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1 **A ratiometric fluorescence amines sensor based on carbon quantum dots-loaded**
2 **electrospun polyvinylidene fluoride film for visual monitoring of food freshness**
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ABSTRACT

Fluorescent sensors for monitoring food freshness have received increasing attention, and carbon quantum dots (CQD) are one of the outstanding fluorescent probes. However, most reported CQD presented fluorescent intensity changes due to their single emission property, which made the color changes too faint for the naked eye. In addition, CQD were generally loaded onto hydrophilic matrixes to construct portable solid sensors for better practical application. However, these sensors might suffer from the adverse impact of high humidity in a fresh food packaging environment. To address these two drawbacks in this study, we firstly synthesized a dual-emission CQD with sensitivity to amines. Then, two hydrophobic electrospun fluorescent films were developed using polyvinylidene fluoride (PVDF) as the film-forming polymer, and CQD as the fluorescent probe. Finally, their microstructures, gas sensitivities, color stabilities and ability to monitor food freshness were investigated.

KEYWORDS: Ratiometric fluorescent sensor; Electrospun film; Food freshness; Intelligent packaging

■ INTRODUCTION

Meats and aquatic foods, such as livestock, poultry, fish and shrimps, are important food sources because they are rich in proteins, fats, minerals and so on. Cold storage (0–4°C) is one of the common preservation methods for fresh meats and aquatic foods, because this non-freezing way can, to the greatest extent, maintain the original taste and nutrition of these foods. However, at the same time, the freshness of these meats and aquatic foods generally decreased rapidly due to microbial contamination, such as *Pseudomonas* and *Bacillus*.

[1](#) In view of food quality and safety, it is important to evaluate the real time freshness of meats and aquatic foods under cold storage in the supply chain.[2](#)

Traditional methods of determining meat and aquatic food quality are mainly based on physicochemical and microbiological analysis.[3](#) However, these methods are usually time-consuming and destructive to food samples. Therefore, they are difficult to apply for monitoring the freshness of meat and aquatic food in real time. To address this problem, some rapid and non-destructive methods have been developed, including near-infrared spectroscopy, hyperspectral imaging, and e-nose systems.[4](#) These methods have been proven to be very effective at evaluating real time quality of meats and aquatic foods. Unfortunately, these methods require expensive equipment and highly trained technicians, which inevitably leads to a high cost for food manufacturers and suppliers.

Nowadays, increasing attention has been paid to portable sensors in a variety of areas, because they are generally simple, economical, and convenient to use. In recent years, various advanced optical sensors [5](#), [6](#) and electrical sensors [7](#), [8](#), [9](#) have shown good potential to achieve in situ and real time monitoring of the freshness of meats and aquatic foods. Compared with electrical sensors, optical sensors exhibit some advantages, including power-free devices, highly visible color changes and generally lower costs. To date, most optical sensors for monitoring the freshness of meats and aquatic foods are based on their sensitivity to

volatile amines. This is because volatile amine gases, such as dimethylamine, trimethylamine and ammonia, are largely generated during protein degradation by microbes, and these volatile amines are regarded as an important freshness indicator.[10](#)

Fluorescent sensors generally have high sensitivities and good stabilities. Of late, some amines-responsive fluorescent sensors have also been developed for monitoring the freshness of aquatic foods.[11](#) Nevertheless, most reported fluorescence sensors rely on the changes of single fluorescence intensity, making their color changes difficult to observe with the naked eye.[12](#) Ratiometric fluorescence sensors can effectively overcome this visual limitation. Ratiometric fluorescence sensors not only exhibit diverse color changes, but also have self-calibration ability to resist interference from the external environment.[13](#) For example, a cellulose-based ratiometric amine-responsive fluorescent sensor was developed using fluorescein isothiocyanate and protoporphyrin IX.[14](#) The sensor presented excellent sensitivity to biogenic amines and the fluorescent color changed from red to yellow-green.

Carbon quantum dots (CQD) are carbon nanomaterials with sizes less than 10 nm. CQD have received great interest due to their low toxicity, low cost, biocompatibility, and fascinating fluorescent properties.[15](#) CQD has also been used to develop aquatic foods freshness sensors. For example, a pH-responsive red single-emission CQD was synthesized and a filter paper was used as a loaded substrate to produce a fluorescent label that could monitor shrimp spoilage.[16](#) N, S-doped single-emission CQD with high selectivity for ammonia was prepared. The CQD was used directly in the form of solution to indicate fish freshness.[17](#) Apart from single-emission CQD, dual-emission CQD was synthesized as a fluorescent probe for volatile amines and successfully produced a fluorescent label that could monitor seafood freshness using cotton paper as a loaded substrate.[18](#) These studies indicated that CQD would be a good candidate to develop food freshness sensors.

In this study, we used a one-step hydrothermal method to synthesize a dual-emission CQD with high amine sensitivity as a ratiometric fluorescent probe. To make a portable hydrophobic sensor for monitoring food freshness in highly humid environments, the synthesized CQD was loaded into electrospun polyvinylidene fluoride (PVDF) film in two different ways. One involved depositing CQD on the surface of PVDF film, labelled CQD/PVDF film. The other was by embedding CQD into PVDF film, labelled as CQD@PVDF film. The microstructure, stability, and gas sensitivity of the two films were investigated and compared; together with their performance in monitoring the freshness of typical meats and aquatic foods. Compared with reported studies, our sensors have several advantages: (1) Compared with ratiometric sensors constructed by using two fluorescent substances, we used a single dual-emission CQD to directly constitute a ratiometric sensor. This fluorescent probe was easier to prepare and more resistant to interference from other factors. (2) Compared with most micron-scale paper-based sensors, we used the electrostatic spinning method to load CQD for the first time. The electrospun nanoscale fibers made the sensors more sensitive to gases. (3) Compared with most hydrophilic paper-based sensors, we used hydrophobic polymers to load the fluorescent probe, namely CQD, which endowed the sensor better stability in fresh food packaging environments with high humidity.

■ MATERIALS AND METHODS

Materials and Reagents. *p*-phenylene diamine (*p*-PD) was purchased from Aladdin Ltd. Sulfuric acid (H₂SO₄, 98%), disodium hydrogen phosphate (Na₂HPO₄), sodium dihydrogen phosphate (NaH₂PO₄), hydrochloric acid (HCL), sodium hydroxide (NaOH), N-N-dimethylformamide (DMF), ethanol and trimethylamine (TMA • H₂O, 25%-27%) were all purchased from Sinopharm Chemical Reagent Co., Ltd. Fresh meat was bought from Gemmellon supermarket (Zhenjiang, China). Polyvinylidene fluoride (PVDF) was purchased from Millipore Co., Ltd. Ultrapure water was used throughout the whole work. All reagents

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89 were analytical reagents without further purification before use.

90 **Synthesis of CQD.** Firstly, 0.216 g of *p*-PD was dissolved in 20 mL C₂H₅OH, and 120 μL of sulfuric acid
91 was added to the above *p*-PD solution. Then, the mixed solution was transferred into a 30 mL Teflon reactor
92 and heated at 200°C in an oven for 3 h.¹⁹ The solution was poured into a 50 mL centrifuge tube and
93 centrifuged at 12000 rpm for 15 min to remove the non-fluorescent precipitates. The obtained solution was
94 then purified by silica gel column chromatography using a mixture of ethanol and ethyl acetate (the volume
95 ratio was 1:1) as eluent to remove the unreacted material. The above steps were repeated **several** times to
96 obtain the purified solution. Finally, the sulfur-doped CQD was obtained after vacuum drying in an oven, **and**
97 the CQD solution was diluted with ethanol to a concentration of 1.0 mg/mL.

98 **Preparation of CQD/PVDF film.** First, a blank PVDF film was prepared using an electrostatic spinning
99 machine (ET-2535M, Yongkang, China). 1.5 g of PVDF powder was dissolved in 10 mL of a double-solvent
100 system (the volume ratio of DMF and acetone was 4:1) at 40°C for 3 h. The obtained solution was defoamed
101 **by ultrasonic** for 35 min. Then, 10 mL of the solution was slowly drawn into 10 mL disposable syringes using
102 metal needles (inner diameter of 0.61 mm). Silicone paper was **covered** on the metal receiver to collect the
103 electrospun fibers. The voltage was set to 18 kV and the distance between the syringe and the receiver was
104 adjusted to 20 cm. At the same time, the relative humidity and temperature were set to 50% and 35°C,
105 respectively. Afterwards, the flow rate of the solution was set to 0.6 mL/h and the receiving roller was
106 controlled to run at 50 r/min. The exhaust system was opened to remove volatile organic solvent gas. At the
107 end of the electrospinning, the obtained PVDF film was placed in a 40°C oven for 1 h to remove residual
108 organic solvents. The film was cut into small square pieces with a side length of 1 cm. The CQD/PVDF film
109 was prepared by dripping 2.5 μL of CQD solution (1.0 mg/mL) onto the surface of the blank PVDF film. Then,

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the CQD/PVDF film was further dried in an oven at 40°C. Finally, the CQD/PVDF film was placed in a silica gel desiccator for further use.

Preparation of CQD@PVDF film. Firstly, 1.5 g of PVDF powder was dissolved in 10 mL of a double-solvent system (the volume ratio of DMF and acetone was 4:1) at 40°C for 3 h. After that, 1 mL of CQD solution (1.0 mg/mL) was slowly added to the above PVDF solution and magnetically stirred for 1 h to fully disperse CQD. Then, the prepared solution was defoamed by ultrasonic for 35 min. The 10 mL of obtained solution was slowly inhaled into 10 mL disposable syringes with metal needles (inner diameter of 0.61 mm). In the environment of 35°C and relative humidity of 50%, the voltage was set to 18 kV and the distance between the syringe and the receiver was adjusted to 20 cm. Afterwards, the flow rate of the solution was set to 0.6 mL/h and the receiving roller was controlled to run at 50 r/min. The exhaust system was opened to remove volatile organic solvent gas. After electrospinning, the CQD@PVDF film was placed in a 40°C oven for 1 h to remove residual organic solvents and stored in a silica gel desiccator for further use. It is worth pointing out that by using the above methods, the CQD weights per unit area of the CQD/PVDF film and CQD@PVDF film were the same.

Response of CQD solution to TMA. Different amounts of TMA solution were added to 3 mL of CQD solution to prepare a series of solutions. After mixing for three minutes, the fluorescence spectra of the mixed solution were measured using a fluorescence spectrophotometer (F98, Prismatic Technology, China).

Stability of composite film. The films were placed in incubators at temperatures of 4 and 25°C. The fluorescent photos of the films were taken in a UV box using a digital camera (EOS 1500D, Canon, Japan). The L^* (lightness), a^* (red-to-green), and b^* (blue-to-yellow) values of the photos were collected using image processing software developed by our group.

Commented [MP8]: Ultrasonic bath make and model

Commented [MP9]: Is this not the exact same process as for the preparation of the CQD/PVDF film and therefore was the receiver not covered in silicone paper? If they are the same process then it is not necessary to repeat the same words but just say that the obtained solution was subsequently treated in the same manner as the CQD/PVDF film.

131 The total color difference (ΔE) was calculated as Eq 1:

132
$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$
 (1)

133 where $\Delta L^* = L^* - L_0^*$, $\Delta a^* = a^* - a_0^*$, $\Delta b^* = b^* - b_0^*$. L^* , a^* and b^* are the color parameters of films after a
134 certain storage time. L_0^* , a_0^* and b_0^* are the initial color parameters of films.

135 **Sensitivity of film to TMA.** TMA was considered to be a representative meat spoilage gas.²⁰ The film
136 strips (1 cm× 1 cm) were placed on top of a testing chamber with a constant temperature (25°C) and relative
137 humidity (75%). The solution of TMA was injected into the testing chamber using a microliter syringe²¹ and
138 left to stand for 1h. The concentration of TMA in the chamber was calculated as Eq 2:

139
$$C = \frac{W_s V_s \rho_s}{M V}$$
 (2)

140 Where C (mol/L) is the concentration of the substance to be tested in the testing chamber; ρ_s is the density of
141 the substance to be tested (g/mL); V_s is the volume of the liquid substance to be measured (mL); W_s is the
142 mass fraction of analyte in the solution; M is the molar mass of the substance to be tested (g/mol); V is the
143 volume of the reaction vessel (L). The images of the films in the UV box were recorded with the camera, and
144 L^* , a^* and b^* values were extracted.

145 **Application in Food Freshness Monitoring.** 90 g of fresh beef (tenderloin), pork (tenderloin), shrimp and
146 salmon were placed in transparent boxes whose tops were attached two types of films and placed in a
147 refrigerator at 4°C. The fluorescence color changes of the film were observed in a UV box and recorded by a
148 camera every 24 h for 7 days. In the meantime, TVB-N values of beef, pork, shrimp and salmon were measured
149 according to GB 5009.228–2015 and GB 5009.228–2016.²² Briefly, 10 g of sample was placed in 75 mL of
150 distilled water and they were broken into homogenates with a homogenizer. The mixture was filtered to obtain
151 a filtrate. Afterwards, the filtrate was transferred to a distillation tube containing 1 g of MgO. 30 ml of boric

acid (20 g/L) was used as the receiving solution. The automatic acid-base titrator (Hanon Instruments, T860, China) titrated boric acid solutions with 0.01 M HCl solution. The TVB-N content was calculated based on the amount of 0.01 M HCl consumed during the titration process and was expressed in mg/100 g. Parallel experiments were performed three times and the average was taken as the final result.

■ RESULTS AND DISCUSSIONS

Characterization of CQD. The morphology and particle size of the as-prepared CQD were investigated using transmission electron microscopy (TEM). CQD dispersed in acetone was drop-cast onto carbon-coated copper grids for TEM measurements. As shown in Figure 1A, the CQD presented a spherical morphology and the average particle size of CQD was around 7.85 nm. The HRTEM image exhibited a clear lattice structure with a pitch of 0.21 nm which was similar to the (100) facet of graphitic carbon (Figure 1B).²³ In addition, the quantum yield (QY) of CQD was measured with quinine sulfate as the standard material (excitation at 360 nm, QY = 54%) was 31%.

Fourier transform infrared (FT-IR) spectrum was obtained to determine groups of CQD. As shown in Figure 1C, three characteristic bands at 1103, 1041 and 994 cm^{-1} were related to the stretching vibration of $\text{O}=\text{S}=\text{O}$, due to the presence of the $-\text{SO}_3\text{H}$ group on CQD.²⁴ The absorption peak at 3416 cm^{-1} corresponded to the O-H stretching vibration.²⁵ Two absorption peaks at 914 and 862 cm^{-1} were attributed to the C-H vibration of the benzene ring bent outward. The absorption peak at 1616 cm^{-1} belonged to the C-C and C-N stretching in the conjugate structure. The absorption peak at 571 cm^{-1} was the bending vibration of the C-S bond and 1381 cm^{-1} was the characteristic stretching band of the C-N bond. These results indicated that sulfur was successfully doped in CQD.

Figure 1D shows the X-ray diffraction (XRD) pattern of CQD. A broad diffraction peak around $2\theta = 28^\circ$ was observed which corresponded to the (002) plane with an interlayer spacing of 0.318 nm.²⁶

174 The Ultraviolet-Visible (UV-Vis) and fluorescence spectra were recorded to study the optical properties. As
175 shown in Figure 1E, the absorption peak at 260 nm was attributed to the π - π^* transition of the conjugated C-
176 C bond. The weak peak at 340 nm is usually attributed to the n- π^* transition of C=O bonds of CQD.[27](#) The
177 absorption band near 350-400 nm was due to the n- π^* transition of the C-O bond.[28](#) The UV-Vis absorbance
178 curve of the as-prepared CQD showed a broad absorption range that could be attributed to the complex energy
179 band structure and random energy levels of CQD.[29](#) The insets of Figure 1E showed that the CQD solution
180 presented orange-yellow color in daylight and yellow color under a 365 nm UV lamp. Figure 1F shows the
181 fluorescence emission spectra of CQD at different excitation wavelengths (360-460 nm). The CQD displayed
182 two maximum emission peaks at 495 and 550 nm under an excitation wavelength of 400 nm. With the increase
183 of excitation wavelength, the emission peak did not produce a large red shift. This fluorescent behavior might
184 be related to the narrow size distribution and surface passivation of CQD.[30](#)

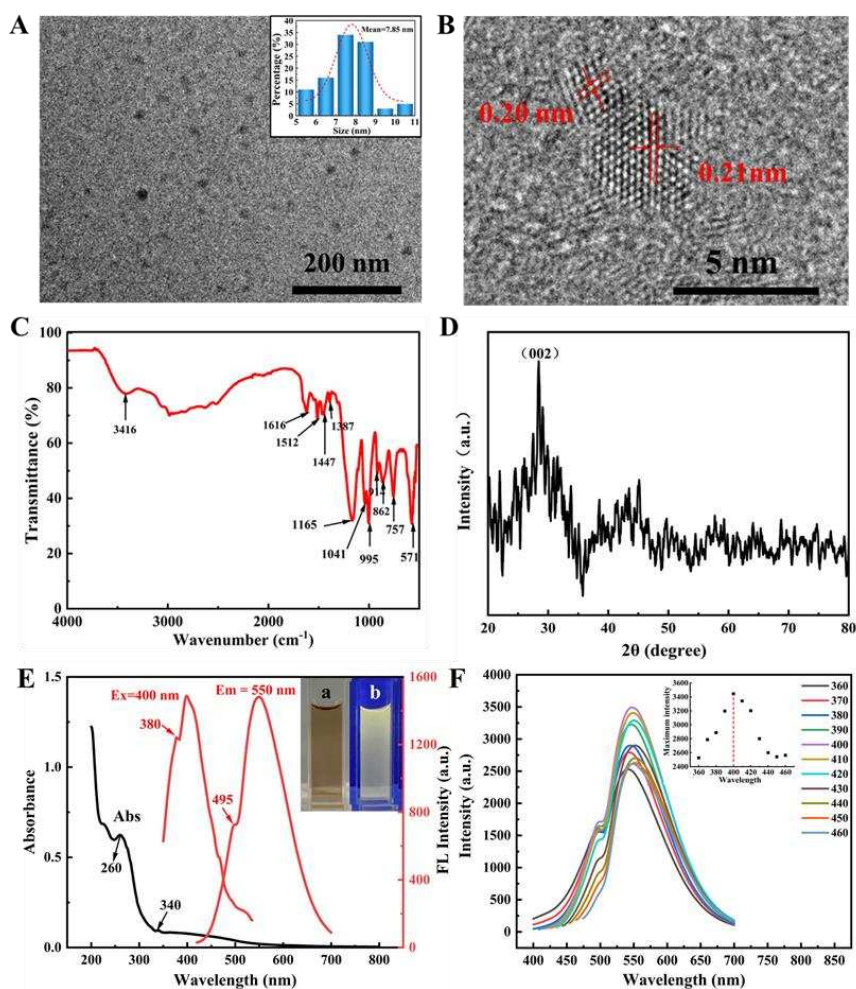


Figure 1. (A) TEM image and particle size distribution of CQD; (B) HRTEM image of CQD; (C) FT-IR spectrum of CQD; (D) XRD of CQD; (E) Fluorescence excitation (Ex), emission (Em) and absorption (Abs) spectra of CQD solution. The insets were photos of CQD solutions under (a) visible light and (b) 365 nm UV light; (F) Fluorescence emission spectra of CQD at different excitation wavelengths.

Response of CQD solution to TMA. The fluorescence spectra of dual-emission CQD in response to different concentrations of TMA solution were determined. As shown in Figure 2A, the emission intensity at 495 nm increased while the emission intensity at 550 nm decreased, with the increase of TMA concentration.

Accordingly, the color of the CQD solution changed from yellow to slightly red under daylight and from yellow to cyan under UV light (365 nm) (Figure 2A insets). According to the fluorescence spectra, the relationship between the fluorescence intensity ratio (F_{495}/F_{550}) and the TMA concentration was determined. As shown in Figure 2B, there was a good linear relationship between F_{495}/F_{550} and TMA concentration in the range of 0-240 μM ($R^2 = 0.9950$). The above results indicated that the dual-emission CQD would be used as a ratiometric nanoprobe for TMA sensing.

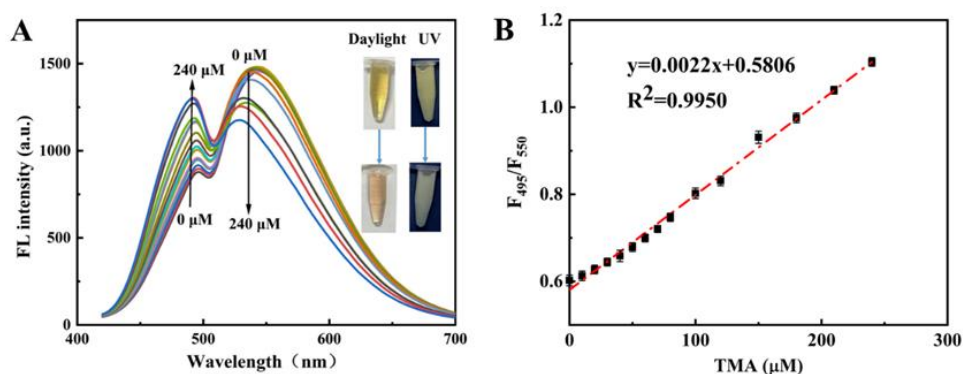


Figure 2. (A) Fluorescence emission spectra of CQD at various concentrations of TMA from 0 to 240 μM . The insets were the color changes of CQD in visible and UV light. (B) The linear relationship between F_{495}/F_{550} and TMA concentrations from 0 to 240 μM .

Response of CQD solution to pH. The pH-sensitive behavior of CQD was studied in phosphate buffer solutions. As shown in Figure 3A, as pH values changed from 3.0 to 11.0, the CQD solutions gradually changed from yellow to cyan-blue under 365 nm UV light. With the increase of pH, the fluorescence intensity at 495 nm gradually increased, while the fluorescence intensity at 550 nm gradually decreased and this fluorescence peak showed a slight blue-shift within pH 3-9 (Figure 3B). The calibration curve between F_{495}/F_{550} of CQD and pH values showed a good linear relationship in the range of pH 5-7 ($R^2 = 0.9765$) (Figure 3C). To give more details of the relation between F_{495}/F_{550} and pH values within 5-7, the pH value was

increased in intervals of 0.2. Similarly, F_{495} increased while F_{550} decreased with the increase of pH (Figure 3E), but a better linear relationship ($R^2 = 0.9850$) was obtained between F_{495}/F_{550} and pH (Figure 3F), indicating that the synthesized CQD could also be used as an accurate pH indicator in the range of pH 5-7.

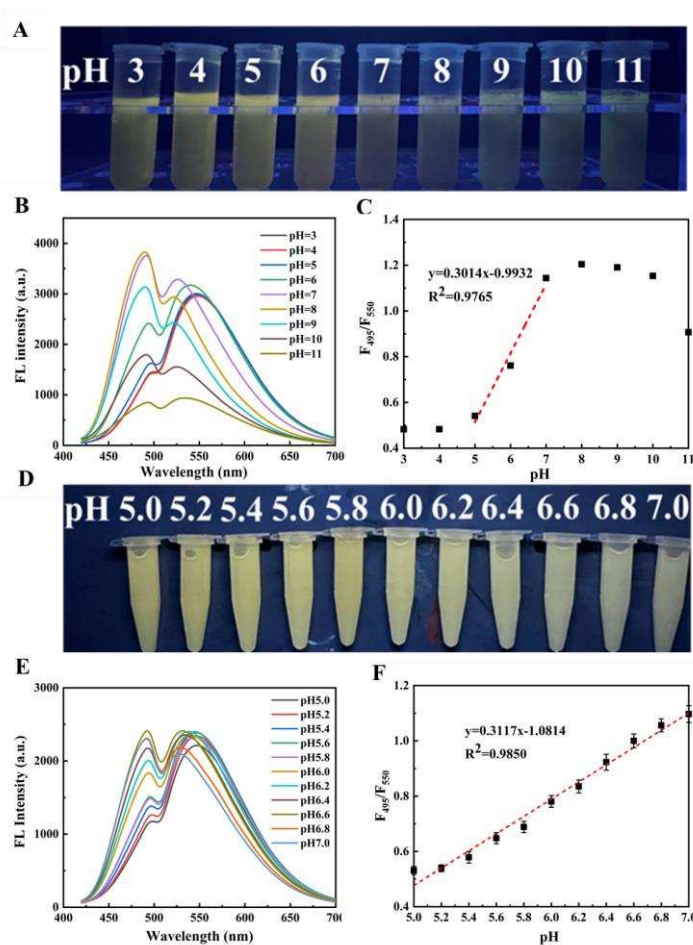


Figure 3. (A) Photographs of CQD solutions with pH values ranging from 3 to 11 under UV light of 365 nm; (B) Fluorescence spectra of CQD solution under pH 3-11 and (C) the change of F_{495}/F_{550} of CQD solution with the increase of pH 3-11 at 400 nm excitation. (D) Photographs of CQD solutions with pH values ranging from 5 to 7 under UV light of 365 nm; (E) Fluorescence spectra of CQD solution under pH 5-7 and (F) the change of F_{495}/F_{550} of CQD solution with the increase of pH 5-7 at 400 nm excitation.

Characterization of fluorescent films. The fabrication of the CQD/PVDF film and CQD@PVDF film is shown in Figure 4A. The synthesized CQD was loaded on the PVDF film through two independent ways. CQD/PVDF film was prepared by depositing CQD on the surface of the electrospun PVDF film, while CQD@PVDF film was prepared by electrospinning CQD-PVDF mixture. The film morphology was characterized by using a field emission scanning electron microscope (JSM-7800M, JEOL, Japan). As shown in Figure 4B, C and D, all films were constituted with rough fibers. Compared with the blank PVDF film with an average fiber diameter of 669 nm, the CQD/PVDF film did not show a significant change in fiber diameter (670 nm) due to the direct addition of CQD to the surface of the blank PVDF film, as shown in Figure 4B and C. However, the CQD@PVDF film in Figure 4D showed a larger fiber diameter (~780 nm) than the blank PVDF film and CQD@PVDF film. This was because, during the squirt flow solvent evaporation process of making the CQD and PVDF mixture, CQD was embedded into the PVDF fiber and thus broke the dense crystal structure of PVDF molecules.

Generally, fresh foods containing high water content would lead to high humidity in the food packaging and this high humidity might lead to the leaching of color agents of the colorimetric sensors. Hence, it was preferable for the colorimetric food freshness sensors to have high hydrophobicity.³¹ The water contact angle (WCA) was used to determine the hydrophilicity and hydrophobicity of the prepared films. As shown in Figure 4E, the WCA value of the blank PVDF film was 134.24°, indicating its intrinsic hydrophobicity due to the large amount of C-F groups.³² Compared with the blank PVDF film, the WCA value of the CQD/PVDF film significantly decreased to 117.52°. This was probably because the hydrophilic amino group of CQD adhered to the surface of the blank PVDF film, making it less hydrophobic. However, there was no significant difference between the WCA value of the CQD@PVDF and blank PVDF film. This was due to the fact that

CQD was mostly embedded into the fibers of PVDF, having a negligible effect on the hydrophobicity of the blank PVDF film. Overall, in this study, the CQD/PVDF and CQD@PVDF films both maintained good hydrophobicity.

The fluorescence images of the films under 400 nm excitation were recorded by a laser confocal microscope (TCS SP5, Leica, Germany). As shown in Figure 5, compared with the blank PVDF film, the CQD/PVDF and CQD@PVDF film had good fluorescence luminescence behavior, indicating that CQD was successfully added to the electrospun film. Compared with the CQD/PVDF film, the fiber morphology of the CQD@PVDF film had a few extra nodules and the distribution of CQD in the CQD@PVDF film was more uniform.

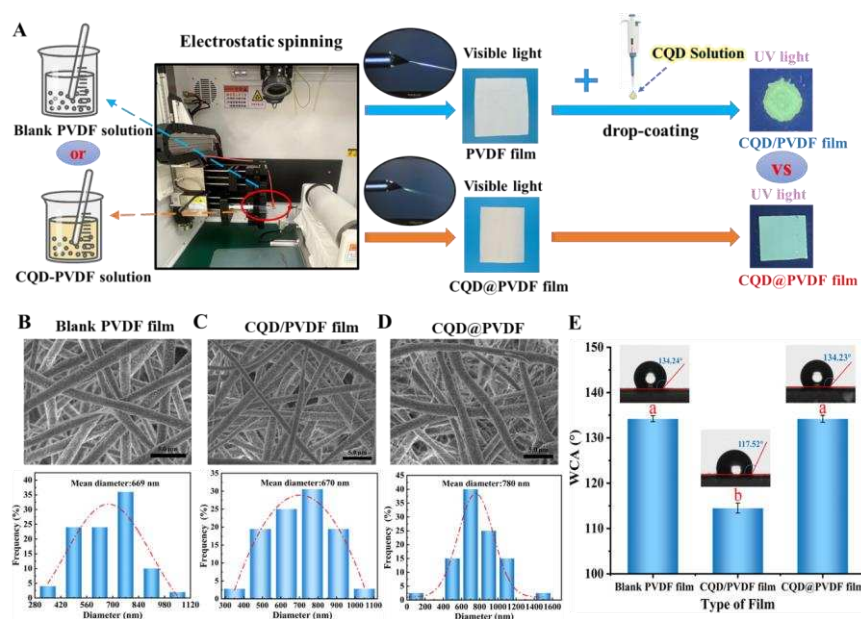


Figure 4. (A) Fabrication of the CQD/PVDF film and CQD@PVDF film; (B) SEM image and fiber diameter of the CQD/PVDF film; (C) SEM image and fiber diameter of the CQD@PVDF film; (D) SEM image and fiber diameter of the blank PVDF film; (E) WCA values and images of films. Data with the same superscript letter in the different columns indicate that they are statistically different ($p > 0.05$). The data (average $\pm$ SD) are results from three independent experiments.

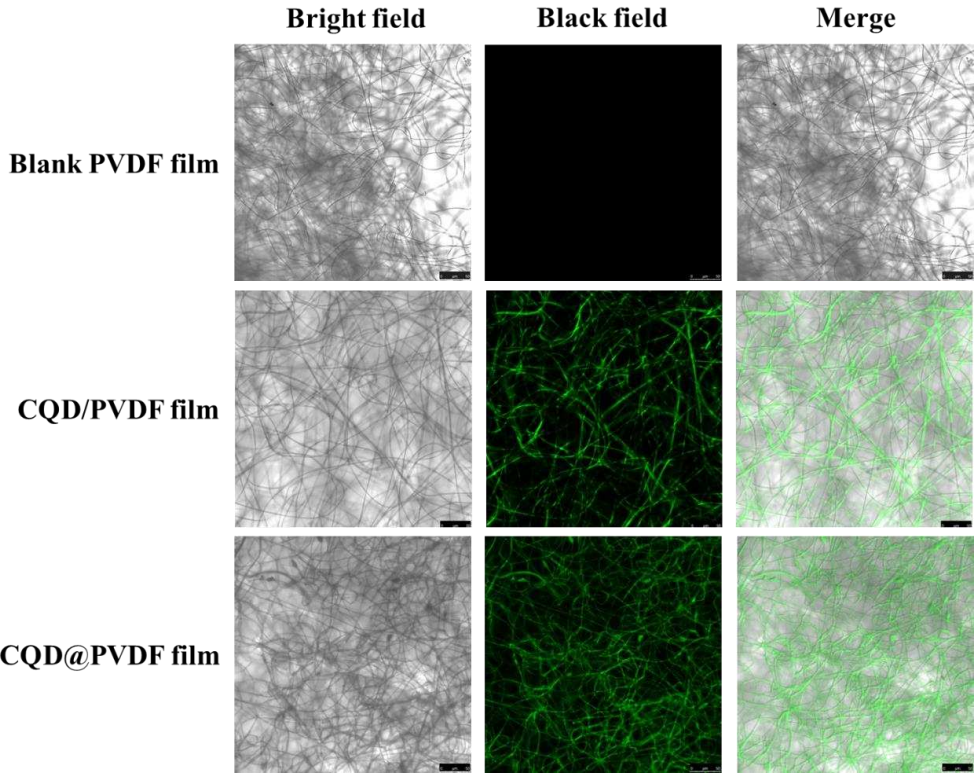


Figure 5. Confocal fluorescence images of three different fiber films. The excitation wavelength of CQD: 400 nm; Emission collection: 450-550 nm; Scale bar: 50 μ m.

Sensitivity of fluorescent films to TMA. The meat spoilage process can produce a variety of amines, and TMA is one of the most representative volatile amines. Hence, the responses of the CQD/PVDF and CQD@PVDF film to TMA were evaluated. As shown in Figure 6A, the fluorescent color of the two films gradually changed from yellow-green to blue with the increase of TMA concentration. This indicated that CQD maintained TMA sensitivity although it existed in a non-liquid environment. The fluorescent color changes of the films were described by using ΔE values. As shown in Figure 6B and C, ΔE values increased progressively with the increase of TMA concentration. Linear relationships between ΔE values of the two

262 films and TMA concentration were found in the TMA concentration range of 0-80.5 μM , and the
 263 corresponding calibration curve for the CQD/PVDF and CQD@PVDF film was expressed as Eqs 3 and 4.

$$264 \quad y = 0.1527x + 0.5859 \quad (R^2 = 0.9726) \quad (3)$$

$$265 \quad y = 0.0904x + 0.3944 \quad (R^2 = 0.9898) \quad (4)$$

266 where x is the concentration of TMA (μM) and y is the ΔE value.

267 Accordingly, the limit of detection (LOD) values of the CQD/PVDF and CQD@PVDF film to TMA were
 268 determined to be 1.04 μM and 2.10 μM based on Eq 5.[33](#)

$$269 \quad \text{LOD} = 3\sigma/N \quad (5)$$

270 where σ is the standard deviation of blank measurements for 13 times, and N is the absolute value of the
 271 slope of the calibration curve.

272 According to the LOD value, it was obvious that CQD/PVDF film was more sensitive to TMA. The reason
 273 was that CQD in CQD@PVDF film was mostly embedded in the fiber and could not fully contact with TMA,
 274 resulting in a lower sensitivity than the CQD/PVDF film with CQD directly exposed to the surface.

275 The film after reaction with TMA was placed at room temperature for 12 h to investigate the reversibility
 276 of fluorescent color change under UV light (365 nm). It could be seen from Figure 6D and E that both the
 277 CQD/PVDF and CQD@PVDF film had good reversibility. The initial fluorescent color of CQD/PVDF and
 278 CQD@PVDF film was yellow-green. After 6 cycle times, the film could still change from yellow-green to
 279 cyan-blue. This good reversibility was because the reaction between TMA and CQD was protonation and
 280 deprotonation processes. As shown in Figure 6F, proton transferred from the sulfonic acid group of CQD to
 281 the nitrogen atom of the TMA molecule, [34](#) and this process was reversible.,

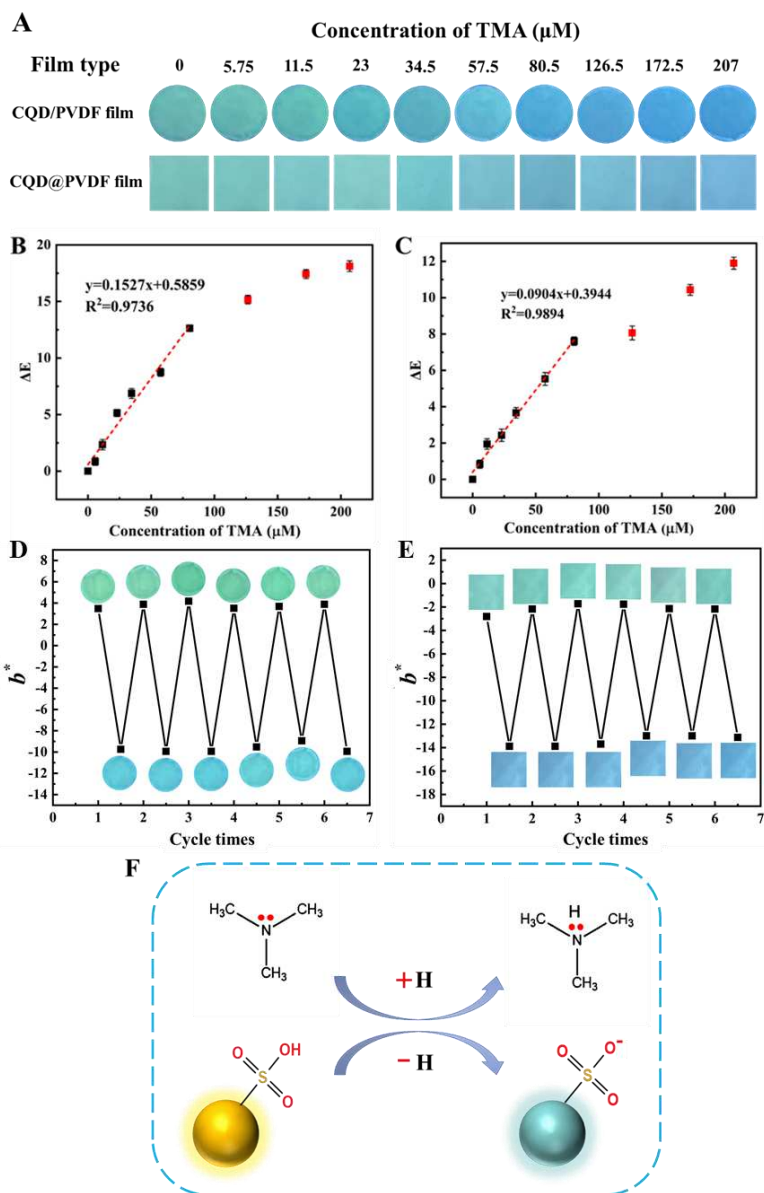


Figure 6. (A) The colors of the films in response to TMA at different concentrations; (B) The plot of ΔE values of the CQD/PVDF film versus the concentration of TMA; (C) The plot of ΔE values of the CQD@PVDF film versus the concentration of TMA; The b^* value and the fluorescent color change of (D) the CQD/PVDF film and (E) the CQD@PVDF film in the TMA-air circulation diagram under 365nm UV light; (F) Principle diagram of TMA and CQD reaction.

Color stability of fluorescent films. The self-stability of films was crucial to their practical application. Figure 7 shows the relative fluorescence color changes (ΔE) of the film. It could be seen that two types of films stored at 4°C had ΔE values lower than 2 in 14 days, indicating that they had outstanding fluorescent color stability. By contrast, the films had higher ΔE values when they were stored at 25°C. On the 14th day, the ΔE values for the CQD/PVDF and CQD@PVDF film were 2.1 and 1.5, respectively. As reported in previous studies, color changes were not visible to naked eyes when the ΔE value was less than 2.³⁵ In this study, the ΔE values were all lower than 5, indicating that the fiber films also had excellent color stability at 25°C. Overall, CQD@PVDF film was more stable than the CQD/PVDF film. The possible reason was that CQD in the CQD@PVDF film was embedded into the fiber, which greatly prevented CQD from aggregation.

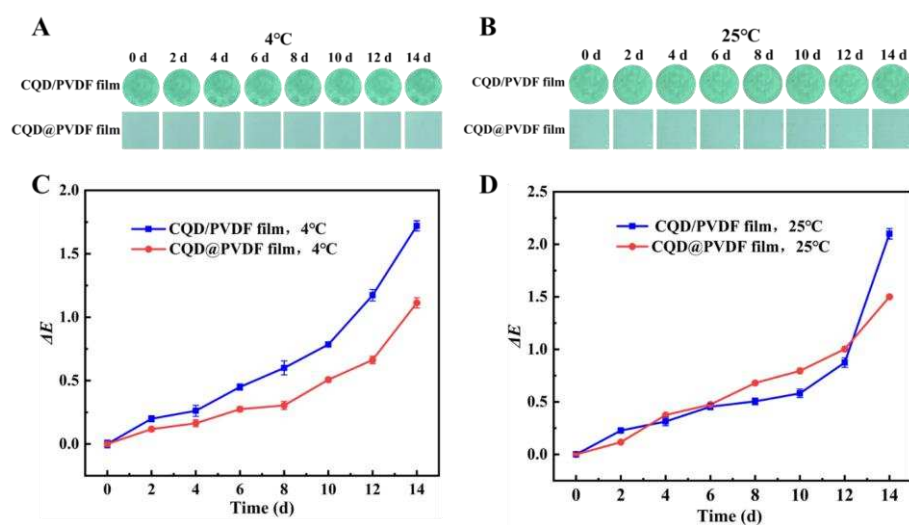


Figure 7. The fluorescent color changes of (A) the CQD/PVDF film and (B) the CQD@PVDF film stored at 4°C and 25°C by 365 nm UV light, and the corresponding ΔE values of (C) the CQD/PVDF film and (D) the CQD@PVDF film.

Selectivity of fluorescent films to amine gases. During meat and fish spoilage, in addition to amine gases, a variety of other volatile gases, such as aldehydes, ketones, acids, esters, sulfides and alkanes, could also be produced.³⁶ According to the previous studies,^{37, 38} some representative components were selected to

investigate the selectivity of films, including ethanol, methanol, acetic acid, ethyl acetate, dichloromethane, cyclohexane, acetone, dimethyl disulfide, dimethylamine and trimethylamine. As shown in Figure 8, in the presence of other gases at a concentration of 500 μM , the ΔE values of the CQD/PVDF and CQD@PVDF film were less than 2. At this time, the color change of the films could not be observed by naked eyes. When amine gases (dimethylamine, trimethylamine) were present at a concentration of 300 μM , the color of the film changed from yellow-green to blue. The ΔE values of the CQD/PVDF and CQD@PVDF film in the presence of dimethylamine were 17.46 and 15.22, respectively, and the ΔE values of the CQD/PVDF and CQD@PVDF film in the presence of trimethylamine were 28.24 and 20.79, respectively. Therefore, the films had high selectivity to amine gases.

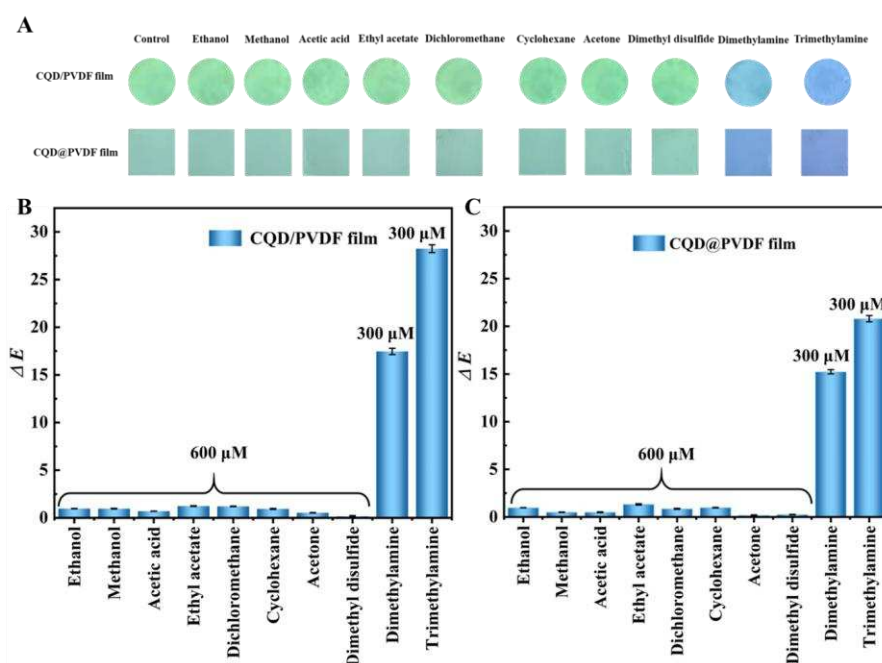


Figure 8. (A) Photographs of the CQD/PVDF and CQD@PVDF film after exposure to different volatile organic compounds under 365 nm UV light; (B) Comparison of ΔE values of the CQD/PVDF film under different volatile compounds; (C) Comparison of ΔE values of the CQD@PVDF film under different volatile compounds.

315 **Application of films.** Firstly, to investigate the self-stability of films in highly humid food packaging,
316 CQD/PVDF film and CQD@PVDF film were attached to the top of a transparent box containing 10 mL of
317 water. The photos of two films and their ΔE value changes with storage time are shown in Figure 9A. The
318 CQD/PVDF film and CQD@PVDF film had ΔE values of 1.7 and 2.9, respectively on the 7th day, indicating
319 that the CQD/PVDF film was less stable than CQD@PVDF film in highly humid environment.

320 The photos of the films used to monitor beef, pork, shrimp, and salmon freshness are shown in Figure 9B.
321 The colors of the films in beef, pork and shrimp changed from yellow-green to blue under 365 nm UV light,
322 while the films in salmon changed to cyan. For both beef, pork, shrimp and salmon, the ΔE of CQD/PVDF
323 film changed more rapidly than that of CQD@PVDF film (Figure 9C-F), which was consistent with the results
324 in Figure 6 that CQD/PVDF had better gas sensitivity than CQD@PVDF film. However, the CQD on the
325 CQD/PVDF film showed visible diffusion phenomenon to some extent, according to the photos on the 7th day
326 (Figure 9B). This was probably because CQD coated on the PVDF film was largely exposed to water vapor
327 generated from foods, and water vapor caused the movement of CQD. Unfortunately, this phenomenon was
328 not beneficial to the indicating ability of films. By contrast, the CQD@PVDF film was stable enough and no
329 diffusion phenomenon was observed in the 7th day (Figure 9B). Hence, in this study, CQD@PVDF film was
330 further used to establish the relation between film color and food freshness.

331 TVB-N values were used to determine the freshness of meats and aquatic foods. Figure 9C shows TVB-N
332 of beef during storage at 4°C for 7 d, and the corresponding ΔE value of the films. TVB-N values increased
333 from 5.59 to 25.67 mg/100 g with time. According to Chinese standard (GB 2707–2016), the maximum value
334 of TVB-N for beef is 15 mg/100 g. In this study, the TVB-N of beef sample reached 15 mg/100 g at nearly
335 5.3 d, when the ΔE value of the CQD@PVDF film was 6.25. Hence, the beef sample could not be consumed

336 if the ΔE value of the CQD@PVDF film was higher than 6.25.

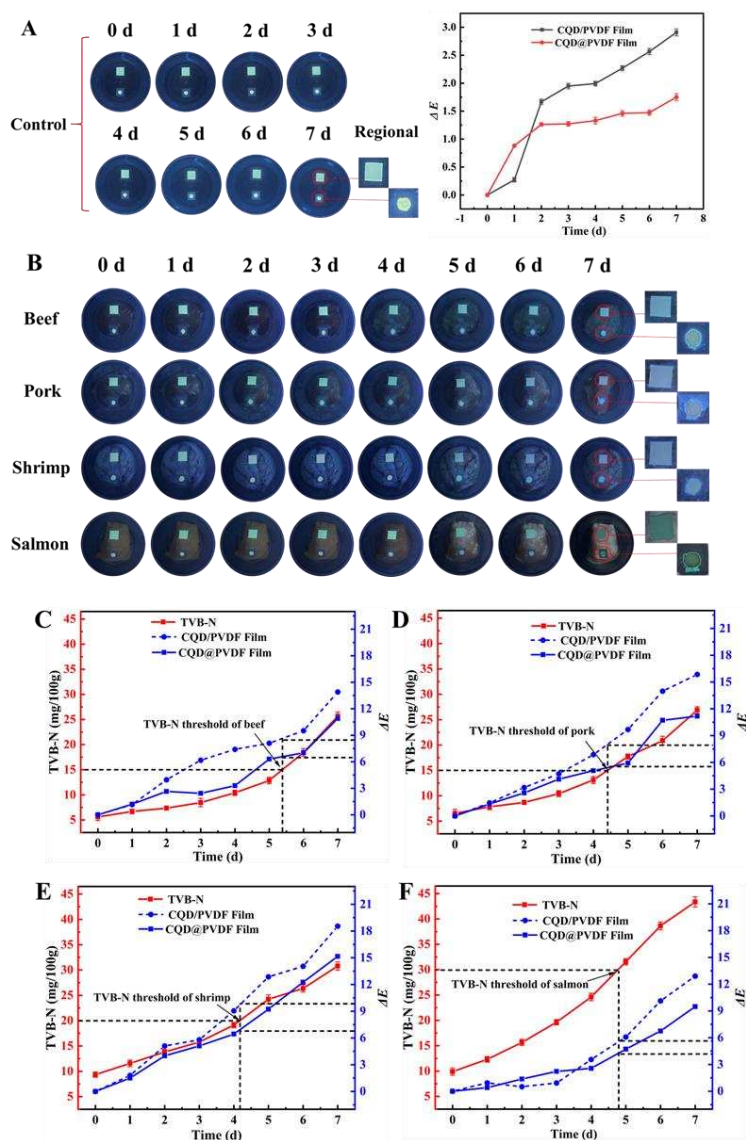
337 Figure 9D shows TVB-N of pork during storage at 4°C for 7 d, and the corresponding ΔE value of the films.
338 TVB-N values increased from 6.53 to 26.86 mg/100 g with time. According to Chinese standard (GB 2707 -
339 2016), the maximum value of TVB-N for pork is 15 mg/100 g. In this study, the TVB-N of pork sample
340 reached 15 mg/100 g at nearly 4.4 d, when the ΔE value of the CQD@PVDF film was 5.65. Hence, the beef
341 sample could not be consumed if the ΔE value of the CQD@PVDF film was higher than 5.65.

342 Figure 9E shows TVB-N of shrimp during storage at 4°C for 7 d, and the corresponding ΔE value of the
343 films. TVB-N values increased from 9.34 to 30.78 mg/100 g with time. According to Chinese standard (GB
344 2707 - 2015), the maximum value of TVB-N for shrimp is 20 mg/100 g. In this study, the TVB-N of shrimp
345 sample reached 20 mg/100 g at nearly 4.2 d, when the ΔE value of the CQD@PVDF film was 6.73. Hence,
346 the shrimp sample could not be consumed if the ΔE value of the CQD@PVDF film was higher than 6.73.

347 Figure 9F shows TVB-N of salmon during storage at 4°C for 7 d, and the corresponding ΔE value of the
348 films. TVB-N values increased from 9.89 to 43.36 mg/100 g with time. According to Chinese standard (GB
349 2707 - 2015), the maximum value of TVB-N for salmon is 30 mg/100 g. In this study, the TVB-N of salmon
350 sample reached 15 mg/100 g at nearly 4.4 d, when the ΔE value of the CQD@PVDF film was 4.30.

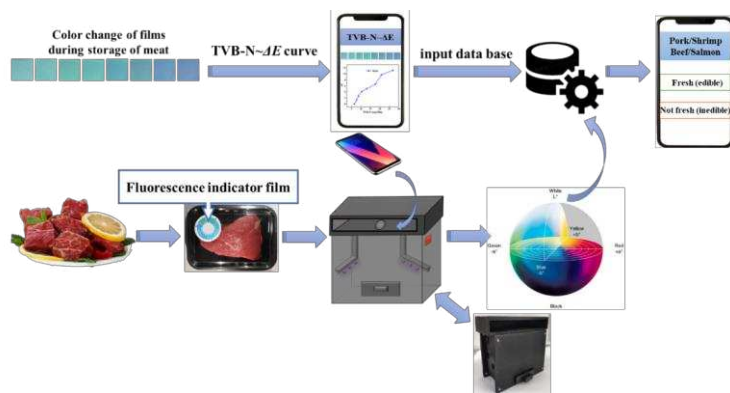
351 In comparison, salmon showed higher TVBN content in the limitation time than beef, pork and shrimp,
352 while the ΔE value of CQD@PVDF film used for salmon (4.30) was lower than the ΔE values of CQD@PVDF
353 film used for beef (6.25), pork (5.65) and shrimp (6.73). This was probably because TVBN represented the
354 total content of volatile basic nitrogen gases, such as TMA, DMA and NH_3 , while during the spoilage of meats
355 and aquatic foods, other acid gases, such as carbon dioxide, could also be generated. As presented in Figure
356 3, since the CQD was sensitive to pH change, acid gases would weaken the color change of CQD in response

to basic gases. As salmon generally has high fat content than beef (tenderloin), pork (tenderloin) and shrimp, more carbon dioxide might be generated due to the degradation of fatty acids. Hence, the CQD@PVDF film would more suitable to be used to monitor the freshness of meats and aquatic foods with low fat content.



361 **Figure 9.** (A) Photographs of the films in 10ml of water simulating a highly humid environment during storage (control) and
 362 change of the ΔE value of the films at 4°C. (B) Photographs of the films under 365 nm UV light during storage at 4°C. (C)
 363 Changes of TVBN values of beef, and the ΔE values of the CQD/PVDF and CQD@PVDF film with time. (D) Changes of
 364 TVB-N values of pork, and the ΔE values of the CQD/PVDF and CQD@PVDF film with time. (E) Changes of TVB-N values
 365 of shrimp, and the ΔE values of the CQD/PVDF and CQD@PVDF film with time. (F) Changes of TVBN values of salmon,
 366 and the ΔE values of the CQD/PVDF and CQD@PVDF film with time.

367 To better utilize ratiometric fluorescence for real time freshness detection and reduce the error of visual
 368 evaluation, we established an intelligent fluorescence sensing system based on a smartphone. By installing the
 369 UV light source in a 3D printed box and connecting the power supply, a portable fluorescent light box was
 370 successfully composed. The specific process was as follows. As shown in Scheme 2, the TVB-N ~ ΔE curve
 371 was first input into the database. Secondly, the smartphone was placed on the camera hole on the top of the
 372 3D printed box. Then, the fluorescent film images captured by the smartphone were used to extract the L^* , a^*
 373 and b^* values of the colors. Then, these data were linked to the TVB-N ~ ΔE curve to determine the freshness
 374 of meats and aquatic foods.



375
 376 **Scheme 2.** Application of smartphone in meats and aquatic foods freshness monitoring.

377 There are several advantages of our fluorescent sensors compared with previously reported sensors, as
 378 shown in **Table 1**. In this study, we synthesized a dual-emission CQD, of which the color change was more
 379 obvious for observation for naked eyes than single-emission CQD.³⁴ Meanwhile, our dual-emission CQD
 380 was obtained by merely one-step heating method, which was much convenient to synthesize than those

381 ratiometric sensors with the need of two fluorescent probes.[39-40](#) Finally, we used electrospinning method to
382 embed CQD into hydrophobic polymer PVDF to get a nano-porous film, which was more suitable for practical
383 use than fluorescent solutions,[11, 34](#) and also show presented better gas sensitivity than those film using cotton
384 paper as the solid matrixes.[18](#) Hence, the CQD@PVDF film would have a good potential for application in
385 intelligent food packaging.

386 **Table 1**
387 A comparison of previously reported works and this work.

No.	Probe	Single / double emission	Analytes	LOD	Linear range	Liquids or solid sensors for use	Food objects	Ref.
1	CDs	single emission	amine	—	—	filter paper	shrimp	16
2	N, S-CDs	single emission	ammonia	—	2 - 80 mmol/L	solution	fish	34
3	InP/ZnS quantum dots	single emission	ammonia	3 ppm	—	solution	fish	11
4	CQDs	single emission	ammonia	0.4 μ M	—	filter paper	shrimp	42
5	BDCH ₂	single emission	amine	—	—	silica gel strip	crawfish fish	43
6	Fluorescein/ RQDs	double emission	ammonia	—	250 - 2.5 $\times$ 10 ⁴ ppm	filter membrane	shrimp	40
7	TPE/PMAA/ RhB	double emission	biogenic amine	—	—	filter paper	fish	44
8	FITC/PpIX	double emission	ammonia	—	5 - 2.5 $\times$ 10 ⁴ ppm	electrospun membranes	shrimp crab	45
9	NACAgNCs /GSH-AuNCs	double emission	spermidine/ spermine	3.85 μ M/ 6.75 μ M	—	cotton paper	shrimp	46
10	N, S-CDs/ CdTe QDs	double emission	biogenic amines	—	1.259 - 5.428 μ M	filter paper	shrimp	41
11	H-CDs	double emission	spermine/ ammonia hydroxide	7 μ M / 137 ppb	—	cotton paper	shrimp	18

12	CQD	double emission	trimethylamine	1.04/2.1 μM	0-80.5 μM	electrospun coating film/ electrospun embedding film	beef pork shrimp salmon	This work
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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

■ AUTHOR INFORMATION

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443 **Notes**

444 The authors declare no competing financial interest.

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453 **■ ABBREVIATIONS USED**

454 CQD, carbon quantum dots; PVDF, polyvinylidene fluoride; LOD, the limit of detection; TEM, transmission
455 electron microscopy; SEM, scanning electron microscopy; FT-IR, Fourier transform infrared; UV-Vis,
456 Ultraviolet-Visible; XRD, X-ray diffraction; WCA, water contact angle

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