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Review Article

Heavy metal ion sensing in water using surface plasmon resonance of metallic nanostructures

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ABSTRACT

Heavy metal contamination in water and other ecosystems is one of the major environmental issues and already gaining significant attention across the world. For monitoring heavy metals in the environmental ecosystem, optical sensors are getting popular due to their high sensitivity and ease of use. Application of nanomaterials in the sensor elements further improves the sensitivity due to their large surface-to-volume ration, high reactivity, high degree of functionalization and size-dependent properties. This article mainly reviews the application of various metallic nanostructures for heavy metal ion sensing based on surface plasmon resonance (SPR). SPR sensors are widely applied in real time monitoring of heavy metals, chemical and biological analytes etc., because of their ability to efficiently detect and quantify these contaminants even at much diluted conditions (ng/L levels). In this article, SPR sensors fabricated with several metallic nanostructures, such as gold and silver, and their shape and size effects on sensor performance for heavy metal ion detection is discussed. Techniques used to improve the performance of such SPR sensors are also reviewed briefly.

Contents

1. Introduction

Heavy metal ion contamination in water is becoming a serious issue across the world due to its potential hazards to human

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health and to the global ecosystem. This necessitates highly sensitive and reliable sensor systems in order to the continuous detection, quantification and monitoring of toxic heavy metal ion levels in soil and water resources (Langford and Ferner, 1999; Goyer, 1993). Governments have formulated environmental laws to keep a check on the amount of heavy metal ion in drainage, considered to be non-detrimental to the environment. Therefore, different types of sensor systems, including optical, electrochemical and field-effect transistor sensors, have been designed and studied for the detection of heavy metal ions both qualitatively and quantitatively, especially in wastewaters (Li et al., 2013). Surface Plasmon Resonance (SPR) spectroscopy is a surface-sensitive technique, which has been widely employed for characterizing the thickness and refraction index of a dielectric medium, typically at the surface of a noble metal (gold, silver) thin film. Due to its high sensitivity SPR sensors has emerged as a powerful sensing technique in the area of chemical and biological sensor applications (Homola, 2008; Willets and Duyne, 2007; Sharma et al., 2007). The use of surface plasmon resonance as an indicator of the ion content can be a useful approach to disseminate the application of continuous water quality management. Metal nanostructures characterized by SPR can be used to detect and quantify various metal ions, like Na^{+}, Pb^{2+}, Cu^{2+}, Hg^{2+}, Cd^{2+}, Zn^{2+}, Pt^{2+}, Ni^{2+}, Al^{3+}, Cr^{3+} and Cr^{6+} present in wastewater (Lukosz et al., 1990). Other methods for quantitatively detecting heavy metal ions include *direct aspiration absorption* and *emission spectroscopy using inductive coupled plasma* (Nie and Emory, 1997). However, these methods require expensive devices and expertize in analysis techniques. Besides, the results are not real-time and portability is an issue as well. Applications of metal nanoparticles and films in the area of SPR sensor design have shown promising results due to their tunable optical properties which greatly depend on the nanoparticle size, shape, inter-particle distance and the dielectric properties of the solvent (Buckle et al., 1993). These variations enabled researchers to develop simple yet sensitive colorimetric sensors for detecting different chemical analytes by observing the shift in their surface plasmon resonance (SPR) peak (Nikitin et al., 1997; Brandenburg and Gombert, 1993). In the early 1980s, SPR technique has been shown for the first time as a simple and cost-effective sensor in the area of gas sensing and thus the development of SPR sensors has become rapid afterwards (Schmitt et al., 2007; Gauglitz et al., 1993). For example, SPR biosensors have become a primary tool in bio-chemistry field for characterizing and quantifying interactions between bio-molecules. At the same time, the application of SPR sensors in other areas, like environmental monitoring, medical diagnostics, food safety and security etc. has gained considerable momentum with scientific publications growing almost exponentially (Goyer, 1993). Here in this article we have reviewed various SPR sensors based on metallic nanostructures used to detect the presence of heavy metal ions in water both qualitatively and quantitatively.

2. Surface plasmon resonance

Surface plasmon resonance (SPR) is a collective oscillation of charge–density that exists at the interface of two media having dielectric constants of opposite signs (for example, a metal and a dielectric), when interaction with an electro-magnetic wave (for example, light) occurs. These oscillations are highly dependent on the angle of incident of the EM (electromagnetic) wave and the angle at which the SPR occurs is called the *surface plasmon resonance angle* (θ_{spr}). Such phenomenon is typically observed when a thin metallic film is deposited on a dielectric medium, like glass. The mobile electrons, known as *surface plasmons*, at the surface of the metal film start to oscillate when resonance occurs between the

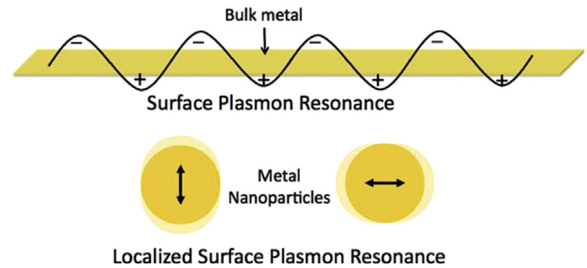

Fig. 1. Schematic illustration depicting the surface plasmon resonance (SPR) and localize surface plasmon resonance (LSPR) phenomena.

wave vector of the incoming EM wave and the wavelength of the oscillation, and hence the term *surface plasmon resonance* (Fig. 1).

In the case of metallic nanoparticles or nanostructures, oscillation of the surface plasmons, sometimes termed as *localized surface plasmons* (LSPs), is confined to the material due to their small size (Sherry et al., 2006). When resonance occurs, upon exciting the LSPs with light (EM wave), the metallic nanoparticle shows enhancement in the local EM fields with strong light scattering resulting an intense surface plasmon absorption band. This collective oscillation of LSPs at resonance results in the *localized surface plasmon resonance* (LSPR) (Sherry et al., 2006; Homola, 2006). The frequency of LSPR is characteristics to the material types, like silver, gold, platinum etc. and is strongly dependent on the shape, size and density of the nanostructures along with their surrounding environment (Hutter and Fendler, 2004). Therefore, small changes in the surrounding dielectric environment, for example, caused by molecular adsorption on the surface of the nanostructure, affect the frequency of LSPR, which can be observed as changes in the light scattering and/or absorption. These changes can be then easily translated to simple optical transmission or reflection measurements with high spectral resolution, enabling the nanostructured LSPRs as excellent sensors for the detection of chemical as well as biological analytes.

3. LSPR based sensors for heavy metal ion detection

LSPR sensors, which are based on the photo-excitation of surface plasmons at the metal nanoparticle surface, comes under the family of refractometric sensors that includes other sensors such as the grating coupler sensor (Lukosz et al., 1990; Brandenburg and Gombert, 1993; Clerc and Lukosz, 1997), the resonant mirror sensor (Buckle et al., 1993; Cush et al., 1993), and several interferometry type sensors (Schmitt et al., 2007; Gauglitz et al., 1993; Heideman and Lambeck, 1999; Heideman et al., 1993; Ymeti et al., 2005). Generally, an SPR sensor responds to the change in the refractive index of its surrounding due to the change in the quantity of interest, which is typically monitored by the SPR frequency shift.

In the quest of quantitatively detecting heavy metal ions in water several sensor devices have been developed till date, which include electrochemical impedance spectroscopy (EIS), anodic stripping voltammetry (ASV), inductively coupled plasma mass spectroscopy (ICP-MS), quartz crystal microbalance spectroscopy (QCM), ion-selective electrodes (ISE) and SPR spectroscopy etc. (Li et al., 2013). All of these devices have their own advantages, like high sensitivity and robustness as well as drawbacks, like need of sophisticated system and too large for field applications etc. Among these sensors, SPR sensors have shown potential for the future in the area of chemical and biological sensors due to its compact size, simple operation and high sensitivity.