, J., 2014. Detection of copper ions in drinking water using the competitive adsorption of proteins. Biosens. Bioelectron. 57, 179–185.

Wei, J., Mu, Y., Song, D., Fang, X., Liu, X., Bu, L., Zhang, H., Zhang, G., Ding, J., Wang, W., 2003. A novel sandwich immunosensing method for measuring cardiac troponin I in sera. Anal. Biochem. 321 (2), 209–216.

Wong, P., Wang, J., 2001. The accumulation of polycyclic aromatic hydrocarbons in lubricating oil over time—a comparison of supercritical fluid and liquid–liquid extraction methods. Environ. Pollut. 112 (3), 407–415.

Wu, C.-M., Lin, L.-Y., 2004. Immobilization of metallothionein as a sensitive biosensor chip for the detection of metal ions by surface plasmon resonance. Biosens. Bioelectron. 20 (4), 864–871.

Wu, L., Chu, H., Koh, W., Li, E., 2010. Highly sensitive graphene biosensors based on surface plasmon resonance. Opt. Express 18 (14), 14395–14400.

Yao, G.-H., Liang, R.-P., Huang, C.-F., Wang, Y., Qiu, J.-D., 2013. Surface plasmon resonance sensor based on magnetic molecularly imprinted polymers amplification for pesticide recognition. Anal. Chem. 85 (24), 11944–11951.

Zeng, K., Yang, T., Zhong, P., Zhou, S., Qu, L., He, J., Jiang, Z., 2007. Development of an indirect competitive immunoassay for parathion in vegetables. Food Chem. 102 (4), 1076–1082.

Zhang, Y., Xu, M., Wang, Y., Toledo, F., Zhou, F., 2007. Studies of metal ion binding by apo-metallothioneins attached onto preformed self-assembled monolayers using a highly sensitive surface plasmon resonance spectrometer. Sens. Actuators B: Chem. 123 (2), 784–792.

Zhao, C.Q., Anis, N.A., Rogers, K.R., Kline Jr, R.H., Wright, J., Eldefrawi, A.T., Eldefrawi, M.E., 1995. Fiber optic immunosensor for polychlorinated biphenyls. J. Agric. Food Chem. 43 (8), 2308–2315.

Zuo, P., Yin, B.-C., Ye, B.-C., 2009. DNAzyme-based microarray for highly sensitive determination of metal ions. Biosens. Bioelectron. 25 (4), 935–939.