Surface Plasmon Resonance Sensor of Toxic Nanoparticles in Aqueous Systems

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Abstract: Given their potential antimicrobial activities, silver nanoparticles are utilised in various consumer goods, such as food packaging, medical devices, wound dressings, clothing, washing machines and refrigerators. However, despite the numerous advantages provided by silver nanoparticles, their use has been hindered by their potential human and environmental toxicity. For example, in rainbow trout, silver nanoparticles can drastically alter the functionality of vital organs, such as the liver, spleen and brain. The levels of silver nanoparticles in aquatic environments should be cautiously monitored to avoid their potential adverse on human health and aquatic organisms. Thus, in this study a sensor based on surface plasmon resonance (SPR) is developed for the rapid detection of trace existent of silver nanoparticles. The developed sensor can differentiate between colloidal silver and silver in solution (silver nitrate). Further analysis showed that, there was a significant difference between two results. The most striking observation to emerge from the data comparison was clearly observed.

Keywords: Surface Plasmon Resonance, Silver Nanoparticles, Real Time Detection, Label-Free Detection, Toxic Nanoparticles

1. Introduction

Sensors based on surface plasmon resonance (SPR) are commonly used in biosensing applications because of their high sensitivity (Jha & Sharma, 2009; Lahav, Auslender, & Abdulhalim, 2008) and reliability (Kadkhodazadeh, Christensen, Beleggia, Mortensen, & Wagner, 2017; Maharana & Jha, 2012; Nguyen, Park, Kang, & Kim, 2015). The SPR sensing method enables the label-free detection of low concentrations of analytes (Liu & Wang, 2009) and is based on changes in SPR coupling conditions caused by changes in refractive index near the metal–sample interface of the sensor. Certain information, such as the presence, concentration or composition of an analyte, can be obtained by analysing the changes in refractive index. In the angular interrogation method, the refractive index of a multi-layered optical system that includes the analyte is measured by calculating the SPR angle. Other methods for the measurement of refractive indices include wavelength, phase and intensity interrogation (Homola, Koudela, & Yee, 1999; Zhang, Fang, Wang, Chen, & Sun, 2016). The angular interrogation method was selected as the focus of this work (Alleyne, Kirk, McPhedran, Nicorovici, & Maystre, 2007) because it has higher sensitivity than the wavelength and intensity interrogation techniques and is simpler than phase interrogation techniques (Salazar, Camacho-León, Rossetto, & Martínez-Chapa, 2013).

One advantage of SPR-based sensing devices is their insensitivity to interference from light scattering within the sensing medium. This insensitivity can be attributed to their small sensing area, given by the penetration depth of the Surface Plasmon Polaritons (SPP), which has been estimated to be between 200 and 300 nm (Raether, 1988).

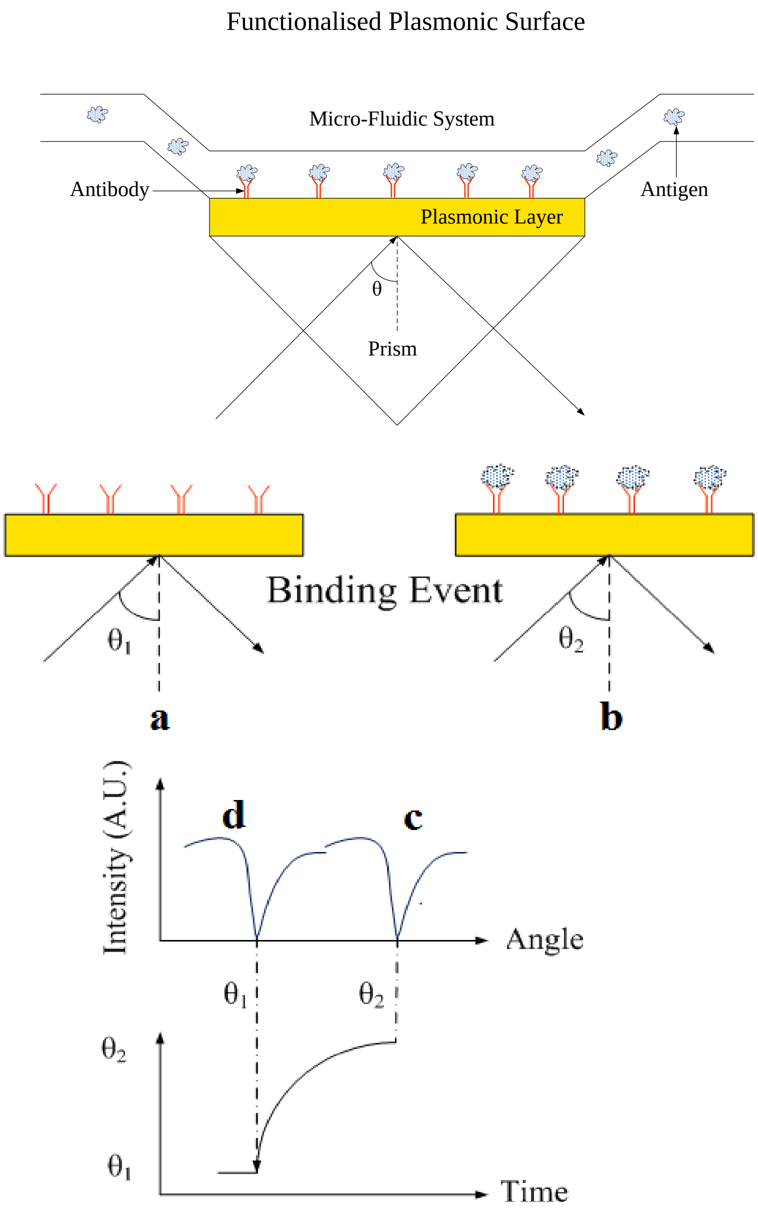


Figure 1: SPR immunoassay technique. (a) and (b) Antibody-functionalised SPR sensor layer on the top of a conventional glass prism/gold plasmonic system. (c) Angles θ_1 and θ_2 before and after the binding event. (d) Change in sensogram following the binding event (Salah, Jenkins, & Handy, 2014).

The SPR response is drastically altered by particulates in areas that are immediately adjacent (<300 nm) to the metal film. This phenomenon facilitates determining the refractive index of area of ~200–300 nm, which was determined on the basis of the penetration depth of surface plasmon (SP) polaritons (Kadkhodazadeh *et al.*, 2017; Karlsson, 2004; Raether, 1988). This only particulate within the area closest (< 300 nm) to the metal film, which cause a significant change in the SPR response. This is advantageous if the refractive index of the analyte suspended in the concern solution. SPR-based sensors generate a signal specific to the fluctuation in refractive index at the sensor surface. One particular example is an SPR-based sensing technique for immunoassays (Mullett, Lai, & Yeung, 2000) used to measure specific antibody–antigen reactions. In this technique, antibodies readily bind to a metallic surface, such as gold (Mullett *et al.*, 2000). This technique enables the transport of antigens into a chamber through a microfluidic channel (Figures 1a, 1b).

In the SPR immunoassay technique, antigens bind to specific local binding sites. The binding event alters the effective refractive index and consequently changes SPR conditions (Figures 1c, 1d). The most common SPR sensor system is based on the Kretschmann configuration (Kretschmann & Raether, 1968; Tudos, 2008) and is widely used for high-sensitivity chemical and biomolecular sensing (Maharana & Jha, 2012). The Figure 1 illustrates the application of the Kretschmann configuration for the detection of analytes in solution. Thiol groups from the disulphide bridges of antibodies are immobilised through covalent bonding to the surface of gold or any other thiol-rich surface (Neves-Petersen, Snabe, Klitgaard, Duroux, & Petersen, 2006). This configuration facilitates the dense packing of antibodies on the sensor surface, thereby providing specific antigen binding sites (Neves-Petersen *et al.*, 2006).

2. Kretschmann Prism Configuration

In the Kretschmann prism configuration, a multi-layered system is placed on the top of a glass prism. This configuration allows incident light rays to couple in the surface plasmon (SP) mode specifically bound to an interface. Extremely thin metal films, such as silver or gold, are typically used as SPs given their optical properties (Nguyen *et al.*, 2015). Film thickness after deposition is easily controllable (Chen & Chen, 1981). Metal films are commonly deposited on glass substrates that are optically coupled to a prism (de Bruijn, Kooyman, & Greve, 1992; Salah *et al.*, 2012). These materials support SP waves when the real component of the dielectric permittivity is negative. SP phenomena is also exhibited by other metals, such as aluminium, copper, chromium, cobalt, nickel, vanadium, platinum, palladium and tungsten, as well as certain semiconductors (Wang, Zhan, Huang, & Hong, 2013).

The physical conditions of surrounding materials determine the amount of light coupled to the SP mode and affect SP conditions, which are tuneable. In the Figure 2, the top dielectric is labelled as the sample environment that contains the analyte of interest. Figure 2 shows that despite its presence at all interfaces between materials, the SP is bound to the interface between the sample environment and plasmonic layers because of coupling effects. Under certain conditions, an electric field E is generated at the interface and rapidly decays in adjacent materials (Tudos, 2008). Moreover, high-density electron gas produces a propagating oscillation.

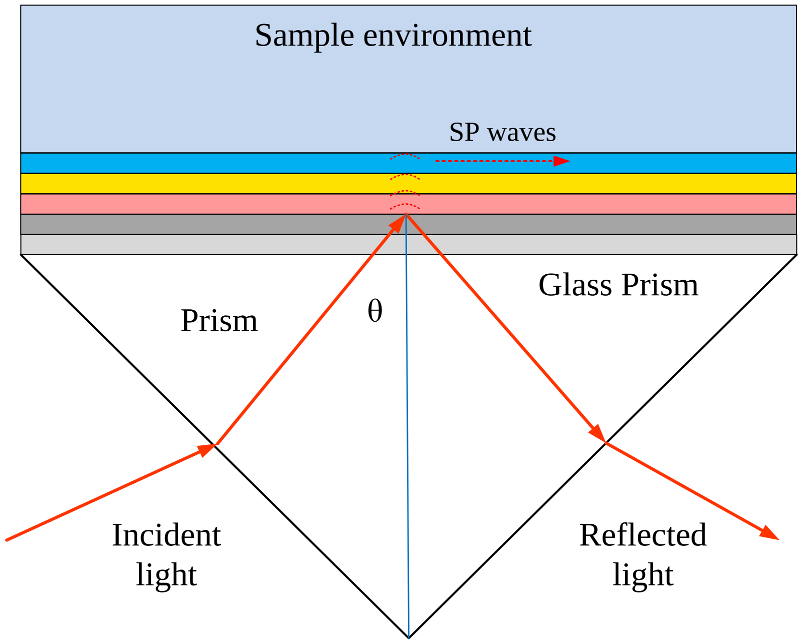


Figure 2: Kretschmann configuration set-up comprising a glass prism, glass substrates and plasmonic layers (Tudos, 2008). The dielectric sample is placed on the top of the set-up. Incident light is refracted towards plasmonic layers at an incidence angle. The evanescent SP wave dominates at the plasmonic–sample environment interface

3. Results and Discussion

3.1 Numerical Results

As shown in the Figure 3, reflectivity and resonance angle are influenced by changes in the real component of the refractive index of the absorbing medium. Our study results are in agreement with those of other workers (Akimoto, Sasaki, Ikebukuro, & Karube, 1999; Durou, Giraudou, & Moutou, 1973; Kotsev, Dushkin, Ilev, & Nagayama, 2003); and similar findings have been obtained for transparent medium (Zhang, 2013). Comparing Figure 3 with a similar image presented by Yingying (2013) shows that the intensity and angular standard interrogation methods can be used to determine the refractive indices of absorptive and transparent media. Thus, we used a novel four-layered system that combines different media to evaluate the angular and intensity interrogation methods. Our system is arranged as Cr (2 nm)/Ag (40 nm)/Au (5 nm)/Gr (0.33 nm) and contains a single graphene layer. In this system, chromium acts as the adhesion layer, silver acts as the plasmonic layer and gold acts as the protective layer. Graphene is used to enhance the sensitivity of the system. The optimised thickness of the silver film is 40 nm in the presence of the 5 nm-thick protective gold layer and is 50 nm in the absence of the gold layer and in the presence of one graphene layer. A comparison of the simulated results revealed that the maximum value of absorption increases as the thickness of the silver layer increases.

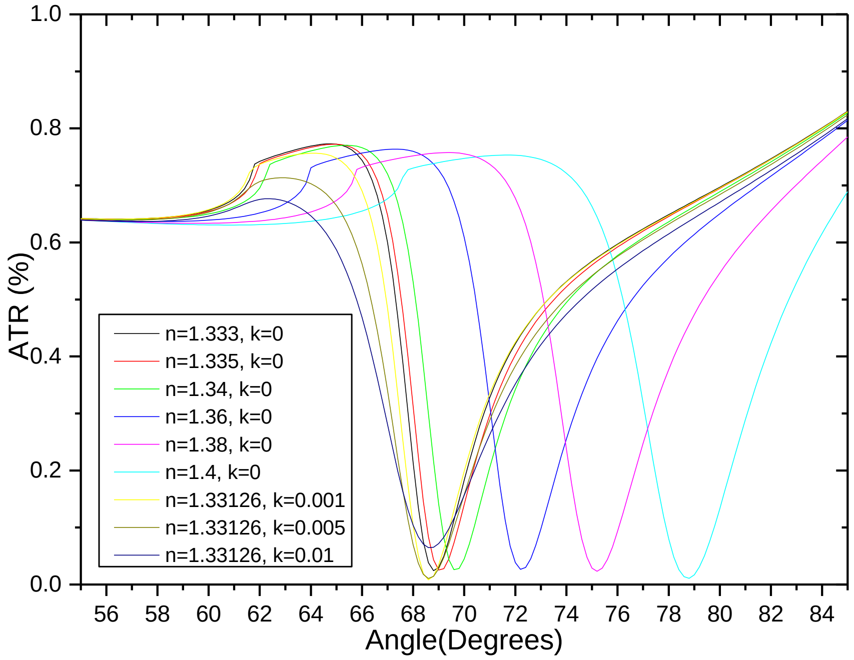


Figure 3: Comparison of the theoretically calculated reflectivity (ATR%) with respect to angle of incident light of different samples with various real and imaginary components

As shown in the Figure 3, intensity interrogation is established with a range of linear measurement values obtained under a sweeping incidence angle. The reflection of SPR and the fixed real component of the refractive index, as well as the changes in imaginary components, are related. Notably, incidence angles can be differentiated at the maximum absorption of the SPR reflectivity curve for samples with the real refractive component indices of 1.33126–1.380. As seen in the Figure 4, the resonance angle shifts as the bulk refractive index of the sensing media increases. Furthermore, the change in the resonance angle is low when the imaginary component is more dominant than the real component. The negligible change in resonance angle, in turn, reduces the sensitivity of the sensor as supported by Figure 3. High values for the imaginary components of the refractive index are associated with broad SPR peaks (Figure 3) and may introduce errors in the determination of resonance angles and consequently cause equivalent noise conditions.

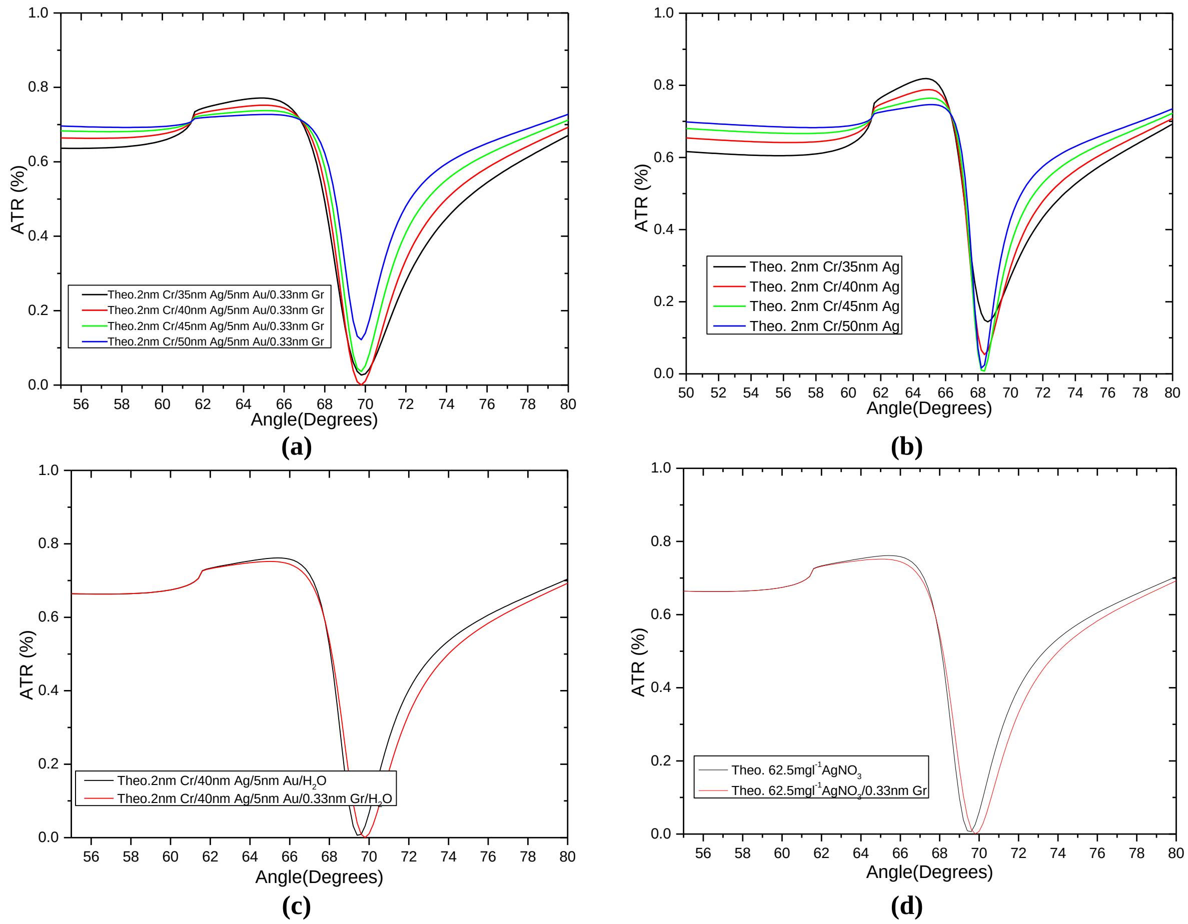
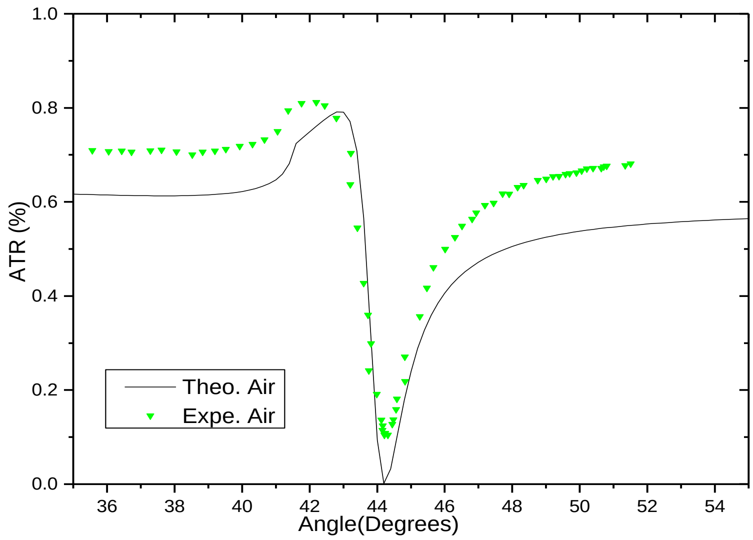


Figure 4: Intensity of reflected light with respect to incidence angle. **(a)** and **(b)** SPR reflectivity from silver layers with different thicknesses in the presence and absence of a 5 nm-thick protective gold or graphene layer. **(c)** and **(d)** Comparison between the SPR results of a multi-layered system with a graphene layer, those of a pure water system and those of a $AgNO_3$ solution system that lacks imaginary components

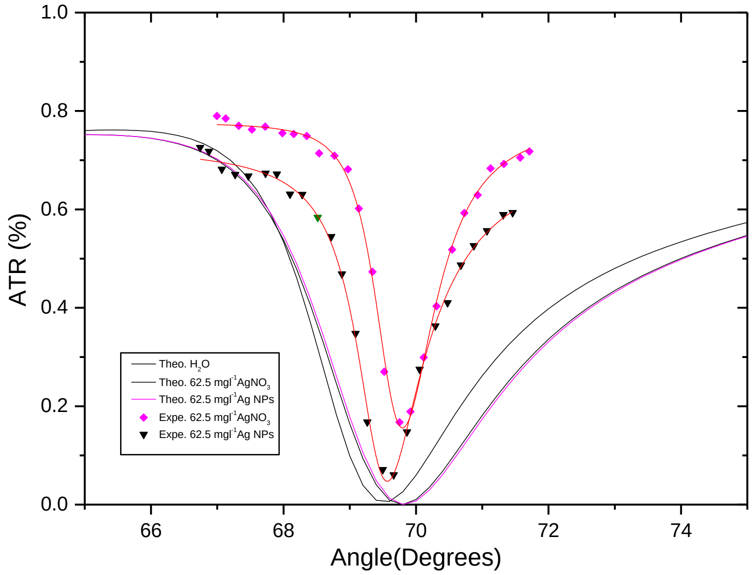
3.2 Experimental and Theoretical Results

A series of experiments were conducted. The Figure 5 (a) shows the first result and the comparison between experimental (green triangles) and theoretical (black solid) results of the multi-layered Cr (2 nm)/Au (50 nm)/Air SPR system under the incidence angles of 35°–56°. The reflectivity of the Cr (2 nm)/Ag (40)/Au (5 nm)/Gr (0.3 nm) SPR system is in good agreement with that of Ag NP and $AgNO_3$ samples with and without imaginary components of the refractive index, respectively. In this case, the absorption maxima from the incident light occur between the incidences angles of 69.0° and 70°. The experimental result, for the 62.5 mg L^{-1} silver sample, shows increased absorption and the same shift in the resonance angle.

Altering the incidence angle yields a range of linear measurement values and changes and measurement sensitivity (Panigrahi, Das, Hassan, & Ray, 2000). Increasing the value of the imaginary component increases that of the real component of the refractive index and reduces the sensitivity of the SPR system. Therefore, the resolution of this interrogation technique can be increased by selecting a wavelength that evades the absorption band of the sample.



(a)



(b)

Figure 5: Comparison of experimental and theoretical results. **(a)** Green triangles represent experimental results, whereas black solid triangles represent theoretical results for the multi-layered Cr (2 nm)/Au (50 nm)/Air SPR system. **(b)** Reflectivity of the Cr (2 nm)/Ag (40)/Au (5 nm)/Gr (0.3 nm) SPR system showing good agreement with that of Ag NPs and $AgNO_3$ (Adegboyega *et al.*, 2012).

4. Conclusions

Recent SPR research has been mainly in the field of biosensor. The sensitivity of the resonance angle to small variations in the electrical refractive index allowed the measurement of low-level correlation reactions to be significantly accurate. This research focused on detecting metallic nanoparticles in water. Experiments have shown that metal nanoparticles can affect the SPR signal at low concentrations. This work numerically and experimentally evaluated the ability of SPR sensors to determine the real component of the refractive index of a sample through two interrogation techniques. The sensitivity of the intensity and angular interrogation techniques can be increased under wavelengths that evade the absorption bands $k(\lambda) \ll n(\lambda)$. In addition, sensitivity is reduced if a plasmonic film with a thickness that has been optimised for the interrogation of a non-absorptive sample is used for the interrogation of an absorptive sample. Notably, the thickness of multi-layered thin films affects the sensitivity of intensity and angular interrogation methods. Therefore, optimal film thickness decreases as sample absorption increases. The resolution of the SPR sensor is maximised under the optimal film thickness.

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