

An irreversible spoilage sensor for protein-based food

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Abstract

Colour changing food spoilage sensors for protein-based food products, such as fish and beef, are mostly based on the halochromic behaviour of pH indicators. However, due to their reversible halochromic nature, these sensors can be manipulated by chemical treatment hiding the true history and quality of deteriorated meat. Therefore, there is a need to create an irreversible and reliable food spoilage sensor, which clearly indicates to consumers if any food degradation or improper storage has occurred, and avoid nefarious food processing companies from disguising spoiled meat as fresh meat. Here, a simple irreversible and halochromic sensor showing spoilage of seafood and meat products is developed. Specifically, chlorophenol red (CPR)-fatty acid particles are dispersed within an ammonia-permeable polymer matrix to form a nontoxic film sensor that shows obvious halochromic behaviour towards bio-amine or total volatile basic nitrogen (TVB-N) given off by deteriorated seafood or meat products. After removal of TVB-N, this sensor does not revert back to its original colour, due to a loss of pi-pi stacking of the original sulfonephthalein molecules. These features make this sensor applicable as a novel and reliable spoilage sensor for protein-based food products.

Key Words: Irreversible; Nontoxic; Meat; Freshness; Sensor; Sulfonephthalein; TVB-N; Ammonia

Traditional food packaging affords many benefits to suppliers, retailers and consumers during the transportation, storage and prior to the end use of food products. Currently, the food packaging industry is facing new challenges, such as counterfeited food products, wider food distribution leading to longer transport times and the consumers' desire to monitor food quality and safety.¹ These challenges have led to the emergence of smart food packaging concepts. Smart food packaging, which provides information about the food or the inner environment surrounding the food, are based on different

techniques including thermochromic labels, radio-frequency identification (RFID) devices^{2, 3}, quick response (QR) codes or two-dimensional (2D) barcodes⁴, gas sensors^{5, 6}, freshness sensors⁷⁻⁹, time-temperature indicators¹⁰ and holograms¹¹. Unexpected food deterioration, especially seafood and meat products, occurs due to inappropriate transportation or storage temperatures. This process can be indicated by the use of spoilage sensors within individual food packaging.

In this area, spoilage sensors based on lactic acid, carbon dioxide, ethanol, biogenic amines or volatile nitrogen compounds generated from food have been used to monitor the shelf life of food products.¹²⁻¹⁵ Biogenic amines or total volatile basic nitrogen (TVB-N), i.e. trimethylamine, dimethylamine and ammonia, have been reported to be important indicative components given off by perishable meat or seafood products.¹⁶⁻¹⁹ Here, pH indicators are typically bound to a medium, such as a film or nanoparticle, and react with TVB-N produced by microorganisms in food to cause colour change, making consumers aware of the deterioration of meat and seafood.^{13, 20} Due to the nontoxicity and obvious halochromic behaviour, sulfonephthaleins, such as bromophenol blue (BPB), chlorophenol red (CPR), bromocresol purple (BCP) and bromothymol blue (BTB), have been widely used as the pH indicators in spoilage sensors for those food products.²¹⁻²⁴ However, due to the chemical nature of the pH indicator, these spoilage sensors all show reversible colour change after TVB-N removal, making their indication towards the true quality of food highly uncertain.^{24, 25} As an example, CPR, as a well-known pH indicator, closes its sulfoxide ring to show yellow when $\text{pH} < 4.8$, and opens its sulfoxide ring to show violet when $\text{pH} > 6.7$.²⁶ This allows the traditional spoilage sensor with CPR as the colorant to change back to yellow from violet through chemical treatment, which would then be indicating an incorrect signal of food quality. In 2017, a scandal arose where food processing companies were found to be disguising rotten meat as fresh meat through chemical manipulation.²⁷ Therefore, it is necessary to develop an irreversible food spoilage sensor that could not be regenerated to indicate the 'safe' colour, through chemical treatment.

Recently, we have reported a nontoxic binary thermochromic system comprising a sulfonephthalein dye and an aliphatic solvent (long-chain ester, acid, or alcohol).²¹ Taking CPR-dodecanoic acid (CPR-DA) as an example, this binary system initially shows red instead of the common colour of yellow when crystallized, due to the π - π stacking form of CPR. CPR would then quickly change from red to purple when it was exposed to an alkaline atmosphere due to its halochromic nature. Therefore, it was envisaged that if this binary system was dispersed evenly throughout a polymeric film, it would potentially change colour due to exposure to TVB-N released from the food during gradual spoilage. When exposed to alkaline TVB-N, this solid binary system shows a purple colour, due to CPRs ring open sulfoxide structure and loss of π - π stacking. After removal of TVB-N or acid treatment, the CPRs revert back to the closed sulfoxide ring structure, but cannot regenerate π - π stacking, making the sensor show the common colour of yellow rather than the initial red. As a result, it is possible to prepare an irreversible halochromic sensor using this binary system.

In this work, we aimed to prepare a nontoxic spoilage sensor that shows irreversible colour change towards perishable protein-based food products, by incorporating this nontoxic CPR-DA binary system into a TVB-N permeable film. Polydimethylsiloxane (PDMS) has been chosen as the film component, due to its transparency, flexibility, biocompatibility and moderate permeability to ammonia gas.²⁸⁻³³ Here, a CPR-DA binary system will be dispersed as particles into crosslinked non-toxic PDMS films. The colour change performance of the obtained films towards ammonium and TVB-N will be investigated, and the irreversibility of colour change and corresponding mechanism will be explained.

Results and discussion

Film formation

Commercial liquid vinylmethylsiloxane-dimethylsiloxane copolymer resin (vinyl-PDMS, VDT-5035, Gelest) were mixed with the (CPR-DA) particles and cast onto polyethylene terephthalate (PET) plastic film before being crosslinked by UV light (Figure 1). The obtained films were classified as F₁ to F₃ according to different dispersed particle size (Figure 2).

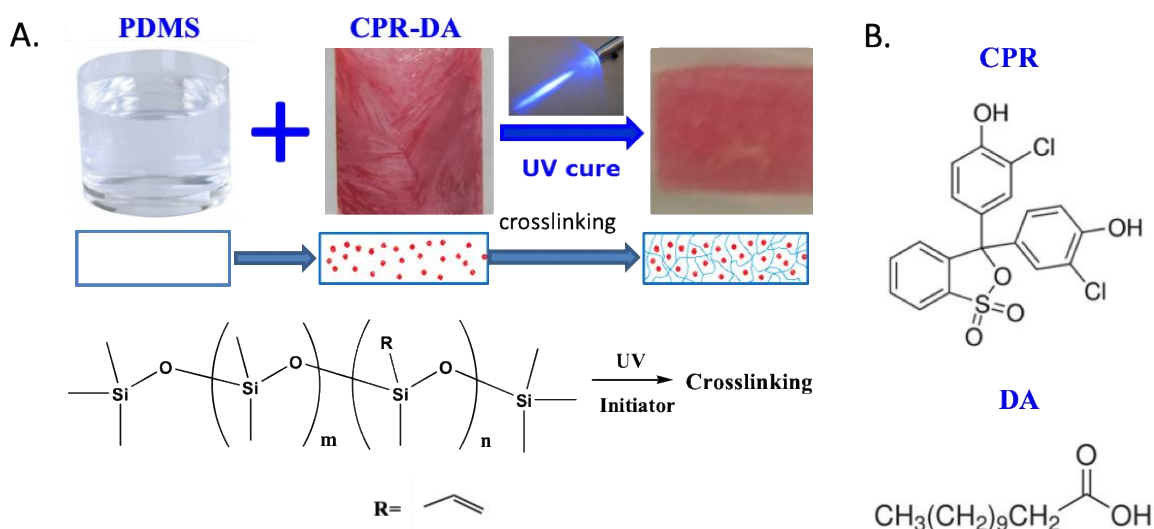


Figure 1. A) Preparation of the hybrid film with PDMS as the polymeric medium and dispersed chlorophenol red-dodecanoic acid (CPR-DA) binary system as the functional particles; B) The molecular structures of CPR and DA.





| Sample | Particle size | Sample | CPR-DA | F ₁ | F ₂ | F ₃ |
|----------------|----------------------|--------|---|--|---|---|
| F ₁ | <90 μm | | | | | |
| F ₂ | 90-425 μm | 25°C |  |  |  |  |
| F ₃ | >425 μm | | | | | |

Figure 2. Left) A summary of the film samples F₁-F₃ containing a range of CPR-DA particle sizes; Right) Photographic images of CPR-DA binary system and film samples (F₁ to F₃) at 25 °C.

The photographic images of the CPR-DA binary system alone and subsequent film samples (F₁-F₃) are shown in Figure 2. All film samples (F₁-F₃) showed a pink colour at 25 °C, below the melting point of DA ($T_m = 43.2$ °C), where the CPR-DA particles remained solid. The pink colour was from the pi-pi stacking structure of CPR formed during the crystallization of DA in a CPR-DA binary system.²¹ Therefore, the longer conjugated pi-pi stackings result in more intense pink colour. Since the colour of CPR-DA particles got paler as the size decreases, the corresponding film samples also exhibited different chromatic intensity. F₃ contains the largest particles with more conjugated pi-pi stackings shows the most intense pink colour among these three samples, while F₁ contains the smallest particles shows the palest colour. However, as the size of the distributed particles increases, the homogeneity of the obtained film deteriorated. F₃ is not homogeneous particularly in the region where the particles are big. Based on the homogeneity and chromatic intensity of the sample, F₂ was chosen for subsequent investigations.

Irreversible halochromic sensor

It has been previously reported that certain food products such as fish and beef, release TVB-N (ammonia, dimethylamine and trimethylamine) upon degradation,^{34, 35} and ammonia gas accounts for the largest proportion of those amines.¹⁹ CPR is well known as a pH indicator component (Figure 3), and its halochromic nature is based on the sulfoxide ring opening or closing as a result of an interaction with OH⁻ or H⁺ respectively.²⁶ To investigate this property further, sample F₂ was treated by ammonia vapor for one minute at 25 °C in a sealed vial by the addition of a number of drops of saturated NH₄OH solution. The colour change and corresponding UV-Vis absorption spectra of F₂ before and after being exposed to ammonia vapor are shown in Figure 4.

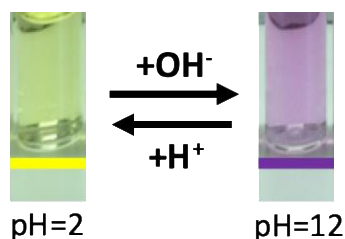


Figure 3. Photographic images of CPR aqueous solution (1mM, pH=2 and pH=12).

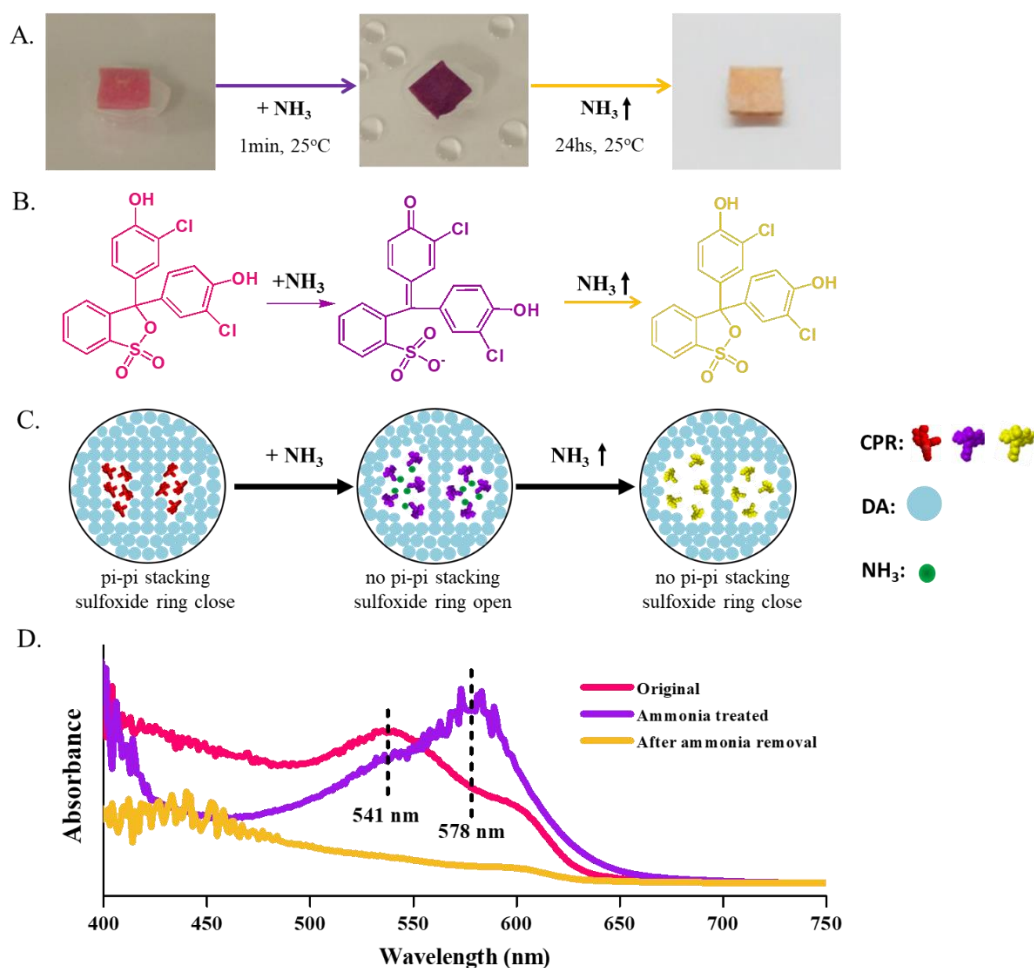


Figure 4. A) The photographic images of original F₂, ammonia vapor (aq. NH₄OH, 1 minute, 25 °C) treated F₂ and F₂ after ammonia vapor removal (24 hours, 25 °C); B) Corresponding molecular structure change of CPR; C) A schematic representation of CPR molecules in corresponding states within CPR-DA particles; D) Corresponding UV-Vis absorption spectra of F₂ at 25 °C.

The original F₂ sample directly changed colour from pink to dark purple with absorption peak shifting from 541 nm to 578 nm due to the sulfoxide ring opening of CPR molecules (Figure 4A&D). The dissociation of the hydrophilic ring-opened CPR from the hydrophobic DA leads to a loss of the pi-pi stacking of CPR molecules, which is responsible for the pink colour in the original sample F₂ (Figure 4B). This experiment clearly confirms the ability of sample F₂ to undergo halochromism under basic conditions. However, DA is an acid and may also react with ammonia which could reduce the accuracy

of the detection. Our early work has indicated that linear chain esters, acids or alcohols can all act the role as DA does.²¹ Therefore, this inaccuracy can be resolved by using base-insensitive solvents such as linear chain esters. After removal of the ammonia, the sample F₂ was stored for a further 24 hours at 25 °C. Sample F₂ was shown to change to an orange-yellow rather than original pink colour (Figure 4A&D).

The obvious colour formation from pink to purple then to orange-yellow in the film can be explained in this way: (1) CPR molecules pi-pi stack in the narrow space on the crystal boundaries of DA in the CPR-DA solid particles and show the pink colour, which is different from the common yellow colour of a ring-closed individual CPR molecule; (2) When CPR molecule is exposed to an alkaline environment, the sulfoxide ring opens and forms a highly hydrophilic ionic structure, which completely separates from the hydrophobic DA. The intermolecular arrangement of CPR molecules no longer arranges to an ordered pi-pi stacking configuration. In this case, CPR showed a deep purple colour; (3) When the alkaline environment is removed or changes, the sulfoxide ring of CPR closes. However, the intermolecular arrangement of CPR molecules cannot return to their original pi-pi stacking form. Therefore, CPR-DA solid particles only show the yellow coloured ring-closed form of the individual CPR molecules (Figure 4C).

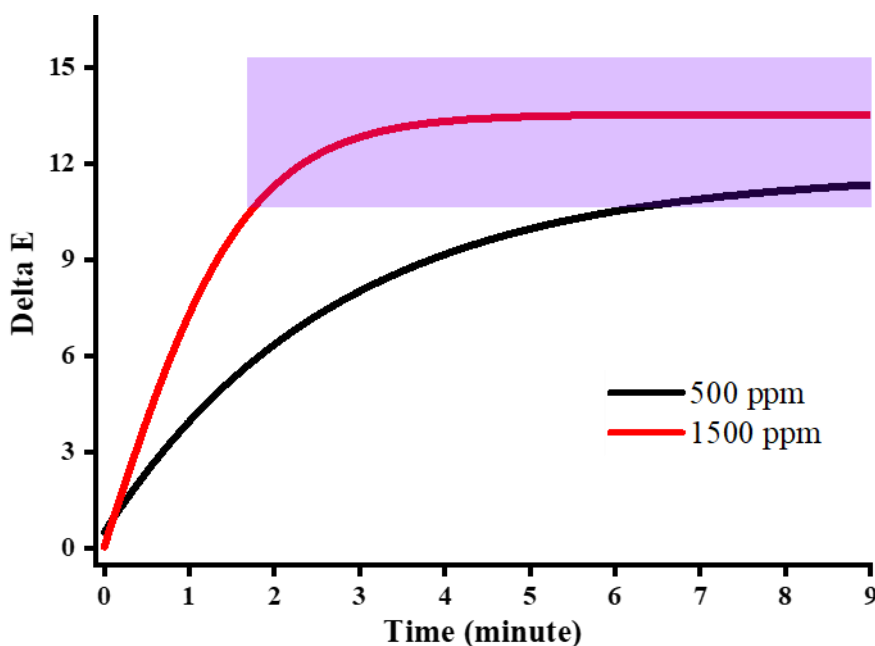


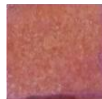





Figure 5. The colour change values (ΔE) of sample F₂ vs. time upon being treated by ammonia with different concentrations (500 ppm and 1500 ppm) in the air.

To investigate the sensitivity level for ammonia detection, sample F₂ was treated by ammonia vapor with two different concentrations at 25 °C and colour change was recorded at different time points. The sample F₂ turned obviously purple after being placed in 500 ppm ammonia vapor for 6 minutes, while it turned into the same colour in only 2 minutes in 1500 ppm ammonia vapor (Figure 5). A value of ΔE above 10 enables the observation of colour difference with a naked eye. The curve of 500 ppm can just

reach above 10 after 6 minutes. Therefore, the detection limit for sample F₂ is about 500 ppm.

| Fish | | | | | | |
|----------------|---|---|---|---|---|---|
| Test time | 0 hour | 24 hours | 48 hours | 72 hours | 96 hours | After removal of TVB-N |
| F ₂ |  |  |  |  |  |  |
| L | 65.13 ± 3.67 | 51.66 ± 3.50 | 53.31 ± 2.96 | 54.80 ± 2.90 | 48.09 ± 2.95 | 74.27 ± 0.78 |
| a | 42.77 ± 6.86 | 39.69 ± 4.31 | 28.74 ± 2.34 | 22.45 ± 4.25 | 25.77 ± 1.65 | 12.88 ± 1.50 |
| b | 28.57 ± 1.46 | 23.51 ± 2.18 | 13.45 ± 6.27 | 7.31 ± 4.28 | -0.69 ± 3.33 | 28.20 ± 2.94 |
| ΔE | 0 | 12.35 | 13.19 | 15.19 | 22.94 | 18.58 |







| Beef | | | | | | |
|----------------|--|--|--|--|--|--|
| Test time | 0 hour | 24 hours | 48 hours | 72 hours | 96 hours | After removal of TVB-N |
| F ₂ |  |  |  |  |  |  |
| L | 63.89 ± 1.89 | 46.80 ± 2.81 | 46.06 ± 4.59 | 54.36 ± 3.31 | 50.17 ± 2.56 | 79.19 ± 1.05 |
| a | 42.87 ± 3.06 | 43.01 ± 1.86 | 29.55 ± 2.83 | 20.14 ± 1.50 | 19.29 ± 0.88 | 7.21 ± 0.66 |
| b | 33.86 ± 2.76 | 15.07 ± 1.30 | 7.88 ± 3.95 | -9.23 ± 1.24 | -12.33 ± 0.79 | 17.06 ± 1.03 |
| ΔE | 0 | 19.24 | 21.62 | 25.92 | 29.07 | 21.53 |

Figure 6. The photographic images and colorimetric parameters (L, a, b and ΔE) of sample F₂ after being placed with raw fish or beef for 0hs, 24hs, 48hs, 72hs and 96hs at 25 °C and after removal of deteriorated fish or beef for 24hs at 25 °C.

To further investigate the halochromic performance of this film towards bio-amines or TVB-N, samples of F₂ were placed with fresh fish or beef mince in sealed Petri dishes at 25 °C. Photographic images of the test sample F₂ in Figure 6, were taken every 24 hours and subsequently calibrated for white balance. The values of L, a, and b for the evaluation of the film colours were from the colour balanced images. It can be seen that the pink sample F₂ exposed to fish and beef gradually changed over the 4-day testing period to a dark purple colour at 25 °C. The colorimetric parameters (L, a, b and ΔE) determined by these images of sample F₂ are summarised in Figure 5. When the sample F₂ and raw fish were placed together over the 4-day period, the values of colorimetric parameters (L, a, and b) changed, with the value of b decreasing the most from 28.57 to -0.69 (blue-shift). When the sample F₂ and raw beef were placed together within the same time span, the value of b dropped more significantly from 33.86 to -12.33.

The colour change was quantified by ΔE values, which indicate the colour difference according to CIE 2000 when the colour of original sample F₂ at 25 °C was set as the reference.³⁶ The ΔE values rose from 0 to 22.94 in fish testing and 0 to 29.07 in beef testing (Figure 6, 7A&7C), indicating that the naked eye can easily recognize such colour changes. When fish or meat is stored at 25 °C, its internal protein structure begins to spoil and release TVB-N. Here the alkaline TVB-N permeates into the test sample causing CPR to open its sulfoxide ring and appear purple. Therefore, the prepared film sample can indirectly alert the consumer of fish or beef spoilage in the package by the colour changing of the sensor.

After removal of the deteriorated fish or beef, the sample F₂ was stored for a further 24 hours at 25 °C. Sample F₂ was also shown to change to an orange-yellow rather than original pink colour (Figure 6, 7A&7C) with a ΔE value of 18.58 in fish testing and 21.53 in beef testing respectively.

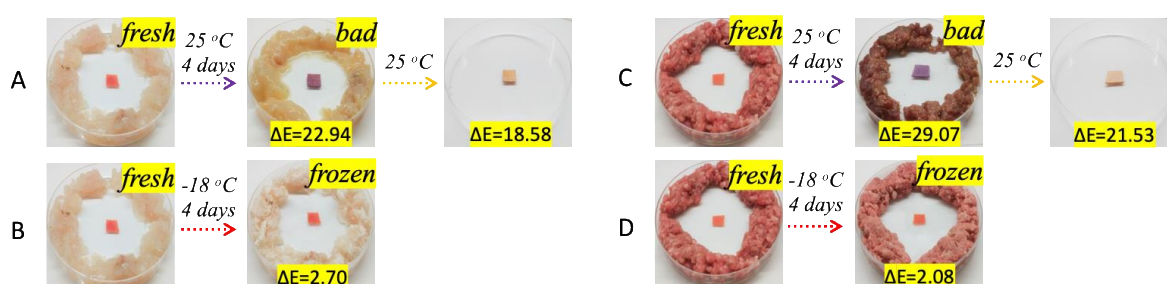


Figure 7. A) Colour change of sample F₂ placed with fresh fish, deteriorated fish and after separation from deteriorated fish at 25 °C; B) Colour change of sample F₂ placed with fresh fish and frozen fish at -18 °C; C) Colour change of sample F₂ placed with fresh beef, deteriorated beef and after separation from deteriorated beef at 25 °C; D) Colour change of sample F₂ placed with fresh beef and frozen beef at -18 °C.

To replicate recommended storage conditions, sample F₂ was placed with fresh fish or beef for 4 days at -18 °C as a baseline (Figure 7B&7D). The samples remained pink in colour with insignificant ΔE values, indicating that fish and beef only released insignificant TVB-N after being stored at the correct storage temperature for 4 days, due to the inhibition of microbial metabolism at low temperature. Therefore, this film has been demonstrated as a halochromic sensor towards practical bio-amines or TVB-N generated from seafood or meat products with an obvious colour change visible to the naked eye. Importantly, the irreversible halochromic nature of this sensor, makes it clear that food degradation, improper storage or product manipulation or substitution has occurred, even after the removal of TVB-N from the sensor.

Conclusion

In conclusion, the first irreversible halochromic sensor showing spoilage of seafood and meat products is reported. This sensor with PDMS as polymeric matrix and dispersed CPR-DA binary systems as

functional particles shows clear colour change from pink to purple towards ammonia and TVB-N released from deteriorated fish or beef due to the sulfoxide ring opening of CPR molecules. After removal of ammonia and TVB-N, the sensor shows an orange-yellow colour rather than original pink colour due to a loss of the pi-pi stacking of CPR molecules, which is responsible for the pink colour in the original sensor. The irreversible halochromic behaviour coupled with the non-toxic nature of the components as well as its ease of preparation, makes this sensor show great potential as a reliable spoilage sensor for protein-based food products.

Experimental

Chemicals and Materials

Chlorophenol red (CPR), dodecanoic acid (DA) and 1-hydroxycyclohexyl-1-phenyl methanone (Irgacure 184) were purchased from Sigma-Aldrich. Vinylmethylsiloxane-dimethylsiloxane copolymer (vinyl-PDMS, VDT-5035) was purchased from Gelest. All the reagents were used as received with no further purification. Polyethylene terephthalate (PET) film was purchased from Polyplex.

Preparation of samples

CPR was dissolved into DA with molar ratio of 1:1000 by sonication. The obtained yellow solution was placed into a freezer (-18 °C) to form a dark red crystallized solid. Finally, the crystallized solid was ground into particles, which were then separated by sieving with 90 µm and 425 µm sieves.

Irgacure 184 photoinitiator (0.02 g, 1.3 wt.% of film sample) was dissolved into vinyl-PDMS liquid (1.0 g, 65.8 wt.% of film sample) by sonication. The clear PDMS solution was preserved in a freezer (-18 °C) until required. CPR-DA particles (0.5g, 32.9 wt.% of film) at three size scales were mixed into cold clear PDMS solution to form homogeneous suspensions by mechanical stirring. These liquid suspensions were casted between two PET films then UV-cured (MODEL UVGL-58 MINERALIGHT lamp, 366 nm) for 1 hour. The PET films were then removed exposing the PDMS-CPR-DA samples ready for testing. The matrix components and the size of particles used in each sample are listed in Figure 2.

Instrumentation and measurements

UV-Vis absorbance spectra were measured on a Shimadzu UV-Mini 1240 spectrophotometer with thermostat.

All digital photographs were white balanced by Photoshop CS6 in Camera Raw file formats.³⁷ The colorimetric parameters L, a and b were determined from the photographs using the same software.

Colour differences (ΔE) were calculated according to CIE2000 from the colorimetric parameters L, a and b.³⁶

Notes

The authors declare no competing financial interest.

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