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Incorporation of surface plasmon resonance with novel valinomycin doped chitosan-graphene oxide thin film for sensing potassium ion

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ABSTRACT

In this study, the combination of novel valinomycin doped chitosan-graphene oxide (C–GO–V) thin film and surface plasmon resonance (SPR) system for potassium ion (K^+) detection has been developed. The novel C–GO–V thin film was deposited on the gold surface using spin coating technique. The system was used to monitor SPR signal for K^+ in solution with and without C–GO–V thin film. The K^+ can be detected by measuring the SPR signal when C–GO–V thin film is exposed to K^+ in solution. The sensor produces a linear response for K^+ ion up to 100 ppm with sensitivity and detection limit of 0.00948° ppm^{-1} and 0.001 ppm, respectively. These results indicate that the C–GO–V film is high potential as a sensor element for K^+ that has been proved by the SPR measurement.

1. Introduction

Potassium ion (K^+) is a mineral necessary and make up about 0.4% mass in the human body [1]. The maintenance of appropriate K^+ concentration is important for many physiological activities in living cells such as nerve transmission, enzyme activation, balancing the pH and regulation of blood pressure [2–4]. However, unbalancing K^+ ion may cause several diseases such as high blood pressure and stroke [5] if excessive and hypokalemia if lack in K^+ [6] in our body system. Therefore, the determination of K^+ is very critical in clinical diagnosis, nutritional analysis and also biochemical application. Recently, there are varieties of techniques in order to determine K^+ ion, such as fluorescence spectrum [7–10], electrochemistry [11–13], calorimetry [14–15], flame photometry [16–17] and so on. However, these method mostly expensive and often take a long time to analysis. Recently, analytical interest has focused on optical sensors that have the advantage of cost-effectiveness, fast measurement capability and no requirement of reference solution [18–19].

Liedberg et al. was the earliest to report the application of the surface plasmon resonance (SPR) technique for chemical sensing [20]. SPR offers an economical, showing ease of operation, rapid detection and excellent sensitivity and selectivity towards ion [21–22]. SPR is an optical process in which light satisfying a resonance condition excites a charge-density wave propagating along the interface between a metal and a dielectric material using a monochromatic and p-polarized light beam [23]. SPR sensing structure for sensing has been generating continuously growing attention from the science community [24–25] and the use of SPR as a metal ion detection had been widely studied [26–31]. However, to the best of our knowledge, SPR is yet applied to K^+ detection in aqueous solution. Hence in this study, we investigate the effect of chitosan-graphene oxide doped with valinomycin to detect the K^+ in aqueous solution using SPR method.

In this study, we created a surface that can sensitively adsorb K^+ in aqueous solution. Chitosan and graphene oxide has been used as a main matrix for our novel active thin film. Chitosan is chosen due to the amine functionality on the chitosan chain, confers both polyelectrolyte and chelate properties, which plays an important role in detecting metal ion [32–37] while graphene oxide is chosen because of their excellent in electrical and optical properties, which make a graphene a strong candidate for a number of potential application like sensing metal ion [38–40]. In order to enhance the sensitivity towards K^+ ion, valinomycin has been doped into the chitosan–graphene oxide matrix. Valinomycin, a potassium ionophore, is envisaged to provide a sensitive determination towards K^+ owing it is a cyclic dodecadepsipeptide, i.e. made of twelve alternating amino acids and esters, with cavity (Fig. 1) which has a strong affinity towards potassium ion [41–42]. The

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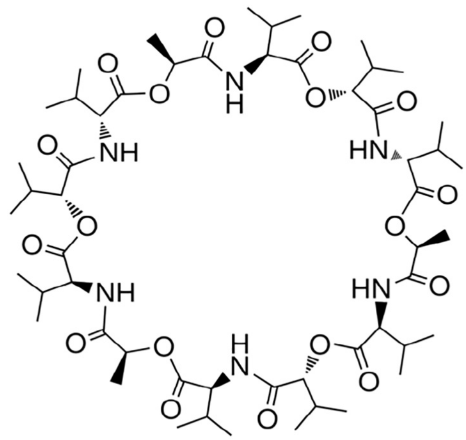

Fig. 1. Structure of valinomycin that used for K^+ detection.

potential of valinomycin doped chitosan-graphene oxide (C–GO–V) thin film as a sensor layer for detection of K^+ in SPR optical sensor is described in this paper.

2. Material and Methods

2.1. Reagent and Materials

Medium molecular weight (MMW) chitosan with MW of 190,000–310,000 and degree of deacetylation 75–85% and acetic acid (assay ≥ 99.7%) were purchased from Sigma Aldrich (St. Louis, MO, USA). The graphene oxide (4 mg/ml) was purchased from Graphenea (Cambridge, MA, USA). The valinomycin was obtained from Fluka (Buchs, Belgium). Atomic Adsorption Spectroscopy standard solution (1000 ppm) of potassium ion was purchased from Merck (Darmstadt, Germany).

2.2. Preparation of Chemicals

All chemical used were of analytical grade and deionized water was used for all solution preparation. A stock valinomycin solution of 2.0 $\times$ 10^{-3} g/ml or 20% *w*/*v* was prepared by dissolving 100 mg of valinomycin in 50 ml deionized water. Potassium standard solution with a concentration of 1000 ppm were diluted using the dilution formula $M_1V_1 = M_2\,V_2$ to produce K^+ solutions with concentration 10, 20, 40, 60, 80, 100 ppm [43].

2.3. Preparation of Thin Film

Glass cover slips (24 mm × 24 mm × 0.1 mm, Menzel-Glaser, Germany) were cleaned using acetone to remove dirt on the surface of the glass slide before any coating process. The glass slides were first deposited with a thin gold layer using an SC7640 sputter coater. Then, spin coating technique (Specialty Coating System, P-6708D) was used to produce a thin layer of C–GO–V film on top of the gold layer. Before the spin coating process, the C–GO–V solution was prepared.

Chitosan–graphene oxide solution was prepared by dissolving 0.40 g of medium molecular weight chitosan and 10 ml graphene oxide in 40 ml of 1% of acetic acid. The solution was stir for 24 h until all chemical dissolved. Immobilization of valinomycin inside the chitosan– graphene oxide is done by mixing 5 ml of 20% *w*/*v* valinomycin with 45 ml chitosan–graphene oxide solution and the mixture was stirred thoroughly for several hours.

Approximately, 1 ml of the solution (C–GO–V) was placed on the top of the gold layer covering the majority of the surface. The glass cover slip was spun at 3000 rev/min for 30 s to produce the thin film.

2.4. Sensing Metal Ion

An optical spectroscopy was designed in the laboratory to test the capability of the thin film for sensing potassium ion based on the principle of surface plasmon resonance (SPR). The schematic diagram of SPR instrument set up as shown in Fig. 2. 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 optical setup consists of a He—Ne laser, an optical stage driven by a stepper motor with a resolution of 0.001° (Newport MM 3000), a polarizer and an optical chopper (SR 540). The He—Ne laser beam was incident on to the prism (refractive index of 1.77861), passed through the sample (derivative thin film), and the reflected beam was detected by a large area photodiode. The signal was then processed by the lock-in amplifier (SR 530).

3. Result and Discussion

3.1. SPR Signal for K^+ on Gold Single Layer

Prior to the measurement, a preliminary SPR test was carried out with deionized water in contact with gold layer. About 2 ml of deionized water was injected into the cell in contact with the gold film. The SPR reflectivity curve for gold film – deionized water is shown in Fig. 3. From the SPR curve, the resonance angle obtained is 53.780°.

The SPR experiment was then carried out for different concentrations of K^+ in aqueous solution, which were injected one after another into the cell to attach with the gold layer. The SPR reflectivity curves for K^+ range from 10 to 100 ppm in contact with the gold film are shown in Fig. 4. The resonance angle for all concentrations of K^+ was monitored. It can be observed that the resonance angle is not changed for all concentrations, as shown in Fig. 5. This is probably due to only a small number of K^+ existing in these concentration solutions to be adsorbed to the only gold surface. Furthermore, this can be attributed by similarity of refractive index for low concentration of metal ion [45].

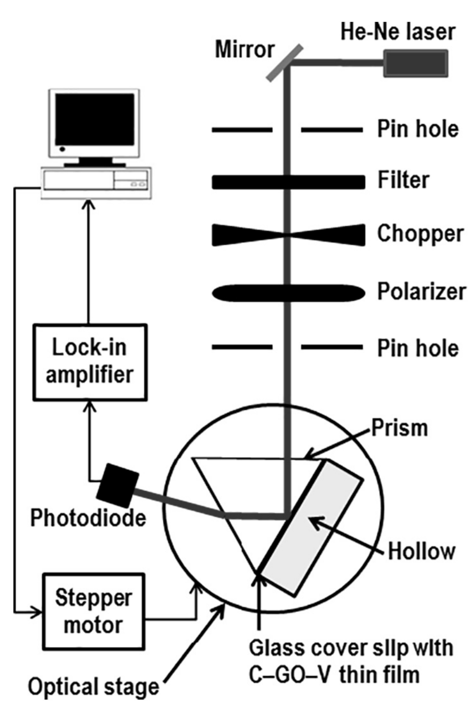

Fig. 2. Experimental set up for angle scan SPR technique [44].