Effect Crosslinking in Sensitivity of Chitosan-Graphene Film Sensor for Detecting Urea Fertilizer

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Abstract

Chitosan/graphene film sensors have been successfully fabrication using electrodeposition method and cross-linked by glutaraldehyde. The effect of graphene addition on chitosan film sensors have proven improve the sensitivity of chitosan film sensors. Chitosan solution added with graphene with variation 0,025 g, 0,05 g, 0,075 g, and 0,1 g. The sensing properties of chitosan/graphene film sensors are tested towards urea concentrations of 1%, 2%, 4%, 6%, and 10%. The measurement results of maximum voltage from chitosan/graphene crosslinked glutaraldehyde (0,6231 V) is greater than pure chitosan sensors (0,121 V). Based on the sensing properties and SEM analysis result obtained that the Chitosan/grafene film sensors with an additional 0,075 g graphene is the best variation, where this Chitosan/graphene film sensors showed good sensitivity and reproducibility, long life time and smoother surface area. In this experiment is also using FT-IR and XRD for characterization.
Keywords: Chitosan, Crosslinking, Electrodeposition, Graphene, Sensor, Urea Fertilizer

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I. INTRODUCTION

Urea fertilizer is a inorganic fertilizers were widely used by farmers. The continuous use of inorganic fertilizers can disrupt soil chemical balance so that soil productivity decreases and can lead excessive residue in the soil. Piles of these fertilizer residues in the soil will become soil toxins which lead the soil to become sick. In this case, land will encourage nutrient losses, environmental pollution and damage natural conditions [1]. In chili plants, excess of urea fertilizer will lead excessive chlorophyll content so that the plant continues to carry out photosynthesis and does not bear fruit and while its lacks the leaves will turn yellow. Therefore, monitoring fertilizer concentration is very important. Conventional methods for detecting urea are usually used such as gas chromatography, calorimetry and fluorometry analysis which did not suitable for rapid analysis [2]. Although this tool looks accurate, but detection using this method is expensive, complex and requires analytical experience [3]. Therefore, alternative method for detecting urea fertilizer that is practical, fast, and cheap with highly expected, that is sensor

Chitosan is the most abundant biodegradable polymer. Chitosan is non-toxic, renewable, and did not have bad impact on humans and environment [4]. Chitosan has amino acid groups and hydroxyl groups which lead chitosan have a high chemical reactivity [5]. This causes electrostatic repulsion between chitosan molecules. The protonation process also lead chitosan to act as a cation polyelectrolyte which allows electrostatic interaction, which can be used as a sensor application [6]. However, pure chitosan has very sensitive properties in environmental conditions and have low mechanical properties [7] and limited electrical conductivity [8]. So that it is necessary to mix with other materials to correct their weaknesses.

One of the materials that has recently developed is Graphene. Graphene is a material composed of sp2 hybridized carbon atoms formed from two infinite layers of layers. Although very thin, graphene had strength exceeds steel. Strong covalent bonding lead graphene to be difficult to stretch [9]. Structures consisting of layers make graphene very conductive [10].

Chitosan has a hydroxyl group (-OH) which is easy to interact with water (H_2O) so that it swelling quickly so it has a low lifetime, to improve the low lifetime of chitosan so it needs to be crosslinked with other materials to make interaction between chitosan and other functional groups, such as anhydride or aldehyde which can be used to produce chitosan material as desired. In crosslinking, the available -NH_2 group will act as an active class and is able to form multiple network bonds in three-dimensional structures [11].

This study presented of effect cross-linking on sensitivity of chitosan-graphene film for detection urea fertilizer, so that we can find out how much urea is needed in chili plants to thrive and produce good fruit and not damage the soil. Chitosan-graphene

biosensor is able to differentiate every concentrations of urea fertilizer in water. It can be proven by the electrical testing which show different response with different urea fertilizer concentration.

II. MATERIALS AND METHODS

A. Materials and Solution Preparation

Chitosan powder with medium molecular weight purchased from Sigma-Aldrich Chemicals. Chitosan solution was prepared by stirring 1.5% chitosan in 2% acetic acid purchased from Merck for 24 h to ensure the chitosan and acetic acid was fully dissolved. While glutaraldehyde purchased from Merck. Synthesis graphene use graphite, H2SO4, $NaNO_3$, $KMnO_4$, H_2O_2, NH_3, $MnSO_4$, $CuSO_4$, ethanol obtained from sigma Aldrich with pure analysis (pa).

B. Synthesis Graphene

Using the Hummers method [12], 2 g of graphite had inserted into beaker glass, added 2 g $NaNO_3$ and 150 ml $H_2SO_{4(l)}$ and stirred for 2 hours in ice bath. 10 grams of $KMnO_{4(s)}$ were added stepwise and stirred for 10 hours at 20°C. Then moved from ice bath and stirred for 48 h at 35°C. Then 200 mL of 5% H_2SO_4 and 10 mL H_2O_2 30% were added and stirred for 1 hour. Then centrifuged at 3000 rpm for 60 minutes to separate between the supernatant and the precipitate. Then added 200 ml of aquadest and ultrasonication on 50/60 Hz for 5 hours. Then 2 gram of $Zn_{(s)}$ was added and stirred for 2 h [13], filtered and dried at 60°C for 24 hours to obtain graphene powder. The graphene powder was characterized by XRD.

C. Sensor Fabrication

Chitosan-graphene solutions were prepared by dissolving chitosan 1,5% and graphene powder in 2% acetic acid using magnetic stirrer with the rotation speed of 300 rpm for 24 h at room temperature. The mass variation of graphene is 0.025, 0.05, 0.075 and 0.1 g, respectively. In this work the fabricated the film sensor was used electrochemical deposition method. The chitosan and chitosan-graphene solutions were coated onto patterned cupper layer using an electrochemical deposition method. The electrochemical deposition was carried out by dipping the substrate in the solution. The dipping process was performed under certain supplied voltage. In this case, ions which are sourced from the solution moved towards the electrode where cations moved towards the cathode and anions moved towards the anode. Thus, the chitosan solution and chitosan-graphene solution was deposited onto substrate surface.

D. Characterization

The surface morphology of pure chitosan and chitosan-graphene were observed using Scaning Electron Microscopy (SEM). To investigate the functional group of pure chitosan and chitosan-graphene cross-linked used Fourier Transform Infrared Spectroscopy (FTIR).

E. Electrical Testing

In the operation, chitosan and chitosan-graphene film sensors were placed into a chamber, equipped with positive and negative aluminium electrodes. Both electrode points were connected to a high resolution multimeter as show in Figurate 1. Then, the sensors were exposed to urea fertilizer with concentration 1%, 2%, 4%, 6% and 10%, respectively.

Fig. 1: Illustration of electrical testing method

III. RESULT AND DISCUSSION

A. Crystal Analysis of Graphene

The crystal structure of graphene was analyzed using XRD. From Figure 2, the analysis shows that graphite formed a peak of 26,525° with d-spacing of 3,357 Å showing high crystallinity properties, tat according to what was previously reported [14]. However, after the oxidation process, the diffraction peaks shifted to peak of 10,486° with d-spacing 8,4296 Å which indicated the

formation of graphene oxide. The loss of a sharp peak becomes a wider peak due the exfoliation of graphite oxide to form graphene oxide.
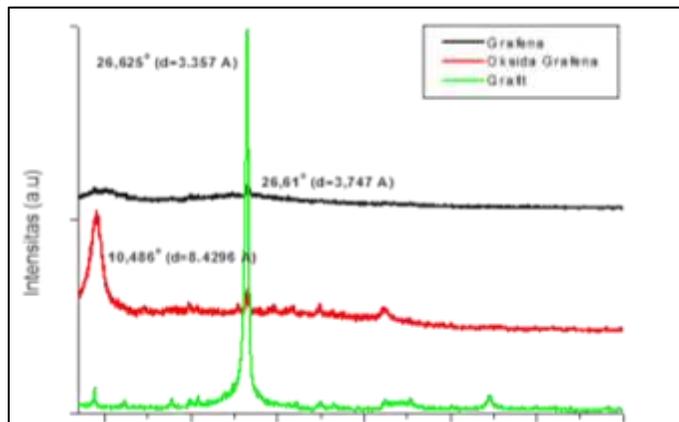

Fig. 2: Pattern of Graphite, Graphene Oxide and Graphene

The presence of functional groups such as hydroxyl groups, epoxy groups, carboxyl groups, and carbonyl groups in graphite oxide could spread the distance between layers to facilitate exfoliation. This seen in the value of d-spacing which is increasingly wide from 3,357Å to 10,487 Å. In addition, the formation of a wider peak shows a decreased crystallinity. This is because entry of functional groups into the structure of graphite will damage the regularity of the structure. However, after reducing graphene oxide the resulting diffraction peaks it decreased to 26.61° with d-spacing 3,747Å. This proves that there has been a reduction which lead several functional groups such as hydroxyl groups, epoxy groups, carboxyl groups, and carbonyl groups to disappear and prove that graphene has been formed. The results of XRD analysis on Graphene are not much different from those previously reported [15,16] , graphene diffraction peaks of about 22-26° and d-spacing of 3.7 Å.

B. *Morphological Analysis of Chitosan-Graphene*

Scanning Electron Microscopy (SEM) analysis to see the surface of chitosan and chitosan/graphene films with various variations of graphene addition. Based on Figure 3 shows the graph is distributed into the chitosan matrix. The graphene can fill the pores contained in polymeric material. With the formation of a unique conductive network making graphene can ideally fill a polymer material where the polymer material depends on its electrical and thermal properties. In SEM image Figure 3.d shows the surface of chitosan/graphene film is much smoother than other films. The smoother surface of 0,075 g addition chitosan/graphene film, it will detect the analyte which is dripped onto the surface of the film sensor more effectively. This also proves that the surface of chitosan/graphene 0,075 g film is stronger and has a lower swelling rate when dripped with urea fertilizer. Thus, the chitosan/graphene sensor with the addition of 0,075 g Grafena can be applied as a new urea fertilizer sensor. While Figure 3 (b), (c), and (e) show that the surface of chitosan/graphene film is uneven or not homogeneous and rough. Figure 3 (a) is the surface of a pure chitosan film which shows a flat and very tight film surface. This proves that chitosan dissolves completely in acetic acid 2%.
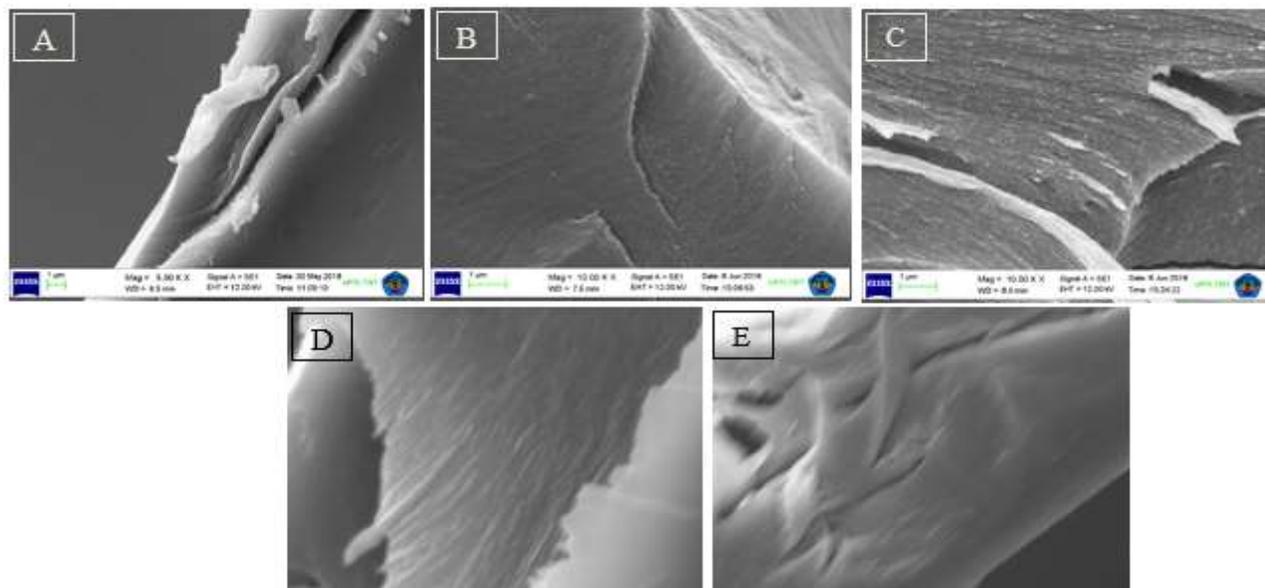

Fig. 3: Image SEM of (A) pure chitosan, (B) 0.025, (C) 0.050, (D) 0,075 and (E) 0,1 g graphene addition to chitosan films

C. Fourier Transform Infrared (FTIR)

Characterization using FTIR was carried out to determine changes in functional groups before and after crosslinking on chitosan and chitosan/graphene and the interactions that occurred between chitosan and graphene. FTIR analysis used Shimadzu IR Prestige-21 tool which was carried out in the wave number range 500 - 4000 cm^{-1}. The sample analyzed was in the form of thin film. The results of FTIR analysis in the sample shows in Figure 4.
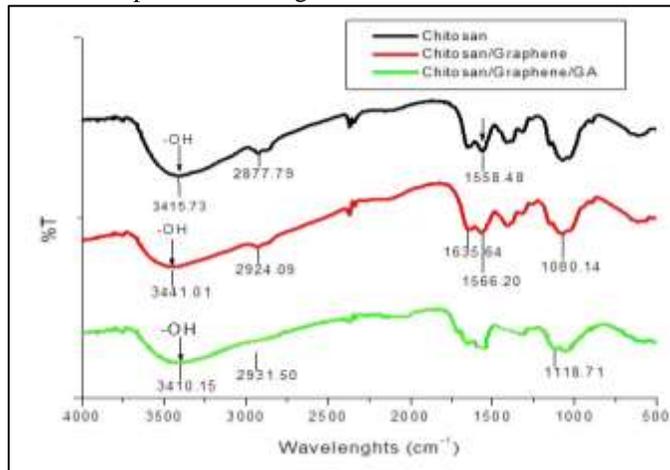

Fig. 4: FTIR spectra from (A) chitosan, (B) chitosan/graphene and (C) chitosan/graphene cross-linked glutaraldyhate

The FTIR spectrum in chitosan shows absorption O-H group at peak 3415.73 cm^{-1} and there is also N-H bending on the primary amine group (-NH$_2$) seen at peak 1558.48 cm^{-1}. Absorption at peak 2877.78 cm^{-1} is a C–H group which shows the stretching vibration of –CH$_2$– groups, the absorption band at 1651 cm^{-1} shows the stretching vibration of C=O and NH deforations in the secondary amide group (NH$_2$) at the peak 1567 cm^{-1} [17]. FTIR spectra on chitosan/graphene shows O-H groups at peak 3441.01 cm^{-1}, N-H bending shows at peak 1566.20 cm^{-1}. The absorption band at 1635.64 cm^{-1} is an O=C-N group which proves that the graphene binds to chitosan [16]. When chitosan/graphene was cross-linked glutaraldehyde the intensity of the O-H group decreases [18]. FTIR spectra on chitosan/grapheme crossliked shows O-H groups at peak 3410.15 cm^{-1}. Based on the results of FT-IR analysis, this proves that crosslinking has occurred between glutaraldehyde and chitosan/graphene film sensors.

D. Performance of the Sensor Film

In acidic media an amino group from chitosan will be protonated to NH$_3^+$ as shows at Figurate 5. This causes electrostatic repulsion between chitosan molecules. The protonation process also lead chitosan to act as a cation polyelectrolyte which allows electrostatic interaction, which can be used as a sensor application [6].

In this study chitosan film sensors were added with graphene to improve the mechanical properties of chitosan. Chitosan film and chitosan/graphene film were produced by electrodeposition method. This electrodeposition method in principle uses direct current, conductive substrate, and anode and cathode.

The resulting chitosan and chitosan/graphene film sensors then crosslinking with crosslinking agents, it was glutaraldehyde. The bond formed here can strength then the mechanical properties of the chitosan film sensor surface produced in chitosan/graphene because of the physical reaction relationship, which will be formed. Hydrogen bonds between amine groups of chitosan and oxygen-containing groups, hydroxyl (-OH) from grapheme shows in figure 6.
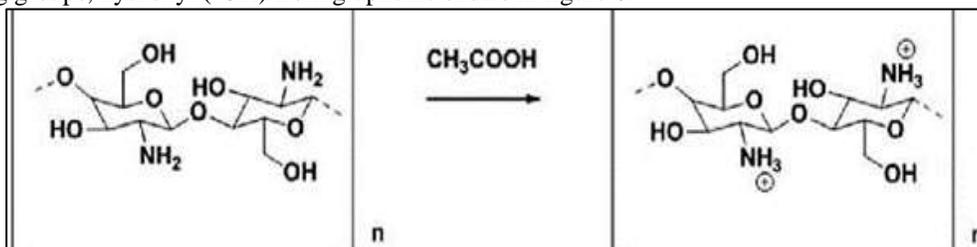

Fig. 5: Protonation amino groups –NH$_2$ to NH$_3^+$

Chitosan/graphene film sensor can differentiate concentration of fertilizers. All the response value shows the significant own value for each urea fertilizer concentration. The performance of chitosan/graphene film sensor shows the decreasing response value with increasing the urea fertilizer concentration, it cause of reduction reaction between potonated amine group (NH$_3^+$) from chitosan to amino group from urea. But this sensor only can used once cause this sensor used drop it methode. So from there, we know this sensor is able to detect and differentiate the urea fertilizer concentrations.
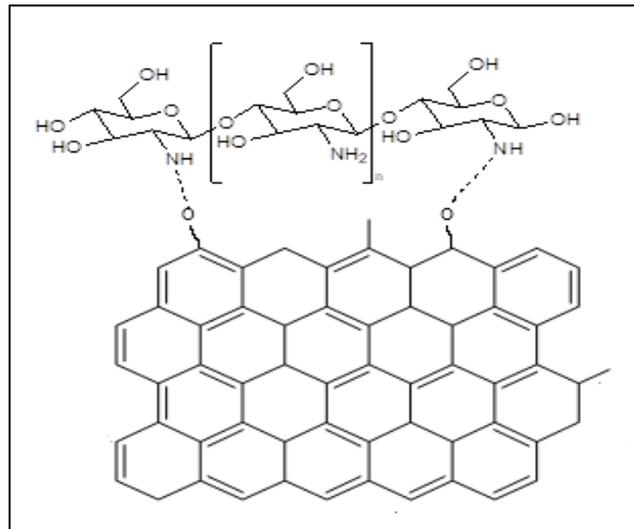
Fig. 6: Interaction between chitosan and graphene

Electrical characteristics of chitosan and chitosan/graphene cross-linked glutaraldehyde film sensors were observed by exposing the sensors towards urea fertilizer concentrations of 1, 2, 4, 6, and 10 %, respectively. As clearly seen in Figure 7, both pure chitosan and chitosan/graphene cross-linked glutaraldehyde film sensors showed fast response, good sensitivity and excellent stability. It is also found that chitosan/graphene cross-linked glutaraldehyde film sensors increased in conductivity which is clearly seen from the maximum responses in output voltage value of chitosan/graphene cross-linked glutaraldehyde film sensors are much higher than pure chitosan. Amongst the variation of graphene, the maximum response of 0,075 g graphene was the highest. This can be explained by the interaction between chitosan and graphene. Since the pKa of chitosan is ~6.3, the hydrogen bonds was broken in acid and electrostatic repulsion would arise between protonated amine groups (NH_3^+) [19]. When sodium TPP was added, the NH_3^+ would interact with OH^- ions [20]. The OH^- ions are mostly linked to NH_3^+ by deprotonation produce $-NH_2$. This interactions lead to increase the electrical conductivity of the films. Whereas, for the addition 0,1 g graphene to chitosan, OH^- has got saturated to interact with NH_3^- and resulting in lower conductivity.
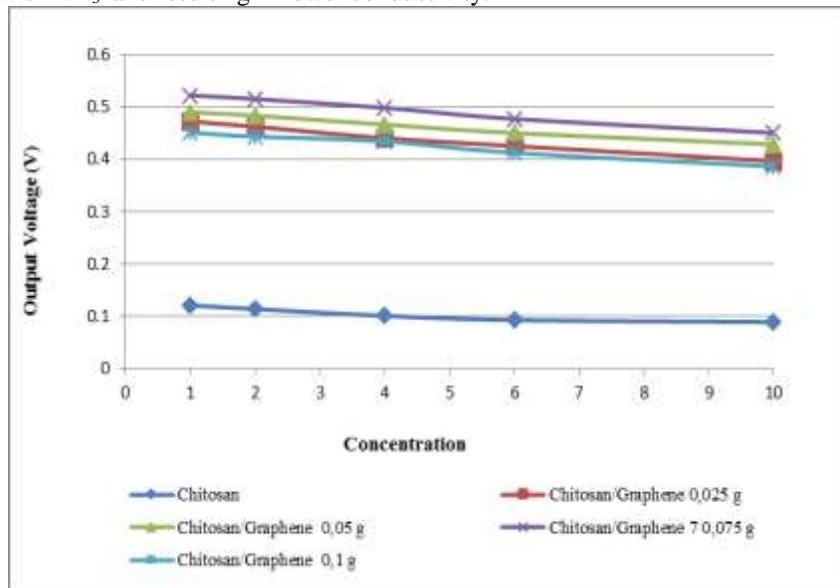

Fig. 7: Electrical characteristics of chitosan/graphene cross-linked film sensors detecting urea fertilizer with various concentration

Figure 8 shows the lifetime of chitosan/graphene cross-linked glutaraldehyde film sensor. Chitosan/graphene cross-linked glutaraldehyde film sensor operate more well for 4 weeks compare to pure chitosan since the maximum responses in output voltage value tend to be the same in every week. It is worth noting that crosslinking degree increased as the concentration of graphene increased when it was crosslinked in acidic. The increases crosslinking degree is capable to decrease the swelling of the films. Therefore, the chitosan/graphene cross-linked glutaraldehyde film sensor exhibit outstanding lifetime due to the low swelling of the films.
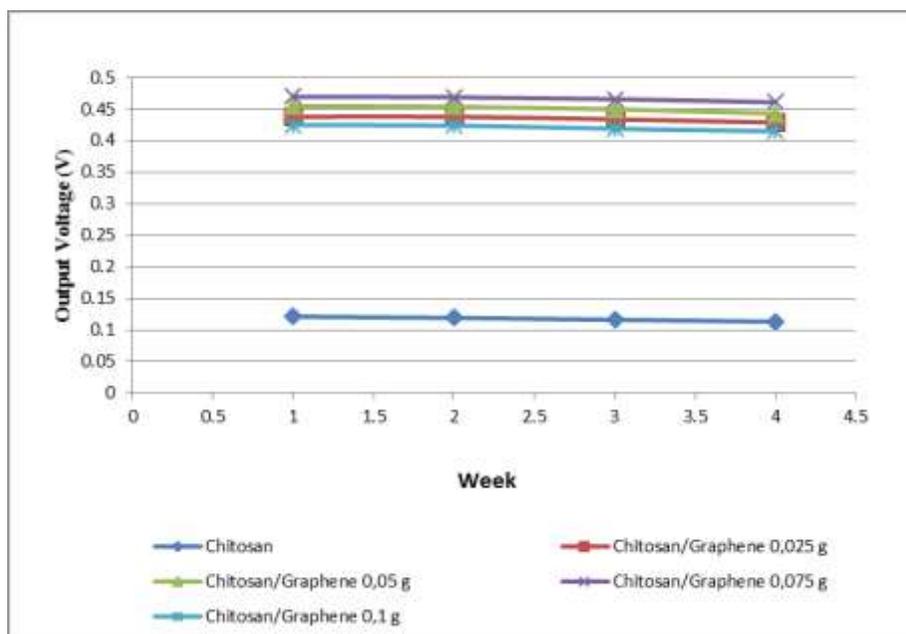
Fig. 8: Lifetime of pure chitosan and chitosan/graphene cross-linked glutaraldehyde film sensors when were exposed towards 1% urea fertilizer

IV. CONCLUSION

In this report, chitosan/graphene has been successfully cross-linked to glutaraldehyde in order to enhance the sensing properties as a novel urea fertilizer sensor. Addition graphene to chitosan solution have proven improve the conductivity sensitivity of chitosan film sensors. Based on measurement results, chitosan/graphene 0,075 g cross-linked glutaraldehyde film exhibits the best sensing properties such as fast response, high conductivity, good repeatability, excellent reproducibility and outstanding lifetime. Therefore, the crosslinking of glutaraldehyde has enhanced the performances of the sensor towards urea fertilizer.

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