

## **Surface Plasmon Resonance Sensing Properties for Chitosan/Carboxyl-Functionalized Graphene Quantum Dots Thin Film**

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**Abstract:** In this study, chitosan/carboxyl-functionalized graphene quantum dots thin film was developed. Sensing properties were explored by using surface plasmon resonance. The experimental surface plasmon resonance curves were obtained for different concentration in a range from 0 to 100 ppm of mercury solution. These results confirmed that the chitosan/carboxyl-functionalized graphene quantum dots thin film shows potential for the detection of mercury using surface plasmon resonance technique.

**Keywords:** Optical properties; Graphene; Chitosan; Quantum Dots; Surface plasmon resonance; Sensing; Mercury ion.

With continuing advances in science and technology, semiconductor-based thin film has become a focus of attraction of researchers. The thin film is a layer of material deposited on glass slip with a thickness ranging from  $10^{-6}$  m and above. Thin film has distinct advantages over thick film due to the properties of the thin film that tightly bound to particle size, shape and surface properties [1]. Other than that, the structural and optical properties depend and can be modified by the deposition thin film process [2]. As deposition conditions apply to thin film and plasma enhancement, crystalline phase composition can be varied to a certain extent.

There are various methods being developed for depositing thin film including evaporative methods, glow-discharge process, gas-phase chemical process, liquid-phase chemical techniques and dip coating [3,4]. However, these methods suffer from a severe drawback such as complex operation, expensive equipment, and expert operators is needed [4]. To overcome the aforementioned drawback, spin coating technique has been used to deposit a layer of material on glass film. Thus, the thickness of the thin film depends on the angular speed of spinning [3]. Graphene is a single layer of graphite or in other words, have one layer of carbon that bonded by  $sp^2$  bond in a honeycomb lattice that can be found in metallic substrate [5]. This unique material has unique physical properties such as high surface area, electrically high conductivity, high transparency, and high thermal stability [6]. In addition, linear energy-momentum relationship and zero bandgaps are the most unique properties of graphene [5]. However, zero bandgaps will give impacts on zero results of optical luminescence that been observed in pristine graphene. After the invention of graphene to GQDs, researchers have discovered of functional conversion give effects on GQDs. Therefore, -COOH functionalized is an excellent option for adjusting the performances of materials [7].

The potential of carboxyl-functionalized graphene quantum dots (CGQDs) thin film will be greatly developed when the composite is in combination with polymeric materials [8]. An organic polymeric material with good optical and mechanical properties has attracted

attention from the scientific community [9]. Chitosan is one of organic polymeric material that consists of the copolymer of glucosamine and N-acetyl glucosamine linked by a  $\beta$ -1,4 glycosidic bond which been derived by alkaline N-deacetylation from chitin [10]. The special characteristics of chitosan are biodegradability, biocompatibility, good film-forming, and good absorption properties, low cost and non-toxicity [2]. Hence, chitosan has been integrated with CGQDs as a thin film to be used in an optical sensor to detect heavy metal ion.

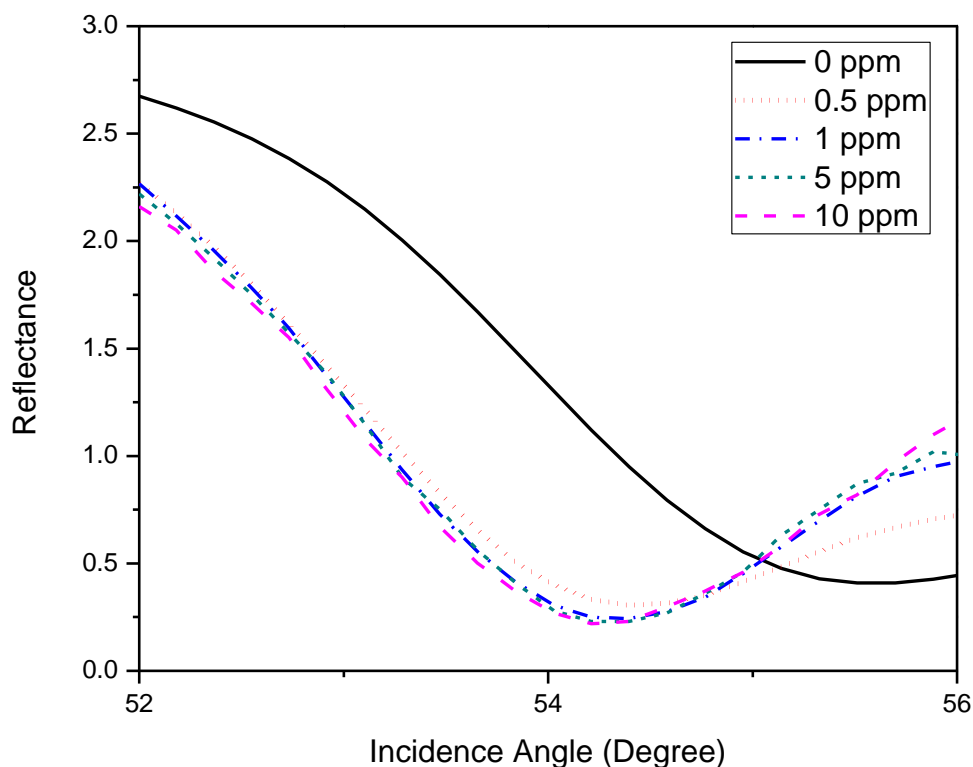
Surface plasmon resonance (SPR) spectroscopy, one of the optical sensor has been developed in various configuration and formats for sensing a variety of target samples, including heavy metal ion [11-13]. This optical sensor is a surface-sensitive technique that been used to characterize the thickness and refractive index of the dielectric medium. This technique was widely used in biological and chemical sensor applications [14-18]. A sharp shadow, called surface plasmon resonance, is observed by the reduction of the intensity of the reflected light at a specific incident angle, which is due to the resonance energy between the incident beam and surface plasmon wave [19]. By developing or depositing a thin film of suitable material on the metal thin film, it will be resulting in a good specificity of the SPR optical sensor to heavy metal ion [20-22].

Although fruitful accomplishments have been achieved worldwide, the study of optical properties of chitosan/carboxyl-functionalized graphene quantum dots (Cs/CGQDs) thin film and its surface plasmon resonance sensing properties is yet to be reported. Therefore in this study, the optical and potential sensing properties of Cs/CGQDs thin film are explored and reported.

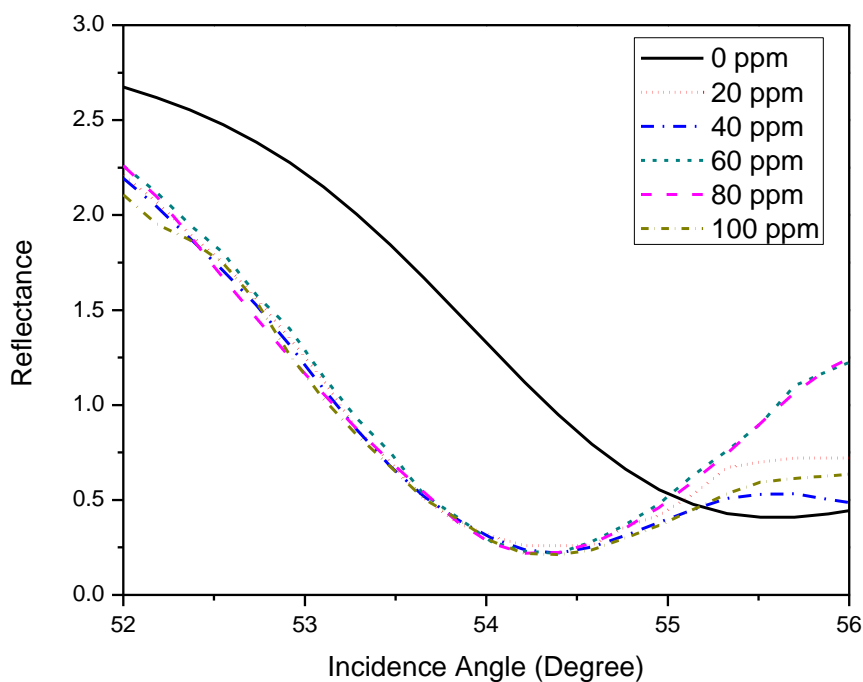
The CGQDs solution was purchased from ASC Material, America, chitosan was purchased from Sigma Aldrich (St. Louis, MO, USA) and acetic acid was also obtained from Aldrich. Firstly, 1 ml of stock acetic acid was diluted by adding deionized water in 100 ml volumetric flask to obtain 1% acetic acid. Next, 50 ml of 1% aqueous acetic acid was used to dissolve 400 mg medium molecular weight chitosan. Then, the solution was stirred to ensure powdered chitosan dissolved completely. Lastly, CGQDs solution was obtained by mixing 10 ml of diluted CGQDs into chitosan solution and stirred. Firstly, the glass cover slip ( $24 \times 24 \times 0.1 \text{ mm}^3$ ) was cleaned by acetone to remove any dirt or fingerprint mark on the surface of the glass film. Next, the glass slip was coated with gold layer by using SC7640 Sputter Coater for 67 seconds. Then, the glass slip underwent another coating process to add another layer. 1000 $\mu$ l of diluted chitosan solution, diluted CGQDs solution and diluted Cs/CGQDs solution were added separately on gold-coated glass cover slip and spun under 3000 rev/min for 30 seconds. Spin coater was used to ensure the glass slip surface coated with chitosan, CGQDs, and Cs/CGQDs solution evenly. For sensing metal ion, SPR measurement has been carried out to determine the potential of Cs/CGQDs thin film for sensing  $\text{Hg}^{2+}$  solution. Figure 1 shows the schematic diagram of the SPR instrument setup. The SPR measurement was carried out by measuring the reflected He-Ne laser beam (632.8 nm, 5 mW) as a function of incident angle. The SPR setup consists of a He-Ne laser, an optical stage driven by a stepper motor with a resolution of  $0.001^\circ$  (Newport MM 3000), a polarizer and an optical chopper (SR 540). The He-Ne laser beam was incident on the prism (refractive index of 1.77861), passed through the thin film and a photodiode. The reflected beam was detected and then processed by the lock-in amplifier (SR 530) [23].

SPR experiment for  $\text{Hg}^{2+}$  solution of concentration ranged from 0.5 ppm to 100 ppm was carried out. The SPR curve of Cs/CGQDs thin film when in contact with different concentration of  $\text{Hg}^{2+}$  solution are shown in Fig. 1(a) and (b). The resonance angle then was determined from the SPR curve of 0.5, 1, 5, 10, 20, 40, 60, 80 and 100 ppm respectively.

To find the resonance angle shift, the resonance angle of  $\text{Hg}^{2+}$  was used and compared with deionized water resonance angle as shown in Table 1. The resonance angle of 0.5 ppm  $\text{Hg}^{2+}$  concentration have slightly shift from deionized water resonance angle when in contact with Cs/CGQDs thin film as shown in Fig. 1. The resonance angle of Cs/CGQDs thin film also shifted further when higher concentration was used until 100 ppm. The resonance angles remain the same for  $\text{Hg}^{2+}$  concentration ranging from 0.5 to 100 ppm.



(a)



(b)

**Figure 1:** SPR Curve gold/Cs/CGQDs thin film in contact with deionized water

**Table 1:** The resonance angle ( ) and shift of resonance angle ( for different concentration of  $Hg^{2+}$  solution in contact of gold/Cs/GQDs thin film

Concentration of mercury ion (ppm)	Resonance Angle, (degree)	Shift of Resonance Angle, (degree)
0	55.5120	0
0.5	54.4049	1.1071
1	54.3216	1.1904
5	54.3097	1.2023
10	54.2978	1.2133
20	54.2859	1.2261
40	54.2740	1.2380
60	54.2621	1.2499
80	54.2502	1.2618
100	54.2411	1.2709

In conclusion, in this study, Cs/CGQDs thin film has been prepared using spin coating technique. The experimental SPR curves were obtained for different concentration (0 to 100 ppm)  $\text{Hg}^{2+}$  solution. These results confirmed that the Cs/CGQDs thin film has the potential for the detection of  $\text{Hg}^{2+}$  using surface plasmon resonance technique.

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