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SPR response of CS-GO nanostructured thin films for selective detection of Pb(II) ions in the Saigon River, Vietnam

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ABSTRACT

The use of surface plasmon resonance (SPR) sensors offers a promising quantitative technique for Pb(II) detection in solutions. This study investigated the SPR response of chitosan/graphene oxide (CS-GO) nanostructured thin films in the presence of Pb(II). Gold (Au) or silver (Ag) films incorporating a CS-GO layer were fabricated and characterized by X-ray diffraction (XRD) analysis. The detection limit of Pb(II) solutions was determined using the SPR sensor on samples from the Saigon River, Vietnam. The XRD analysis revealed little difference in the crystallinity for Au/CS-GO and Ag/CS-GO films. The SPR sensitivity towards the Pb(II) ion solution was 1.332° ppm^{-1} for Ag/CS-GO, which was slightly higher than that for the Au/CS-GO, which was 1.222° ppm^{-1}. Compared to the Ag/CS-GO film, the Au/CS-GO film was reusable up to three times for all concentrations of Pb(II). Upon exposure to water samples from the Saigon River, both of the films successfully detected Pb(II) even with the interference of other metals. The CS-GO fabricated on the thin films favours the binding potential with the Pb(II) ions. Thus, the proposed Au/CS-GO film may be an economic solution due to higher reusability and higher sensitivity for the detection of Pb(II) in the polluted water.

Keywords: SPR; Toxic metals; Thin films; Chitosan; Graphene oxide; Polluted water

1. Introduction

Hazardous industrial wastewater polluted by metal ions such as Pb(II), Cu(II), Ni(II), Zn(II) and Hg(II) has detrimental implications for public health as well as for ecological systems. The toxic metals, which originate from industries such as metal plating, mining, electroplating and metal finishing, are generally non-biodegradable and may bio-accumulate in living tissues and can cause headaches, fever, nausea, diarrhoea, lung cancer, kidney cancer, damage to the cardiovascular system and even death in humans [1–3]. The World Health Organization (WHO) has set the drinking water quality guidelines that are used as an international benchmark and lists the permissible limit of Pb(II) at 10 ppb to safeguard human health worldwide [4]. The most well-known techniques in the detection of the presence heavy metals, including Pb(II), are atomic absorption spectrometry [5], inductively coupled plasma mass spectrometry [6], anodic stripping voltammetry [7] and microprobe analysis [8]. However, these techniques generally require expensive equipment, tedious pretreatment steps and longer initiation times [9,10].

In environmental studies, surface plasmon resonance (SPR) sensors are an optical sensing technique that has been used for the detection of heavy metals in water. It has been

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highlighted by Maharana et al. [11] that SPR sensors have apparent advantages over the conventional techniques. They are an inexpensive, simple, reliable procedure with a high sensitivity towards toxic metal ions. In the SPR process, a p-polarized light causes the excitation of a charge density wave along the metal-dielectric material interface at an incidence angle and thus satisfies a resonance condition [12]. In other words, when the wave vector of incident light couples with the wave vector of the surface plasmon wave (SPW) at the incident angle, a sharp dip is produced at the point of reflectance [13]. The excitation light of the SPW on a thin metallic layer, such as gold (Au) or silver (Ag), follows the Kretchmann configuration design [14]. Selection of the metallic layer is important to ensure sensors with a high sensitivity response. Homola and co-workers [12] demonstrated the propagation length for Ag to be approximately twice that of Au in the near infrared region (NIR) wavelength, which demonstrates an intrinsic sensitivity enhancement over Au. It has been reported also in [15] that Ag has higher sensitivity for the SPR sensor technique, but more effort is needed to improve the stability of Ag. Thus, to enhance sensitivity, a top coat can be used over Ag to reduce the oxidization process that usually occurs [16]. Recently, chitosan (CS), an active dielectric material, has been coated on top of the metallic layer to help increase the sensitivity of the SPR sensors. CS is a polymer that has attracted great attention due to its excellent biocompatibility and biodegradability. CS has been utilized in many applications, including wound dressing, tissue engineering, drug delivery, cosmetics and agriculture [17]. Application of CS as standalone based material has low mechanical properties and poor solubility in normal solvents due to the strong hydrogen bonding between amino ($–NH_2$) and hydroxyl (–OH) groups in CS. Thus, glutaraldehyde reagents will be used in this study for cross-linking the CS as a simple modification approach to improve its properties. To further improve the properties of CS, graphene oxide (GO) is compatible for the cross-linking process due to its epoxy groups. The graphene has a single two-dimensional (2D) plane of carbon atoms forming a hexagonal lattice structure that more strongly confined SPR than other metallic layers [18]. GO is a product of graphene oxidation which has many functional groups, such as hydroxyl (–OH), epoxy (–O) and carboxyl (–COOH) [19]. These functional groups influence a large specific surface area, have a high π-conjugation structure and make GO sheets more hydrophilic for dispersion in water compared with graphene [20]. The emergence of GO as a suitable candidate for the dielectric layer in the SPR sensing technique has recently attracted the attention of researchers. Studies on CS-GO as a candidate for sensitivity enhancement are comparatively scarce even though this active layer has the ability to bind with the metal ions in the water samples.

The Saigon River is located in Ho Chi Minh City (HCMC) in the south of Vietnam and has a total length of approximately 280 km. In 2010, water consumers in HCMC approached over eight million. As is the case many other large cities in developing countries, HCMC is facing challenges that come with rapid urbanization and industrialization [21]. It has been reported that almost 60% of wastewater discharged from industry and hospitals into the Saigon River is not treated [22]. The water of the Saigon and Dong Nai rivers is used as the drinking water for the population of HCMC, with limited purification or controls on industrial and domestic waste discharge [22,23]. Moreover, the majority of industries are located around HCMC, causing the serious depletion of the city's surface water quality; and the Saigon River has been polluted with many toxic metals, such as Al, Fe, Cd and Pb, all of which cause adverse health impacts [24].

In this study, we fabricate the Au or Ag thin films with the CS-GO mixture, which operates as an active layer, and observe the response of the SPR sensors. The objectives of this study are to establish the characterization, sensitivity and reusability of the Au/CS-GO and Ag/CS-GO thin films for Pb(II) detection using the SPR sensor technique. The response of the thin films will be further studied to detect Pb(II) in the water samples from the selected case study, the Saigon River.

2. Methods

2.1. Study site and sampling

Fig. 1 shows the sampling point of the Saigon River, Vietnam. The case study area is located at a longitude of 106° 42′ 31″ and a latitude of 10° 45′ 15″. A study at the same location by Nguyen-Thi et al. [25] found that the river is being polluted by active navigation activity and urbanization activity along the river. The study area is close to the mouth of the river and is known as the 'Saigon Port'. Nguyen-Thi et al. [25] stated that this location is a downstream area and is much more polluted compared to the upstream area. At the sampling points, 200 ml wastewater samples were taken using the grab sampling method and were stored in air tight plastic containers. The wastewater sample was kept at 4°C in a polystyrene box while it was transported to the laboratory. Upon arrival, the sample was continuously kept at 4°C until used [26].

2.2. Experimental and testing setup

Two samples of Au/CS-GO and Ag/CS-GO thin films were prepared on top of the glass substrates at room temperature. Glass cover slips or glass substrates (Menzel-Glaser, Germany) 24 mm × 24 mm thick in the 0.13–0.16 mm range were used. The glass substrates were cleaned using acetone before coating with the active layer. First, each glass substrate was coated with either gold (Au) or silver (Ag) to approximately 50 nm of thickness. Au was sputter-coated on the top of the substrates using an E-1010 Ion Sputter (Hitachi, USA) instrument with a 99.99% pure Au target. The sputter machine was operated at 100 V AC Hz with an ion current of 15 mA and under a vacuum pressure of 10 Pa for 300 s. Ag was deposited using a PVD 75 Sputter Coater (Kurt J. Lesker, USA) controlled by a film thickness monitor, located 35 mm from the Ag foil target (99.99 % in purity) and at a rotational speed of 10 rpm for 360 s. The sputtering was carried out at a power of 50 W under an argon pressure of approximately 5×10^{-3} torr at room temperature.

Commercial graphene oxide (GO) with a concentration of 2 mg/ml was purchased in solution form (Aldrich, USA). The solution was dissolved in water to prepare a 1 mg/ml concentration of GO. Then, the chitosan (CS) solution was prepared by adding 0.40 g of medium molecular weight chitosan (75–85% deacetylated - Aldrich, USA) to 50 ml of

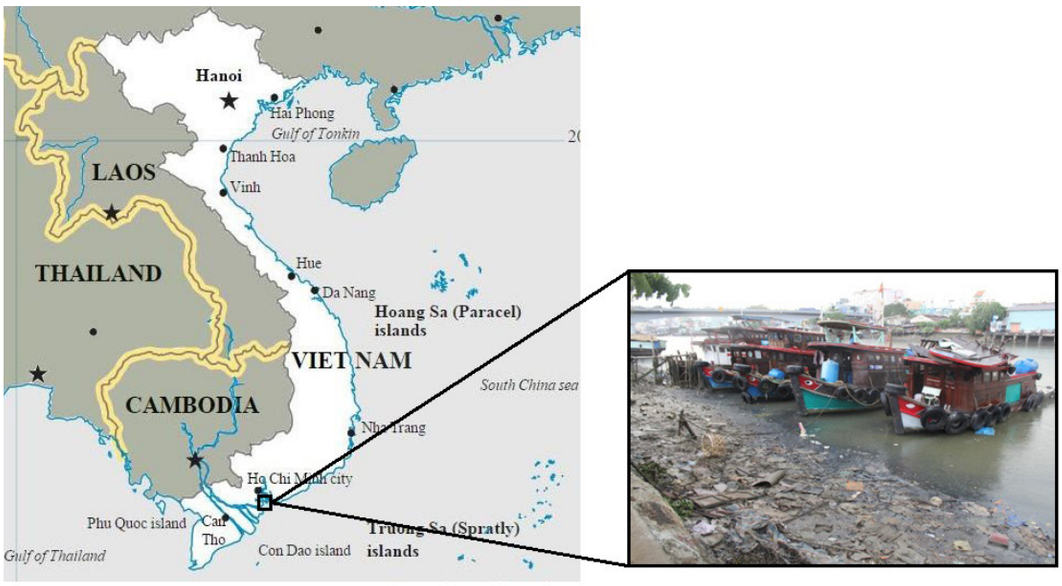

Fig. 1. Map of Saigon River in Ho Chi Minh City, Vietnam. The right picture shows the polluted sampling sites of Saigon River.

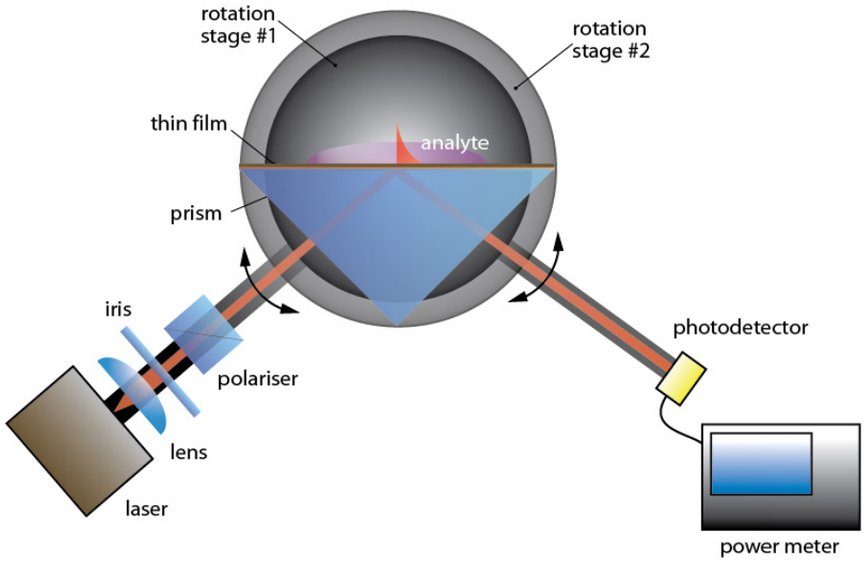

Fig. 2. SPR experimental setup (Adapted from [27]).

1% acetic acid (Aldrich, USA) and continually stirred for 24 h. Next, 0.05 ml of glutaraldehyde (Aldrich, USA) and 3 ml of GO with a concentration of 1 mg/ml were added to 45 ml of the chitosan solution and stirred for another hour. This mixture of chitosan and GO was sonicated for 10 min at 53°C to remove air bubbles. The Au/CS-GO thin film was prepared by coating the Au substrates surfaces with the CS-GO mixture solution. Approximately 0.55 ml of the mixture was coated using a WS-400BX-6NPP spin coater (Laurell Technologies, USA) operating at 6000 rev/min for 30 s. Then, for the Ag/CS-GO thin film, the same procedure was used. The thin films were then characterized by XRD analysis using a D-5000 diffractometer (Siemens, USA) with CuKα radiation (λ = 1.5406 A) and an angular scanning range (2θ) from 20° to 60°. Both films were further analysed using SPR sensors operated under a laser wavelength of 850 nm.

The arrangement of SPR experimental setup shown in Fig. 2 includes a prism, two rotation stages, a laser, a lens, an iris, a polarizer, a photodetector and an optical power meter. Fig. 2 is adapted from our previously published paper in Lokman et al. [27]. The prepared thin films were placed on the right-angle prism model N-BK7 (Thorlabs, USA) using a refractive-index-matching gel known as glycerine (Aldrich, USA). The laser light source is incident to the prism, which is in contact with the film, and its reflectance

is determined by a photodetector and then processed by the optical power meter.

Starting with an initial concentration of 1000 ppm of standard Pb(II) solution, different concentrations are prepared at 0.03 ppm, 0.10 ppm, 0.50 ppm, 1 ppm, 3 ppm and 5 ppm using a dilution process. Approximately 0.50 ml analytes of deionized (DI) water or lead Pb(II) solution ranging from 0.03 to 5 ppm are placed on top of the thin films. The prism is positioned on top of a motorized rotation stage with two worm drives, model CR1/M-Z7E (Thorlabs, USA). The laser light is rotated to enable the excited light through the prism and the S120VC photodetector (Thorlabs, Malaysia) is then aligned corresponding to the reflectance angle. The laser with 1 mW output power is used to transmit light into the right-angle prism. The transmitted light was coupled using an aspheric lens, model C240TME-B (Thorlabs, USA), which was optimized with an SM1D12 iris (Thorlabs, USA) and polarized using a polarized beam splitter, model number PBS202 (Thorlabs, USA). The change in the reflected light corresponding to the SPR response of the thin films interacting with the analytes was detected using the photodetector and measured using the PM100D optical power meter (Thorlabs, USA).

The SPR curves of both films in contact with the pure DI water and with different concentrations of Pb(II), ranging from 0.03 to 5 ppm, were plotted. The reflectance, R reaches its minimum value at the resonance and simultaneously, the incidence angle was recorded and used to plot the SPR curves. The initial incidence angle (θ) was measured when the coated surface of the thin films made contact with the pure DI water (as a baseline). As the concentration of Pb(II) increased, the new incidence angle was determined and the difference in the incidence angles (Δθ) was recorded. Finally, the SPR sensitivity was further calculated by the Δθ over the concentration of the Pb(II).

For the reusability test, the Au/CS-GO thin film was exposed to all six concentrations of Pb(II) from 0.03 to 5 ppm, which were prepared earlier with up to five replicates. After the first replicate or reusability test, any remaining Pb(II) solution on the thin film is removed by using a lint-free wipe and rinsed with DI water before the subsequent reusability test is carried out. This step was repeated with the Ag/CS-GO thin film.

The amount of Pb(II) in the five water samples taken from Saigon River was tested using the inductively coupled plasma-atomic emission spectrometry (ICP-AES) method conducted by ALS Technicem (M) Sdn. Bhd. located in Shah Alam, Selangor. Then, using both thin films, Au/CS-GO and Ag/CS-GO thin films, we conducted the experiment to confirm the applicability of the SPR sensors in the detection of Pb(II) in real water samples. In the laboratory, synthetic water sample were spiked with Pb(II) at a similar concentration of 0.60 ppm, following the detection results of the ICP-AES method. The prepared sample was then tested with the proposed thin films to establish the SPR curves.

3. Results and discussion

3.1. Characterization study

The X-ray diffraction (XRD) patterns of the Au/CS-GO and Ag/CS-GO thin films are presented in Fig. 3. The XRD signals for both thin films exhibited a broad peak in the 2θ range between 20.0° to 30.0° attributed to the general amorphous peak of chitosan as reported by Wang et al. [28]. Two diffraction peaks for the Au/CS-GO thin film showed the most prominent peaks located at (2θ = 38.45° and 44.83°) can be indexed to the planes (111) and (200), respectively. A similar result was reported by Folarin et al. (2011) for Au. The planes matched the Joint Committee on Powder Diffraction Standards (JCPDS-file no. 00-04-0478) of face-centred cubic (fcc) crystal structures ascribed to Au. The strongest prominent peak at the (111) plane attributes to 93.71 nm of the crystallite size following the Debye-Scherrer equation [29]:

$$D = \frac{k\lambda}{\beta\cos\theta} \quad (1)$$

where k is the Scherrer constant (0.94), λ is the wavelength of the X-rays (1.5406A), β is the full width at half maximum (FWHM) and θ is the Bragg angle.

The diffraction peaks for the Ag/CS-GO were similar to those for the Au/CS-GO thin films, where the two strongest prominent peaks were located at similar angles of (2θ = 38.40° and 44.60°) for the (111) and (200), respectively. The peaks closely matched the Joint Committee on Powder Diffraction Standards (JCPDS-file no. 00-004-0783) entitled to Ag with a face-centred cubic (fcc) crystal structure. Choi et al. (2003) also reported the same peaks ascribed to Ag. Analysis of the most prominent peak (111) accounted for a crystallite size of 90.10 nm, just slightly smaller than that for Au/CS-GO. It can be summarized that from the XRD, the structural analysis of both thin films confirms that the fabrication does not differ much because the same coated material was used, namely, chitosan-graphene oxide. Thus, it is expected that the performance of the Au/CS-GO thin film is on a par with that of the Au/CS-GO.

Figs. 4a and 4b show the SPR curves of the Au/CS-GO and Ag/CS-GO thin films, respectively, with pure DI water and different concentrations of Pb(II) ranging from 0.03 to 5 ppm. In Fig. 4a the trend of the SPR curves for the Au/CS-GO thin film shifted to the left starting from DI water to the other incremental concentrations of Pb(II). Initially, when the thin film was in contact with the DI water, the minimum reflectance was found at the incidence angle of

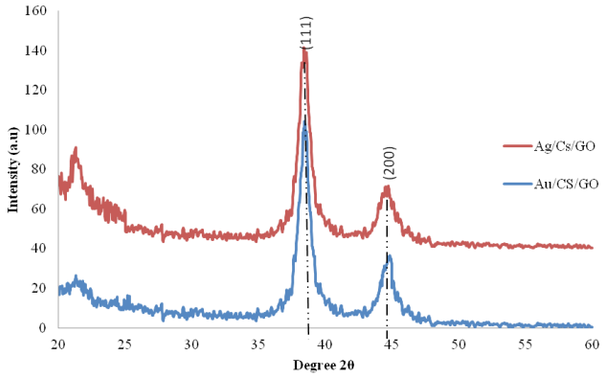

Fig. 3. The X-ray diffraction (XRD) patterns of the Au/CS-GO and Ag/CS-GO thin films.

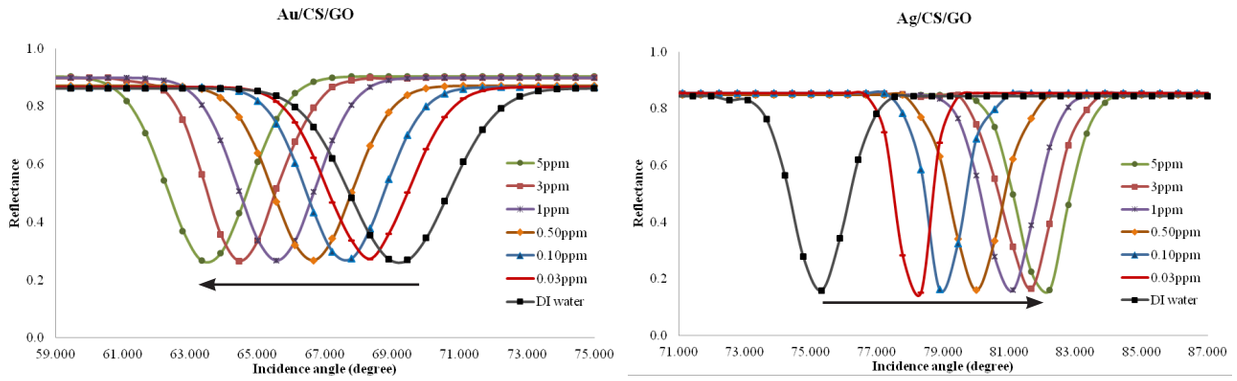

Fig. 4. The SPR curves of the (a) Au/CS-GO and (b) Ag/CS-GO thin films.

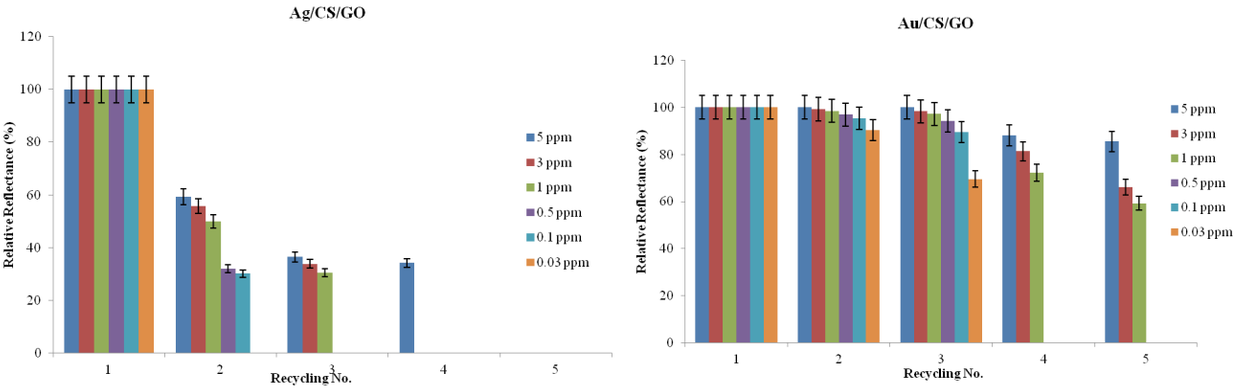

Fig. 5. The reusability of the (a) Au/CS-GO and (b) Ag/CS-GO thin films.

69.44°. The Δθ progressively increased to 1.11°, 1.66°, 2.77°, 3.88°, 5.55° and 6.11° for Pb(II) concentrations of 0.03 ppm, 0.10 ppm, 0.50 ppm, 1 ppm, 3 ppm and 5 ppm, respectively. Thus, the SPR sensitivity at 5 ppm of Pb(II) was measured to be 1.222° ppm^{-1}.

The SPR curves for the Ag/CS-GO thin films in Fig. 4b were shifted to the right from the DI water to higher concentrations of Pb(II). However, a similar increasing trend of Δθ was observed at 3.01°, 3.57°, 4.68°, 5.79°, 6.35° and 6.90° for Pb(II) concentrations of 0.03 ppm, 0.10 ppm, 0.50 ppm, 1 ppm, 3 ppm and 5 ppm, respectively. As the result, the Ag/CS-GO thin film attained slightly higher SPR sensitivity than the Au/CS-GO film, where 1.38° ppm^{-1} was obtained. Compared to Fig. 4a, the width of the SPR curves for Ag/CS-GO were narrower and the reflectance dip reached the lowest point. The stated features of the SPR curves correspond to higher sensitivity [30].

The trend of the SPR curves with increment concentrations of Pb(II) shifted either to the left or right corresponding to an increase in Δθ due to the metal ions that were absorbed onto the surface of the metal thin film [31]. Meanwhile, higher SPR sensitivity may be achieved if the SPR sensor was operated at a longer wavelength (NIR), which would attain deeper laser light penetration and coat the substrate with an active metal layer, such as Ag, that possesses a higher modulus of the real part of the dielectric constant [32]. In the present study, the SPR sensor was designed to operate at an 850 nm (NIR range) wavelength and introduced Ag as the active layer on the substrate. Moreover, CS, with abundant amounts of hydroxyl and amino groups, possesses a suitable configuration for excellent adsorption of heavy metals [33]. Thus, the result shows comparably good SPR sensitivity for both Au/CS-GO and Ag/CS-GO thin films. The corresponding limit of detection for this study is 0.03 ppm, which indicates that the SPR sensors techniques with both thin films are capable of tracing the Pb(II) accumulated in water even at a low concentration.

Recycling experiments were carried out five times to observe the reusability ability of the thin films in contact with the Pb(II) ranging from 0.03 to 5 ppm. The reusability performance of the Au/CS-GO and Ag/CS-GO films are shown in Figs. 5a and 5b, respectively. In terms of trends, it was found that the percentage of relative reflectance declined with increasing the times the films were reused for both films. The Au/CS-GO shows a good percentage of relative reflectance for all the concentrations of Pb(II) up to the third reusability test, compared to only one time for Ag/CS-GO. The Au/CS-GO film still showed a good response at the fourth and fifth reusability tests, measured at almost 70% for 1–5 ppm of Pb(II). Unfortunately, the Ag/CS-GO film shows no response the fifth time even with a higher trace concentration of Pb(II). Meanwhile, magnitudes of the error bars for all recycling numbers represent the stability for Au/CS-GO compared to Ag/CS-GO. The reusability of

Table 1
The concentrations of Pb(II) ions for five samples

Sample	Concentration (ppm)
1	0.600
2	0.620
3	0.600
4	0.590
5	0.610
Mean	0.600

the thin films is important to ensure the proposed method is potentially economic [30].

The water sample from the Saigon River was tested using the inductively coupled plasma-atomic emission spectrometry (ICP-AES) method conducted by ALS Technicem (M) Sdn. Bhd. (located in Shah Alam, Selangor), and the amount of Pb(II) concentration accumulated in the sample was measured to be 0.60 ppm on average, as shown in Table 1.

This value was over the permissible limits of Pb (II)Pb(II) concentration sets by Environmental Quality Act (EQA) with of 0.10–0.50 ppm only and the World Health Organization (WHO) with of 0.01 ppm only. Therefore, the water sample was clearly polluted and unsafe to for consumers. Thus, by using both thin films, Au/CS-GO and Ag/CS-GO thin films, we conduct the experiment to conform the applicability of the SPR sensors in the detection of Pb (II)Pb(II) in real water samples. In the laboratory, the synthetic water samples were spiked with Pb (II)Pb(II) at the a similar concentration (0.60 ppm Pb (II)Pb(II) solution), as detected from the ICP-AES results. The prepared sample was then tested with the proposed thin films to establish the SPR curves. These curves were referred as a baseline for further analysation analysis with the real water samples from the Saigon River.

Fig. 6 shows the SPR curves for both thin films tested on with the synthetic water sample and the real water sample (from the Saigon River). It can be seen that the incidence angle for the Au/CS-GO and Ag/CS-GO thin films on the synthetic water sample were marked at 66.67° and 80.00°, respectively. They were in agreement with the SPR curves in the previous section (Figs. 4a,b) because the incidence angle for the synthetic water samples were located in between 0.50–1.00 ppm in the previous section.

The SPR curves for both thin films on with the river water samples were then plotted, and the curvesy matched very well with the synthetic sample. This implies that the river water sample had a concentration of 0.60 ppm, which exactly matched to the result from the ICP-AES method. Upon exposure to the Au/CS-GO thin film, the reflectance for the synthetic water sample and river water sample were measured to be 0.268 and 0.322, respectively, and accounted for 16.81% of the percentage difference. Whereas the SPR curve for the Ag/CS-GO thin film was narrower and sharper than that of the Au/CS-GO; therefore, thus the minimum reflectance point for the synthetic sample was 0.160, and the minimum reflectance and for the river water sample was slightly higher, which measured at 0.284. Thus, the percentage difference was calculated as 43.55%, almost twice that

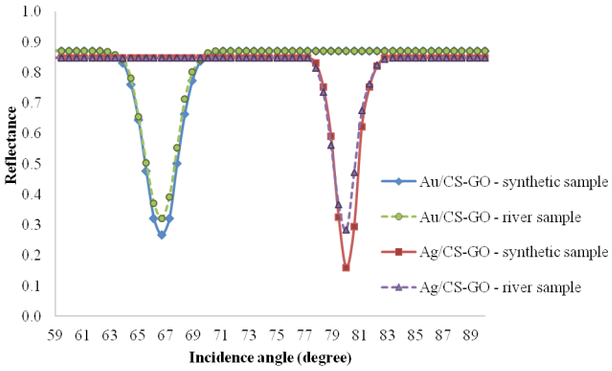

Fig. 6. The SPR curves of the (a) Au/CS-GO and (b) Ag/CS-GO thin films for water samples from the Saigon River.

from Au/CS-GO. It can be depicted therefore, that the Au/CS-GO film is more stable when in contact with the river water samples.

4. Conclusion

It was found that the SPR sensors with Au/CS-GO and Ag/CS-GO thin films are capable of detecting down to 0.03 ppm of Pb(II). Both thin films exhibit great sensitivity mainly due to the CS-GO that binds strongly to the Pb(II) ion. However, the Au/CS-GO demonstrates better reusability with up to three times compared to the reusability of the Ag/CS-GO. In the river water samples, both thin films show good results on the detection of Pb(II), which opens a new avenue for fabricating excellent thin films for environmental applications. In this study, the Au/CS-GO demonstrated comparable sensitivity with Ag/CS-GO, but showed higher reusability results. Thus, we concluded that Au/CS-GO is more suitable to apply with the SPR sensors because it possesses high sensitivity, reusability and as a result, is more economical.

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