Development of Surface Plasmon Resonance Spectroscopy
for Metal Ion Detection

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Surface plasmon resonance (SPR) spectroscopy has emerged as an optical sensor for sensing a variety of analytes, including metal ions. However, despite its numerous advantages, which include very high sensitivity, simple sample preparation, low cost, fast measurement capability, no requirement for reference solution, high reproducibility, ability to monitor kinetic behaviour, label-free detection, and nondestructiveness, the SPR optical sensor has to compete with existing methods especially in terms of sensitivity and selective detection. A critical review of the use of SPR in metal ion detection is presented. It describes the instrument and different developments on active layers or recognition molecules for sensitivity and selectivity improvements. In conclusion, progress in SPR optical sensor technology will further expand SPR detection abilities and allow SPR sensing to be used widely including in environmental monitoring as an effective metal ion sensor in the future.

1. Introduction

Metal ions are very important in biological systems as they play an essential role in enzymes. Metal ions can effectively control an enzyme-catalysed reaction by modifying electron flow in a substrate or enzyme.[1] Metal ions such as the potassium (K^+) ion are essential for detecting cardiovascular diseases, as K^+ ion quantity regularities allow the disease to be identified early.[2] On the other hand, zinc (Zn^{2+}) as the second most abundant transition metal after iron (Fe^{2+}), at approximately 2 to 3 g in total, is important in enzyme regulators, DNA binding, catalytic centres, and structural cofactors. Zn^{2+} disorder can lead to Alzheimer's disease, amyotrophic lateral sclerosis (ALS), Guam ALS-Parkinsonism dementia, Parkinson's disease, hypoxia-ischemia, and epilepsy,[3] while lack of Fe^{2+} can cause paediatric iron deficiency anaemia.[4] Other metal ions such as magnesium (Mg^{2+}) and copper (Cu^{2+}) concentrations and distributions are tightly controlled. For example, Mg^{2+} is essential as an enzyme activator for neuromuscular excitability and cell permeability. Besides, Mg^{2+} also plays an important role in cellular proliferation and apoptosis.[5] Cu^{2+} is a crucial micronutrient in cellular homeostasis,

gene transcription, and neural signal transmission.[6]   Another metal ion that is important in biological systems is nickel (Ni^{2+}). It is considered to play a role in physiological processes as a cofactor in the absorption of iron from the intestine. It is also reported that the lack of nickel in the human body can lead to certain liver and kidney diseases.[7]

However, metal ions can also be very harmful to biological systems owing to their highly toxic properties. Metal ion imbalance can lead to many diseases that are related to the abnormal accumulation of metal ions in a cell.[8]   Such metal ions include lead, mercury, cadmium, chromium, and arsenic. Lead (Pb^{2+}) ions at a very low concentration, for example, can damage the brain, central nervous system, and kidneys in adults or children,[9] while mercury (Hg^{2+}) can cause loss of myelinated nerve fibres, autonomic dysfunction, and abnormal central nervous system cell division.[10] The most toxic metal ion is cadmium (Cd^{2+}). It is not required even in trace amounts in the human body, and excessive exposure to Cd^{2+} can damage bones, kidneys, liver, intestines, and the brain.[11]   Chromium ion, on the other hand, can exist in several forms of "valence states", which are divalent, trivalent, and hexavalent. At trace levels, Cr^{3+} is essential to human health. However, Cr^{5+} is known to be very toxic owing to its high mobility in aqueous solutions, and exposure to Cr^{5+} can increase the risk of lung cancer even at low concentrations.[12]   Last but not the least, arsenic can lead to serious damage to biological systems, including the dermal, cardiovascular, renal, nervous, hepatic, endocrine, and haematological systems.[13]

Metal ion determination in the environment is a challenging subject because the concentration ranges set by standards and guidelines are related to toxicity. Most of the metal ion permissible limits are in the range of ppt to ppm levels. Therefore, an effective technique is needed for carrying out repetitive analyses in metal ion detection for environmental protection, quality control, general public health, and industrial operations.

To date, several sensors have been developed for sensing metal ions in aqueous solutions, namely, atomic absorption spectroscopy,[14] inductively coupled plasma mass spectrometry,[15] inductively coupled plasma atomic emission spectrometry,[16] anodic stripping voltammetry (ASV),[17] X-ray fluorescence spectrometry,[18] and instrumental neutron activation analysis.[19] Although these sensors have their own advantages, each has one or more disadvantages, which include destructiveness, high cost, interference effect, complicated sample treatment, and long measurement time.[20]   To overcome the disadvantages of these conventional methods, researchers have focused on other methods such as optical sensors.

Surface plasmon resonance (SPR) is one of the favourable optical tools that are mainly used for the detection of biochemical interaction. SPR measurement is also widely used in chemistry and biochemistry to characterise biological surfaces and to observe and track any binding events owing to its advantages. For example, the biomolecular interaction kinetic can be measured in real time, and unlabelled analyte molecule adsorption to the surface can be tracked with a high degree of SPR surface sensitivity. Moreover, when applied to a biosensor and a chemical sensor, SPR has many advantages that include low cost, low mass, high sensitivity, and linear properties.

2.   SPR Principal Operation

Basically, light will be partially refracted and partially reflected as it passes through a material of high refractive index to a material of lower refractive index. When the incident angle of the incident light is greater than the critical angle, there will be no light refracted as total internal reflection occurs. SPR operation is based on this principle, by adding the interface between media with a metal thin film and the light is monochromatic and p-polarised.

Free electrons on the surfaces of a metal thin film, which are present between the metal and the dielectric medium, can be excited by the incident monochromatic and p-polarised light. When total internal reflection occurs, part of the electromagnetic field component will penetrate through the prism, which is defined as an evanescent field. If the metal layer is sufficiently thin, the field can reach the interface between the metal and the dielectric medium. As a result, the free electrons on the metal surface are excited, and a surface plasmon wave is formed, which propagates along the metal surface. At a specific incident angle, resonance occurs where the incident light momentum is equivalent to the momentum of the surface plasmon wave. Consequently, the intensity of the reflected light decreases. This angle is called the SPR or resonance angle (θ_{SPR}). The plasmon wave is the sensing component that interacts optically with the metal surface. This wave has a high sensitivity towards the changes in the surface refractive index. Changes in the optical properties of the surface will affect the SPR angle. Thus, SPR can be used for sensing purposes.

Surface plasmon requires a coupler as it does not couple with the outside electromagnetic radiation. The simplest coupler for surface plasmon excitation is the prism coupler. Figure 1 shows the Kretschmann configuration of the coupler while the schematic diagram for the SPR setup is shown in Fig. 2. The Kretschmann configuration is commonly used because it is the most efficient. A metal film was placed directly on the horizontal surface of the film (~50 nm) and the incident beam passed through the film to excite the surface plasmon at the bottom of the film. A lock-in amplifier and chopper were used in the setup to enhance the signal-to-noise-ratio (SNR) of the measurement, while a filter was used to modulate the intensity of the incident light.

3.   SPR as Metal Ion Sensor

3.1   Modification of SPR and gold thin film

In 2001, Ock *et al.* developed the squarylium dye (SQ dye) containing a polymeric thin film to be incorporated with SPR for Cu^{2+} detection.[21] A high sensitivity for Cu^{2+} ion detection ranging from 1.0 pM to 10 mM was reported. The complexation of the Cu^{2+} ion and the SQ dye changes the refractive index and gives an effective detection in SPR measurement with high sensitivity and selectivity. On the other hand, Lee *et al.* reported that a highly selective response to Li^{2+} was observed when the azacrown indoaniline (ACIA) dye was used as an active layer.[22] They studied the effect of the complexation of a metal ion with ACIA on absorption
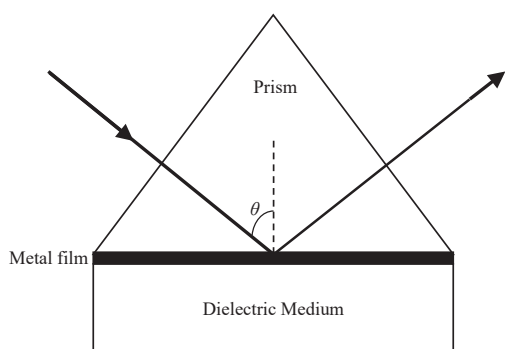
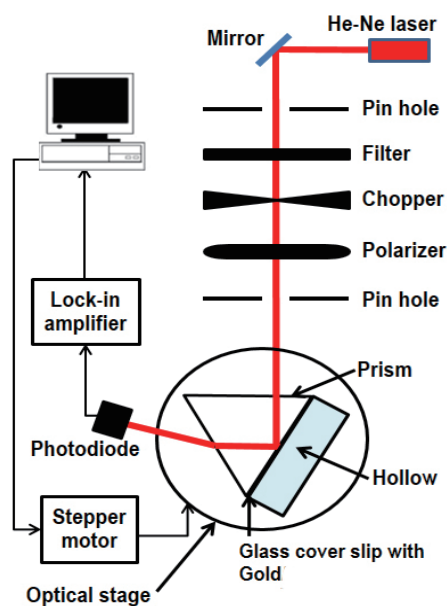Fig. 1.   Kretschmann configuration of SPR prism coupler.

Fig. 2.   (Color online) SPR spectroscopy setup.

spectra by the Pariser–Parr–Pople (PPp-MO) method. The ACIA dye was reported to carry the monoazacrown moiety and showed sensitivity to metal ion complexation. The insertion of other metal ions such as K^+, Ca^{2+}, and Na^{2+} up to 10 nM did not have any effect towards the shift of the resonance angle.

Hur *et al.* in 2002 fabricated the dithiosquarylium (DTSQ) dye containing a polymeric film as a Ag^+-sensing membrane.[23] The interaction between DTSQ and Ag^+ effectively changed the refractive index, and a good selectivity of Ag^+ detection appeared in a wide concentration range from 10 nM to 10 pM. They reported that the increase in the refractive index of the sensing membrane appeared to be caused by the decrease in the absorption coefficient around the wavelength of the SPR probe beam and proposed that the maximum wavelength, Λ_{max} control of the DTSQ dye can offer a novel strategy for the highly sensitive metal ion detection.

Later in 2003, May and Russel developed a novel technique for cadmium ion detection by combining the metal-sensitive enzyme urease with the SPR method.[24] The urease was modified with *N*-succinimidyl 3-(2-pyridyldithiol) propionate (SPDP) before being deposited on a gold-coated glass SPR sensor disk. When exposed to trace levels of cadmium ions, a linear relationship between the change in the SPR signal and the concentration of cadmium ions in the range of 0 to 10 ppm was obtained. It was considered that the Cd^{2+} bound on the active nickel site of urease. They proved that SPR is capable of detecting Cd^{2+} by using urease as a heavy metal bioreceptor without the need for activity assays.

In 2004, Chah *et al.* reported that Hg^{2+} can be spotted by using the SPR signal with a gold film treated by 1,6-hexaneithiol (HDT).[25] A gold surface modified by HDT promoted the adsorption of mercuric ion and improved the SPR signal. The thiol molecules on the HDT-

modified gold surface attracted the mercuric ion with the adsorption equilibrium ratio of 1:3 up to 20 µM, a point where the area illuminated by the incident light became saturated. The SPR signal did not change at a higher concentration. Moreover, they also reported that quantification from the SPR signal of Hg^{2+} was in the concentration range from 1.0 nM to 1.0 mM, and it selectively detected Hg^{2+} when present in a mixture containing Ni^{2+}, Pb^{2+}, Cu^{2+}, and Zn^{2+} ions. Yu *et al.* also developed a Hg^{2+} sensor by monitoring the binding interaction between Hg^{2+} with polypyrrole (PPy) and 2-mercaptobenzothiazole (2-MBT).[26] The chemical binding of aqueous Hg^{2+} ions with a PPy thin film deposited on a gold surface was monitored and an increase in the SPR angle of $(780 \pm 10) \times 10^{-40}$ at 10 ppm Hg^{2+} was reported. Between 0.1 and 10 ppm, a linear dynamic range was observed. After Hg^{2+} absorption to the polymer, 2-MBT was injected with a solution that produced further binding interaction with the Hg^{2+} bound on PPy, which improved the detection limit to 0.01 ppm. On the other hand, a protein coated on a metallic film was reported by Wu and Lin.[27] Metallothionein (MT) was immobilised onto a carboxymethylated dextran matrix as a biosensor with sensitivity in the detection of Cd^{2+}, Zn^{2+}, and Ni^{2+} but not Ca^{2+}, Mg^{2+}, and Mn^{2+}. The MT chip could differentiate Cd^{2+} effectively by controlling the presence of NaCl in the reaction buffer by 1 mM. The metal ion binding affinity towards immobilised MT was in the order of $Cd^{2+} > Zn^{2+} > Ni^{2+}$.

In 2005, Wu and Lin advanced their research by immobilising bovine serum albumin into the same matrix, which increased the sensitivity of metal ion detection.[28] The same as the MT chip, the albumin-based sensor could detect Cd^{2+}, Zn^{2+}, and Ni^{2+} but not Ca^{2+}, Mg^{2+}, and Mn^{2+}. The albumin-based sensor sensitivity was increased to 10 nM and the binding affinity followed the $Ni^{2+} > Zn^{2+} > Cd^{2+}$ order. In the same year, Forzani *et al.* built a high-resolution differential SPR sensor by dividing the sensor surface into two parts, namely, reference area and sensing area.[29] By using a quadrant cell photodetector, the difference in the SPR angle between the two areas was detected as the differential signal. The differential signal changed with the presence of metal ions owing to a specific binding of the metal ions onto the sensing area coated with particular peptides. They reported that the peptide NH_2–Gly–Gly–His–COOH was coated in the sensing area to detect Cu^{2+} with a detection limit of 1.6 nM, whereas the peptide NH_2–$(His)_6$–COOH was used to sense Ni^{2+} with a detection limit of 41 pM.

Moon *et al.* in 2006 reported that a thin gold film that was modified with 1,6-hexanedithiol (HDT) is capable of sensing Pt^{2+}.[30] The thiolated surface is selective towards other metal ions, such as Cu^{2+}, Ni^{2+}, and Cd^{2+}. The concentration of Pt^{2+} in the range of 0.1 µM to 1.0 mM caused the SPR angle shift to increase logarithmically. The rate of Pt^{2+} absorption accelerated until the surface coverage reached around 17%. Then, the adsorption profile followed the Langmuirian behaviour with surface coverage. It was considered that the hydrophobic thiolated surface absorbed the heavy metal ions by a cooperative mechanism. Moreover, they reduced the hydrophobicity of the thiol-functionalised surface by composing HDT with 11-mercaptoundecanoic acid to form a self-assembled monolayer (SAM). The addition of hydrophilic groups to the surface did improve the rate of adsorption of Pt^{2+}. They concluded that the adsorption of metal ions is strongly dependent on the hydrophilicity/hydrophobicity of the surface.

Zhang *et al.* in 2007 improved the MT-based sensor reported by Wu and Lin in 2004.[31] Instead of a dextran film, they suggested the attachment of MT onto the preformed SAM. In

comparison with the preformed SAM, the dextran film is nonuniform and relatively thick, causing the detection limit reported earlier to be not particularly low (~2 μM). In their report, MT molecules were firstly attached onto preformed alkanethiol SAM. The MT was then treated with glycine–HCl just before the SPR analyses with heavy metal ions. The compact MT film formation with a uniform surface orientation gave low detection levels of Cd^{2+} and Hg^{2+} at approximately 0.1 and 5 μM, respectively. Then, in 2007, SPR was used to detect arsenic when Forzani *et al.* modified a gold surface with three different recognition elements, namely, glutathione (GSH), dithiothreitol (DTT), and *N*-(dithiocarboxy)-*N*-methyl-D-glucamine (dTGluc).[32] The thiol-containing compound was able to distinguish arsenic levels when used as a sensor probe. They compared DTT, GSH, and dTGluc for arsenic detection and reported that DTT has a stronger affinity for arsenic and a better response while quantifying both As^{3+} and As^{5+}. Most of the arsenic detection methods that require chemical pretreatment can also be avoided by using DTT in the SPR sensor, thus allowing the in situ reduction of arsenate. Hong *et al.* in the same year compared two types of SAMs, which were 2-aminoethane thiolhydrochloride (AET) and 6-aminohexane thiolhydrochloride (AHT) for Cu^{2+} detection in the range of 0.1 μM to 1.0 mM.[33] Both AET and AHT are capable of detecting Cu^{2+} in the presence of Zn^{2+} and Ni^{2+}, which are divalent and have similar atomic radii. The high density of AET SAM on the gold thin film caused the AET-Au sensor to exhibit a clearer cut SPR response than AHT-Au on Cu^{2+} detection. They concluded that AET-Au is more suitable as an SPR sensor than AHT-Au to detect Cu^{2+} with concentration ranging from 100 nM to 1.0 mM.

Potassium plays an important role in membrane transport, and the precise detection of potassium ions is very crucial. In 2008, Chen *et al.* used calix[4]crown to modify a gold chip to be incorporated with SPR spectroscopy.[34] It was reported that the calix[4]crown was assembled as a monolayer on the gold surface. From their report, the K^+ ion concentration can be monitored at a wide range of 1 pM to 0.1 mM with the highest sensitivity (1 pM) and selectivity over other alkali and alkaline earth metal ions near the neutral pH (6–8).

In another interesting work, gold nanoparticles (Au NPs) were used to combine with SPR to enhance the selective detection of a sensor. Fahnestock *et al.* in 2009 reported that the best Au NP size was 10 nm and it was able to selectively detect hexachromium (Cr^{6+}) ions.[35] They found that the absorption of Cr^{6+} was unaffected by the existence of trivalent chromium (Cr^{3+}) ions. The detection limit for Cr^{6+} was 10 ppm and the sensitivity was 0.022 nM/ppm at an optimum pH of between 6.2 and 6.8. They also reported that Na^+ affected the Cr^{6+} absorption the most, which followed the order of $Na^+ > Mg^{2+} > Ca^{2+} > K^+$ and $Cl^- < SO_4^{2-} < PO_4^{2-}$ for cations and anions, respectively.

On the other hand, Wang *et al.* used a mercury-specific oligonucleotide (MSO), which is thymine (T)-rich, to modify the Au NPs that enhanced the sensing of mercury ions.[36] They immobilised the MSO probe on the Au NP film by forming a Au–S bond between DNA and the gold thin film. When Hg^{2+} was present, the MSO probe took Hg^{2+} via the Hg^{2+}-mediated coordination of T–Hg^{2+}–T base pairs. The Hg^{2+} limit of detection for direct immobilisation was 0.3 μM. It improved to 5 nM when they employed part complementary DNA (PCS)-modified Au NP labels. Besides that, the sensor also exhibited an admirable selectivity over other metal ions such as Pb^{2+}, Cd^{2+}, Mg^{2+}, Ca^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+}, Fe^{3+}, and Al^{3+}. The following year, Chang *et*

al. improved the SPR sensor for Hg^{2+} sensing by using thiol-modified oligonucleotides and gold nanoparticles.[37] They developed a Hg^{2+} sensor with highly selective and sensitive detection, and also took the advantages of $T–Hg^{2+}–T$ coordination chemistry. They reported that the detection limit for Hg^{2+} was 1 nM, which was lower than those of other recently developed methods. Moreover, they observed a linear correlation between the measured SPR reflectivity and the Hg^{2+} concentration logarithms at a range between 5 and 5000 nM. The SPR system also offered a high selectivity over other divalent metal ions up to micromolar concentration levels. This turn-on detection approach has numerous significant advantages compared with the turn-off detection.

Since 2011, researchers have started to focus on the recognition element investigation for developing a highly sensitive polymer through a rapid and simple preparation. A high-performance SPR sensor to detect Cu^{2+} and Hg^{2+} was developed by Fen *et al.* when they deposited a thin crosslinked chitosan on the surface of a gold film.[38] By using the spin coating technique, the crosslinked chitosan layer can be easily prepared within less than a minute. The gold/crosslinked chitosan interface had a high sensitivity, which was 0.00743 ppm^{-1} for Hg^{2+} and 0.00654 ppm^{-1} for Cu^{2+}. The detection limits for both heavy metal ions were 2.5 μM–0.5 mM and 7.9 μM–1.6 mM, respectively. In the same year, Fen *et al.* also studied other essential heavy metal ions with high toxicity potential, which were Zn^{2+}, Cu^{2+}, and Mn^{2+}.[39] They found that the detection between these metal ions was between 0.5 and 100 ppm, where the resonance angle changes were directly proportional to the heavy metal ion solution concentration in this range. The kinetic behaviour of these metal ions was also studied and divided into two groups. For concentrations between 0 and 5 ppm, the kinetic reaction completed at approximately 100 s, and for concentrations above 10 ppm, a more complex kinetic reaction was observed and completed at approximately 500 s. The sensitivity of these studied heavy metal ions for this sensor layer followed the $Cu^{2+} > Zn^{2+} > Mn^{2+}$ order. In the same year, Abdi *et al.* modified the gold surface with a conducting polymer composite, polypyrrole–chitosan (PPy–CHI) for sensing Hg^{2+} and Pb^{2+}.[40] They found that the resonance angle changed with varying ion concentrations in the range of part per million (0.5–12 ppm). This sensor also had a higher sensitivity towards Pb^{2+} than Hg^{2+}. As a result, the selective binding of Pb^{2+} to chitosan can be utilised to detect heavy metal ions in water at lower concentrations. Meanwhile, Sadrolhosseini *et al.* used PPy–CHI to detect Zn(II) and Ni(II) in aqueous solutions.[41] They used an electrochemical method to coat the gold layer with PPy–CHI. The sensitivity of the SPR-based sensor with PPy–CHI as a sensing layer was about 0.01 ppm.

In the following year, Fen *et al.* developed a sensor that is sensitive and selective towards Pb^{2+} detection by immobilising p-tert-butylcalix[4]arene-tetrakis (BCAT) in a chitosan thin film.[42] The BCAT–chitosan thin film was coated on the gold layer by the spin coating technique. From their report, the BCAT–chitosan thin film helped the adsorption of Pb^{2+}, and thus improved the shift of the SPR angle. As a result, the concentration of Pb^{2+} in the range between 0.01 nM and 0.24 μM can be quantified. They also found a linear relationship between the shift of the SPR angle and the Pb^{2+} concentration up to 1 ppm with a sensitivity of 0.04503° ppm^{-1}. Moreover, Pb^{2+} can also be differentiated from Cu^{2+}, Hg^{2+}, Zn^{2+}, and Mn^{2+} as it is preferentially adsorbed by the BCAT–chitosan. The SPR sensor for Pb^{2+} detection was improved again by Pelossof *et al.*[43] They used Pb^{2+}-dependent DNAzyme and hemin/

G-quadruplex as the recognition element. A complex containing the Pb^{2+}-dependent DNAzyme arrangement and ribonuclease-containing nucleic acid arrangement linked to a G-rich domain "caged" in the complex structure was assembled on gold-coated glass surfaces. When Pb^{2+} is present, the DNAzyme undergoes cleavage that releases the G-rich sequence that will self-assemble into the hemin/G-quadruplex label. The sensing surface refractive index changes with the hemin/G-quadruplex, and thus enables the SPR detection of Pb^{2+}. Furthermore, they also amplified the detection of Pb^{2+} by immobilising the recognition element on Au NP, which causes the detection limit of Pb^{2+} to become 5 fM. A high-sensitivity SPR sensor for Ni(II) ion detection was developed by Kim *et al.*[44] In order to detect Ni^{2+} ions, they designed a surface sandwich assay that involved two different ligands that are selective to Ni^{2+}, polyhistidine and *N*-[5-(3'-maleimidopropylamido)-1-carboxypentyl]iminodiacetic acid (NTA). NTA was deposited on a gold thin film that was first modified with alkanedithiol, before the Ni^{2+} ion adsorption. The polyhistidine-functionalised quasispherical gold nanoparticles then adsorbed onto surface Ni(II)–NTA complexes to improve the SPR sensitivity. This sensor has the ability to detect Ni^{2+} at a very low concentration, i.e., about 50 parts per trillion (211 pM), which is an amazing improvement. They also confirmed the selectivity of Ni^{2+} ions by the sandwich assay when other divalent cations such as Zn(II), Pb(II), and Cu(II) were used to compare the measurements, as some of them individually possess binding affinities towards either NTA or histidine moieties.

Fen *et al.* then built a Pb(II) ion sensor by using a crosslinked chitosan thin film.[45] They prepared a crosslinked chitosan solution by the homogenous reaction of chitosan in an aqueous acetic acid solution and used glutaraldehyde as a crosslinker. By the spin coating technique, crosslinked chitosan was deposited on the surface of the gold thin film. They reported that as the Pb(II) ion concentration increased, the SPR resonance angle decreased. This sensor was reported to have a sensitivity of 0.00483° ppm^{-1}. It was believed that the Pb(II) ion interacted with the primary amino and aldehyde terminal (imino bound) of the crosslinked chitosan thin film that was formed by crosslinking chitosan with glutaraldehyde.

In 2014, polypyrrole multiwalled carbon nanotubes (PPy-MWCNTs) were used by Sadrolhosseini *et al.* to modify a gold layer.[46] The SPR sensor is capable of detecting trace amounts of Pb, Fe, and Hg ions. The sensitivity and accuracy of the sensor were enhanced by the application of PPy-MWCNTs, such that the angle shift increased relative to the angle shift of the PPy sensing layer to measure the concentration of the above-mentioned ions. The limit of detection of this sensor is about 0.1 ppm and the sensor prefers Hg ions over Pb or Fe ions. A high-sensitivity SPR response of a gold/chitosan/graphene oxide nanostructure thin film was developed by Lokman *et al.* as a metal ion sensor to detect Pb(II) ions.[47] In this project, the Au/CS/GO thin film was characterised and compared with the Au/CS thin film in all aspects, from surface morphology to SPR response. From their report, the integration of GO in the prepared Au/CS thin film was successful and confirmed by XRD, field-emission scanning electron microscopy (FESEM), and AFM analyses. For the surface morphology characterisation using FESEM, two different morphologies were observed in the FESEM micrograph for Au/CS and Au/CS/GO nanostructure thin films. By incorporating GO, the fine distribution of average-size chitosan particles transformed into a rough fractured sheet covering the chitosan, where the defect and roughness of the GO contribute to the improvement of the

interaction between the sensing layer and the metal molecules. Later, on the metal ion detection part, Au/CS and Au/CS/GO thin films were used with different concentrations of Pb(II) ion, ranging from 0.03 to 5 ppm. From the result, it can be seen that the SPR response for both sensors was generally very sensitive towards Pb(II) ions with a detection limit of 0.03 ppm, as there was no response shown by the thin films below 0.03 ppm. In addition, the minimum reflectance angle for the Au/CS thin film with deionized (DI) water occurred at an incidence angle of 69.44°, and as the concentration of Pb(II) ion increased, the incidence angle decreased with a maximum angle shift of 3.88°. Compared with the Au/CS/GO thin film, the minimum reflectance angle of DI water is at 68.89°, and as the concentration of the Pb(II) ion increased, the incidence angle decreased with a maximum angle shift of 5.56°. By comparing the result, the changes in the incidence angle were more distinct for the Au/CS/GO thin film than for the Au/CS thin film. This indicates that the Au/CS/GO nanostructure thin film has the potential to measure a wide range of heavy metal ions. The sensitivity of the Au/CS/GO thin film was also higher than that of the Au/CS thin film, at about 1.11200 and 0.77600 ppm^{-1}, respectively. They concluded that the surface roughness of the Au/CS/GO nanostructure thin film improved the adsorption of Pb(II) ions onto the thin film, and thus increased the sensitivity of the sensor.

In the following year, Fen *et al.* developed an SPR sensor to determine zinc ions by using novel chitosan and chitosan-tetrabutyl thiuram disulfide (Chitosan–TBTDS) as the active layers.[48] In their review, the presence of the amine functionality that is crucial for metal ion adsorption was the reason why they chose chitosan. TBTDS was doped into the chitosan matrix as it has sulfur donor atoms that have stronger binding affinity towards Zn^{2+}, and thus enhanced the sensitivity and selectivity for sensing Zn^{2+}. The result of the preliminary test on deionised water showed that the resonance angle for the gold-only thin film was lower than that for gold/chitosan and gold/chitosan/TBTDS thin films. For the SPR result of Zn^{2+} ion with Au/chitosan, the change in resonance angle increased as the Zn^{2+} ion concentration was increased. This showed the binding of Zn^{2+} with the detection limit of 0.5 mg/l. With the addition of TBTDS, a similar increasing trend was observed but with a higher resonance angle change and a lower detection limit of 0.1 mg/l. From the results, it can be seen that the sensitivity of chitosan–TBTDS was higher than that of the chitosan layer only with sensitivities of 0.032 and 0.013° (mg/l)$^{-1}$, respectively. For the selectivity test, the Au/chitosan/TBTDS nanolayer was run with various types of metal ions, namely, Zn^{2+}, Mn^{2+}, Cu^{2+}, Hg^{2+}, and Pb^{2+}. The results showed that the Zn^{2+} ion had the greatest resonance angle change and Mn^{2+} had the lowest. In addition, the selective detection of Zn^{2+} in the mixed metal ion solution was carried out with a solution containing Zn^{2+}, which had a higher resonance angle change than the metal ion solution without the Zn^{2+} ion. Also, in 2015, Verma and Gupta used silver (Ag) metal and indium tin oxide (ITO) to incorporate with an SPR thin film.[49] The thin film was modified with the coating of a pyrrole/chitosan composite. This sensor is capable of detecting trace amounts of Hg^{2+}, Cd^{2+}, and Pb^{2+} in polluted water. They fabricated four types of sensing probe, i.e., pyrrole/chitosan/ITO/Ag, pyrrole/ITO/Ag, pyrrole/chitosan/Ag, and pyrrole/Ag. From their investigation, the pyrrole/chitosan/ITO/Ag-coated fibre optic probe was the most sensitive in detecting all heavy metal ions. Furthermore, the detection limits for Cd^{2+}, Pb^{2+}, and Hg^{2+} were 0.129, 0.158, and 0.293 nM, respectively. It was also found that pyrrole/chitosan/ITO/Ag had a higher sensitivity towards Cd^{2+} than other heavy metal ions.

Peralta-Domínguez *et al.* developed the schiff base derivative used for copper sensing through colorometric and SPR techniques.[50] In their project, a schiff base compound known as 5-chloro-2-[(1E,2E)]-3-(4-(dimethylamino)phenyl)-allyidene)amino]phenol (S1) was prepared by using a standard condensation method of imine derivatives. From the investigation, it was clearly shown that S1 was very selective towards Cu^{2+} ions. A clear distinction of colour changes can be seen after the addition of metal ion solutions into S1 (in MeCN). The change in colour was believed to be induced by the formation of a S1–Cu^{2+} complex. In addition, the absorption spectra showed a new absorption peak at 530 nm, which was redshifted around 123 nm with respect to the free S1. For the sensing technique using SPR spectroscopy, a standard Krenchman configuration was implemented with a silver film used as a source of plasmon resonance. It was directly in contact with the S1 solution without modifying the active layer, which was then tested with different concentrations of Cu^{2+} ions. From the SPR result, it can be observed that as the concentration of Cu^{2+} is increased, the SPR curve became broader and shifted to the right. The limit of detection for this technique was observed to be as low as 1.5 μM. As a conclusion, they stated that the colorimetric sensor produces a spectroscopic limit of detection of 0.12 μM, and the limit of detection evaluated by the naked eyes is 2 μM.

In 2017, Sadrolhosseini *et al.* used a polypyrrole-chitosan/nickel-ferrite nanoparticle (PPy–Chi/$NiFe_2O_4$–NP) composite layer for heavy metal ions using SPR.[51] They prepared the polypyrrole-chitosan/nickel-ferrite nanoparticle composite layer by using an electrochemical method to detect nickel, iron, cobalt, aluminium, manganese, mercury, and lead ions. The detection limit for Fe, Co, Al, and Mn ions obtained was 0.001 ppm and that for Hg and Pb was 0.4 ppm. The selectivity follows the order of Ni > Fe > Co > Al > Mn > Hg > Pb. The PPy–Chi/$NiFe_2O_4$–NP sensitivity was greater than those of polypyrrole and polypyrrole chitosan as it could detect the paramagnetic materials strongly. In the latest work, Zainudin *et al.* modified the gold surface with valinomycin-doped chitosan-graphene oxide (C–GO–V) for potassium ion detection.[52] They used the spin coating technique to deposit the novel C–GO–V on the gold surface. As a result, the sensor was able to detect K^+ ions with a linear response up to 100 ppm. The sensitivity and selectivity of the sensor were 0.001 ppm and 0.00948° ppm^{-1}, respectively. This proved that the C–GO–V film has a high potential in K^+ ion detection by SPR measurement.

3.2 Incorporation of SPR with other methods

Instead of modifying the gold surface, researchers also studied the sensitivity of SPR by using different light sources. Eum *et al.* used a NIR light source on SPR to sense K^+ ions.[53] SPR sensors that detected K^+ ions using a gold thin film were assembled at two different incident wavelengths, 670 and 830 nm. They reported that at the 670 nm wavelength, no resonance was detected owing to the thickness of the sensing film as the K^+ ion concentrations varied from 1 nM to 1 M. When the light source changed to NIR light sources (830 nm), a resonance point was detected even though the film was too thick. Besides that, when compared with the resonance point by using a gold thin film, the resonance angle enhanced by 0.2° at low concentration and 2.8° at 1 M concentration.

Another approach in the quantitative detection of heavy metals ions was developed by Wang *et al.*[54] They combined SPR with ASV. They reported that SPR and ASV were combined to

detect heavy metal ions in water. Signals from both SPR and electrochemical current were used to identify the amount and type of metal ions. Their system was capable of detecting lead, copper, and mercury, and the detection limit was in the range of part per million to sub-part per billion. The SPR signal is unaffected by background current and no additional step is needed to remove oxygen compared with ASV. Besides that, the required SPR sampling area is small and effective in making a very compact and arrayed sensing practicable. Moreover, when compared, the SPR sensor uses a mercury-free gold electrode that is environmentally friendly, while ASV uses a typical mercury-coated electrode.

In 2008, Chen *et al.* developed wavelength-resolved SPR spectroscopy for the detection of uranyl ion.[55] They used a white light source for the SPR sensing system based on the wavelength shift and sensing film of calix[6]arene. The combination of the wavelength-resolved SPR and the calix[6]arene film showed a stable and sensitive detection for uranyl ion. In order to obtain multiple wavelengths, a white lamp was used. To ensure that the SPR phenomenon occurs, the angle was adjusted and fixed at a suitable angle. They stated that the binding of the uranyl ion onto the active layer film induces the SPR wavelength shift with a concentration range between 1 pM and 1 μM.

Later in 2009, Panta *et al.* proposed magnetohydrodynamic (MHD) convection to be combined with SPR and ASV for detection sensitivity improvement.[56] When tested for metal ion sensing, the mercury ion can be detected down to 1 fM in an aqueous solution by using this combination. Mercury ions were electroplated onto a gold sensing surface and detected quantitatively by applying a potential scan. They recorded the SPR angle shift and the electrochemical current signal for the identification and quantification of the mercury ions. By applying an MHD convection in the presence of a magnetic field and supporting electrolytes, namely, 1 mM nitric acid and 10 mM potassium nitrate, the detection sensitivity was enhanced. The experimental results demonstrated that the SPR angle shifts of the 1 fM to 1 mM mercury ions were enhanced by 10 to 60% with the flux density B of 0.71 T.

An SPR-based fibre optic sensor for the detection of mercury by using a gold nanoparticle PVA-hybrid was developed in 2016. Rather than applying the Krenchmann configuration setup, Raj *et al.* developed a fibre-optic-based SPR system that uses a white light source.[57] The fibre was coated with silver by thermal evaporation and coated with a AuNP-PVA hybrid film as the sensing layer. The SPR spectra were plotted for a mercury concentration of 0 to 25×10^{-6} M, and the sensing studies showed a good response for the aqueous solution where the shift in the resonance wavelength of SPR spectra increases with mercury concentration. The sensing mechanism was confirmed by conducting three experiments without coating the sensing layer.

In a recent work, Castillo *et al.* combined the SPR sensor based on gold nanoparticles and the cold vapour generation technique for the detection of mercury ions in aqueous samples.[58] The sensor reacted with the alteration of the signal generated by the solutions when mercury reacted with sodium borohydride. They reported that the detection limit for this device was 172 ng/L, which was better than 91 ng/L obtained with atomic fluorescence, a common technique for mercury detection. In summary, the SPR sensor has encouraged researchers to develop a recognition element to improve the sensitivity and selectivity of SPR in metal ion detection. Table 1 shows the summary of findings of recognition molecules with specific metal ions targeted by researchers from 2001 until 2017, whereas Table 2 contains the summary of SPR combinations with other methods.

Table 1
Recognition elements reported with particular metal ions.

Metal ion	Detection limit/range	Active layers/recognition elements	Reference
Cu^{2+}	1.0 pM–10 mM	Squarylium dye containing polymeric thin film	21
Li^{2+}	—	Azacrown indoaniline dye	22
Ag^{2+}	1 mM–10 pM	Dithiosquarylium dye	23
Cd^{2+}	20–90 µM	Urease modified with *N*-succinimidyl 3-(2-pyridyldithiol) propionate	24
Hg^{2+}	1.0 nM–1.0 mM	1,6-hexanedithiol	25
Hg^{2+}	0.5–50 µM	Polypyrrole and 2-mercaptobenzo-thiazole	26
Cd^{2+}, Zn^{2+}, Ni^{2+}	2.0 µM–1.0 mM	Immobilize methallothionein onto a carboxymethylated dextran matrix	27
Cd^{2+}, Zn^{2+}, Ni^{2+}	10 nM	Immobilize bovine serum albumin onto a carboxymethylated dextran matrix	28
Cu^{2+}, Ni^{2+}	Cu^{2+}: 1.6 nM Ni^{2+}: 41 pM	Cu^{2+}: NH_2–Gly–Gly–His–COOH Ni^{2+}: NH_2–$(His)_6$–COOH	29
Pt^{2+}	0.1µM–1mM	Thin-gold-film-coated glass modified with 1,6-hexanedithiol	30
Cd^{2+}, Hg^{2+}	Cd^{2+}: 0.1 µM Hg^{2+}: 5.0 µM	Methallothionein crosslinked onto preformed SAM; treated with glycine-HCl	31
As, As^{3+}, As^{5+}	~10 µM	Glutathione, dithiothreitol, and *N*-(dithiocabocy)-*N*-methyl-D-glucamine	32
Cu^{2+}	0.1 µM–1.0 mM (selective)	2-aminoethane thiolhydrochloride and 6-aminohexane thiolhydrochloride	33
K^+	1 pM– 10 mM	Calix[4]crown-5 derivatives	34
Cr^{6+}	0.2–5.0 mM	Gold nanoparticles-chitosan composite	35
Hg^{2+}	5.0 nM (selective)	Mercury-specific oligonucleotide probe and AuNP	36
Hg^{2+}	1 nM	Thiol-modified oligonucleotides and AuNP	37
Hg^{2+}, Cu^{2+}	Hg^{2+}: 2.5 µM–0.5 mM Cu^{2+}: 7.9 µM–1.6 mM	MMW chitosan (glutaraldehyde-crosslinked)	38
Cu^{2+}, Zn^{2+}, Mn^{2+}	~8.0 µM–2.0 mM	MMW chitosan (glutaraldehyde-crosslinked)	39
Hg^{2+}, Pb^{2+}	2.5–60 µM	Polypyrrole-chitosan conducting polymer composite	40
Zn^{2+}, Ni^{2+}	Zn^{2+}: 15 µM Ni^{2+}: 17 µM	polypyrrole-chitosan	41
Pb^{2+}	0.01 nM–0.24 µM	p-tert-butylcalix[4]arene-tetrakis (BCAT) immobilized in chitosan	42
Pb^{2+}	5 fM	hemin/G-quadruplex	43
Ni^{2+}	0.85 nM	*N*-[5-(3′-maleimidopropylamido)-1-carboxypentyl]iminodiacetic acid (NTA) and polyhistidine	44
Pb^{2+}	2.4 µM–48 mM	Crosslinked chitosan	45
Hg^{2+},Pb^{2+}, Fe^{2+}	Hg^{2+}: 0.49 µM Pb^{2+}: 0.48 µM Fe^{2+}: 1.79 µM	Polypyrrole multiwalled carbon nanotube	46
Pb^{2+}	0.14–0.24 µM	Gold–chitosan–graphene oxide (Au/CS/GO)	47
Zn^{2+}	1.52 µM	Chitosan and chitosan–tetrabutyl thiuram disulfide	48
Cd^{2+}, Pb^{2+}, Hg^{2+}	Cd^{2+}: 0.129 nM Pb^{2+}: 0.158 nM Hg^{2+}: 0.293 nM	Silver (Ag) and indium tin oxide (ITO) coated with pyrrole and chitosan composite	49
Cu^{2+}	1 µM	5-Chloro-2-[(1E,2E)-3-(4(dimethylamino) phenyl)allylidene)amino)]phenol	50
Ni^{2+}, Fe^{2+}, Co^{2+}, Al^{2+}, Mn^{2+}, Hg^{2+}, Pb^{2+}	Co^{2+}, Ni^{2+}: 0.017 µM Mn^{2+}, Fe^{2+}: 0.018 µM Al^{2+}: 0.037 µM Hg^{2+}, Pb^{2+}: 1.94 µM	Polypyrrole-chitosan/nickel-ferrite nanoparticles	51
K^+	25.57 nM	Valinomycin-doped chitosan-graphene oxide	52

Table 2
Recognition element and combination of SPR with other techniques.

Metal ion	Detection limit/range	Active layers/ recognition elements	Modification/combination with other techniques	Reference
K^+	0.1 µM – 1 M	—	NIR light sources	53
Pb^{2+}, Cu^{2+}, Hg^{2+}	Cu^{2+}: 1.6 nM–1.6 µM Pb^{2+}, Hg^{2+}: 0.5 nM–5 µM	—	Mercury-free gold electrode (SPR combined with ASV)	54
Uranyl ion	1 pM–1 µM	Calix[6]arene	White light sources	55
Hg^{2+}	1 fM	—	Gold working electron and magnet (combination of SPR, ASV and MHD convection)	56
Hg^{2+}	1 µM	AuNPs–PVA hybrid	Silica fiber	57
Hg^{2+}	0.857 nM	SPR-based Au NPs	Cold vapor generation technique	58

4.　Trends in SPR Development and Future Research

SPR-based sensors for metal ion sensing have been developed substantially since 2001. Owing to the presence of metal ions in the environment, SPR has encouraged researchers to continuously concentrate on the improvement of the sensitivity and selectivity of SPR-based sensors in metal ion sensing. The important issue is to detect metal ions at concentrations below the danger limit for human health and the ecosystem. Researchers are now concentrating on SPR sensitivity improvement for the quantitative detection of metal ions. By modifying the sensing surface, the SPR sensitivity could be increased. Some researchers also focus on combining SPR with other methods of enhancing its sensitivity. However, SPR as a sensor for metal ions has yet to be used in a real-life situation as SPR has to compete with other existing methods.

The modification of the gold thin film is a crucial aspect in SPR as it defines the sensitivity and selectivity of the sensor towards metal ions. Recently, cellulose has been reported as a good absorbent for metal ions.[59–64] Cellulose is an abundant natural polymer that can be obtained from various natural sources. Owing to its unique features including low density, nonabrasiness, combustibility, nontoxicity, low cost, and biodegradable properties, cellulose has attracted the attention of many researchers. Now, it is being developed as a metal ion absorbent. Besides that, to increase cellulose potential, pretreatment can be made to modify the surface of fibres. Thus, we expect a good incorporation of cellulose with SPR to increase the SPR potential in metal ion sensing.[65]

5.　Conclusion

In this paper, we reviewed the chronological, collective and systematic evolution of SPR in metal ion sensing. Various modifications of the metal surface to increase the sensitivity and selectivity were discussed in detail. To conclude, SPR has a high sensitivity to sense metal ions

as low as pM to μM. It is also fast and label-free, and metal ion concentration can be measured in real time with small sample consumption. Furthermore, SPR also exhibits a strong capacity as it can determine real water samples directly compared with the common method. We assume that further research in SPR detection will expand the detection abilities and allow SPR sensing to be used widely including in environmental monitoring as an effective metal ion sensor.

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