DOI: 10.19884/j.1672-5220.202505008

Dual Fluorescent Hydrogel Derived from Cross-Linked Chitosan-Salicylaldehyde-Eu (Ⅲ) for Visual Detection of Volatile Amine and Meat Freshness

WANG Yanmin, ZHANG Xuan *
College of Chemistry and Chemical Engineering, Donghua University, Shanghai 201620, China

Abstract: Based on cross-linked chitosan (CS)-salicylaldehyde (SA)-Eu (Ⅲ), a dual fluorescent hydrogel, designated as Eu-SA-CS, was successfully fabricated. The Eu-SA-CS hydrogel exhibited a green fluorescence around 500 nm, whereas a red fluorescence around 600 nm was observed upon exposure to volatile amines such as triethylamine (TEA). There was a good linear relationship between the fluorescence intensity ratio and TEA volume concentration (0−40 μL/L). Furthermore, the hydrogel could be used to indicate the meat freshness by a change in fluorescence color from green (fresh) to red (spoiled). These results revealed that the present Eu-SA-CS hydrogel could serve as a smart green-red fluorescent signal label for real-time monitoring of meat freshness.

Keywords: dual fluorescent hydrogel; volatile amine detection; meat freshness

CLC number: O652; Q811.4 **Document code**: A

Article ID: 1672-5220(2026)03-0057-07

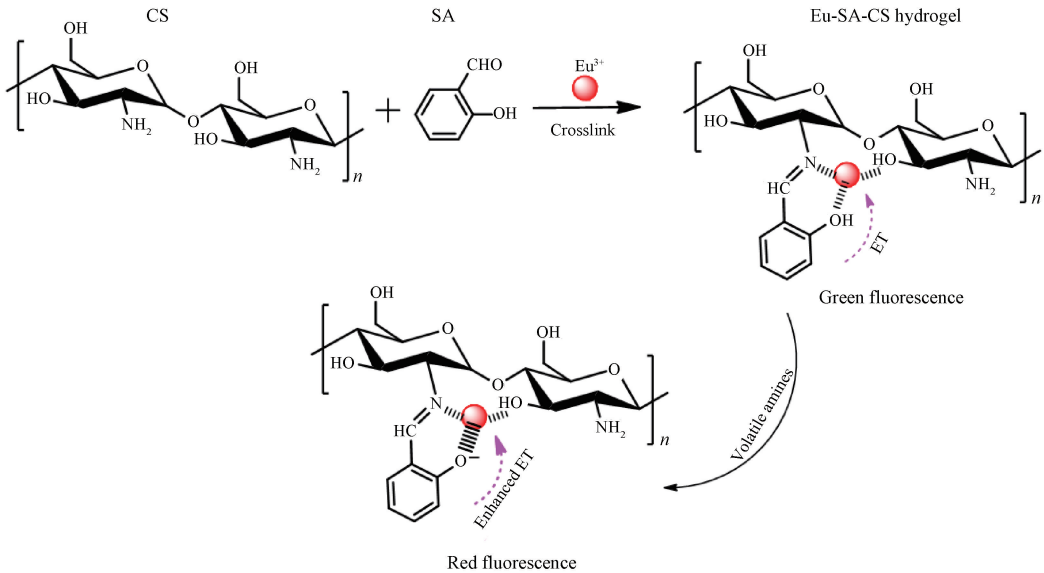
Open Science Identity (OSID)

0 Introduction

To meet the increasing requirement for food safety and freshness, the quality evaluation of meat products has become particularly important because meat (fish, shrimp, pork, etc.) is the main protein source for human beings. Generally, volatile and biogenic amines (ammonia, methylamine, histamine, etc.) produced from protein degradation are considered key indicators of food quality[1-3]. In this regard, the development of detection methods for on-site and real-time monitoring of volatile amines is crucial to evaluate the meat spoilage. Traditional analytical methods require expensive instruments and involve inherent operational complexity[4-6]. Fluorescence sensing is a sensitive and visual detection technique and has attracted much attention in amine detection and food safety control due to its simplicity[7-9]. However, most fluorescent sensors reported for volatile amine detection worked in solution, and inconvenient to monitor the volatile amines and food freshness in situ[10-15]. Fluorescent hydrogel is a promising polymer material with a three-dimensional network structure and has demonstrated great potential for portable and wearable sensors[16-18]. Additionally, the development of dual fluorescent hydrogels is more promising because dual-wavelength emissions can be directly used for ratiometric fluorescent sensors. The ratiometric mode would enhance the detection accuracy by avoiding the signal fluctuations of the instrument through the self-calibration of two distinct signals. But only a few ratiometric fluorescent hydrogels for volatile amine detection were reported[17].

In this study, based on biocompatible chitosan (CS) polymer matrix, combined with Eu (Ⅲ) and salicylaldehyde (SA) fluorescence centers, a dual fluorescent hydrogel, designated as Eu-SA-CS, was successfully fabricated for meat freshness monitoring. The present Eu-SA-CS hydrogel was facilely fabricated by crosslinking via glutaraldehyde and showed amine-sensitive green-red dual fluorescence (Fig. 1). Triethylamine (TEA), a typical volatile amine, was used as a model analyte to verify the sensing performance. Relying on the silimar amine-responsive behavior, it can serve as an intelligent fluorescent label for monitoring meat freshness, where the green fluorescence distinctly turned red with meat spoilage.

Received date: 2025-05-16
Foundation item: Research Foundation from National Innovation Center of Advanced Dyeing & Finishing Technology, China (No. 2022GCJJ10)
* Correspondence should be addressed to ZHANG Xuan, email: xzhang@dhu.edu.cn
Citation: Wang Y M, Zhang X. Dual fluorescent hydrogel derived from cross-linked chitosan-salicylaldehyde-Eu (Ⅲ) for visual detection of volatile amine and meat freshness[J]. *Journal of Donghua University (English Edition)*, 2026, 43(3): 57-63.



ET—energy transfer.

Fig. 1 Fabrication process of Eu-SA-CS hydrogel and possible response mechanism to volatile amines

1 Materials and Methods

1.1 Materials and characterizations

CS (degree of deacetylation > 90%), SA, ammonia ($NH_3 \cdot H_2O$, mass fraction of 25%), hydrazine (N_2H_4, mass fraction of 85%) and aniline were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Dimethylamine ($(CH_3)_2NH$) and TEA were purchased from Aladdin Reagent (Shanghai) Co., Ltd., China. $Eu(NO_3)_3 \cdot 6H_2O$ was purchased from Sigma Aldrich Shanghai Trading Co., Ltd., China. Other common reagents were obtained from commercial suppliers. All the reagents were used without further purification.

The Fourier transform infrared (FTIR) spectra of hydrogels were recorded on an FTIR instrument (PerkinElmer Spectrum Two, PerkinElmer, Inc., USA). The fluorescence spectra of hydrogels were recorded on a spectrophotometer (Shimadzu RF-6000, Shimadzu Corporation, Japan).

1.2 Preparation of fluorescent hydrogels

CS (0.30 g) was dissolved in 10 mL aqueous glacial acetic acid (a volume ratio of 1%) and stirred at 30 ℃ for 2 h to get a homogeneous solution. An aqueous solution of $Eu(NO_3)_3 \cdot 6H_2O$ (0.19 g in 1 mL H_2O) was then added to the above CS solution and stirred for 30 min. Subsequently, the SA solution (83 μL in 1 mL ethanol) was added under stirring for 30 min, and aqueous glutaraldehyde solution (a volume ratio of 1%, 2 mL) was added and kept stirring for another 5 min to improve the crosslinking of the hydrogel. The obtained fresh hydrogel was left to stand for 24 h, and transferred into a freezer incubation at −18 ℃ for 12 h. The Eu-SA-CS hydrogel was finally obtained by a controlled thawing process at an ambient temperature for 1 h. Other hydrogels were similarly prepared without Eu (Ⅲ) (denoted as SA-CS), without SA (denoted as Eu-CS), or without both Eu (Ⅲ) and SA (denoted as CS). All hydrogels were preserved under refrigerated conditions at 4 ℃ for further experimental investigations.

1.3 Application of Eu-SA-CS hydrogel in monitoring of meat freshness

Fresh meat samples (shrimp, fish, and pork) were purchased from a local supermarket. The meat sample and Eu-SA-CS hydrogel were co-encapsulated within a 25 mm × 10 mm transparent chamber for a certain time at various temperatures of 25, 15, 4, and −18 ℃, respectively. Fluorescent hydrogels were photographed at regular intervals to record color changes and thereby monitor the meat freshness.

2 Results and Discussion

2.1 Structural characterization of fluorescent hydrogels

Figure 2 shows the FTIR spectra of Eu-SA-CS, SA-CS and CS. Both Eu-SA-CS and SA-CS exhibit the characteristic peaks of CS. For SA-CS, a distinct band at 1 632 cm^{-1} is observed, corresponding to the C═N vibration characteristic of imines[19]. This indicates the formation of imine bonds between SA and CS in the hydrogel network. For Eu-SA-CS, the absorption band of C═N shifts to 1 622 cm^{-1}, suggesting C═N is involved in the coordination with Eu^{3+}.

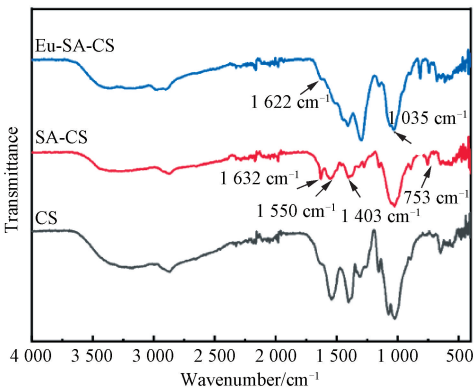


Fig. 2 FTIR spectra of Eu-SA-CS, SA-CS and CS

2.2 Luminescent properties of fluorescent hydrogels

Figure 3 shows the fluorescence spectra of CS, SA-CS, Eu-CS and Eu-SA-CS, where the excitation wavelength λ_{ex} is 390 nm, and the insets are corresponding fluorescence photographs obtained under a 365 nm lamp. Single blue emission at 475 nm and green emission around 500 nm are observed from CS and SA-CS, respectively. Besides short-wavelength emission around 480 nm, a series of emissions around 580 – 700 nm with the strongest peak of 615 nm is observed from Eu-CS and Eu-SA-CS. The long-wavelength emissions from Eu-CS and Eu-SA-CS could be ascribed to characteristic peaks of Eu^{3+} at 590 nm ($^5D_0 \rightarrow {}^7F_1$), 615 nm ($^5D_0 \rightarrow {}^7F_2$), and 693 nm ($^5D_0 \rightarrow {}^7F_4$)[20]. Interestingly, with exposure to TEA, the fluorescence of Eu-SA-CS dramatically turns red from green (Fig. 3(d) and inset), where the emissions from Eu^{3+} are sharply enhanced. However, other hydrogels do not undergo an obvious fluorescence color change and almost remain at the original emission upon exposure to TEA (Figs. 3(a)–(c) and insets). This indicates that Eu-SA-CS can be used as a dual fluorescent sensor for amine detection.

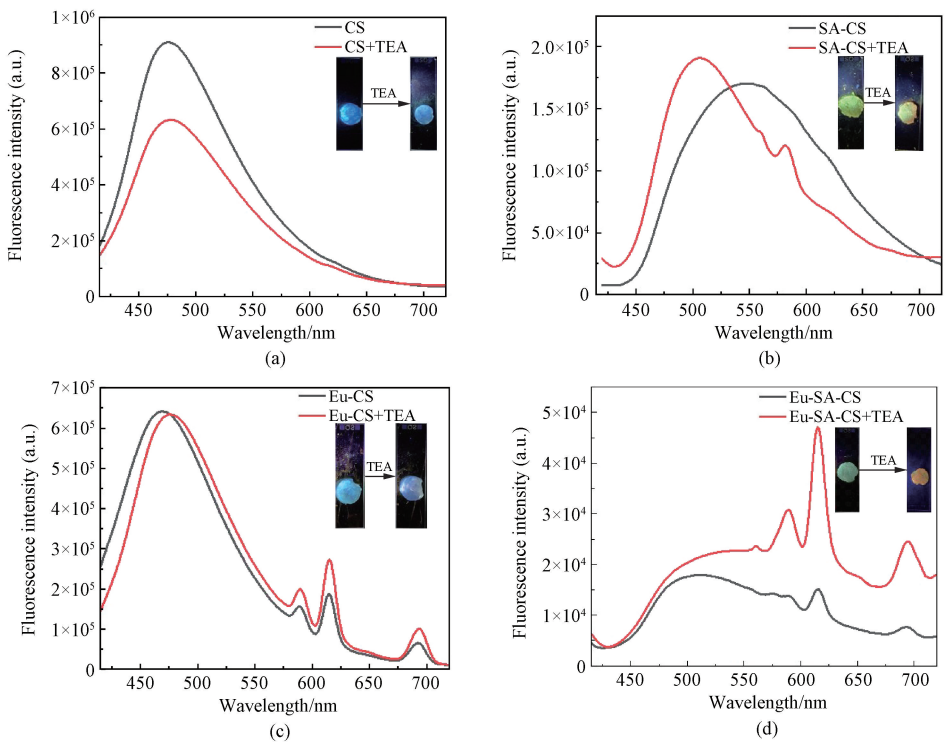


Fig. 3 Fluorescence emission spectra of hydrogels in the absence and presence of TEA: (a) CS; (b) SA-CS; (c) Eu-CS; (d) Eu-SA-CS

2.3 Fluorescence responses toward volatile amine

The dual fluorescence response of Eu-SA-CS toward various volatile amines was investigated. The results are shown in Fig. 4. It can be seen that both TEA and $(CH_3)_2NH$ strongly enhance the red fluorescence emission of Eu^{3+}. The fluorescence intensity ratios I_{615}/I_{490} are about 27 and 16, respectively (Fig. 4(b)), where I_{615} and I_{490} denote the fluorescence intensities of Eu^{3+} (red emission) and SA (green emission). Other amines such as N_2H_4, aniline, and $NH_3 \cdot H_2O$ induce a slight increase in the I_{615}/I_{490} ratio. Such fluorescence enhancement could be attributed to the deprotonation of SA induced by basic volatile amines, followed by enhanced ET between the SA anion and Eu^{3+}, which greatly enhances the fluorescence emission of Eu^{3+}[21]. The response mechanism has been illustrated in Fig. 1. Based on the enhancement effect of the I_{615}/I_{490} ratio, TEA was selected as a model volatile amine for further study in this work.

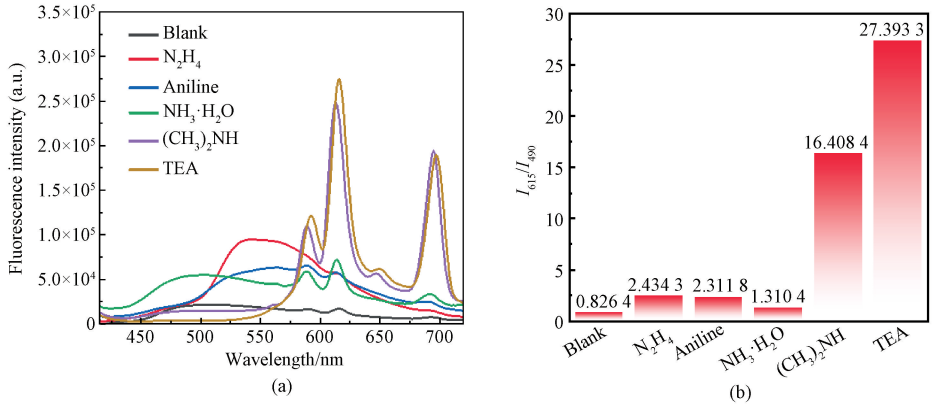


Fig. 4 Fluorescence changes of Eu-SA-CS upon exposure to various volatile amines: (a) fluorescence spectra; (b) fluorescence intensity ratio I_{615}/I_{490}

The response time was firstly investigated by fluorescence spectra of Eu-SA-CS with exposure to TEA vapor at different time. As shown in Fig. 5 (a), the fluorescence emission of Eu-SA-CS at 615 nm sharply increases with increasing exposure time and levels off after 60 min. The I_{615}/I_{490} ratio also reflects a similar enhancement trend within 60 min (Fig. 5 (c)), meanwhile, the fluorescence color gradually turns red from the original green (Fig. 5 (d)). For comparison, the fluorescence change of Eu-SA-CS was also investigated upon exposure to H_2O vapor. It can be noted that the fluorescence spectra, I_{615}/I_{490} ratio, and color remain almost unchanged in H_2O vapor (Figs. 5 (b) – (d)). Therefore, the response time was selected to be 60 min.

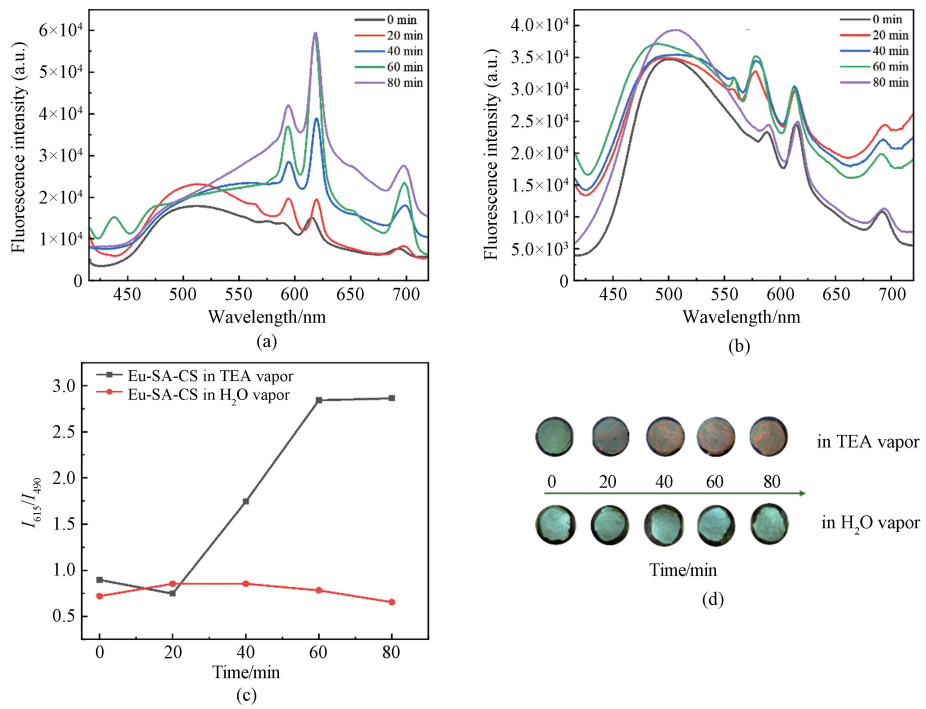


Fig. 5 Fluorescence changes of Eu-SA-CS with response time: (a) fluorescence spectra upon exposure to TEA vapor; (b) fluorescence spectra upon exposure to H_2O vapor; (c) change of I_{615}/I_{490} ratio; (d) change of fluorescence color

The fluorescence spectra of Eu-SA-CS hydrogels were recorded at various TEA vapor volume concentrations (0 – 50.0 μL/L), where λ_{ex} = 390 nm and the exposure time is 60 min. As shown in Fig. 6, the fluorescence intensity at 615 nm increases with increasing TEA vapor volume concentration, and the I_{615}/I_{490} ratio linearly increases in 0 – 40.0 μL/L TEA vapor (coefficient of determination R^2 = 0.990 05). This revealed that Eu-SA-CS could be used as a ratiometric fluorescent sensor for volatile amine, and a smart fluorescent label for monitoring meat freshness.

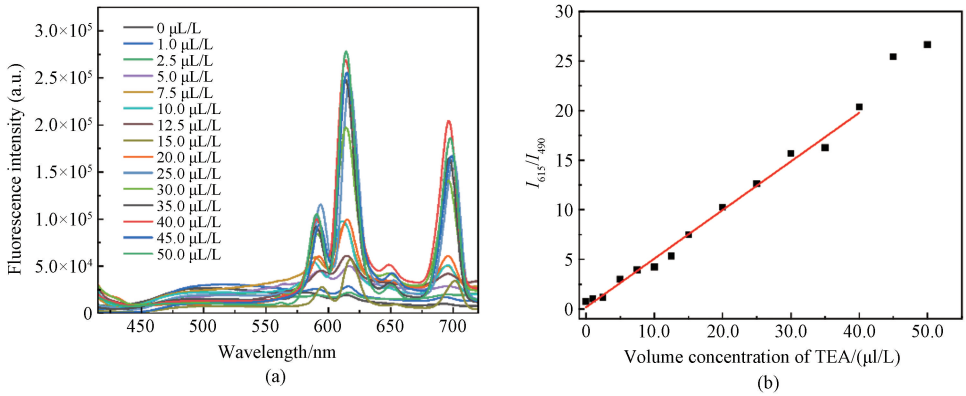


Fig. 6 Fluorescence response characters of Eu-SA-CS upon exposure to various volume concentrations of TEA vapor: (a) fluorescence spectra; (b) corresponding linear correlation between I_{615}/I_{490} and TEA volume concentration

2.4 Application in monitoring meat freshness

During the process of meat spoilage, microorganisms decompose free amino acids into amines such as histamine, dimethylamine, and trimethylamine. The distinct fluorescence color change of Eu-SA-CS toward volatile amines makes it a potential smart fluorescent label for monitoring meat freshness. To detect the meat freshness, the meat samples were stored in a sealed container with the hydrogel together at a controlled temperature and time[22]. As shown in Fig. 7, at 25 ℃, the original green fluorescence of the Eu-SA-CS decreases and red fluorescence increases with increasing exposure time, with the fluorescence photographs taken under a 365 nm lamp. The distinct red fluorescence is observed after 18, 24, and 72 h for fish, shrimp, and pork samples, respectively. This indicated that these meat samples spoiled during storage.

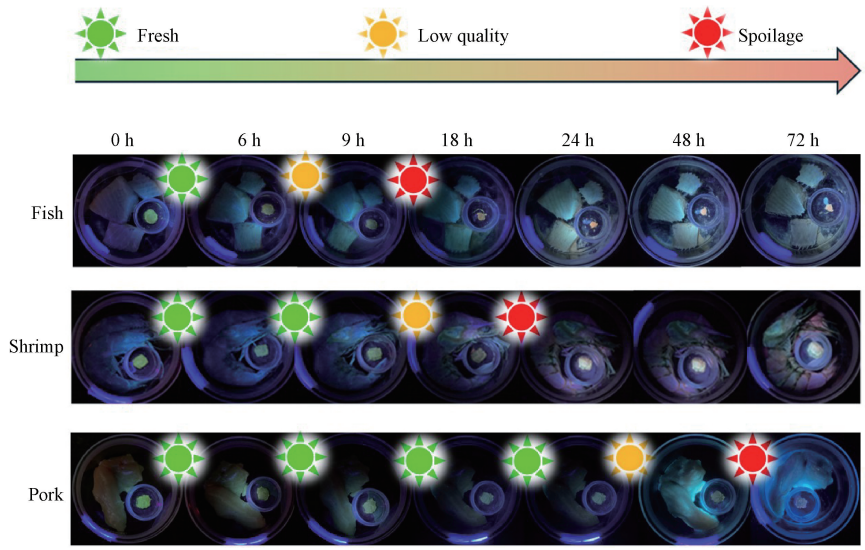


Fig. 7 Fluorescence changes of Eu-SA-CS in monitoring freshness of meat samples at 25 ℃

To examine the effect of storage temperature on food freshness, the shrimp sample was further investigated at various temperatures ranging from 15 to −18 ℃. As shown in Fig. 8, the fluorescence color of Eu-SA-CS changes with prolonged storage time and lower temperature, with the fluorescence photographs taken under a 365 nm lamp. For example, the shrimp spoils after 48 h at 15 ℃ and is of low quality after 72 h at 4 ℃, whereas it remains fresh even after 72 h at −18 ℃. These results demonstrated that Eu-SA-CS could serve as a smart fluorescent label for meat freshness monitoring via fluorescence color changes.

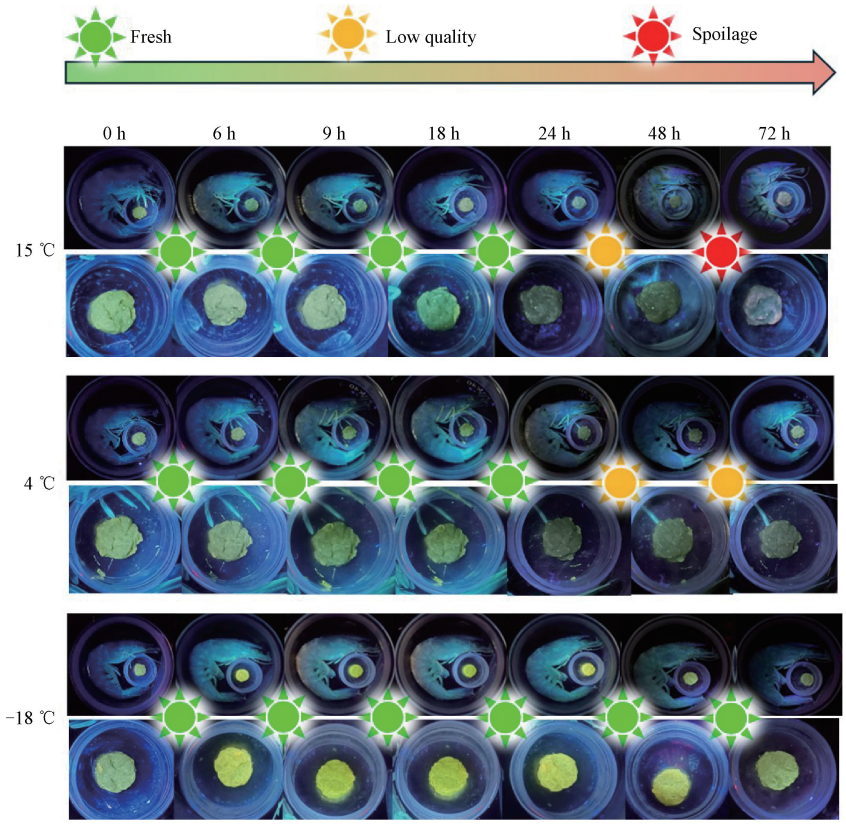


Fig. 8 Fluorescence changes of Eu-SA-CS in monitoring freshness of shrimp samples at different temperatures

3 Conclusions

In conclusion, a novel CS-based dual fluorescent hydrogel (Eu-SA-CS) was facilely fabricated by incorporating Eu^{3+} and SA luminescent centers and cross-linking with glutaraldehyde. Eu-SA-CS exhibited a distinct fluorescence color change from green to red with exposing to volatile amines such as TEA. A good linear relationship was obtained between the fluorescence intensity ratio I_{615}/I_{490} and TEA volume concentration (0–40.0 μL/L). Furthermore, Eu-SA-CS was successfully used to monitor the meat freshness during storage by a change in fluorescence color from green (fresh) to red (spoiled).

References

[1] Andre R S, Mercante L A, Facure M H M, et al. Recent progress in amine gas sensors for food quality monitoring: novel architectures for sensing materials and systems[J]. *ACS Sensors*, 2022, 7(8): 2104-2131.

[2] Ding T, Li Y L. Biogenic amines are important indices for characterizing the freshness and hygienic quality of aquatic products: a review [J]. *LWT-Food Science and Technology*, 2024, 194: 115793.

[3] Zeng Q Y, Wang Y F, Javeed A, et al. Preparation and properties of polyvinyl alcohol/chitosan-based hydrogel with dual pH/NH_3 sensor for naked-eye monitoring of seafood freshness [J]. *International Journal of Biological Macromolecules*, 2024, 263: 130440.

[4] Gao H, Yang F, Zhu B Q, et al. Optimization of HS-SPME-GC-MS for the determination of volatile flavor compounds in Ningxiang pork[J]. *Foods*, 2023, 12(2): 297.

[5] Fang Z Q, Xu Y F, Duan L, et al. Freshness evaluation of grass carp by volatile biogenic amines monitored by secondary electrospray ionization ion mobility spectrometry [J]. *Microchemical Journal*, 2023, 195: 109483.

[6] Adımcılar V, Öztekin N, Bedia Erim F. A direct and sensitive analysis method for biogenic amines in dairy products by capillary electrophoresis coupled with contactless conductivity detection [J]. *Food Analytical Methods*, 2018, 11(5): 1374-1379.

[7] Zhao J H, Xu W X, Li B, et al. Portable fluorogenic probe for monitoring of volatile amine vapour and food spoilage[J]. *Chinese Chemical Letters*, 2024, 35(3): 108579.

[8] Li Z Y, Hou S T, Zhang H N, et al. Recent advances in fluorescent and colorimetric sensing for volatile organic amines and biogenic amines in food [J]. *Advanced Agrochem*, 2023, 2(1): 79-87.

[9] Yang L F, Xie J, Ding Z Y. Recent studies of

metal-organic frameworks as meat freshness sensors[J]. *Microchemical Journal*, 2025, 212: 113184.
[10] Liu X Y, Li Z L, Wang Z Y, et al. BCNO quantum dots-based ratiometric fluorescence platform integrated with portable device: hypoxanthine sensing for on-site assessment of meat freshness with deep learning[J]. *Chemical Engineering Journal*, 2024, 480: 147917.
[11] Yang Z, Tong F, Peng Z W, et al. Development of colorimetric/fluorescent two-channel intelligent response labels to monitor shrimp freshness[J]. *Food Hydrocolloids*, 2023, 135: 108125.
[12] Ye H, Koo S, Zhu B T, et al. Real-time fluorescence screening platform for meat freshness [J]. *Analytical Chemistry*, 2022, 94(44): 15423-15432.
[13] Chen L J, Wang J Y, Zhao X, et al. Biogenic amine-responsive ratiometric fluorescent microneedle sensor for real-time visualization of meat freshness[J]. *Food Chemistry*, 2025, 482: 144144.
[14] Zhao J S, Ni Y S, Tan L J, et al. Recent advances in meat freshness "magnifier": fluorescence sensing [J]. *Critical Reviews in Food Science and Nutrition*, 2024, 64(31): 11626-11642.
[15] Li H Y, Li M, Zhang S Q, et al. Packaged europium/fluorescein-based hydrogen bond organic framework as ratiometric fluorescent probe for visual real-time monitoring of seafood freshness[J]. *Talanta*, 2024, 272: 125809.
[16] Zhong K L, Zhao Y F, He Y Q, et al. A sensing label or gel loaded with an NIR emission fluorescence probe for ultra-fast detection of volatile amine and fish freshness [J]. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2024, 318: 124501.
[17] Jia P, He X M, Yang J Y, et al. Dual-emission MOF-based ratiometric platform and sensory hydrogel for visible detection of biogenic amines in food spoilage[J]. *Sensors and Actuators B: Chemical*, 2023, 374: 132803.
[18] Liu Y N, Xiao Y Q, Shang M H, et al. Smart fluorescent tag based on amine response for non-contact and visual monitoring of seafood freshness [J]. *Chemical Engineering Journal*, 2022, 428: 132647.
[19] Wang Y A, Liu T, Zhong G Q. Synthesis, characterization and applications of copper(II) complexes with Schiff bases derived from chitooligosaccharide and iodosubstituted salicylaldehyde [J]. *Carbohydrate Polymers*, 2019, 224: 115151.
[20] Xu Y S, Zhang X X, Zhang W J, et al. Fluorescent detector for NH_3 based on responsive europium(III)-salicylic acid complex hydrogels [J]. *Journal of Photochemistry and Photobiology A: Chemistry*, 2021, 404: 112901.
[21] Wang Y, Zhang W J. Fluorescent color conversion of luminous hydrogel upon stimulation of basic molecule[J]. *Journal of Photochemistry and Photobiology A: Chemistry*, 2019, 385: 112086.
[22] Liu Y N, He Y Q, Li H, et al. Biogenic amines detection in meat and meat products: the mechanisms, applications, and future trends[J]. *Journal of Future Foods*, 2024, 4(1): 21-36.

基于交联壳聚糖-水杨醛-铕离子(III)双重荧光水凝胶可视化检测挥发性胺和肉新鲜度

汪艳敏, 张 煊*
东华大学 化学与化工学院, 上海 201620

摘 要: 基于交联壳聚糖(chitosan, CS)-水杨醛(salicylaldehyde, SA)-铕离子(III)(Eu(III)),成功制备了一种双重荧光水凝胶,Eu-SA-CS。该水凝胶在约 500 nm 处发射绿色荧光,但在暴露于三乙胺等挥发性胺时则在约 600 nm 处发射红色荧光。研究发现荧光发射强度比与三乙胺体积浓度(0~40 μL/L)存在良好线性关系。此外,该水凝胶可通过荧光发射颜色的改变来指示肉新鲜度,即荧光由绿色变为红色则表明肉由新鲜发生了变质。以上结果表明,本研究制备的水凝胶 Eu-SA-CS 可作为一种灵敏的绿-红荧光信号标签,用于肉新鲜度的实时监测。

关键词: 双重荧光水凝胶;挥发性胺检测;肉新鲜度