Hexadecyltrimethylammonium Bromide Modified Nanocrystalline Cellulose/Graphene Oxide Composite Thin Film Incorporated with Surface Plasmon Resonance Spectroscopy for Sensing Copper Ion

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Abstract: In this research, hexadecyltrimethylammonium bromide modified nanocrystalline cellulose/graphene oxide composite (CTA-NCC/GO) layer was prepared by using spin coating technique on gold-coated glass layer was prepared. The composite was used to detect copper ion using surface plasmon resonance spectroscopy and the sensor detection limit was 0.01 ppm until 0.5 ppm.

***Keywords*:** Surface plasmon resonance, Nanocrystalline Cellulose, Graphene oxide, Sensing, Copper ion

INTRODUCTION

After iron and zinc, the most abundant transition metal ion is copper. It is reported that copper and some proteins is essential in producing about 20 enzymes important for life [1]. Moreover, it is reported that copper is very important to help in producing bones, tissue formation, cellular respiration, and brain functions [2]. However, excess exposure copper in various ways such as in drinking water or other environmental sources could lead human to serious diseases such as Alzheimer, Parkinson, and Wilson disease. In human blood, copper is limited to 23.6 μM while in drinking water, it is limited to 15-30 μM. Hence, it is crucial to monitor copper at low concentration. Nanocrystalline cellulose is the most abundant polymer that contained negative charge on their surface [3]. To enhanced cellulose properties, hydroxyl functional group in cellulose can be modified by using several methods [4–8]. In this work, NCC has been made to be partially hydrophobic by modification of NCC with hexadecyltrimethylammonium bromide (CTAB) using method reported by Abitbol et al. [9], and incorporated with SPR sensor for Cu^{2+} sensing.

MATERIALS AND METHODS

Graphene oxide, hexadecyltrimethylammonium bromide (CTA), copper ion solution (1000 ppm) and nanocrystalline cellulose (NCC) were purchased from Sigma Aldrich (St. Louis, MO, USA). All chemical were analytical grade and deionized water was used for all solution preparation. To prepare CTA-NCC, previous method reported by Abitbol et al. was used. First, 5 g of NCC was diluted in 100 ml (0.1 wt.% suspension) are mixed with 0.1 wt.% CTA. The obtained CTA-NCC solution then was centrifuge for 10 minutes and repeated 3 times. To prepare CTA-NCC/GO, the process begins by dispersing 1 ml of the GO into 1 ml of CTA-NCC to produce CTA-NCC/GO and sonicated in bath sonicator at a temperature of 70˚C for about 1 hour. To dilute the copper solution, copper standard solution of 1000 ppm concentration was diluted with deionized water by using dilution formula $M_1V_1=M_2V_2$ and the prepared solution were 0.01, 0.05, 0.08, 0.1, 0.5, 1, 5, 10, and 20 ppm.

Substrate glass with area of 24 mm x 24 mm and thickness 0.13-0.16 mm were purchased from Menzel-Glaser. The substrate first was cleaned with acetone to remove dirt and fingerprint marks on the glass surface. Then, gold layer were deposited on the glass surface using SC7640 Sputter Coater. To dispersed CTA-NCC/GO solution uniformly on top of the gold layer, spin coating technique was

used. About 1 ml of CTA-NCC/GO solution was placed on the gold layer surface and the glass slip was spun at 6000 rpm at 30 seconds using spin coater P-6708D.
Surface plasmon resonance spectroscopy (SPR) was used to test the ability of the thin film in sensing copper ion. The thin film is sandwiched between the glass film and the dielectric layer which is copper solution. The copper ion solution with concentration of 0.01 ppm until 20 ppm then was injected into the hollow one by one and the reflected beam was recorded [10].

RESULTS AND DISCUSSION

SPR experiment for Cu^{2+} solution of concentration ranged from 0.01 ppm to 20 ppm was carried out. The SPR curve of CTA-NCC/GO thin film when in contact with different concentration of Cu^{2+} solution are shown in Fig. 1. The resonance angle then was determined from the SPR curve of 0, 0.01, 0.05, 0.08, 0.1, 0.5, 1, 5, 10, and 20 ppm respectively.
To find the resonance angle shift, the resonance angle of Cu^{2+} was used and compared with deionized water resonance angle as shown in Table 1. The resonance angle of 0.01 ppm Cu^{2+} concentration have slightly shift from deionized water resonance angle when in contact with CTA-NCC/GO thin film as shown in Fig. 1. The resonance angle of CTA-NCC/GO thin film also shifted further when higher concentration was used until 0.5 ppm. The resonance angles remain the same for Cu^{2+} concentration ranging from 0.5 to 20 ppm.

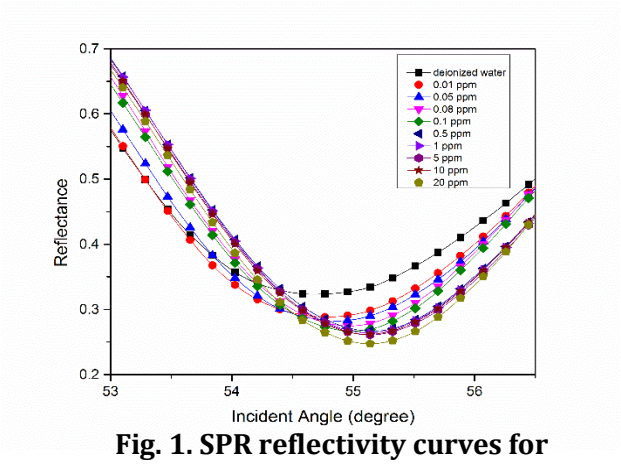

Fig. 1. SPR reflectivity curves for CTA-NCC/GO thin film in contact with Cu^{2+}solution of 0.01-20 ppm

Table 1. Resonance angle and angle shift for all Cu^{2+} solution concentration in contact with CTA-NCC/GO thin film

Concentration	Resonance angle	Angle shift
0	54.6769	0
0.01	54.7732	0.0963
0.05	54.8496	0.1727
0.08	54.9584	0.2815
0.1	54.9773	0.3004
0.5	55.1456	0.4687
1	55.1456	0.4687
5	55.1456	0.4687
10	55.1456	0.4687
20	55.1456	0.4687

CONCLUSIONS

CTA-NCC/GO composite thin film was prepared using spin coating technique. Variation in resonance angle shift from 0.01 to 0.5 ppm confirmed that CTA-NCC/GO had adsorbed Cu^{2+} in aqueous solution and can be used to detect Cu^{2+}.

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