Sodium tripolyphosphate cross-linked chitosan based sensor for enhancing sensing properties towards acetone

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Abstract. In this report, sensing properties of sodium tripolyphosphate (TPP) cross-linked chitosan based sensor has been successfully enhanced towards acetone. Chitosan solutions were cross-linked with sodium TPP in variation of 0.1%, 0.5%, 1% and 1.5% w/v, respectively. The sensors were fabricated in film form using an electrochemical deposition method. The sensing properties of the sensors were observed by exposing the pure chitosan and sodium TPP cross-linked chitosan sensors towards acetone concentrations of 5, 10, 50, 100 and 200 ppm. The measurement results revealed that the maximum response in output voltage value of pure chitosan sensor was 0.35 V while sodium TPP crosslinked chitosan sensors were above 0.35 V towards 5 ppm acetone concentration. When the sensors were exposed towards acetone concentration of 200 ppm, the maximum response of pure chitosan was 0.45 V while sodium TPP crosslinked chitosan sensors were above 0.35 V towards 5 ppm acetone concentration. When the sensors were exposed towards acetone concentration of 200 ppm, the maximum response of pure chitosan was 0.45 V while sodium TPP crosslinked chitosan sensors were above 0.45 V. Amongst the variation of sodium TPP, the maximum response of 1% sodium TPP was the highest since the maximum response was 0.4 V and 0.6 V towards 5 ppm and 200 ppm acetone concentration, respectively. While the maximum responses of other sodium TPP concentrations were under 0.4 V and 0.6 V towards 5 ppm and 200 ppm acetone concentration. Moreover, 1% sodium TPP cross-linked chitosan based sensor showed good reproducibility and outstanding lifetime. Therefore, 1% sodium TPP cross-linked chitosan based sensor has exhibited remarkable sensing properties as a novel acetone sensor.

1. Introduction

In recent years, the detection of volatile organic compounds (VOCs) has become a serious task all over the world owing to their manifold hazardous effects on environmental safety and human health.
Acetone is one of the amongst VOC which is extensively used to purify paraffin, dissolve plastic and dehydrate tissues in pharmaceutics. Although acetone is regarded as one having relatively low toxic effects, but some studies reveal that it has anesthetic effects on the central nervous system and may cause damage to the liver, kidney and pancreas in the human beings. Furthermore, it is known acetone is a product obtained from fatty acid metabolism, which is an important biomarker for diabetes diagnosis. Hence, a new effective method with low cost, portable and real-time detection of acetone concentration is extremely expected [1–3].

Chitosan is an abundant cationic natural biopolymer [4] derived simply by alkaline N-deacetylation from chitin [5]. Chitosan has been used widely in sensor application [6] due to its good film-forming properties [7–9], low cost and biodegradability [10]. However, limited electrical conductivity [11], low mechanical strength [12], high swelling [13] and poor stability [14] have limited its application in sensor application. Chitosan can be modified by chemical modifications through a cross-linking to overcome these obstacles [15,16]. Chitosan contains abundant free −NH$_2$ and −OH groups [8,17] that provides to enhance solubility and reactivity [16]. Chitosan is soluble in acidic condition due to the protonation of its amino groups (−NH$_3^+$) with pK$_a$ value ~6.3 so it behaves as a polycation and may favor electrostatic interactions [18]. In cross-linking, the available −NH$_2$ groups act as active sites and are capable of forming a number of linkages in three dimensional network structure [19]. However, cross-linking agents that are commonly used such as glutaraldehyde, epichlorohydrine and ethylene glycol diglycidyl ether are not preferred because of their toxicity [20]. Thus, the preference is given to non-toxic polyanion crosslinkers such as sodium tripolyphosphate (TPP) [21]. Sodium tripolyphosphate (TPP) is a non-toxic polyanion which can interact with positively charged amino groups of chitosan via electrostatic forces to form ionic cross-linked networks due to its high net negative charges [22,23]. Hence, the aim of this study is focus on interaction of sodium TPP cross-linked chitosan as a novel acetone sensor which leads to the improvement sensing properties such as conductivity, swelling, repeatability, lifetime, reproducibility and stability since the sensing mechanism toward acetone has been discussed in our previous work [24].

2. Methodology

2.1. Materials and Solution Preparation
Chitosan powder (medium molecular grade) purchased from Sigma Aldrich was used as a sensor material. Chitosan solution was prepared (1.75% w/v) by dissolving chitosan powder in 2% acetic acied (Glacial) obtained from Merck Millipore. The solution was stirred using a magnetic stirrer with rotation speed of 300 rpm for 24h at room temperature. While sodium TPP (technical grade) purchased from Merck was used as a cross-linker in variation of 0.1%, 0.5%, 1% and 1.5% w/v, respectively. The pH of pure chitosan and 0.1%, 0.5%, 1% and 1.5% w/v sodium TPP cross-linked chitosan are 3.4, 7.3, 8.3, 8.6 and 9.0, respectively.

2.2. Sensor Fabrication
A gold layer was coated onto an epoxy substrate surface and patterned by a printing method. Then, pure chitosan and sodium TPP cross-linked chitosan solutions were coated onto the patterned gold layer using an electrochemical deposition method [25,26] as shown in figure 1. The deposited wet film was annealed in a vacuum oven Memert at 205°C for 20 minutes.

2.3. Characterization
The surface morphology of pure chitosan and sodium TPP cross-linked chitosan films were observed using Scanning Electron Microscopy (SEM: Hitachi TM3000) while Fourier Transform Infrared Spectroscopy (FTIR: SHIMADZU IRPrestige21) was used to investigate the functional group of pure chitosan and sodium TPP cross-linked chitosan films.
2.4. Electrical Testing
The pure chitosan and sodium TPP cross-linked chitosan sensors was inserted into a testing chamber and equipped with positive and negative electrode. Both electrode points were connected to a high resolution multimeter. Then, the sensors were exposed to acetone gas with concentration of 5, 10, 50, 100, 200 ppm respectively to observe the sensing properties such as response, recovery, conductivity, repeatability, reproducibility, stability and lifetime.

3. Results and Discussion
Surface morphology of pure chitosan and sodium TPP cross-linked chitosan films using SEM are shown in figure 2. It clearly shows that surface of pure chitosan (1.75% w/v) film seems to be rough and porous due to the grain growth which was largely distributed over the surface. Meanwhile, when chitosan was cross-linked by OH and P,O, ions in sodium TPP solution, its grain size reduced. As a result, the sodium TPP cross-linked chitosan films have a low surface roughness and form a solid surface. It can be seen that the higher concentration of sodium TPP, the more even and solid surface of films occur. When the sensors were exposed towards acetone, this solid surface may enhance electrons to be transferred faster from one particle to another and leads to produce higher electrical conductivity. However, the surface of 1% sodium TPP cross-linked chitosan film appears the most even and solid since the surface of 1.5% sodium TPP cross-linked chitosan film becomes uneven or wavy. This wavy surface occurred due to weak bond between sodium TPP cross-linked chitosan film and gold layer electrode which may cause the film is lower in conductivity. Therefore, it attests that 1% sodium TPP cross-linked chitosan film is applicable for a novel acetone sensor.

![Figure 1. Illustration of electrochemical deposition method.](image)

![Figure 2. Surface Morphology of (A) pure chitosan, (B) 0.1 %, (C) 0.5%, (D) 1% and (E) 1.5% sodium TPP cross-linked chitosan films using SEM.](image)
Figure 3 shows the FTIR spectrum of pure chitosan and sodium TPP cross-linked chitosan films. The FTIR spectrum of pure chitosan shows the absorption band at 3275 cm\(^{-1}\) which indicates the combined broad non-symmetric band of \(-\text{OH}\) and \(-\text{NH}\) groups [27] while the peak of absorption band at 2877 cm\(^{-1}\) shows the \(-\text{CH}\) stretching vibration. C=O stretching in amide I vibration group appears at the absorption band of 1651 cm\(^{-1}\) and N-H deformation in amide II group vibration (NH\(_2\)) as the active site of the film occurs at 1566 cm\(^{-1}\). The peak at 1315 cm\(^{-1}\) identifies vibration range of the C-N amine and absorption band at 1150 cm\(^{-1}\) indicates C-O asymmetric. Meanwhile, the FTIR spectra of sodium TPP cross-linked chitosan films becomes wider at the band of 3421 cm\(^{-1}\) which indicates hydrogen bonding is enhanced [31]. The peaks at 1651 cm\(^{-1}\) and 1566 cm\(^{-1}\) disappear and appear new bands at 1662 cm\(^{-1}\) and 1589 cm\(^{-1}\). This could be attributed to the linkage between the OH\(^-\) and phosphoric ions with ammonium ions of chitosan. Sodium TPP cross-linked chitosan films also shows a peak for P=O at 1157 cm\(^{-1}\).

![Figure 3. FTIR spectra of (A) pure chitosan, (B) 0.1 %, (C) 0.5%, (D) 1% and (E) 1.5% sodium TPP cross-linked chitosan films](image)

Electrical characteristics of pure chitosan and sodium TPP cross-linked chitosan sensors were observed by exposing the sensors towards acetone concentrations of 5, 10, 50, 100, and 200 ppm, respectively. As clearly seen in figure 4, both pure chitosan and sodium cross-linked chitosan sensors showed fast response, complete recovery and excellent stability. It is also found that sodium TPP cross-linked chitosan sensors increased in conductivity which is clearly seen from the maximum responses in output voltage value of sodium TPP cross-linked chitosan sensors are much higher than pure chitosan. Amongst the variation of sodium TPP, the maximum response of 1% sodium TPP was the highest. This can be explained by the interaction between chitosan and sodium TPP. 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\(_3^+\)) [28]. When sodium TPP was added, the NH\(_3^+\) would interact with OH\(^-\) and P\(_2\)O\(_{10}\)^{1-} ions [29]. The OH\(^-\) ions are mostly linked to NH\(_3^+\) by deprotonation produce \(-\text{NH}_2\) while P\(_2\)O\(_{10}\)^{1-} ions linked by ionic crosslinked produce H\(^+\) ions. This interactions lead to increase the electrical conductivity of the films. Whereas, for 1.5% sodium TPP cross-linked chitosan, OH\(^-\) and P\(_2\)O\(_{10}\)^{1-} ions has got saturated to interact with NH\(_3^+\) and resulting in lower conductivity. Futhermore, 1% sodium TPP cross-linked chitosan sensor exhibits the best repeatability since the maximum responses were relative similar for five times continuously measurement within one day. This is worth noting that 1% sodium TPP cross-linked chitosan sensor offers the best electrical characteristics to be used as a novel acetone sensor.
Figure 4. Electrical characteristics of (A) pure chitosan, (B) 0.1%, (C) 0.5%, (D) 1% and (E) 1.5% sodium TPP cross-linked chitosan film sensors.

Figure 5. Reproducibility of pure chitosan and sodium TPP cross-linked chitosan film sensors when were exposed towards (A) 5 ppm and (B) 200 ppm acetone concentration.

The reproducibility of pure chitosan and sodium TPP cross-linked chitosan sensors were observed by exposing five different sensors towards 5 ppm and 200 ppm acetone concentration. It is found that sodium TPP cross-linked chitosan sensors are more reproducible than pure chitosan. Nonetheless, 1% sodium TPP cross-linked chitosan demonstrates the most excellent reproducibility which can be seen
in figure 5. This indicates that 1% sodium TPP was homogeneously cross-linked with chitosan solution and produce the most reproducible sensors.

![Figure 5](image1.png)

Figure 6. Lifetime of of pure chitosan and sodium TPP cross-linked chitosan film sensors when were exposed towards (A) 5 ppm and (B) 200 ppm acetone concentration.

While figure 6 shows the lifetime of pure chitosan and sodium TPP cross-linked chitosan sensors. Sodium TPP cross-linked chitosan sensors 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 sodium TPP increased when it was crosslinked in acidic. The increases crosslinking degree is capable to decrease the swelling of the films. Therefore, the sodium TPP cross-linked chitosan sensors exhibit outstanding lifetime due to the low swelling of the films.

4. Conclusion

In this report, sodium TPP has been successfully cross-linked to chitosan solution in order to enhance the sensing properties as a novel acetone sensor. Based on measurement results, 1% w/v sodium TPP cross-linked chitosan film exhibits the best sensing properties such as fast response, complete recovery, high conductivity, good repeatability, excellent reproducibility and outstanding lifetime. Therefore, the crosslinking of sodium TPP has enhanced the performances of the sensor towards acetone.

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References

[1] Xu X, Chen Y, Zhang G, Ma S, Lu Y, Bian H and Chen Q 2017 J. Alloys Compd. 703 572–9
[2] Lian X, Li Y, Tong X, Zou Y, Liu X, An D and Wang Q 2017 Appl. Surf. Sci. 407 447–55
[3] Shaikh F I, Chikhale L P, Mulla I S and Suryavanshi S S 2017 Ceram. Int. 43 10307–15
[4] Gogoi P, Thakur A J, Devi R R, Das B and Maji T K 2016 J. Environ. Chem. Eng. 4 4248–57
[5] Shi T, Yang D, Yang H, Ye J and Cheng Q 2017 Appl. Clay Sci. 142 100–8
[6] Ni K, Chan C C, Chen L, Dong X, Huang R and Ma Q 2017 Opt. Fiber Technol. 33 56–9
[7] Rui L, Xie M, Hu B, Zhou L, Yin D and Zeng X 2017 Carbohydr. Polym. 173 473–81
[8] Zhang K, Hu R, Fan G and Li G 2017 Sensors Actuators B Chem. 243 721–30
[9] Leceta I, Arana P, Guerrero P and de la Caba K 2014 Mater. Lett. 128 125–7
[10] Fen Y W, Yunus W M M, Yusof N A, Ishak N S, Omar N A S and Zainudin A A 2015 Opt. - Int. J. Light Electron Opt. 126 4688–92
[11] Janaki V, Oh B-T, Shanthi K, Lee K-J, Ramasamy A K and Kamala-Kannan S 2012 Synth. Met. 162 974–80
[12] Zhang C, Wen H, Huang Y and Shi W 2017 *Int. J. Biol. Macromol.* **97** 635–41
[13] Jawad A H, Azharul Islam M and Hameed B H 2017 *Int. J. Biol. Macromol.* **95** 743–9
[14] Kim U-J, Lee Y R, Kang T H, Choi J W, Kimura S and Wada M 2017 *Carbohydr. Polym.* **163** 34–42
[15] Alshahrani A A, Al-Zoubi H, Nghiem L D and in het Panhuis M 2017 *Desalination* **418** 60–70
[16] Mokhena T C and Luyt A S 2017 *J. Clean. Prod.* **156** 470–9
[17] Ayad M M, Salahuddin N A, Minisy I M and Amer W A 2014 *Sensors Actuators B Chem.* **202** 144–53
[18] Sacco P, Paoletti S, Cok M, Asaro F, Abrami M, Grassi M and Donati I 2016 *Int. J. Biol. Macromol.* **92** 476–83
[19] Delavar Z and Shojaei A 2017 *Carbohydr. Polym.* **167** 219–28
[20] Ma S, Chen Z, Qiao F, Sun Y, Yang X, Deng X, Cen L, Cai Q, Wu M, Zhang X and Gao P 2014 *J. Dent.* **42** 1603–12
[21] Sarkar S D, Farrugia B L, Dargaville T R and Dhara S 2013 *Mater. Sci. Eng. C* **33** 1446–54
[22] Hejjaji E M A, Smith A M and Morris G A 2017 *Int. J. Biol. Macromol.* **95** 564–73
[23] Xiao B, Ma P, Ma L, Chen Q, Si X, Walter L and Merlin D 2017 *J. Colloid Interface Sci.* **490** 520–8
[24] Nasution T I, Nainggolan I, Hutagalung S D, Ahmad K R and Ahmad Z A 2013 *Sensors Actuators B Chem.* **177** 522–8
[25] Liu H, Lu D, Li P, Chen Y, Zhou Y and Lu T 2014 *J. Electroanal. Chem.* **717–718** 125–30
[26] Wang Z, Zhang X, Gu J, Yang H, Nie J and Ma G 2014 *Carbohydr. Polym.* **103** 38–45
[27] Rumansyah T I N and R A and Y M and I N and M B and R 2017 *IOP Conf. Ser. Mater. Sci. Eng.* **180** 12018
[28] Emanet M, Kazanç E, Çobandede Z and Çulha M 2016 *Carbohydr. Polym.* **151** 313–20
[29] Lee S-T, Mi F-L, Shen Y-J and Shyu S-S 2001 *Polymer (Guildf).* **42** 1879–92