Chitosan nano film a chemical sensor: Preparation, characterization and application for detection of Nickel ions in aqueous solution

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Abstract. The effects of Dimethyl Glyoxan (DMG) loaded chitosan-nano film (NFCh) chemical sensor for detection Ni\(^{2+}\) ions in aqueous solution were studied. The films, prepared by solvent casting technique with the following compositions of the casting solutions in DMG, chitosan, STPP. The DMG was successfully loaded into NFCh as confirmed by UV–Vis spectrophotometry. Interaction of NFCh with nickel ions provides obvious colorimetric change from red to violet, enabling easy detect with the naked eye. Sensor was exhibited good selectivity with sensitive. In addition, the sensing details were evaluated using UV–Vis spectroscopy. The physico-mechanical properties of NFCh i.e tensile strength, elongation and thicknesses were studied. NFCh with electron withdrawing group at organic ligand showed high selectivity for detection of ion nickel over other interfering anions.

1. Introduction
Nowadays the increase of environmental problems and concerns, caused by contaminations with heavy metals. Nickel (Ni\(^{2+}\)) is one of the toxic heavy metals in wastewater, which has been paid considerable attention due to its toxicity, carcinogenicity, and cumulative adverse characteristics. The Ni\(^{2+}\) pollution, which stem from metal smelting, mining, metal processing, and battery manufacturing [1,2], is concentrated and cumulated in living organisms. High concentration of Ni\(^{2+}\) in human beings would cause serious consequences containing headache, heart damage and even cancer [3]. Thus, it is crucial to eliminate Ni\(^{2+}\) from the water and wastewater for protecting the public safe and the environment. Moreover, nickel can cause a skin disorder known as nickel-eczema [4]. Therefore, it is important to develop simple, sensitive methods for the determination of nickel (II) in different environmental matrices.

Currently, various methods have been applied in the removal of Ni\(^{2+}\), such as adsorption [5], ion exchange [6], electrooxidation [7], biologi [8] solvent extraction in imping stream rotating packed bed [9], spectrophotometric [10], atomic absorption spectrometry [11] and ion-coupling plasma [12], liquid chromatographic[13], colorimetry[14]. Among these techniques, ultraviolet-visible spectrophotometry and colorimetry has been widely used because of its advantages in speed, accuracy, simplicity, versatility, and cost-effectiveness [12].

The colorimetric approach can detect various kinds of molecules in a short time. Sensors based on colorimetric approach are significant while analyzing its ideal characteristics. Earlier sensor are mean to be a bulk and complex one, requiring different functional blocks such as transducer, processing unit, a detection unit etc. Leading to a delayed sensor response. Current technology based on colorimetry is
all about the miniaturization of size, cost, in-situ and without any additional instruments. A colorimetric sensor is used for instantaneous detection of analyte and shows a color change, which can be detected visually.

Colorimetric detection of the pathogen has been done using silicon by the interference phenomenon exhibited by it when subjected to different layers. The challenges such as usage of harmful chemicals in sensor platform, cost of the instruments, label free detection, real time analysis, single step detection and portability will be a hurdle for existing conventional sensors available in the market. Colorimetric sensors can gain wide range acceptance in these challenging fields.

Colorimetric sensors are an attractive choice for rapid on-site detection of a pollutant. A number of such sensors have been developed with the colorimetric reagent trapped within a polymer matrix, for the detection of various analytes like nitrite ion [15], iron [16], plumbum [17] and cobalt [18]. Most of them involved the use of the liquid colorimetric/fluorometric reagents as ligand the signaling unit.

Natesh et al [19] investigation simple, rapid, sensitive and reproducible method for the determination of nickel (II) using two imine ligands, (E)-Ni(2-hydroxy-5-nitrobenzylidene)isonicotinoylhydrazone and 2-(4-fluoro benzylideneamino) benzenethiol. The ligands react with Ni^{2+} at pH 4.0 and 4.7 to form red and pale purple complexes respectively with a stoichiometric ratio's of 1:1. The complexes obeyed Beer's law in the range of 0.8-20.0 mg L^{-1} with an excellent linearity depicted by correlation coefficient value of 0.9996. The molar absorptivity were found to be 5.1 \times 10^{4}, 6.3 \times 10^{4} L mol^{-1} cm^{-1} and 0.98, 0.91 ng cm^{-2} for the red or pale purple complex systems. The limit of detection for Ni^{2+} was noted as 0.89 and 0.82 ng L^{-1}.

One of the important elements in the production of a rapid optical sensor is the membrane utilized as the sensing platform. Without the membrane, the optical sensor is literally not functioning. The membrane specific surfaces are used as the binding sites for the adsorption of optical ligand and to maintain their stability and activity over the shelf-life of the sensor.

Chitosan (CS) is a well-known adsorbent in various applications since it has a strong chelation potential for heavy metals due to the presence of amine and hydroxyl groups in the polymer. However, pure chitosan membrane is poor in mechanical strength and has low chemical stability. To improve the mechanical strength of chitosan, chitosan modified by ionic gelation of chitosan and tripolyphosphate.

Nano chitosan films produced from the acid dissolution of chitosan possess numerous desirable physicochemical and biological properties. These properties show high variation in relation to several factors such as the degree of acetylation, the viscosity of the solution, drying temperature, the percentage of acid dissolution and most important type of composite if the films are supposed to be composted with other ingredients. These parameters are responsible for variation in important physicochemical and biological properties including tensile strength and strain, barrier properties, wettability, thermal stability, roughness, antimicrobial and antioxidant attributes. In addition, these attributes define the application areas of chitosan-based films such as food packaging, adsorption studies, biomedical applications (wound dressing), agriculture etc.

Kocak et al [20] synthesized nano-chitosan Schiff base was applied to the preparation of a modified carbon paste electrode and used to remove lead (II) by using differential pulse anodic stripping voltammetry (DPASV). Raju et al [21]. have demonstrated an electrode based chitosan-zinc oxide film biosensor for the detection of cholesterol. Ravikumar et al [8] have utilized a CS-Ni film based optical intermodal sensor for detection of hexa-histidine tagged proteins.

2. Materials and Methods

2.1 Materials
Chitosan with Degree of deacetylation: 92% were provided by Laboratory Chemistry BATAN, Jakarta, Sodium Tripolyphosphate (TPP), DMG, NiCl; was obtained from Merck.

2.2 Preparation
Preparation of cross-linked chitosan nanoemulsion chitosan with different molecular weight was weighed and dissolved in acetic acid aqueous solution (1% v/v) to obtain the concentration range of 0.5-4.0 mg mL⁻¹ (w/v). TPP was dissolved in deionized water with gradient of 0.25 mg mL⁻¹ and concentration of 0.5-2.5 mg mL⁻¹ was obtained. A certain amount of emulsifier was added to the chitosan acetic acid solution (150 mL) and stirred continued until it was fully dissolved, and the pH of the solution was adjusted to 4.8. 50 mL sodium tripolyphosphate solution (w/v) was slowly added to the chitosan solution by mechanical stirring at 500 rpm/min after fully emulsifying, and the stirring continued until the solution was completely cross-linked. After centrifugation (12000 rpm, 30 min), the cross-linked chitosan polymer was washed three times with deionized water, and the precipitates were suspended in deionized water for future analysis. To investigate the influence of different variables and optimum the chitosan particulates, the Plackett-Burman Design (PBD), Central Composite Design (CCD) and Response Surface Methodology (RSM) was used with the software Design-Expert (version 7.1.3) in the present study. 2.3 Particle size and scanning electron microscope (SEM, X-ray Diffraction (XRD) analysis Nanoemulsion size and zeta potential were determined with Delsa Nano C Analyzer (Beckman Coulter Co., Ltd). After cross-linked by TPP, the nanoemulsion were isolated by ACCEPTED MAN.

2.3 Preparation of nanoemulsion chitosan

Chitosan films were prepared according to previous studies by Cunli et al. (20019) with some modifications. Chitosan film solutions, were prepared by dissolving 0.5 gram of chitosan in 100 mL glacial acetic acid 1% and homogenized with an homogenizer at 600 rpm for 15 min and the pH of the solution was adjusted to 4.8. The solution was kept at room temperature for 24 h. 60 mL sodium tripolyphosphate solution 0.5% (w/v) was slowly added, drop by drop to the chitosan solution by mechanical stirring at 500 rpm. After fully emulsifying, and the stirring continued until the solution was completely cross-linked, chitosan nanoemulsion are left in the freezer for 24 hours. After that it is removed from the freezer and allowed to melt then centrifugation at 6000 rpm for 15 minutes to separate the water contained in chitosan naoemulsion. The nanoemulsion chitosan was washed three times with deionized water, and the emulsion were suspended in deionized water. Characterization with FTIR and XRD.

2.4 Preparation DMG chitosan film

DMG chitosan film are obtained by adding 10 mL DMG solution at a fixed concentration to 10 mL nanoemulsion chitosan measured the weight, and stirred at 600 rpm room temperature (25 ± 1°C). DMG chitosan film were casted onto (2 x 4) cm rectangular glass plates, and dried for 48 h at ambient conditions (25°C). Dried films were stored in desicators at 25°C and 57% relative. The color change DMG chitosan film was then observed with the spectrophotometer at 465 nm. DMG chitosan film preparation with variable pH (6-10), time of mixing (20-60 min), concentration DMG (10-100 ppm). Two replicates of most of the DMG chitosan film were used in the adsorption tests. The adsorption capacity of the films was calculated using the following equation:

\[
q = \frac{(Co-Ce)V}{W}
\]

where \( q \) represents the adsorption capacity (mg of DMG/g nanoemulsion chitosan), \( V \) is the volume of the DMG and \( W \) is the weight of nanoemulsion chitosan \( Co \) is initial concentration DMG, and \( Ce \) is concentration DMG after adsorption.

2.5 Determination of physical properties

Characterization DMG chitosan film for TS and WVP were conditioned for 2 days in an environmental chamber set a 50% RH and 25°C before testing. Films for the other properties also were stored at the same conditions prior to testing.
2.5.1 Film thickness. Film thickness was determined with a hand-held micrometer. Fifteen thickness measurements taken on each tensile testing sample along the length of the strip with the mean used in tensile strength (TS) were randomly taken on each testing sample. Similarly, 5 measurements were taken on each WVP sample 1 at the center and 4 around the perimeter and the mean values were used in WVP calculation.

2.5.2 Tensile strength and percentage elongation at break. TS and E were evaluated with Universal Testing Machine. Initial grip separation was set at 50 mm and cross head speed was set at 500 mm/min. TS was calculated by dividing the maximum load by the cross sectional area of the sample. Ev was calculated as the percentage change by dividing film elongation at the moment of rupture by initial gage length (50 mm). TS and E measurements for each type of film were replicated 3 × with individually prepared films as the replicated experimental units and each replicate being the mean of 7 tested sampling units from the same film.

2.5.3 Water solubility. Water solubility was calculated as the percentage of soluble manner to initial dry matter in each film sample, solubility is defined as the content of dry matter solubilized after 24 h immersion in water. The initial dry matter content of each film was determined by drying to constant weight in an oven at 105°C. Film disks (2 cm diameter) were cut, weighed (Mi), and immersed in 50 mL of water. After 24 h of immersion at 20°C with agitation (60 rpm), the samples were taken out and dried to constant weight (Mf) in an oven the samples were taken out and dried to constant weight (Mf) in an oven at 105°C, to determine the weight of dry matter that was not solubilized in water. The solubility of each film was then determined as follows:

\[
\text{Solubility in water (\%) = } \left( \frac{M_i - M_f}{M_i} \right) \times 100
\]

where \(M_i\) is the initial mass and \(M_f\) is the final mass of the sample. Three replicates were obtained for each sample.

2.5.4 Colorimetric test and quantification of Ni using DMG chitosan film. Standard working solutions of \(\text{Ni}^{2+}\) were prepared in the range from 10 to 50 mg L\(^{-1}\) by diluting a stock solution (100 mg L\(^{-1}\)) with double distillwater. DMG chitosan film it was immersed to each standard solution (10 mL) for an appropriate time (15 min) at room temperature. Three repeats were done at each concentration of nickel standard at each nickel. After DMG film were placed in the sample holders inside the box, were allowed to stand for 0.5 h, and the color change was then observed with the spectrophotometer at 465 nm.

2.5.5 Analysis of real samples. Four real samples were analyzed by using the DMG chitosan - films for quantification of nickel. These consisted of four water samples from the electroplating industry, mining industry, agro industry. All the water samples were preliminarily tested using the DMG chitosan - film in order to assess the nickel concentrations approximately. Wastewater sample was diluted with aquabidest and adjusted to pH 9, Real samples were also analysed using AAS.

2.5.6 Stability of the DMG chitosan-films. The stability of the green colorimetric sensors was evaluated by preparing sensors using the optimum conditions, in one batch. Three of them were tested with nickel solution (1 mg L\(^{-1}\)) on the day of preparation, while the others were kept to evaluate their stability. They were vacuum sealed in packs of three sensors (63 packs in total). Twenty-one packs in one ziplock plastic bag were then stored in the freezer (−18°C), and in desiccator (Acrylic D50-A, Northman, Thailand), as well as at ambient conditions. One pack (three sensors) was taken from each storage condition for nickel test every day for one week, and monitoring then continued on a weekly basis to 3 weeks, and thereafter at every month for a year.
3 Results and Discussion

3.1 Characterization chitosan and chitosan nanoemulsion

3.1.1 XRD. The diffraction pattern of chitosan and chitosan nanoemulsion is as shown in Figure 1. From the results of XRD characterization, chitosan diffraction patterns were carried out where the diffraction pattern showed a peak at $2\Theta = 10.18^\circ; 20.26^\circ; 72.57^\circ$ and $88.21^\circ$.

![Figure 1. The diffraction pattern of chitosan and chitosan nanoemulsion](image)

According to Sivakami et al., (2013), chitosan has 2 characteristic peaks at $2\Theta = 10^\circ$ and $20^\circ$, and the chitosan diffraction pattern obtained also shows the most prominent peak at $2\Theta = 10.18^\circ; 20.26^\circ$ where the peak is a typical peak of semi-crystalline chitosan. In the obtained chitosan emulsion diffraction pattern, it can be seen that there is a significant decrease in peak intensity. The results obtained were in accordance with the references where the chitosan nanoparticle diffraction pattern will experience a significant decrease in peak intensity, which proves that there has been a cross bond between chitosan and STPP which can be associated with modifications in molecular arrangement in the crystal. As well as a decrease in the intensity of chitosan characteristic peaks on the diffraction pattern of chitosan nanoemulsion showed an increase in amorphous properties in chitosan nanoemulsion.

The results obtained prove that chitosan nanoemulsion have lower crystallinity than chitosan which can be seen from the XRD diffraction pattern obtained. Chitosan nanoemulsion show a peak at $2\Theta=14.29^\circ; 22.18^\circ; 30.81^\circ$ and $72.53^\circ$, the main peak in the chitosan nanoemulsion diffraction pattern obtained was in accordance with the results of Anbu et al., namely at $2\Theta=14.93^\circ; 25^\circ; 30.49^\circ$ and $65.65^\circ$. The peak arises because chitosan nanoemulsion consist of a dense polymer chain network structure and are cross-linked with STPP. At $2\Theta=22.18^\circ$ it has a weak peak and width where it shows the amorphous characteristics of nanoemulsion. These results are in accordance with the results of Dai lam et al. [22] where at $2\Theta=25^\circ$ showed weak and wide peaks which showed amorphous characteristics of nanoemulsion.

3.1.2 FTIR Analysis. FTIR analysis was carried out to confirm the occurrence of crosslinking between Cluster $\text{HPO}_4^-$ from STPP with amino groups from chitosan and also to determine the functional groups present in chitosan nanoemulsion show in Figure 2. The chitosan spectrum obtained shows some characteristic peaks at wave number $3412.08 \text{ cm}^{-1}$, it is thought to be a stretching group $\text{–NH}_2$ and $\text{-OH}$; at wave number $2924.09 \text{ cm}^{-1}$ there is stretching C-H. There is a stretching of carbonyl group (C = O) at wave number $1745.58 \text{ cm}^{-1}$. At wave number $1463.97 \text{ cm}^{-1}$, there is a CH group bending, and at wave
number 1317.38 cm\(^{-1}\) there is tertiary amide stretching. At wave number 1159.52 cm\(^{-1}\), indicates the presence of an amino group (NH\(_2\)) and P = O. At wave number 890 cm\(^{-1}\) there is bending C-H.

![FTIR spectrum](image)

**Figure 2.** FTIR spectrum (a) Chitosan and (b) Chitosan Nanoemulsion

While the FTIR spectrum of chitosan nanoemulsion shows characteristic peaks at wave number 3425.58 cm\(^{-1}\) there is a stretching of vibration groups -NH\(_2\) and –OH, at wave number 2924.09 cm\(^{-1}\) there is stretching of the peak C-H that appears to appear weaker; at wave number 1651.07 cm\(^{-1}\) and 1554.63 cm\(^{-1}\) where the peak is thought to be stretching CO and stretching –NH\(_2\) asymmetric. The appearance of these 2 peaks indicates that there has been an interaction between amino groups from chitosan and phosphate groups from STPP, so it can be concluded that the emergence of these peaks shows the formation of chitosan nanoemulsion and the presence of inter and intramolecular forces in chitosan nanoemulsion. At wave number 1409.96 cm\(^{-1}\) there is stretching of C-H. At wave number 1303.88 cm\(^{-1}\) there is amide III stretching. At wave number 1151 cm\(^{-1}\) there are amino groups –NH\(_2\) the peak that appears to be weaker. Chitosan nanoemulsion also show peak P = O at wave number 1115.36 cm\(^{-1}\). At wave number 890 cm\(^{-1}\) there is bending C. The loss and weakening of chitosan characteristic peaks in the spectrum of chitosan nanoemulsion is due to the crosslinking between ammonium ions from chitosan and phosphate ions from STPP.

3.2. **Physical and thermal properties**

3.2.1. **Thickness and water solubility.** Homogeneous, flexible and transparent films were obtained from control and test solutions. The thin films with pink until red colour were easily removed from the cast plate and the thickness of films varied between 0.27 and 0.062 mm, as shown in Table 1. Table 1 also shows the solubility and moisture content values obtained for chitosan films.

| No. | Code number | Thickness (mm) | Solubility in water (%) |
|-----|-------------|----------------|-------------------------|
| 1   | Chitosan    | 0.30           | 23.67                   |
| 2   | DMG pH 7    | 0.34           | 24.12                   |
| 3   | DMG pH 9    | 0.30           | 18.65                   |
| 4   | DMG t       | 0.31           | 18.78                   |
| 5   | DMG t       | 0.28           | 21.85                   |
| 6   | DMG C       | 0.27           | 15.43                   |
| 7   | DMG C       | 0.34           | 21.80                   |
Even though we already use prints which is made of glass material that has flat surface, film thickness still varies. This varying thickness can be caused by the dye is lost during the immersion process thus affecting the thickness of the film after the process cross-connect. The thickness of the film in the middle is thicker compared to the edge of the film. That matter can be caused by a decrease in mobility macromolecules and intramolecular distances which are caused by an increase in chitosan concentration when evaporation of solvents through the entire layer at the stage film formation (Krzyzanowska, 1975).

The higher solubility of the control film is attributed to the water binding capacity of functional groups of chitosan (Ojagh et al., 2010). The increase of DMG concentration (10–90 ppm) in chitosan film, as shown in Table 1, leads to a significant decrease (p < 0.05) of moisture content values due to the hydrophobic nature of DMG, indicating that there was major variation of the total void volume. However, the films solubility was not affected by the incorporation of DMG (p > 0.05). Similar results were obtained by other authors when a hydrophobic agent was incorporated into chitosan films, such as α-tocopherol or cinnamon essential oil, carvacrol, (Martins et al., 2012; Ojagh et al., 2010). Burt (2004), while the major DMG components present hydrophilic zones in their structure (Yamakoshi et al., 1999).

One of the major problems of polysaccharide films is their water sensitivity, which is evaluated by different methods such as sorption and water activity, moisture content, solubility, contact angles and through the measurement of the water permeability (Martins et al., 2012). Solubility of films in water may also provide insight into the behaviour of a film in aqueous environments, being a measure of its water resistance, hence related to the hydrophilicity of the material.

3.2.2 Tensile strength and Elongation. TS DMG chitosan film containing DMG show that TS increased with increase DMG. The increase may be attributed to development of cross linking between DMG and chitosan. In our results, TS of DMG chitosan film increased 80% with addition DMG at level 10 %, which resulted in the strongest film in the experimental range tested. At higher levels of added DMG, TS decreased. This may indicate that the increased ratio DMG to chitosan resulted in steric hindrances preventing the hydroxyl group on DMG from recting with amino groups on chitosan.

Percentage elongation at break, a measure of extensibility for DMG chitosan films decreased from 60 to 150% as the amount of DMG increased from 1-10%. In general, increased TS of DMG chitosan films due to cross linking has been often accompanied by reduced film elongation, resulting in less elastic films.

3.2.3 Biodegradable DMG chitosan film. The films showed fast biodegradability and increased biodegradation rate through visual analysis of the films, with loss of mass between 35 % and 38 %, indicating a good alternative to the use of non-biodegradable polymers and inadequate discarding of these materials into the environment. A similar result was observed by Medina Jaramillo et al. (2016) in cassava starch films with yerba mate extract, with rapid biodegradability of the material in 12 days, demonstrating the importance of development biodegradable packaging and substitution packaging obtained from non-biodegradable polymers.

Seligra et al. (2016) also observed a rapid degradation in the first 15 days for starch films, but at the end of the 30 days study the films showed a significant degradation. Biodegradable films obtained from starch and glycerol, which compounds exhibit hydrophilic character, can present high loss of mass during the process of biodegradation due to increased water absorption. The increased water absorption promotes the growth of microorganisms naturally present in the soil, that act on the source of carbohydrate and results in a greater and more rapid degradation of these materials.

3.3 Preparation DMG chitosan film

3.3.1 Effect of pH. The pH of the aqueous solution is an important parameter in controlling the adsorption process of DMG. When pH is increased from 5 to 8, the colour removal increases slightly from 76 to 82 % and then decreases slightly up to pH 8. There is significant decrease of 19% in colour removal in the pH range of 8-10. The effect of solution pH on the uptake of CR is presented in Figure 1. As shown in
the Figure, the capacity of chitosan nanoemulsion decreased from pH 8 to pH 10 and reached 12.40 mg/g maximum capacity adsorption at pH 8. Condition for percentage uptake of DMG using chitosan nanoemulsion. The solution DMG of pH 8 was then selected for other optimization experiment.

![Figure 3](image-url)  
**Figure 3.** The effect of pH on the removal of DMG solution using chitosan nanoemulsion

3.3.2 Effect of Contact Time. The adsorption experiments to evaluate the contact time effect on percentage uptake of DMG were brought within 30 minutes to 80 minutes. The experiments were conducted under the standard conditions; temperature of 298°C, pH 8.0 and the concentration DMG solution 10 mM. As shown in Figure 2, percentage uptake of DMG increased rapidly within 120 minutes and remained constant after 180 minutes indicating an equilibrium state. At the contact time of 180 minutes, the capacity adsorption of Citosan nanoemulsion for DMG 10 mM is 15.88 mg/g, respectively. A contact time at 180 minutes was then selected for other optimization experiment.

![Figure 4](image-url)  
**Figure 4.** The effect of contact time on the adsorption of DMG using chitosan nanoemulsion

3.4. Performance of Ni-sensor

Although the formation of a red-pink complex of nickel (II) ions and DMG was visible by naked-eye on the chitosan film spectrophotometric measurements were also performed. DMG chitosan containing 10 mM of DMG using 20 kV at 20 cm delivered most uniform film with the best sensing property and the least amount of added DMG in nanoemulsion chitosan. This composition was therefore used in the preparation of the film and tested for nickel detection. A good linear relationship between reflectance signal and nickel concentrations ranging between 1 and 10 ppm was observed with a $R^2$ value of 0.9855. However, at concentrations lower than 1 ppm, the color change of sensor were small and did not allow a significant difference to be measured. Therefore, it was concluded that the chitosan film containing
DMG could be used for detecting nickel (II) ions in concentration levels of 1–10 ppm quantitatively by the simple dipping method.

4. Conclusions

Chitosan film containing dimethylglyoxime (DMG) to serve as an optical sensor for nickel (II) ion were prepared for the first time. All DMG solutions were spun at the electrical potential of 20 kV, the working distance of 20 cm, and a flow rate of 1.2 mL/h. With the increasing content of DMG, the effect of added DMG content on the fiber size was found to be quite small. ATR-FTIR analysis indicated that the interaction between PCL and DMG was weak. The prepared electrospun fibers could be used as sensor for nickel (II) ions in the concentration as low as 1 ppm with a good linear response between 1 and 10 ppm. Acknowledgements This work was supported by the Chulalongkorn University Graduate School, Thesis Grant, Thailand Tobacco Monopoly, and The Center for Petroleum Petrochemicals and Advanced Materials.

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