Article

Cellulose and Vanadium Plasmonic Sensor to Measure Ni^{2+} Ions

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Abstract: A novel vanadium–cellulose composite thin film-based on angular interrogation surface plasmon resonance (SPR) sensor for ppb-level detection of Ni(II) ion was developed. Experimental results show that the sensor has a linear response to the Ni(II) ion concentrations in the range of 2–50 ppb with a determination coefficient (R^2) of 0.9910. This SPR sensor can attain a maximum sensitivity ($0.068^\circ \text{ ppb}^{-1}$), binding affinity constant ($1.819 \times 10^6 \text{ M}^{-1}$), detection accuracy ($0.3034 \text{ degree}^{-1}$), and signal-to-noise-ratio (0.0276) for Ni(II) ion detection. The optical properties of thin-film targeting Ni(II) ions in different concentrations were obtained by fitting the SPR reflectance curves using the WinSpall program. All in all, the proposed Au/MPA/V–CNCs–CTA thin-film-based surface plasmon resonance sensor exhibits better sensing performance than the previous film-based sensor and demonstrates a wide and promising technology candidate for environmental monitoring applications in the future.

Keywords: vanadium; cellulose; optical sensor; surface plasmon resonance; nickel ion

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1. Introduction

The rapid growth in the industrial revolution, particularly in the production of stainless steel, kitchenware, and hard-wearing plating, has led to an enormous demand for nickel [1]. Some market watchers also believe that nickel demand will increase as electric vehicle production ramps up [2]. Moreover, it is worth noting that there are around 3000 alloys containing nickel that are in everyday use [3–5]. Although the toxicity of nickel is low, occupational and casual exposures to nickel are mainly occurred, lead to health problems. Occupational exposure is associated with the workers that engaged in refining, electroplating, and welding, which may develop severe chronic diseases of the upper respiratory tract, including hypertrophic rhinitis, nasal sinusitis, anosmia, nasal polypsis, and perforation of the nasal septum. While casual exposure to nickel occurs mainly in the use of shiny things such as coins, watches, jewelry, zippers, exposure causes nickel allergies and dermatitis [6–11]. Generally, the concentration of nickel is very high in food compared to the environment [12–14]. The recommended daily intake for nickel is only 0.3 mg, which offers essential trace nutrients for the human body in the involvement of biological processes such as respiration, metabolism, and biosynthesis [15,16]. Despite all that, the most absorbed nickel comes from drinking water and tap water due to the use of nickel-containing plumbing fittings. On the other hand, bioaccumulation of nickel can occur in fish or agriculture, and humans at the highest levels of the food chain, which will receive harmful effects and cause chronic or acute illness when the amount is exces-

sive, $>20 \mu\text{g/L}$ [17–19]. The nickel-ion quantification at low concentrations thus became increasingly important.

Several standard techniques have been developed over the years for measuring the total nickel amounts include atomic absorption spectroscopy, inductively coupled plasma spectrometry, anodic stripping voltammetry, and X-ray fluorescence spectroscopy [20–23]. Overall, these existing methods have their advantages as having very highly sensitive and good accuracy; nevertheless, they have some limitations, such as time-consuming, expensive equipment, and the requirement of complex operation [24–28]. Hence, the detection of nickel using a very simple and high-sensitive method is of utmost demand. Recently, a very sensitive fluorescence sensor composed of a magnetic core-amino silica shell-fluorescein was successfully applied for the selective and sensitive nanomolar detection of nickel ions [22]. Another fluorescence method-based on imidazole-modified carbon dots with a detection limit of 0.93 nM [29]. A new strategy using a colorimetric sensor in both solution and paper-based membrane for the Ni ions determination was developed, resulting in the detection limit of 36 nM and 83 nM , respectively [30]. To date, only two techniques, fluorescence and colorimetric, are being investigated, yet they require a rather complicated operating process. Optical sensors offer clear advantages when compared to other methods such as easy handling, rapid analysis without pre-sampling, and high sensitivity of small analytes [31–35].

Surface plasmon resonance sensors stand out as attractive to detect nickel sensitively since nickel ions normally occur at very low-levels in the environment. Several reports have indicated the detection of nickel ion in this technique; however, many of them are not sensitive to detecting trace level concentrations in an aqueous solution. In recent studies, Daniyal et al. (2019) successfully reported the modification of SPR sensors using graphene/nanocrystalline cellulose for nickel ions detection, but the detection limit of the sensor is only achieved at 0.01 ppm with low sensitivity [36]. Then, there is a growing demand for the development of surface plasmon resonance with enhanced sensitivity and detection limits. The basis of this is an SPR sensor dependent on measuring any increment of resonance angle related to the change of the refractive index at the sensor surface. At this point, it is desirable to modify the sensor surface with other novel materials to enhance the sensing properties.

To date, cellulose nanocrystals (CNCs) derived from natural renewable resources meet the requirement of being good alternative sensor elements [37–39]. They possess desirable mechanical and chemical characteristics, such as high surface area, high tensile strength, high stiffness, and lack of apparent toxicity [40–44]. In spite of having its outstanding properties, CNCs were surface-modified with cetyltrimethylammonium bromide (CTAB) through hydroxyl groups to generate their moderate hydrophobic, simultaneously serves as a promising matrix for attaching nanoparticles [45–47]. On the other hand, metal salt nanostructures, namely vanadium salts—also known as ammonium metavanadate (NH_4VO_3)—have played ideal reagents in the laboratory and analytical chemistry, which find widespread usage in the detection of drugs, gaseous, and N-acetyltransferase activity in humans [48]. Moreover, they also serve as precursors of various medicinal agents and production of catalysts on account of their low-cost, mild reaction conditions, high yield, and operational simplicity. Hence, it is expected that vanadium–cellulose composite-based thin films can further improve the sensing performance of the SPR sensor.

The main of the present work is to enable the potential detection of Ni(II) ion using vanadium incorporated in modified cellulose nanocrystal. To the best of our knowledge, this is the first report that utilizes vanadium salts-CNCs in detecting nickel ions, with the obtained detection limit of nickel ion at 2 ppb .

2. Materials and Methods

2.1. Reagents and Materials

Ammonium metavanadate, hexadecyltrimethylammonium bromide (CTA), nickel ion (Ni(II)) solution (1000 ppm), and 3-mercaptopropionic acid (MPA) were purchased

from Sigma-Aldrich, a leading Life Science and High Technology company in Germany. Cellulose nanocrystals (CNCs) were purchased from CelluForce, a clean-tech company that operates the world's largest CNC plant in Canada and a leader in the development and commercial production of CNCs.

2.2. Deposition of MPA/V-CNCs Composite Thin Film

A self-assembled monolayer (SAM) was developed by immersing the gold film in 10 mM MPA solution for 24 h and then rinsed with ethanol, followed by deionized water (DW). To form the last layer, 1 mL of V-CNCs-CTA composite solution was dropped onto Au/MPA thin film, followed by spinning at a speed of 6000 rpm for 20 s using a spin coater P-6708D.

2.3. Experimental of SPR Setup

A Kretschmann model was exhibited to define the principle of SPR sensors, which included experimental setup of He-Ne laser beam, a rotating stage driven by a stepper motor, a polarizer, an optical chopper, a custom-made o-ring, a photodetector, and a lock-in amplifier (Figure 1). The SPR experiment was then initiated by evaporating a derivative sensor film on the prism surface and placed on a rotating stage. After the setup was ready, 1 mL of deionized water (DW) was injected into the o-ring to obtain the baseline signal. The DW was then injected out for the next use of different concentrations of Ni(II) ion solution. To prepare Ni(II) ion solution at different concentrations of 50, 20, 10, 8, 6, 4, and 2 ppb, the Ni(II) ion stock solution was diluted in DW using dilution formula of $M_1V_1 = M_2V_2$. The target solution was injected one after another into the o-ring to be in contact with the sensor surface. Finally, the prism was rotated with respect to the beam of the laser light source and the reflected light was detected in different angles by the photodetector. In this angular interrogation technique, the excitation of surface plasmon will occur at a certain incident angle, where the momentum of plasmon resonates with the momentum of light, resulting in a decrease in the reflectance (known as resonance angle). This resonance angle can be increased by increasing the refractive index of the sensing layer caused by the binding of the Ni(II) ion. The WinSpall software was used throughout this study to characterize sample properties such as thickness and the refractive index of the thin film [49–54].

Figure 1. Schematic of the surface plasmon resonance device.

3. Results and Discussion

3.1. Sensor Surface Functionalization

Figure 2 shows the comparison of the SPR reflectance curve observed after the introduction of Ni(II) ion at two different concentrations, i.e., 8 ppb and 10 ppb. These concentrations were chosen as they represent the concentrations that are near the detection limit obtained from previous work [36]. First, from Figure 2a, there was no increment in resonance angle when a bare Au film interacted with two respective concentrations of

Ni(II) ion. This is because the refractive indices of 8 and 10 ppb of Ni(II) ion concentrations were almost similar to the refractive index of deionized water (DW), thus did not change the refractive index of the metal surface. A similar phenomenon was observed for MPA-self-assembled monolayer-modified Au film when tested with Ni(II) ion concentration, as depicted in Figure 2b. When the V layer assisted the Au film surface (Figure 2c), an increase in resonance angle was observed upon introduction of the first lowest concentration of Ni(II) ion, 8 ppb. However, when 10 ppb of Ni(II) ion was introduced to the prior Au/V thin film, there was no increment in resonance angle. This was due to the unsuccessful binding of Ni(II) ion due to no interaction force between Ni(II) ion and the sensing layer, thus tends to cause the degradation of the sensing layer after twice introduction of Ni(II) ion solution. Next, the Au/CNC and Au/CNC-CTA thin film were also tested with 8 ppb and 10 ppb of Ni(II) ion. The obtained reflectance curve, as shown in Figure 2d,e, respectively, resulting in a very small increase in resonance angle when detecting low concentrations of Ni(II) ion.

Figure 2. Cont.

Figure 2. The surface plasmon resonance (SPR) reflectance curve for (a) Au; (b) Au/3-mercaptopropionic acid (MPA); (c) Au/V; (d) Au/cellulose nanocrystals (CNCs); (e) Au/CNCs–hexadecyltrimethylammonium bromide (CTA); (f) Au/V–CNCs; (g) Au/V–CNCs–CTA; (h) Au/MPA/V–CNCs; (i) Au/MPA/V–CNCs–CTA thin film when detecting 8 ppb and 10 ppb of Ni(II) ion solution.

Compared to the individual V, CNCs, CNCs–CTA, the composite layer of V–CNCs and V–CNCs–CTA was done. Figure 2f shows no increment in resonance angle with the addition of CNCs, indicating the non-functional of CNCs onto Au/V thin film because of electrostatic repulsion of the resultant positive charge of V–CNCs composite against Ni(II) ion. On the other hand, V–CNCs–CTA caused a small increase in resonance angle upon the binding of 8 ppb of Ni(II) ion (Figure 2g). However, an introduction of 10 ppb of Ni(II) ion, a similar resonance angle value was observed. This suggests that the interaction of Ni(II) ion does not change the refractive index of Au/V–CNCs–CTA thin film. It is, therefore, likely that a self-assembled monolayer of MPA is required to support the deposition of a thin sensing layer for increased surface refractive index.

The first self-assembled monolayer of MPA for the development of Au/MPA/V–CNCs gives a small increase in resonance angle for detection of 8 ppb and 10 ppb of Ni(II) ion (Figure 2h). Yet, with the modification of CNCs with CTA, the Au/MPA/V–CNCs–CTA shows a greater increase in resonance angle to the higher value due to the excellent plasmonic enhancement (Figure 2i). The interactions with 8 ppb of Ni(II) ion successfully resulted in an increase in resonance angle of 0.534° from the reference signal and again, increased further by 0.655° with the addition of 10 ppb of Ni(II) ion. The increase in resonance angle was proportional to the concentration of Ni(II) binding to the surface functionalization of MPA/V–CNCs–CTA on the gold film. This phenomenon, also relevant to the conformational change in the analytes bound to the sensor film, suggests the increase in the thickness of the absorbed sensor film. Therefore, the self-assembled monolayer of MPA with the attached layer of V–CNCs–CTA showed a better performance than other thin films.

3.2. SPR Reflectance Curve for Au/MPA/V-CNCs-CTA Thin Film

Next, the proposed Au/MPA/V-CNCs-CTA thin film was tested with different concentrations of Ni(II), as shown in Figure 3. Note that the concentration of Ni(II) ion was reduced to 2 ppb to obtain the lowest detectable concentration. It can be observed from the figure that the corresponding resonance angle for DW was found to be 53.6592° . Next, the surface-functionalization of MPA/V-CNCs-CTA manages to increase the resonance angle of each Ni(II) ion concentration detection, which was again associated with changes in the refractive index of the sensing medium. The increase in the resonance angles corresponding to 2 ppb, 4 ppb, 6 ppb, 8 ppb, 10 ppb, 20 ppb, and 50 ppb of Ni(II) ion was measured from the resonance angle of DW, yielded a value as shown in Table 1. The increase in the resonance angle was mainly due to the attachment of the Ni(II) ion onto the sensing surface. This means that when the sensing layer was exposed to the Ni(II) ion solution, the chemical absorption will induce a change in the sensing layer's refractive index, which changes the value of the resonance angle. It is believed that the change of resonance angle's value was associated with the change of the refractive index real part of the sensor surface [55–57]. It is also worth noting that the change in reflected intensity was associated with the change in the imaginary part and thickness of the sensor layer as the Ni(II) ion concentrations were varied.

Figure 3. The SPR reflectance curves of Au/MPA/V-CNCs-CTA thin film when detecting Ni(II) ion solution ranged from 2 ppb to 50 ppb.

Table 1. The increment of resonance angle for Au/MPA/V-CNCs-CTA thin film when detecting Ni(II) ion solution ranged from 2 ppb to 50 ppb.

Ni(II) ion Concentration (ppb)	Resonance Angle (Degree)	Resonance Angle Increment (Degree)
0	53.6592	0
2	53.7502	0.0910
4	53.9389	0.2797
6	54.1210	0.4618
8	54.2120	0.5528
10	54.3031	0.6439
20	54.3941	0.7349
50	54.4982	0.8390

To validate this observation, the experimental reflectance curves were then fitted using the WinSpall program (Figure 4). The complex refractive index of the gold layer was obtained when contacted deionized water (refractive index = 1.333), with n and k values of

0.1750 + 3.6796i and the thickness of 47 nm. This value is in good agreement with the one reported in [58]. The determination of these values thus allows further finding for refractive index real part and imaginary part and the thickness of the V-CNCs-CTA sensing layer. In this case, it is good to conclude that the real part of the refractive index of the sensing layer increases as the concentration of Ni(II) ion increases, which is contrary to the imaginary part. This is due to the strong interaction between the evanescent fields and sensing medium, which in turn increases the real part of the wave vector of the surface plasmon wave (k_{sp}). The real part of k_{sp} will be large when the refractive index is large to meet the resonance condition at the larger value of the resonance angle [59,60]. Similarly, the observed effect of the binding can be attributed to the increase in layer thickness, as shown in Table 2. On the other hand, the imaginary part of the refractive index is slightly reduced, leading to less energy loss due to electronic damping. In this work, the formation of V-CNCs-CTA clearly remarkable changes in the reaction of Ni(II) ion, which was probably due to the easy oxidization of vanadium salts in the presence of modified cellulose nanocrystals. This is because the reaction between vanadium salts and a reducing agent such as cellulose nanocrystals could generate heat and products that may be flammable, combustible, or otherwise reactive to give vanadium oxide.

3.3. Sensitivity and Binding Affinity

Sensitivity in the SPR performance mainly depends on the increase in the resonance angle with the change in the refractive of the sensing medium. For a better sensor, sensitivity should be as high as possible. With the help of Figure 5a, the sensitivity of the proposed sensor could be determined. A maximum sensitivity of 0.068° ppb^{−1} was obtained at the lower range of Ni(II) ion concentrations, from 0–10 ppb. Table 3 shows that this proposed sensor outperforms the best sensitivity and detection limit reported so far. An appreciable enhancement in the sensitivity and limit of detection was obtained because of the self-assembly method, which provided a much better distribution of V-CNCs-CTA for improved analyte-binding property. The inclusion of CNCs-CTA provided a larger active surface area in V film, thus allowing the interaction of van der Waals and hydrogen bonds between hydroxyl groups and oxygen atoms.

Table 2. The real part of the refractive index, the imaginary part of the refractive index, and the thickness of the proposed sensor film when exposed to Ni(II) ion solution ranged from 2 ppb to 50 ppb.

Ni(II) Ion			Au Film			V-CTA-CNC Layer		
Concentration (ppb)	Refractive Index		Refractive Index		Thickness (nm)	Refractive Index		Thickness (nm)
	n	k	n	k		n	k	
0	1.3330	0	0.17501	3.6796	47	1.340	0.176	7.30
2	1.3332	0.001	0.17501	3.7126	47	1.349	0.148	7.33
4	1.3338	0.001	0.17501	3.7256	47	1.380	0.148	7.73
6	1.3339	0.001	0.17501	3.7566	47	1.436	0.148	8.59
8	1.3345	0.001	0.17501	3.7766	47	1.453	0.138	9.10
10	1.3348	0.001	0.17501	3.7766	47	1.475	0.138	9.10
20	1.3350	0.001	0.17501	3.7776	47	1.483	0.136	9.59
50	1.3353	0.001	0.17501	3.7776	47	1.487	0.136	9.79

Binding affinity measurement was another parameter used to evaluate the strength of the binding interaction between a single Ni(II) ion to its binding partner, V/CNCs-CTA sensing film. Figure 5b shows the increment in resonance angle plotted against Ni(II) ion concentration, which was nonlinearly fitted in Origin 9 with the help of the following Sips equation [61]:

$$\theta = \frac{\theta_{\max} KC^n}{1 + KC^n} \quad (1)$$

where K is the binding affinity constant, C is the concentration of the Ni(II) ion, θ is the resonance angle at maximum binding sites, n is the heterogeneity factor of the system, which varies from 0 and 1. The system heterogeneity means that the adsorbent

or the adsorbate, or both are heterogeneous. When $n = 1$, this model converts to the Langmuir model, which implies homogenous adsorption, and if it is greater than 1, the system is said to be heterogeneous. The higher the value of n , the more heterogeneous is the system [62,63]. However, in some cases, when the value of n is greater than 1, this model may be identified as describing a cooperative interaction with adsorbates at one site of the adsorbent influencing different binding sites on the same adsorbent [64]. Evaluation of the experimental fitting yielded an n of 2.04, thus indicating the cooperative manifestations of the adsorptive Ni(II) ions on the heterogeneous surface of Au/MPA/V-CNCs-CTA thin film. Furthermore, the K value reported in this study had a higher affinity constant of 0.0310 ppb^{-1} ($1.819 \times 10^6 \text{ M}^{-1}$) compared to other existing SPR sensors [65,66] (see Table 3).

Figure 4. Cont.

Figure 4. Fitting experimental data to theoretical data for Au/MPA/V-CNCs-CTA thin film when detecting (a) DW and (b) 2 ppb; (c) 4 ppb; (d) 6 ppb; (e) 8 ppb; (f) 10 ppb; (g) 20 ppb; (h) 50 ppb of Ni(II) ion solution.

Figure 5. Plot of resonance angle increment with Ni(II) ion concentration for (a) sensitivity and (b) binding affinity measurements.

Table 3. Surface plasmon resonance for Ni(II) ion detection presented in the previous report.

Materials Used	LOD ¹	Sensitivity	Binding Affinity	SNR ²	Ref.
CTA-NCC/GO ³	10 ppb	0.001° ppb ^{−1}	$1.620 \times 10^3 \text{ M}^{-1}$	0.0191	[36]
PPy-CHI ⁴	10 ppb	-	$1.672 \times 10^4 \text{ M}^{-1}$	-	[65]
AgNPs-3MPS ⁵	500 ppb	-	-	-	[66]
V-CNCs-CTA ⁶	2 ppb	0.068° ppb ^{−1}	$1.819 \times 10^6 \text{ M}^{-1}$	0.0276	This work

¹ limit of detection, ² signal–noise–ratio, ³ nanocrystalline cellulose–graphene oxide, ⁴ polypyrrole–chitosan, ⁵ silver nanoparticles capped with 3-mercaptopropylsulfonic acid sodium salt, ⁶ vanadium–cellulose nanocrystals–hexadecyltrimethylammonium bromide.

3.4. SPR parameters

In addition to sensitivity and binding affinity parameters, full width at half maximum (FWHM) is also an important parameter, which the value should be as small as possible for a good sensor. A smaller value of FWHM implies a narrow and sharp reflectance curve, signifying a better detection accuracy of measurements [67–69]. The variation of FWHM with respect to Ni(II) ion concentrations is shown in Figure 6. It was observed that after the detection of 2 ppb of Ni(II) ion, the FWHM increased until the detection of 20 ppb of Ni(II) ion. The reason for this was due to the increase in the thickness of the sensing layer, which leads to damping of incident light in the sensing layer, which in turn resulted in broadening of the reflectance curve [70–74]. The smallest FWHM was obtained at the detection of 2 ppb of Ni(II) ion, for which the detection accuracy (DA) was maximum. DA was inversely proportional to the FWHM. As is clearly shown in Figure 5, the proposed sensor showed the highest DA when exposed to 2 ppb of Ni(II) ion.

Figure 6. Full width at half maximum and detection accuracy of Au/MPA/V-CNCs-CTA thin film when detecting Ni(II) ion solution ranged from 2 ppb to 50 ppb.

Figure 7 demonstrates the variation of SNR with the concentration of Ni(II) ion. The SNR is an important measurement to reduce the sensor's noise or improve the sensor intensity, indicated by higher SNR. The SNR can be calculated using the following equation:

$$SNR = \frac{\Delta\theta_{SPR}}{FWHM} = \Delta\theta_{SPR} \times DA, \quad (2)$$

As a result, the SNR increases through the detection of Ni(II) ions. In addition, when comparing to other SNR of the SPR sensor in Table 3, the SNR of the Au/MPA/V-CNCs-CTA thin-film-based SPR sensor is increased. The increased SNR can result in faster detection of analyte concentrations that were previously lost in the noise. At the end of this study, the overall performance parameter analysis of the proposed sensor with respect to Ni(II) ion concentrations is given in Table 4.

Figure 7. Signal-to-noise-ratio of Au/MPA/V-CNCs-CTA thin film when detecting Ni(II) ion solution ranged from 2 ppb to 50 ppb.

Table 4. Full width at half maximum (FWHM), detection accuracy (DA), and SNR of Au/MPA/V-CNCs-CTA thin film with respect to Ni(II) ion concentrations.

Ni(II) Ion Concentration (ppb)	FWHM (Degree)	DA (Degree ⁻¹)	SNR
0	3.3299	0.3003	0
2	3.2952	0.3034	0.0276
4	3.4513	0.2897	0.0810
6	3.5033	0.2854	0.1317
8	3.6767	0.2719	0.1503
10	3.5727	0.2799	0.1802
20	3.9195	0.2551	0.1874
50	3.6420	0.2745	0.2303

4. Conclusions

A novel Au/MPA/V-CNCs-CTA thin-film-based SPR sensor was successfully utilized for Ni(II) ion detection ranging from 2 to 50 ppb. The proposed sensor displayed excellent detection at a low ppb-level compared to other reported work so far. The sensor also exhibits a maximum sensitivity of $0.068^\circ \text{ppb}^{-1}$ as well as a strong binding affinity, determined from Sips isotherm model calculation. Importantly, this proposed sensor successfully achieved a better detection limit, sensitivity, binding affinity as well as high DA and SNR measurements. The Au/MPA/V-CNCs-CTA thin-film-based SPR sensor is hence proposed to have high potential in the detection of Ni(II) ions in real samples and other related applications.

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