

# 基于比色传感器可视化检测虾的新鲜度

宋光杰<sup>1#</sup>, 王 蕾<sup>1#</sup>, 田颜清<sup>1,2</sup>

(1. 南方科技大学材料科学与工程系,  
2. 广东省可持续仿生材料与绿色能源重点实验室, 深圳 518055)

**摘要** 生物胺是虾类腐败的代谢副产物, 监测生物胺水平对评估食品质量至关重要. 目前, 大多数生物胺检测方法存在程序耗时、操作复杂和结果延迟等局限性. 近年来, 比色分析技术因其分析时间短、操作简单、适合现场检测等优点而备受关注. 本文通过在滤纸和电纺纳米纤维膜(ENFs)上分别添加天然活性成分姜黄素(CUR)及其衍生物硼络合物BFCUR, 开发了一系列生物胺类比色传感器平台. 通过分析这些传感器与生物胺接触时的颜色反应差异, 筛选出检测性能优越的比色传感器, 并进一步应用于虾类腐败过程的视觉监测和指示.

**关键词** 虾的新鲜度; 比色分析; 生物胺; 传感器

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## Visual Detection of Shrimp Freshness via Colorimetric Sensors

SONG Guangjie<sup>1#</sup>, WANG Lei<sup>1#</sup>, TIAN Yanqing<sup>1,2\*</sup>

(1. Department of Materials Science and Engineering,  
2. Guangdong Provincial Key Laboratory of Sustainable Biomimetic Materials and Green Energy,  
Southern University of Science and Technology, Shenzhen 518055, China)

**Abstract** Monitoring biogenic amines, which are metabolic byproducts of shrimp spoilage, is crucial for assessing food quality. Currently, most detection methods for biogenic amines suffer from limitations such as time-consuming procedures, complex operations, and delayed results. Colorimetric analysis techniques have gained attention in recent years due to their advantages of short analysis time, simple operation, and suitability for on-site testing. This study successfully developed a series of colorimetric sensor platforms for biogenic amines by loading the natural active ingredient curcumin (CUR) and its derivative of Boron complex BFCUR onto filter paper and electrospun nanofibre films (ENFs), respectively. By analyzing the color response differences of these sensors upon contact with biogenic amines, the colorimetric sensors with superior detection performance were selected and further applied to the visual monitoring and indication of shrimp spoilage processes.

**Keywords** Shrimp freshness; Colorimetric analysis; Biogenic amine; Sensor

## 1 Introduction

Food freshness detection is an important prerequisite for food safety. During the spoilage of food such as

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联系人简介: 田颜清, 男, 博士, 教授, 主要从事荧光生物传感器方面的研究. E-mail: tianyq@sustech.edu.cn

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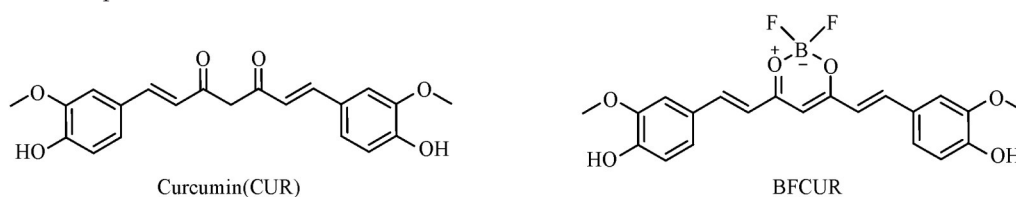
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# 共同第一作者.

meat, fish and shrimp, ammonia and biogenic amines can accumulate in food due to the presence of bacteria that can decarboxylate certain free amino acids<sup>[1]</sup>. Ammonia and biogenic amines are recognized as typical biomarkers for freshness monitoring of protein-containing foods<sup>[2–4]</sup>. Methods have been established for the detection of ammonia and biogenic amines, such as solid phase microextraction chromatography and flow injection analysis photometry<sup>[5,6]</sup>. Although these methods could accurately detect ammonia and biogenic amines, they were only suitable for laboratory and research use due to their complexity and cost.

Colorimetric analysis, which identifies substances by characteristic color reactions, has received widespread attention for its simplicity and ease of use<sup>[7,8]</sup>. Although colorimetric sensors for detecting food freshness have been reported, the dye molecules used in these sensors often require complex and costly synthesis processes<sup>[9,10]</sup>. This has limited their practical application, thus, cost-effective dyes are required. Natural product dye molecules have the advantage of being highly biocompatible, rich in structural diversity, environmentally friendly and cost-controlled<sup>[11–13]</sup>. However, colorimetric sensors based on these molecules have not yet received much attention<sup>[14–16]</sup>. Curcumin (CUR) is a natural compound with pharmacological properties that can be simply extracted from the rhizome of *Curcuma longa*<sup>[17,18]</sup>. CUR-based fluorescent sensors have been developed due to their favorable chemosensing properties and low cost<sup>[14–16,19–22]</sup>. The diphenol group and 1,3-dione structure in CUR molecules confer unique potential for chemical modification, enabling the derivation of diverse compounds with distinct optical properties through structural transformation (Scheme 1)<sup>[23,24]</sup>. Under alkaline conditions (pH>8), the two phenolic groups in the CUR molecule undergo deprotonation, forming phenoxy anions<sup>[25–30]</sup>. After deprotonation, CUR's UV absorption peak shifts significantly from 430 nm to 465 nm. Since 465 nm remains within the human eye's yellow light sensitivity range (450–570 nm), no discernible color difference is observed by the naked eye<sup>[31–33]</sup>.

Previously, we synthesized a boron complex of CUR (BFCUR) using CUR as a raw material and applied it to breath ammonia detection (Scheme 1)<sup>[34]</sup>. Compared to CUR, the strong electronegativity of boron atoms in the BFCUR molecule significantly enhances intramolecular charge transfer (ICT) effects, resulting in a pronounced red shift in its UV absorption peak [Fig.S1, see the Supporting Information (SI) of this paper]. We loaded BFCUR onto filter paper and found that it exhibited a more pronounced response to ammonia gas than CUR. Given that high detection sensitivity is closely related to the specific surface area of the sensor loading material<sup>[35–37]</sup>, electrospun nanofibre films (ENFs) are considered ideal chemical sensing materials due to their high porosity and specific surface area<sup>[38,39]</sup>. Therefore, we further incorporated BFCUR into poly(vinylpyrrolidone) (PVP) microfibers *via* electrospinning to obtain BFCUR-loaded ENFs, enabling visual detection of shrimp freshness.



Scheme 1 Molecular structures of CUR and BFCUR

## 2 Experimental

### 2.1 Reagents and Solvents

All reagents were purchased from commercial sources and used without further purification. The solutions of metal ions were prepared from deionized water. All the measurement samples were prepared from deionized water at room temperature.

## 2.2 Instruments

$^1\text{H}$  NMR spectrum measurement was performed on high performance digital FT-NMR spectrometer AVANCE 600III (Bruker Corporation), using  $\text{CDCl}_3$  as solvent. HRMS spectrum was obtained on a Thermo LTQ Orbitrap XL Mass Spectrometer (Thermo Fisher Scientific). UV-Vis spectra were measured utilizing a PerkinElmer Lambda 25 UV/Vis spectrophotometer (PerkinElmer). Fluorescence measurements were performed on a Horiba FluoroMax-4 spectrofluorophotometer (Horiba Company).

## 2.3 Preparation of CUR-based and BFCUR-based Test Papers

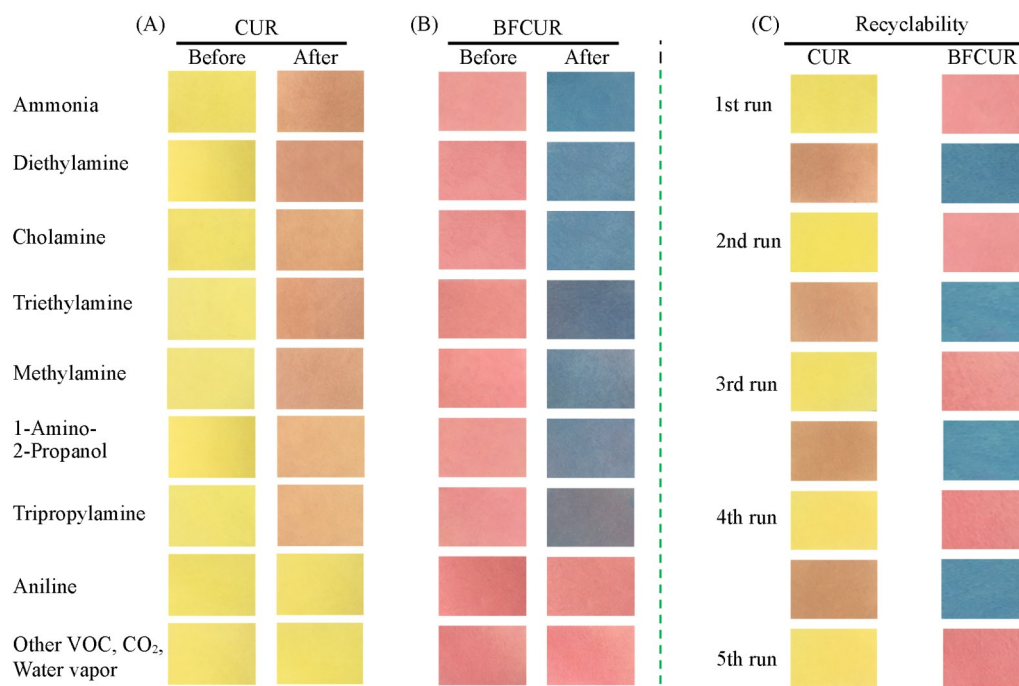
CUR and BFCUR were dissolved in a dichloromethane/tetrahydrofuran mixture (1:1, volume ratio), then the pre-cut strip filter papers were infiltrated for 2 s, and the test papers were obtained after drying in air.

## 2.4 Preparation of BFCUR-based Nanofibers

2.0 g of Polyvinyl pyrrolidone (PVP,  $M_w=1300000$ ) was dissolved in 8 g of DMF (*N,N*-Dimethylformamide) and stirred for 6 h at room temperature. Then, DMF solution of BFCUR was mixed with the above solution for 2 h. After fully dissolving, 2 mL of the mixture was loaded into a 5 mL plastic syringe to prepare electrospinning. The electrospinning conditions were as follows: air humidity: 50%; temperature: 35 °C; distance between the needle and receiving device: 20 cm; injection rate: 2 mL/h; voltage: 20 kV.

## 3 Results and Discussion

Test strips loaded with CUR and BFCUR were prepared for the detection of ammonia and volatile amines. Exposure of CUR-loaded filter paper to ammonia or individual volatile amines resulted in an immediate change in the color of the test strips from yellow to brown, with the magnitude of the color change dependent on the basicity of the amine [Fig.1 (A)]. BFCUR-loaded filter paper strips showed more pronounced color changes

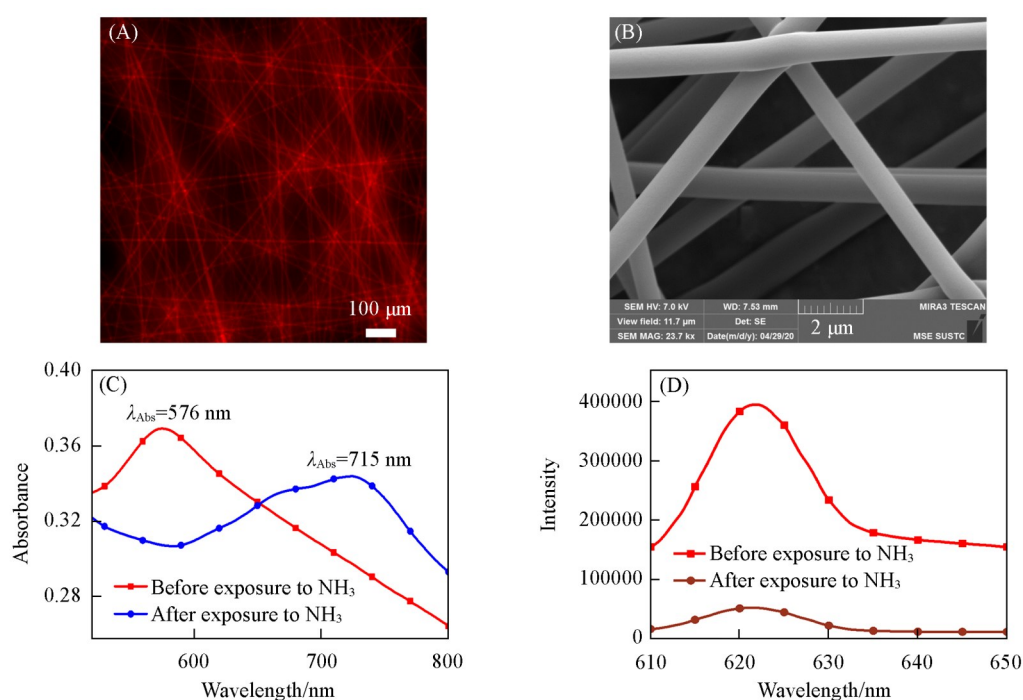


**Fig. 1** Visual color changes of CUR-loaded filter paper strips(A) and BFCUR-loaded filter paper strips(B) after exposure to ammonia or volatile amines vapors, visual color changes of CUR-loaded filter paper strips(C) and BFCUR-loaded filter paper strips(D) after repeated exposure to ammonia vapor and degassing

(A, B) Other VOC depicted in the figure include the following: *n*-hexane, toluene, chloroform, tetrahydrofuran, acetone, and methanol.

than CUR-loaded filter paper strips (Fig.S2 in the SI). BFCUR-loaded filter paper strips changed color from pink to blue, whereas CUR-loaded ones changed color from yellow to brown under the same conditions [Fig.1(B)]. In addition, filter paper strips loaded with CUR or BFCUR returned to their original color after degassing under vacuum. After five cycles, CUR-loaded filter paper strips [Fig.1(C)] and BFCUR-loaded filter paper strips [Fig.1(D)] demonstrated good stability and continued to respond to ammonia effectively. Furthermore, no significant color change was observed when these test strips were exposed to other volatile organic compounds (VOC), indicating that such test strips exhibit selective responsiveness to ammonia vapor [Fig.1(B)]. Therefore, CUR- or BFCUR-loaded filter paper strips showed good potential as a rapid visual test for monitoring ammonia and volatile biogenic amines in food.

To further improve sensitivity to the detection of amine vapors, BFCUR was incorporated into ENFs using PVP as the matrix. Fluorescence images and the morphology of nanofibers were characterized by inverted fluorescence microscopy [Fig.2(A)] and scanning electron microscopy (SEM) [Fig.2(B)], respectively. The results showed that the fibers of BFCUR-ENF had a diameter from 200 nm to 600 nm and emitted red fluorescence under UV excitation. The BFCUR-ENF showed a continuous three-dimensional structure with a high specific surface area, allowing analytes to diffuse through the film, which in turn facilitates the response to ammonia and volatile amine vapors.

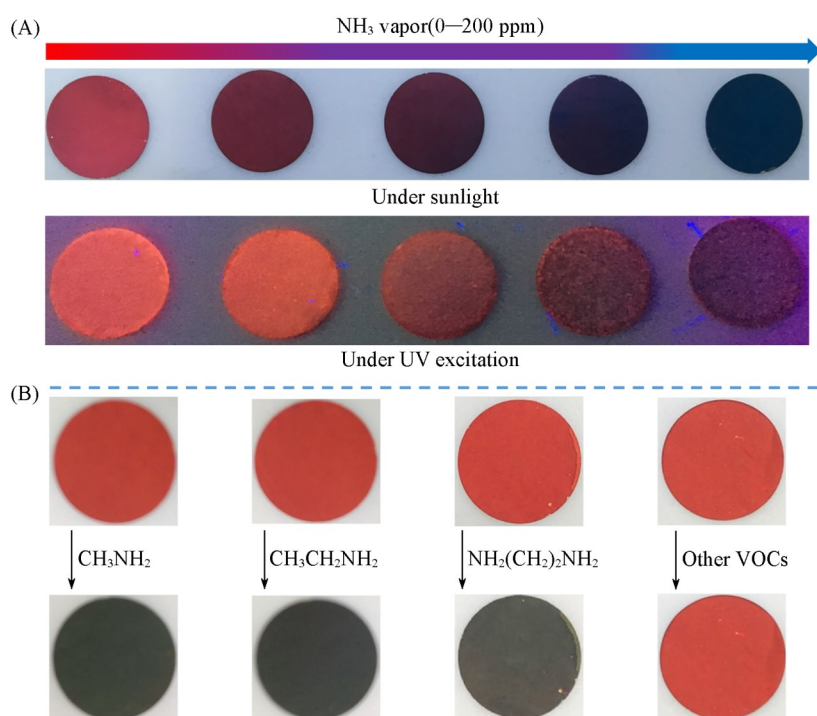


**Fig. 2** Fluorescence microscopy images of BFCUR-ENFs(A), SEM images of BFCUR-ENFs(B), UV spectra of BFCUR-ENFs before and after exposure to ammonia(C) and fluorescence emission spectra of BFCUR-ENFs before and after exposure to ammonia(D)

BFCUR is a D- $\pi$ -A- $\pi$ -D conjugated system with two intramolecular charge transfer (ICT) centers, the electron acceptors and donors were located centrally and terminally. After exposure to ammonia, deprotonation of the phenol groups in BFCUR resulted in formation of phenolate groups which enhanced ICT (Fig.S3 in the SI), leading a bathochromic shift in UV absorption from 576 nm to 715 nm, and a visual color change from pink to blue [Fig.2(C)], the red fluorescence at 622 nm was quenched by ammonia as UV absorption at 576 nm decreased [Fig.2(D)].

Colorimetric analysis can be performed without the need for sophisticated instruments. BFCUR-ENF

immediately changes from pink to blue upon exposure to ammonia vapor, while red solid-state fluorescence is simultaneously quenched. When exposed to ammonia vapor at varying concentrations, the optical properties of BFCUR-ENF material exhibit significant concentration-dependent changes: under visible light, the surface color reversibly shifts from an initial pink hue to deep blue as ammonia concentration increases; under UV light, its solid-state fluorescence color shows a negative correlation with ammonia concentration, with red fluorescence diminishing as ammonia vapor concentration rises [Fig. 3 (A)]. Both of these dual-mode response phenomena can be utilized for ammonia detection. Similar visual color changes were obtained when the sensor was exposed to the vapor of other biogenic amines, such as methylamine, ethylamine and ethylenediamine [Fig. 3(B)]. No significant color changes were observed when the BFCUR-ENF was exposed to VOCs such as *n*-hexane, toluene, chloroform, tetrahydrofuran, acetone, and methanol [Fig. 3(B)]. After repeated cycles of exposure to ethylamine and degassing, the BFCUR-ENF was able to return to its original state (Fig. S3). To verify the concern on long-term stability, the sensor was continuously exposed to ammonia under ambient conditions [15.28 °C, 45%–76% (RH%)] for 5 d. The results show that the blue-black state remained highly stable throughout this period without signal degradation, and the sensor fully recovered to its original red color after degassing (Fig. S4 in the SI). This demonstrates long-term stability and reversible performance under extended amine exposure, supporting its practical durability.

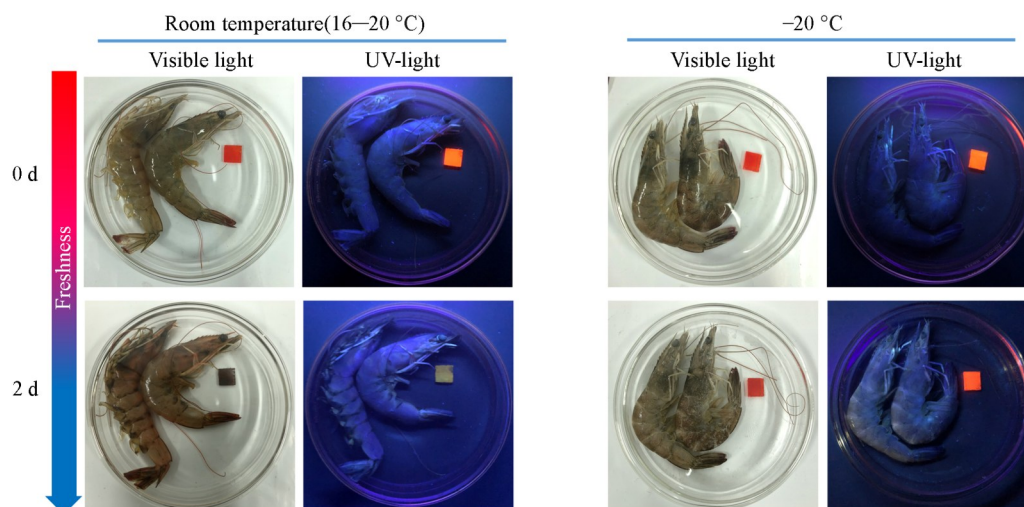


**Fig. 3** Color changes of BFCUR-ENF sensors

(A) After exposure to different concentrations of ammonia vapor under sunlight and UV light excitation (365 nm); (B) after exposure to methylamine, ethylamine and ethylenediamine, other VOCs depicted in the figure include the following: *n*-hexane, toluene, chloroform, tetrahydrofuran, acetone, and methanol.

The colorimetric signal of the sensor film is closely related to its ultraviolet absorption characteristics. The response performance to ammonia was evaluated through UV absorption titration experiments. Results demonstrated that BFCUR-ENF exhibits a wide detection range for ammonia [0–500000 ppb (part per billion)], with a detection limit as low as 50 ppb (Fig. S5 in the SI). During the fresh stage of shrimp, the released ammonia concentration is generally below 100 ppb; whereas upon entering the initial spoilage stage, the ammonia concentration gradually increases from approximately 100 ppb to 10000 ppb. Therefore, BFCUR-ENF

is applicable for monitoring the freshness of shrimp. To demonstrate this, fresh shrimp were placed in containers with BFCUR-ENF and kept at two different temperatures (room temperature and  $-20^{\circ}\text{C}$ ) for 2 d. After storing at room temperature for 2 d, the color of BFCUR-ENF changed from pink to deep blue, and the red fluorescence was quenched. After storing at  $-20^{\circ}\text{C}$  for 2 d, the color and fluorescence of BFCUR-ENF showed no significant changes. This result indicates that BFCUR-ENF offers a convenient tool for assessing shrimp freshness (Fig.4).



**Fig. 4** Color changes in BFCUR-ENF sensors stored with fresh shrimps at room temperature and  $-20^{\circ}\text{C}$  under visible and UV light

## 4 Conclusions

A series of colorimetric sensors responsive to ammonia or volatile amines was prepared based on CUR and BFCUR. Filter paper strips loaded with BFCUR exhibited a more pronounced color change than those loaded with CUR. BFCUR-ENF exhibited a more intense ammonia color response than BFCUR-loaded filter paper. As the ammonia vapor concentration increases, a distinct color change in BFCUR-ENF is observed, accompanied by the gradual quenching of its red solid-state fluorescence. BFCUR-ENF not only responds to ammonia vapor but also detects other amine vapors, including methylamine, ethylamine, and ethylenediamine. It also demonstrates excellent reusability. The application of the colorimetric sensors in ambient and cold storage (for fresh shrimp) demonstrated that BFCUR-ENF could be a simple, rapid, portable tool for the visual, non-contact monitoring of shrimp freshness.

The Supporting Information of this paper see <http://www.cjcu.jlu.edu.cn/CN/10.7503/cjcu20250293>.

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