

LED-Light-Driven Active Packaging Based on a Scalable $\text{g-C}_3\text{N}_4/\text{TiO}_2$ Nanocomposite for Ethylene Scavenging and Plum Preservation

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Highlights

- ◆ Facile aqueous mixing method yields scalable g-C₃N₄/TiO₂ photocatalysts.
- ◆ Active PVA films achieve efficient LED-driven ethylene scavenging.
- ◆ The packaging delays plum ripening and suppresses surface browning.
- ◆ Novel active packaging extends 'Wushan' plum shelf life by 3-5 days.

Journal Pre-proof

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Abstract

The mitigation of ethylene-induced postharvest losses in climacteric fruits requires the development of efficient, scalable, and economically viable active packaging. This study presents a green, simple nanomanufacturing approach—utilizing a facile aqueous mixing method—to produce a visible-light-driven graphitic carbon nitride/titanium dioxide (g-C₃N₄/TiO₂) photocatalyst tailored for ethylene scavenging. By optimizing the synthesis parameters (including the precursor calcination temperature of 500 °C and a g-C₃N₄-to-TiO₂ mass ratio of 1:8) with comprehensive characterization (SEM, XRD, EPR, PL, XPS), a highly functional heterostructure was engineered and subsequently incorporated into a polyvinyl alcohol (PVA) matrix to fabricate an active composite

film. The optimized catalyst powder and the resulting functional film (g/T/P_{opt}) demonstrated significant ethylene degradation capacities of ~40 % and ~33 %, respectively, within 10 hours under energy-efficient LED illumination. Crucially, the practical application of this active packaging was validated in the postharvest storage of ‘Wushan’ plums. The composite packaging effectively regulated the storage microenvironment by reducing ethylene accumulation by 29 % compared to the PVA control, which consequently delayed the ripening process and extended the commercial shelf life of the fruit by 3–5 d. This work provides a commercially scalable and green manufacturing pathway for advanced photocatalytic active packaging, offering a sustainable technological solution to reduce food waste in the supply chain.

Keywords

LED-light photocatalysis; Ethylene photodegradation; Composite packaging; Plum postharvest storage

1. Introduction

Ethylene (C_2H_4) is a plant hormone critical to enzyme synthesis and protein processes associated with fruit ripening^[1]. Even minimal ethylene exposure can accelerate the maturation and aging of climacteric fruits, causing irreversible damage to their texture, composition, and nutritional quality^[2]. Studies indicate that ethylene increases respiration rates and water loss in climacteric fruits, leading to softening and shortened storage life. Removing ethylene from postharvest environments reduces weight loss, slows softening, and delays the accumulation of soluble solids, thereby decelerating the ripening process^[3]. This practice is essential for reducing spoilage and improving economic efficiency in the fruit and vegetable industry. The 'Wushan' plum (*Prunus salicina*), a commercially important fruit, is particularly susceptible to ethylene-induced quality degradation, necessitating effective strategies for ethylene removal from the storage environment.

Photocatalytic oxidation has emerged as a promising, eco-friendly technology that degrades ethylene into harmless CO_2 and H_2O under light irradiation, offering a sustainable alternative to traditional preservation methods^[4,5]. The $g-C_3N_4/TiO_2$ heterostructure is a particularly effective system, as it pairs the stability and strong oxidative power of titanium dioxide (TiO_2) with the visible-light harvesting capability of graphitic carbon nitride ($g-C_3N_4$). This combination not only extends the catalyst's activity into the visible spectrum, suitable for practical LED-lit storage environments, but also promotes the separation of photogenerated electron-hole (e^-h^+) pairs, a key factor in enhancing quantum efficiency^[6,7]. Indeed, high-performance $g-C_3N_4/TiO_2$ composites, often prepared via wet-chemical routes such as the sol-gel method, have demonstrated excellent efficacy in postharvest applications^[8,9].

However, a critical barrier to the widespread commercialization of such technologies is the complexity and potential cost of the synthesis process. Wet-chemical methods like sol-gel often involve multiple steps, organic solvents, and expensive precursors, which can present challenges for large-scale, industrial production^[10–12].

Consequently, there is a compelling need to explore simpler, more scalable, and economically viable synthesis routes. In recent years, green wet-chemical approaches (such as using water as the dispersion medium, followed by ultrasonic dispersion and drying to achieve composite formation) have emerged as an attractive alternative due to their operational simplicity, environmental friendliness and potential for scalable production. While this approach is straightforward, a systematic investigation into its effectiveness for producing functional g-C₃N₄/TiO₂ heterostructures for active packaging applications is currently lacking.

This study, therefore, aims to address this gap by focusing on the materials science of a scalable synthesis method. The objectives of this work are fourfold: (i) to synthesize a g-C₃N₄/TiO₂ composite photocatalyst using a simple and green aqueous mixing method; (ii) to systematically optimize the key synthesis parameters, namely the precursor calcination temperature and component mass ratio; (iii) to conduct a comprehensive characterization of the optimized material to elucidate the structure-property relationships governing its photocatalytic activity; and (iv) to fabricate a PVA (polyvinyl alcohol)-based composite film and perform a proof-of-concept application in the postharvest preservation of 'Wushan' plums to validate the material's real-world functionality.

2. Materials and methods

2.1. Materials

Urea (99 %), potassium hydroxide (KOH, 95 %), titanium dioxide (TiO₂, P25, 99.8 %), and polyvinyl alcohol (PVA, 1799 type, alcoholysis degree 98-99 %) were obtained from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). All other chemicals and solvents were of analytical grade. Deionized water was used throughout all experiments.

2.2. Synthesis of g-C₃N₄/TiO₂ (g/T) photocatalysts

2.2.1. Synthesis of g-C₃N₄ by thermal polymerization

Graphitic carbon nitride (g-C₃N₄) was synthesized via thermal polymerization of urea. Briefly, 15 g of urea was dissolved in an aqueous KOH solution (0.01 g KOH in 30 mL of deionized water) and stirred thoroughly. The mixture was then left to evaporate overnight in an oven at 60 °C. The dried residue was calcined in a muffle furnace at 200 °C for 12 h, followed by heating at 450 °C, 500 °C, 550 °C, or 600 °C for an additional 3 h to produce g-C₃N₄ samples at distinct precursor calcination temperatures.

2.2.2. Preparation of g-C₃N₄/TiO₂ composites by aqueous mixing

The g/T composites were prepared via a simple physical mixing method using the g-C₃N₄ powders from section 2.2.1 and commercial TiO₂ (P25). For each composite, a 0.2 g sample of a specific g-C₃N₄ powder was dispersed in 50 mL deionized water using an ultrasonic homogenizer for 5 min. Separately, the corresponding mass of TiO₂ (P25) was dispersed in 150 mL deionized water to achieve the desired mass ratio. The g-C₃N₄ suspension was then gradually added to the TiO₂ suspension under continuous stirring for 3 h. The resulting mixture was filtered, washed, and dried at 60 °C to yield the final g/T composites.

To optimize the composite structure, two series of materials were prepared: (i) Temperature Series: Using g-C₃N₄ calcined at 450 °C, 500 °C, 550 °C, and 600 °C (labeled g/T-450, g/T-500, g/T-550 and g/T-600), all at a fixed mass ratio. (ii) Ratio Series: Using the optimized g-C₃N₄ (calcined at 500 °C), composites were prepared with g-C₃N₄:TiO₂ mass ratios of 1:20, 1:12, 1:10, 1:8, 1:6, 1:4, 1:2, and 1:1 (labeled g/T₂₀, g/T₁₂, g/T₁₀, g/T₈, g/T₆, g/T₄, g/T₂, g/T₁).

2.3. Characterization of g/T photocatalysts

The surface morphology and elemental composition of the photocatalysts were analyzed using scanning electron microscopy (SEM, Phenom Pro, Phenom World, Netherlands) equipped with energy-dispersive spectroscopy (EDS). Crystal structures were determined by an X-ray diffractometer (XRD, Rigaku Ultima IV, Japan) over a 2θ range of 10-80°. Optical properties were measured with a UV-Vis

spectrophotometer (Cary 5000, Agilent, China), and the band gap energy (E_g) was calculated using the Tauc plot equation. Chemical composition and functional groups were analyzed by FT-IR spectroscopy (Spectrum 100, PerkinElmer, USA). Photoluminescence (PL) spectroscopy (FLS1000, Edinburgh Instruments, UK) at an excitation wavelength of 320 nm was used to evaluate the separation efficiency of photogenerated electron-hole pairs. Surface elemental composition and chemical states were examined by X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Scientific, USA). An electron paramagnetic resonance (EPR) spectrometer (EMXplus-9.5/12, Bruker, UK) was used to detect superoxide radicals ($\bullet\text{O}_2^-$) and hydroxyl radicals ($\bullet\text{OH}$) using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as a spin-trapping agent. Considering the extremely short half-life of DMPO-radical adducts, the mild intensity of the practical LED source was insufficient to accumulate a detectable instantaneous steady-state radical concentration within the short testing window. Therefore, an accelerated testing protocol using a 100 W mercury lamp (200-2000 nm) for 3 min was employed to overcome the instrument detection limit and explicitly validate the thermodynamic radical-generation pathway of the catalyst.

2.4. Photocatalytic degradation of ethylene by g/T photocatalysts

0.5 g of the as-prepared photocatalyst was placed in a 500 mL transparent airtight plastic container with approximately 110 ppm of ethylene. Ethylene concentrations were measured using an ethylene detector (F950, Felix Instruments, USA) under LED illumination (light intensity $\sim 80 \text{ W/m}^2$, wavelength: 400~700 nm, details of the emission spectrum can be found in our previous work^[13]) every 2 h over a 10-hour period. Each test was performed in triplicate. This light intensity was selected to accelerate the materials-level screening to clearly differentiate the photocatalytic performance of the various synthesized powders. Kinetic analysis was conducted using a simplified Langmuir-Hinshelwood pseudo-first-order model^[14]:

$$\ln(C_0/C) = kt \quad (1)$$

Here, C_0 and C represent the initial ethylene concentration and the concentration

after irradiation, respectively. k is the apparent degradation rate constant, reflecting the reaction rate, and t is the reaction time.

2.5. Preparation of g-C₃N₄/TiO₂/PVA (g/T/P) package film

To prepare the g/T/P solution, an appropriate amount of g/T particles was dispersed in 30 mL of deionized water followed by 5 min of ultrasonication. Separately, 10 g of PVA was dissolved in 210 mL of deionized water at 90 °C and maintained under stirring until full dissolution. The g/T solution was then added to the PVA solution with continuous stirring to achieve a homogeneous mixture, forming a stable g/T/P film solution. The resulting solution was then poured into a 25 cm × 25 cm plastic petri dish and dried to produce membranes with a solid content of ~ 5 mg/cm². The proportions of g/T to PVA were varied (1 %, 2.5 %, 5 %, 7 %, and 10 %), and the resulting membranes were labeled as X % g/T/P, where X represents the mass percentage of g/T in PVA.

Control PVA membranes were prepared using the same method without adding g/T. Similarly, TiO₂/PVA and g-C₃N₄/PVA membranes were prepared by replacing g/T with TiO₂ or g-C₃N₄, respectively, maintaining the same proportions as g/T to PVA.

2.6. Characterization of g/T/P package film

The films' microscopic morphology and elemental distribution were examined using SEM and EDS. Crystal structure and chemical composition were analyzed by XRD and FTIR, respectively. UV-Vis transmittance was measured with a dual-beam spectrophotometer (TU-1950, P&G, China). Tensile strength (TS) and elongation at break (EAB) were determined using an electronic universal testing machine (ETM503A, Shenzhen Wance Testing Equipment Co., Ltd, China) following the GB1040.3-2006 standard. The water vapor transmission rate (WVT) was measured according to GB/T 1037-2021 at 25 °C and 75 % RH. The oxygen transmission rate (OTR) was determined with an OTR tester (C230, Labthink, China) according to GB/T 19789-2021 at 25 °C and 85 % RH.

2.7. Photocatalytic degradation of ethylene by g/T/P package film

The photocatalytic activity of the prepared PVA, TiO₂/PVA, g-C₃N₄/PVA and g/T/P films was assessed with similar procedure as described in Section 2.4.

2.8. Proof-of-concept validation: Plum fruit preservation experiment

Prunus salicina ‘Wushan plum’ fruits were sourced from Wushan County, Chongqing, and selected for uniform size, absence of pests and diseases, and similar maturity. The fruits were transported to the laboratory on the same day of picking and stored overnight under cold storage conditions. The fruit were removed from storage and acclimated to room temperature on the following day. To simulate practical postharvest storage and sales conditions, surface stains were gently removed using a hair dryer but without any disinfection treatment.

The fruit were randomly divided into five groups (approx. 200 fruits per group): (i) Control (unpacked), (ii) PVA (sealed in pure PVA packaging), (iii) TiO₂/PVA (sealed in TiO₂/PVA packaging), (iv) g-C₃N₄/PVA (sealed in g-C₃N₄/PVA packaging), and (v) g/T/P (sealed in the optimized g/T/P_{opt} packaging).

All fruit groups were stored at 25 ± 2 °C with a relative humidity of 52 ± 2 % RH and under continuous LED illumination. A key parameter in this proof-of-concept validation was the light intensity. The materials-level screening (Section 2.4) utilized a higher intensity (~ 80 W/m²) to accelerate catalyst evaluation. However, preliminary trials confirmed that this intensity generated excessive surface heat, causing thermal stress and abiotic damage to the plum epidermis. Therefore, an application-relevant, non-destructive light intensity of ~ 20 W/m² was selected for the fruit preservation experiment, ensuring that all observed effects were attributable to the photocatalytic and not thermal artifacts.

To validate the packaging's functionality, a comprehensive assessment of fruit quality was performed at regular intervals during the 11-day storage period. Key parameters measured included: (i) Atmospheric composition: Gas content (ethylene, CO₂, O₂) within the sealed bags. (ii) Physical attributes: Sensory qualities, surface color (L*, a*, b*, ΔE), firmness, weight loss, and decay rate. (iii) Biochemical and nutritional

markers: Ascorbic acid (AA) content, titratable acidity (TA), and soluble solids (SS) content. The detailed, step-by-step analytical protocols for each of these measurements are provided in the Supplementary Information (Section S3).

2.9. Statistical analysis

The data were expressed as mean $\pm$ standard deviation. Data organization was performed using Microsoft Excel 2019, and graphs were generated using Origin 2021. Statistical analyses were conducted using SPSS 27.0, employing one-way analysis of variance (ANOVA). Significant differences among means were determined using Duncan's test, with a significance level set at $p < 0.05$.

3. Results and discussion

3.1. Construction of the optimal g/T photocatalyst

Calcination temperature and composite ratio critically influence the photocatalyst performance by controlling surface area, light absorption, and e^-h^+ recombination, thus determining efficiency^[15]. Therefore, these parameters were systematically optimized to achieve the highest photocatalytic efficiency for ethylene degradation under LED illumination. The detailed optimization process, which examines the effects of different calcination temperatures and composite ratios, is described in the Supplementary Information (see Section S1, Figs. S1a-d and Table S1). The optimization study identified a calcination temperature of 500 °C and a g-C₃N₄-to-TiO₂ mass ratio of 1:8 as the ideal conditions. The photocatalyst prepared under these conditions, hereafter referred to as g/T_{opt}, was selected for all subsequent characterizations and applications.

Fig. 1(a) compares the ethylene degradation performance of g/T_{opt} with other materials. The Control group (empty container) showed negligible ethylene degradation over 10 h, indicating ethylene photochemical stability. Both TiO₂ and g-C₃N₄ degraded ~12 % of ethylene in 10 h under LED irradiation, while g/T_{opt} exhibited more than three times (~40 %) the efficiency of these single materials.

Ethylene degradation kinetics followed pseudo-first-order behavior (Fig. 1b). The rate constants (k) were 0.012 h⁻¹, 0.013 h⁻¹, and 0.050 h⁻¹ for TiO₂, g-C₃N₄, and g/T_{opt},

respectively, with g/T_{opt} showing a fourfold improvement over the single materials (Table S1). This significant enhancement underscores the effectiveness of the composite structure in boosting photocatalytic efficiency. To investigate the mechanisms behind this enhancement, g/T_{opt} and other representative samples were selected for detailed characterization.

To assess the reusability of the g/T_{opt} photocatalyst, three cycles of ethylene degradation tests were conducted under LED illumination. Fig. 1(c) shows g/T_{opt} maintained consistent ethylene degradation rates across three cycles, and proves g/T_{opt} robustness and practicality.

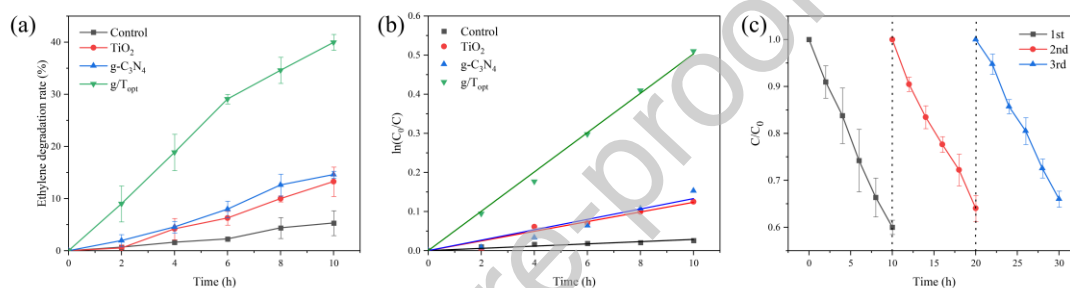


Fig. 1 Ethylene degradation by different materials (a) and their kinetic behaviors (b) (the k values and R^2 are presented in Table S1), and reusability test for g/T_{opt} (c).

3.2. Characterization of g/T photocatalysts

3.2.1. Physicochemical properties

SEM was used to analyze the surface morphology of TiO_2 , $g\text{-C}_3\text{N}_4$, and g/T_{opt} to assess compositional effects. As shown in Fig. 2(a), TiO_2 exhibited irregular granular structures and significant agglomeration, likely due to its small particle size and high surface energy, which promote aggregation^[16]. $g\text{-C}_3\text{N}_4$ exhibited layered morphology with smooth surfaces (Fig. 2b). In Fig. 2(c) and S2(b), the SEM image of g/T_{opt} revealed a nanosheet structure with $g\text{-C}_3\text{N}_4$ irregularly distributed across the TiO_2 surface. The EDS pattern in Fig. 2(d) confirmed the elemental composition of g/T_{opt} , revealing the presence of C, N, O and Ti elements with uniform distribution. SEM images of the samples g/T series prepared at various composite ratios and calcination temperatures

(Fig. S2) show little difference, only g/T_{opt} (Fig. S2(b)) clearly reveals that the nanosheets are irregularly distributed across the TiO_2 surface.

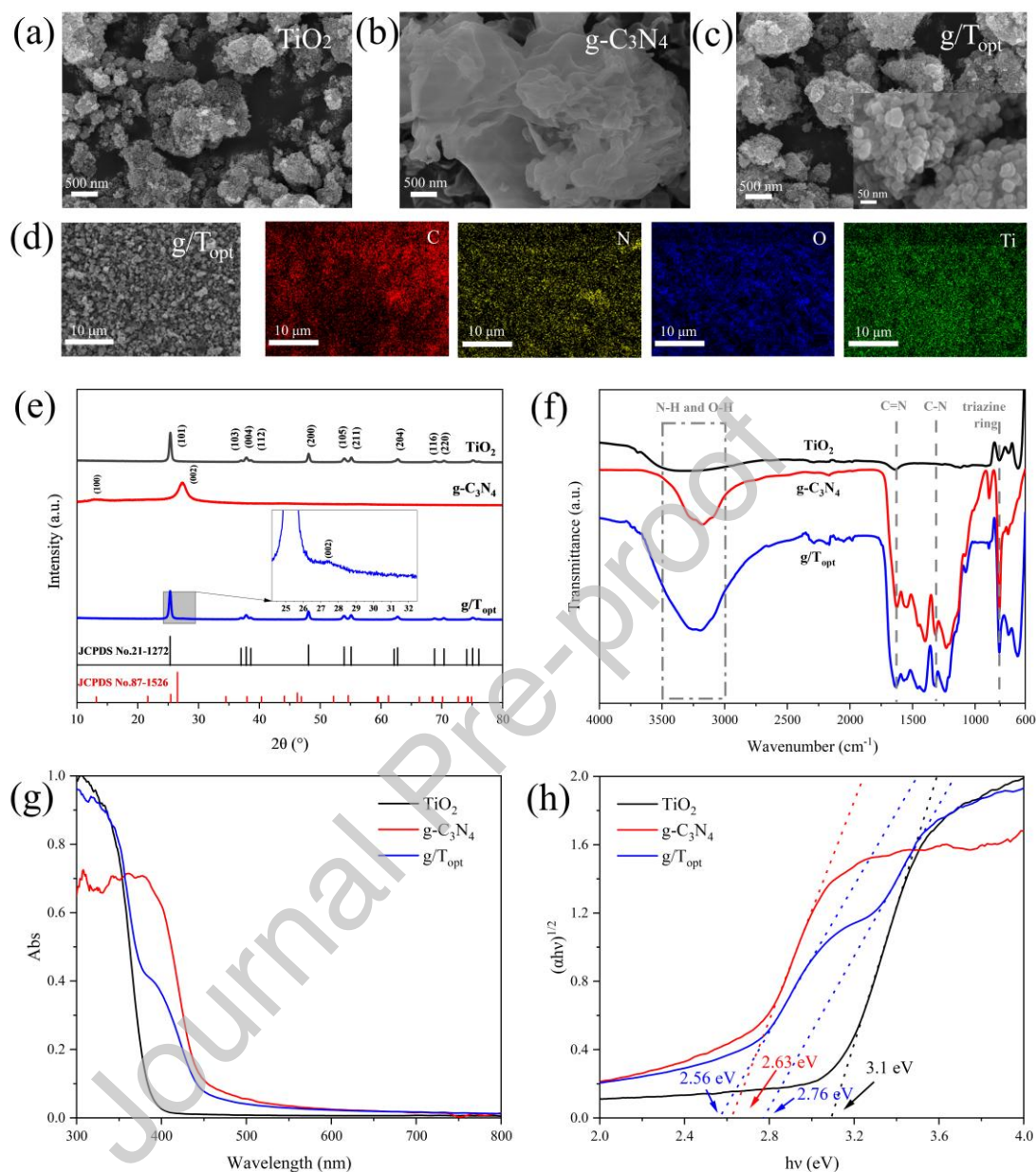


Fig. 2 SEM images of photocatalysts (a-c), EDS of g/T_{opt} (d), XRD patterns (e), FTIR spectra (f), UV-Vis spectra (g) and Tauc plots (h).

XRD was used to determine the crystal structure of the materials. As illustrated in Fig. 2(e), the XRD pattern of $g-C_3N_4$ displayed two characteristic peaks at 13.1° and 27.1° , corresponding to the (100) and (002) planes (JCPDS No. 87-1526). The 13.1° peak was attributed to the N-bridged tri-s-triazine units, while the 27.1° peak was due to the stacking of C-N bonds in aromatic structures^[17]. The XRD pattern of TiO_2 (black

curve) matched the diffraction peaks of anatase TiO_2 (JCPDS No. 21-1272), with corresponding crystal planes labeled in Fig. 2(e). The g/T_{opt} composite exhibited distinct diffraction peaks of both $\text{g-C}_3\text{N}_4$ and TiO_2 , confirming composite formation. All g/T samples showed characteristic peaks of both components (Fig. S3). Notably, the diffraction peaks of $\text{g-C}_3\text{N}_4$ in g/T composites were weaker compared to those of TiO_2 , reflecting its lower content and crystallinity^[18]. The g/T_1 sample showed stronger $\text{g-C}_3\text{N}_4$ peaks from higher content. No extraneous peaks appeared in the XRD patterns, confirming the high-purity synthesis of all materials.

FTIR analysis was performed to investigate the chemical composition and identify the functional groups of the photocatalysts. Fig. 2(f) illustrates the FTIR spectra of TiO_2 , $\text{g-C}_3\text{N}_4$, and g/T_{opt} . The characteristic bands at $600\text{-}700\text{ cm}^{-1}$ in TiO_2 were attributed to the stretching vibrations of Ti-O and Ti-O-Ti bonds. For $\text{g-C}_3\text{N}_4$, peaks at $3000\text{-}3500\text{ cm}^{-1}$ corresponded to the stretching vibrations of free amino groups (N-H) and hydroxyl group (O-H). Peaks in the $1200\text{-}1700\text{ cm}^{-1}$ range represented the typical stretching modes of carbon-nitrogen heterocycles, such as C-N and C=N bonds^[19]. Additionally, the peak at 808 cm^{-1} was associated with triazine unit vibrations^[20]. The g/T_{opt} spectrum showed all characteristic peaks of $\text{g-C}_3\text{N}_4$ and TiO_2 , confirming their successful integration. The FT-IR spectra of g/T composites incorporating $\text{g-C}_3\text{N}_4$ precursors calcined at $450\text{ }^\circ\text{C}$ (Fig. S4) revealed weak $\text{g-C}_3\text{N}_4$ peaks, suggesting incomplete urea polymerization or the presence of intermediate products. As the calcination temperature increased, the polymerization degree improved, leading to the formation of triazine groups and the tri-s-triazine structure of $\text{g-C}_3\text{N}_4$. Distinct characteristic peaks were observed at $500\text{ }^\circ\text{C}$, indicating the complete formation of $\text{g-C}_3\text{N}_4$ ^[21]. The FT-IR analysis of g/T composites with varying composite ratios revealed that when the $\text{g-C}_3\text{N}_4$ content was low, its characteristic peaks were less prominent. However, at a $\text{g-C}_3\text{N}_4$ -to- TiO_2 ratio of 1:8, the characteristic structure of $\text{g-C}_3\text{N}_4$ became well-defined, further supporting the selection of this ratio as optimal.

3.2.2. Optical properties and photocatalytic mechanism

The UV-Vis spectra were used to assess the light absorption range and performance of the photocatalysts. As shown in Fig. 2(g), pure TiO_2 exhibited strong absorption only in the UV region with an absorption edge at approximately 400 nm. In contrast, pure g- C_3N_4 showed an obvious red-shift with significant visible light absorption. Upon combination, g/ T_{opt} and g/T series demonstrated noticeably stronger visible absorption than TiO_2 (Fig. S5(a)), which is beneficial for improving light utilization and photocatalytic activity. As shown in Fig. 2(h), the corresponding optical band gaps (E_g) were calculated using Tauc plots (Fig. 2(h) and Fig. S5(b)). The E_g values of TiO_2 and g- C_3N_4 were determined to be 3.1 eV and 2.63 eV, respectively. Interestingly, all the g/T series composites exhibited two distinct band gaps. For instance, the g/ T_{opt} composite displayed two E_g values at 2.76 eV and 2.56 eV. The emergence of these dual band gaps, deviating from those of the pure components, strongly indicates the successful formation of a heterojunction with intimate interfacial electronic interactions between g- C_3N_4 and TiO_2 .

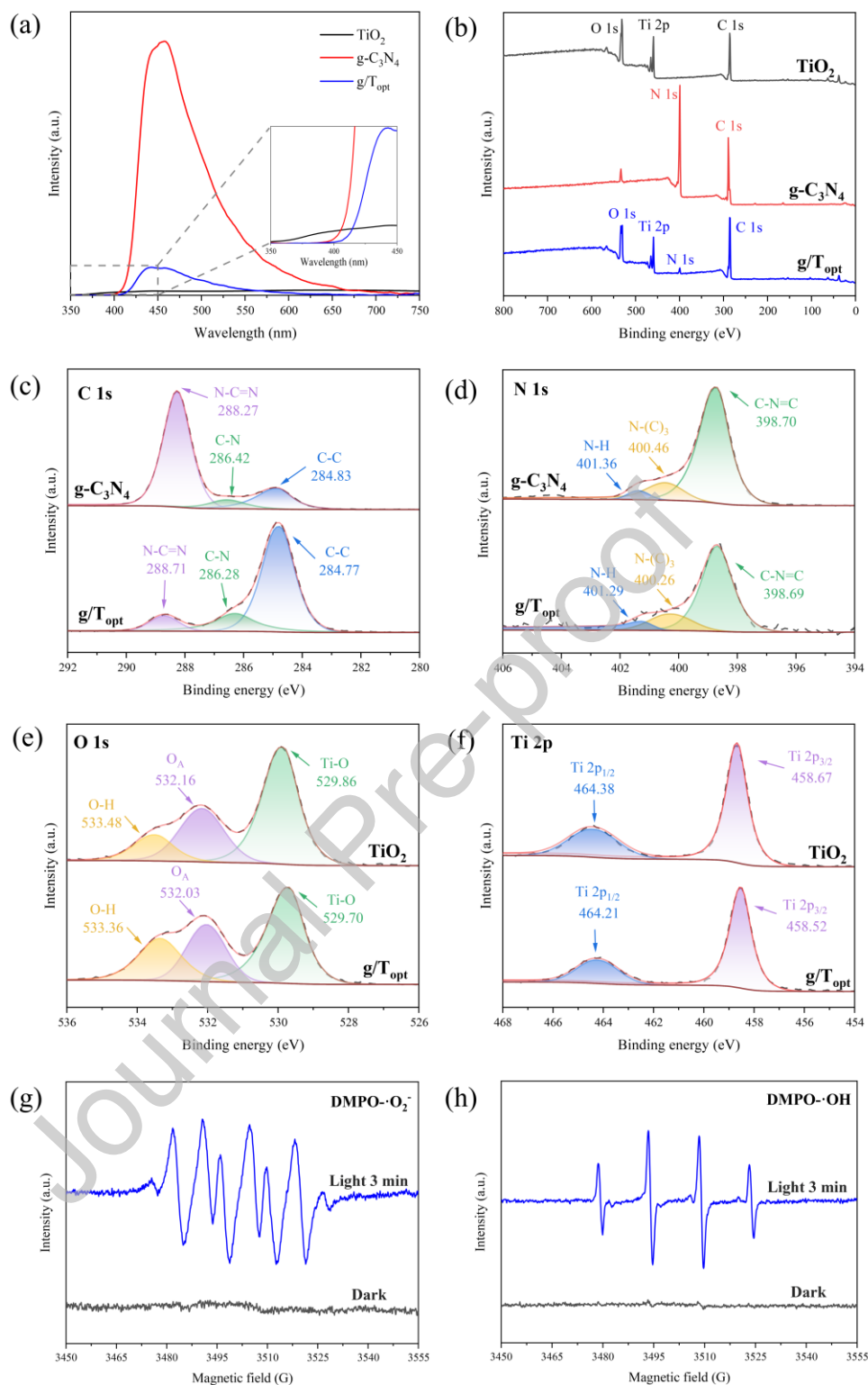


Fig. 3 PL spectra (a), XPS spectra: survey (b), C 1s (c), N 1s (d), O 1s (e), Ti 2p (f), and EPR spectra of $\text{DMPO}\cdot\text{O}_2^-$ (g) and $\text{DMPO}\cdot\text{OH}$ (h) for $g\text{-T}_{\text{opt}}$.

PL spectroscopy measured e^-h^+ recombination rates, where lower intensity indicated reduced carrier recombination and higher photocatalytic efficiency^[22]. As

shown in Fig. 3(a), pure g-C₃N₄ displayed a pronounced emission peak at approximately 462 nm, indicating a quick recombination^[23]. Despite its strong absorption in the visible region (Fig. 3(a)), g-C₃N₄ had a high PL intensity, indicating low photogenerated carrier separation efficiency. In the UV light range, the PL intensity of the g/T_{opt} was significantly quenched compared to that of pristine TiO₂, as shown in the inset. The PL spectrum of g/T_{opt} showed a similar peak position to g-C₃N₄ but with significantly quenched intensity. This suppression of photoluminescence strongly implies that the simple synthesis route can successfully promote the separation of photogenerated e⁻-h⁺ pairs, a key requirement for photocatalysis, by inhibiting their rapid recombination. The PL spectra of the g/T series materials (Fig. S6) confirmed consistent improvements in carrier separation while retaining the g-C₃N₄ structure.

XPS was employed to analyze the elemental composition and chemical states of the materials. The XPS survey spectrum of g/T_{opt} (Fig. 3(b)) confirmed the presence of C, N, O and Ti elements, consistent with the EDS results. Compared with pure g-C₃N₄ and TiO₂, no new peaks corresponding to Ti-C or Ti-N covalent bonds were detected in g/T_{opt}; instead, distinct binding energy shifts were observed, revealing strong interfacial electronic interactions. Specifically, in the C 1s spectrum (Fig. 3(c)), the characteristic N-C=N peak of g/T_{opt} shifted positively from 288.27 eV (pure g-C₃N₄) to 288.71 eV, indicating decreased electron density around the triazine ring carbon centers^[24]. Meanwhile, the C-N and C-C peaks exhibited slight negative shifts (286.42 → 286.28 eV and 284.83 → 284.77 eV, respectively). In the N 1s spectrum (Fig. 3(d)), all peaks shifted to lower binding energies: C-N=C (398.70 → 398.69 eV), N-(C)₃ (400.46 → 400.26 eV), and N-H (401.36 → 401.29 eV)^[25]. This divergent behavior suggests that the interfacial interaction is localized at the triazine ring carbon centers, inducing a site-selective electron redistribution within the g-C₃N₄ framework. Conversely, in the O 1s spectrum (Fig. 3(e)), peaks for lattice oxygen (Ti-O, 529.70 eV), adsorbed oxygen (O_A, 532.03 eV), and surface hydroxyls (O-H, 533.36 eV) all shifted to lower binding energies compared to pure TiO₂^[26]. Similarly, the Ti 2p spectrum (Fig. 3(f)) showed

negative shifts for the Ti^{4+} characteristic peaks (458.52 eV and 464.21 eV vs. 458.67 eV and 464.38 eV). The positive shift of the N-C=N carbon skeleton and the concurrent negative shifts of Ti and O species indicate an interfacial electron redistribution from the g-C₃N₄ triazine rings toward the TiO₂ phase, establishing an intimate electronic coupling and a built-in electric field at the heterojunction interface.

To explicitly elucidate the specific charge transfer pathway under illumination, the absolute conduction band (E_{CB}) and valence band (E_{VB}) potentials of the individual components were estimated using the classic Mulliken electronegativity empirical formulas: $E_{\text{CB}} = X - E_{\text{e}} - 0.5E_{\text{g}}$ and $E_{\text{VB}} = E_{\text{CB}} + E_{\text{g}}$, where X represents the absolute electronegativity (4.73 eV for g-C₃N₄ and 5.80 eV for TiO₂), and E_{e} is the energy of free electrons on the hydrogen scale (~ 4.50 eV)^[27]. Based on the E_{g} values obtained from the Tauc plots, the E_{CB} and E_{VB} of g-C₃N₄ were calculated as -1.085 eV and +1.545 eV (vs. NHE), respectively. Meanwhile, the E_{CB} and E_{VB} of TiO₂ were determined as -0.25 eV and +2.85 eV (vs. NHE).

Based on these absolute potentials, the thermodynamic feasibility of reactive oxygen species (ROS) generation can be rigorously deduced. If the g/T_{opt} composite followed a conventional Type-II charge transfer pathway, photogenerated electrons would accumulate on the E_{CB} of TiO₂ (-0.25 eV). This potential is thermodynamically insufficient to reduce O₂ to superoxide radicals (-0.33 V vs. NHE). Similarly, holes accumulating on the E_{VB} of g-C₃N₄ (+1.545 eV) could not oxidize surface hydroxyls into hydroxyl radicals (+1.99 V vs. NHE).

To experimentally validate this theoretical analysis, EPR spectroscopy was employed to detect the ROS generated by g/T_{opt}. As shown in Figs. 3(g) and 3(h), no obvious signals were observed under dark conditions. However, after 3 min of light irradiation, characteristic signals prominently appeared: a sextet signal for the DMPO- $\bullet\text{O}_2^-$ adduct (Fig. 3g) and a quartet signal for the DMPO- $\bullet\text{OH}$ adduct (Fig. 3h)^[28]. The explicit detection of both $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ radicals strongly contradicts the Type-II assumption and provides definitive physical evidence for a direct Z-scheme charge

transfer mechanism. It should be noted that while an accelerated broad-spectrum irradiation was utilized to achieve the transient radical concentration required for EPR detection, this intrinsic Z-scheme radical-generation mechanism remains entirely valid under the specific visible-light-driven application conditions. Given that the g/T_{opt} composite exhibits strong visible-light absorption (Fig. 2(g)) and successfully achieves the macroscopic degradation of ethylene under the commercial LED, this practical performance confirms that the mild illumination is highly capable of supplying a sufficient and continuous generation of ROS to drive the photocatalytic process.

In this heterojunction, the relatively useless photogenerated electrons in the TiO₂ CB preferentially recombine with the holes in the g-C₃N₄ VB at the interface. Consequently, the highly reductive electrons in the g-C₃N₄ CB (-1.085 eV) and the highly oxidative holes in the TiO₂ VB (+2.85 eV) are spatially separated and preserved. Mechanistically, •O₂⁻ originates from the reduction of dissolved O₂ by these highly reductive electrons, while •OH is mainly produced through the oxidation of H₂O or surface hydroxyl groups by the preserved holes. In combination with the XPS results, which reveal the presence of abundant adsorbed oxygen and hydroxyl species on the surface of g/T_{opt}, the EPR findings further confirm that these surface active sites act as efficient precursors for ROS generation upon illumination. Therefore, the synergistic oxidative action of •O₂⁻ and •OH radicals is identified as the core mechanism underlying the superior ethylene degradation performance of the g/T_{opt} based active packaging.

3.3. Construction of the optimal g/T/P package film

To translate the optimized g/T_{opt} powder from a laboratory material into a practical, scalable format for a proof-of-concept application, the photocatalyst was incorporated into a robust PVA polymer matrix. The effect of the g/T_{opt}-to-PVA loading ratio on the photocatalytic degradation performance of ethylene was subsequently investigated. As shown in the Supplementary Information (Section S2) and Fig. S7, a 2.5 % g/T_{opt} loading achieved a maximal photocatalytic efficiency. This configuration, referred to as g/T/P_{opt}, was selected as the optimal functional package for subsequent experiments.

PVA, TiO_2/PVA and $\text{g-C}_3\text{N}_4/\text{PVA}$ films exhibited ethylene degradation rates below 15 % after 10 h (Fig. 4(a)), demonstrating low photocatalytic activity. In contrast, the $\text{g/T/P}_{\text{opt}}$ film significantly improved the photocatalytic performance ($\sim 33\%$). The constant rate k of $\text{g/T/P}_{\text{opt}}$ was 5.95, 2.57, and 2.42 times higher than those of PVA, TiO_2/PVA , and $\text{g-C}_3\text{N}_4/\text{PVA}$ films, respectively (Fig. 4(b) and Table S2). Although $\text{g/T/P}_{\text{opt}}$ showed slightly lower photocatalytic activity than pure g/T_{opt} , this likely resulted from the low g/T_{opt} content in the composite film. Nonetheless, $\text{g/T/P}_{\text{opt}}$ significantly improved the ethylene degradation versus control films, demonstrating its effectiveness as functional packaging.

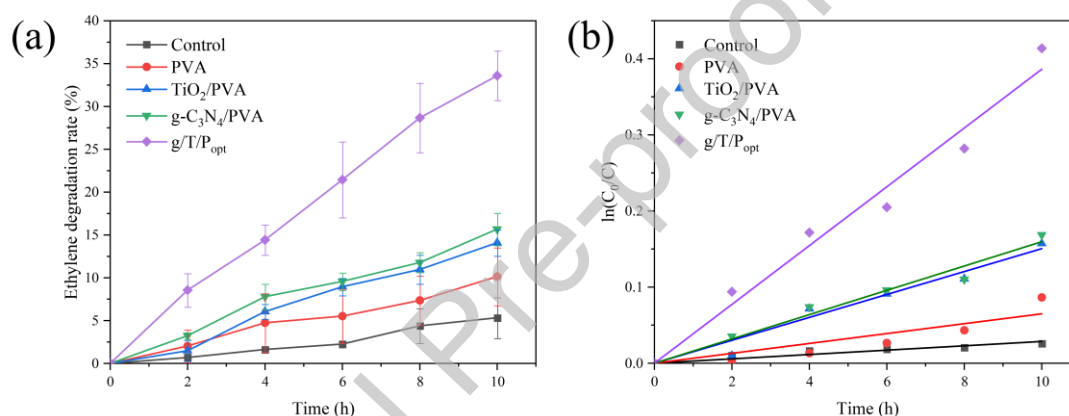


Fig. 4 Photocatalytic degradation performance of the as-prepared materials (a) and their corresponding results of kinetic analysis (b).

3.4. Characterization of g/T/P package

3.4.1. Physicochemical properties

The smooth and uniform surface observed in the SEM images (Figs. 5(a-c)) indicates the uniform dispersion of the catalyst nanoparticles within the PVA matrix. This is attributed to the excellent compatibility and strong interfacial adhesion between the catalysts and the polymer, which effectively prevents the aggregation of the particles. EDS analysis confirmed the uniform distribution of C, N, O and Ti on the $\text{g/T/P}_{\text{opt}}$ surface (Fig. 5(d)). SEM and cross-sectional images of g/T/P materials series with varying g/T_{opt} loadings were also investigated (Fig. S8). As the g/T_{opt} loading increased, the particle aggregation became more apparent on the membrane surface,

reducing the compatibility between g/T_{opt} and PVA. Notably, g/T/P_{opt} with 2.5 % g/T_{opt} showed no aggregation and maintained excellent PVA compatibility. Ethylene degradation tests (Fig. S7) revealed 1 % g/T/P underutilized g/T_{opt}'s photocatalytic activity, whereas g/T/P_{opt} showed optimal performance and was selected for further study.

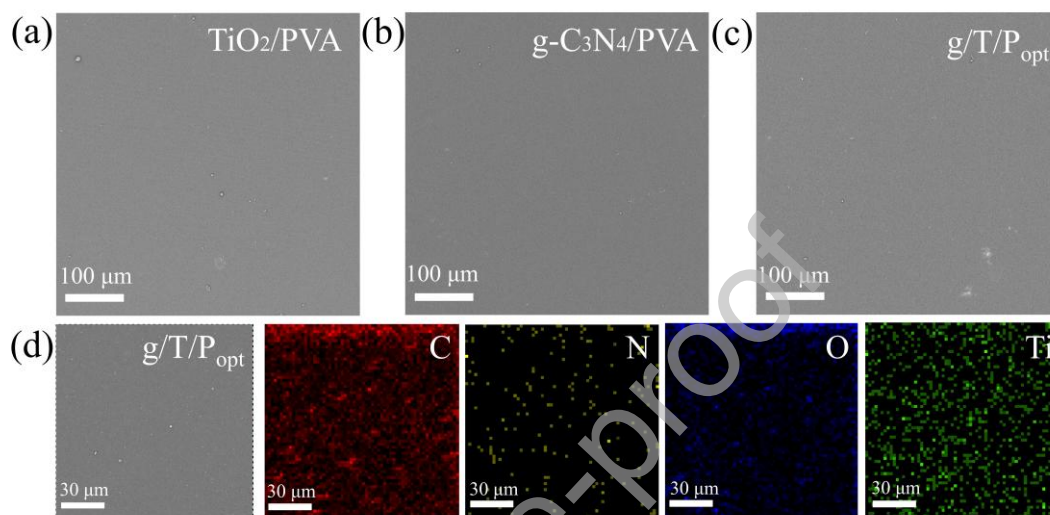


Fig. 5 SEM of different materials' film (a-c) and EDS of g/T/P_{opt} (d).

XRD patterns of the films are presented in Fig. 6(a). All film samples exhibited a broad diffraction peak at $2\theta=19^\circ$, corresponding to the (101) crystal plane of PVA. This peak originated from the semi-crystalline regions of PVA, which are maintained by extensive intra- and inter-molecular hydrogen bonding between the abundant hydroxyl (-OH) functional groups on adjacent polymer chains^[29]. The g/T/P_{opt}'s diffraction peaks matched anatase TiO₂ characteristics (JCPDS No. 21-1272). However, no distinct peaks corresponding to g-C₃N₄ were observed, suggesting low crystallinity and content. The weaker crystallization peak at 19° in g/T/P_{opt} versus the pure PVA control suggests that the embedding of g/T_{opt} nanoparticles disrupted the original hydrogen-bonded stacking of PVA chains. The PVA hydroxyl groups competitively formed new physical interactions with the nanoparticle surfaces, thereby inhibiting PVA crystallization during film formation^[30,31]. Importantly, g/T/P_{opt} showed no additional peaks versus g/T_{opt}, confirming its structural and chemical stability. Physical bonding between g/T_{opt} and PVA maintains the photocatalyst integrity, enabling fruit preservation applications.

Fig. 6(b) showed that the FTIR spectrum of g/T/P_{opt} matched that of PVA, indicating that g/T_{opt} was embedded into the PVA matrix without forming new chemical bonds^[32]. The absence of new peaks indicates without forming new covalent bonds between the materials. The FTIR spectra of the films with varying g/T_{opt} content exhibited similar characteristics (Fig. S9). Minor peak shifts without shape alteration suggested interfacial interactions between g/T_{opt} and PVA^[33]. The shifts indicated a stable physical incorporation of g/T_{opt} in the PVA matrix, preserving its molecular structure.

3.4.2. Transmittance

Light transmittance is a critical factor for packaging materials and the results for the different films are presented in Fig. 6(c). Pure PVA displayed high light transmittance but poor UV-blocking capability (200-400 nm). Incorporating TiO₂, g-C₃N₄ and g/T_{opt} decreased transmittance via enhanced light scattering from their layered structures. Despite this, the g/T/P_{opt} films showed enhanced UV-blocking versus pure PVA, effectively protecting fruits and vegetables from UV-induced damage. Notably, the transmittance decreased as the g/T_{opt} content increased, as observed in Fig. S10. The 1 % g/T/P film demonstrated a markedly enhanced UV-blocking (200-400 nm) effect versus the pristine PVA film. The 2.5 % g/T/P demonstrated optimal UV-blocking effect, balancing light transmittance and UV protection to keep fresh produce quality.

3.4.3. Mechanical performance

Packaging materials require adequate mechanical strength to prevent food damage. The tensile strength (TS) and elongation at break (EAB) of the films were presented in Fig. 6(d). The TS of TiO₂/PVA, g-C₃N₄/PVA and g/T/P_{opt} films showed comparable values to pure PVA, confirming good photocatalyst dispersion without affecting matrix rigidity. However, differences were observed in the EAB. While the g-C₃N₄/PVA and g/T/P_{opt} films retained EAB values similar to the pristine PVA film, the TiO₂/PVA film exhibited a reduction in EAB, likely resulting from weak TiO₂ and PVA interfacial bonding and defect formation^[34].

3.4.4. Gas barrier properties

Gas barrier properties are critical for packaging. As shown in Fig. 6(e), all films containing photocatalysts demonstrated a beneficial reduction in oxygen transmission rate (OTR) compared to pure PVA, attributed to the nanoparticles creating a more tortuous diffusion path for O₂ molecules. However, the water vapor transmission rate (WVT) for the g/T/P_{opt} film was slightly increased compared to pure PVA. This is a known trade-off, as the hydrophilic nature of the incorporated oxide catalyst can interact with water molecules and facilitate their diffusion. The diminished PVA (101) crystalline peak at $2\theta=19^\circ$ g/T/P_{opt} (Fig. 6(a)) reflects reduced crystallinity and increased amorphous fraction, which facilitates water diffusion and sorption, thereby contributing to elevated WVT^[35,36]. While this indicates a compromise in the film's passive barrier function, its primary intended function is as an active photocatalytic scavenger.

3.4.5. Reusability

To validate the reusability of g/T/P_{opt} functional packaging, ethylene degradation performance was also tested over three cycles under LED lamp irradiation. Fig. 6(f) confirmed g/T/P_{opt}'s stable ethylene degradation across three cycles, demonstrating its practical potential for fruit preservation.

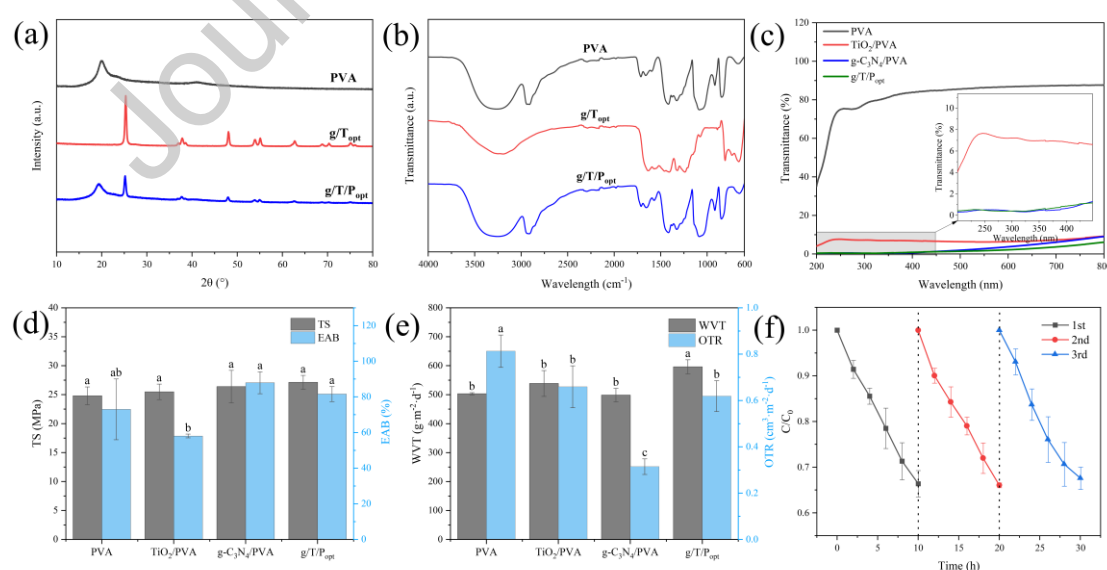


Fig. 6 XRD (a), FT-IR (b), light transmittance (c), TS and EAB (d), WVT and OTR (e) of different films, and reusability of g/T/P_{opt} (f).

3.5. Application of g/T/P packaging in plums preservation

3.5.1. Gas content in bags

The primary function of the active packaging—its ability to scavenge ethylene in a real-world scenario—was validated by measuring the gas content within the sealed plum packages. As depicted in Fig. 7(a), ethylene accumulation occurred in all groups, but the g/T/P group consistently maintained the lowest ethylene concentration. By day 11, ethylene levels in the g/T/P bag were 29 % lower than in the PVA control bag. This result is a successful proof-of-concept, demonstrating that the g/T_{opt} catalyst, when embedded in the PVA film, remains functional and effectively degrades ethylene produced by the fruit under LED illumination. Figs. 7(b-c) show that plum respiration caused CO₂ accumulation and O₂ depletion in all groups during storage. The g/T/P group maintained lower CO₂ and higher O₂ levels than the controls during storage. The gas concentrations (ethylene, CO₂ and O₂) within packages exhibited some variation among replicate samples, primarily arising from inherent differences in respiratory metabolism among individual fruits, transient disturbances to package integrity during sampling and potential microbial interference during late storage. Notably, all treatment groups employed standardized packaging and measurement protocols, ensuring that these sources of variation were randomly and equally distributed across groups. Under this experimental design, the g/T/P group consistently displayed the lowest ethylene concentration, the lowest CO₂ accumulation and relatively higher O₂ levels across all replicates, indicating effective suppression of ethylene generation and respiratory intensity.

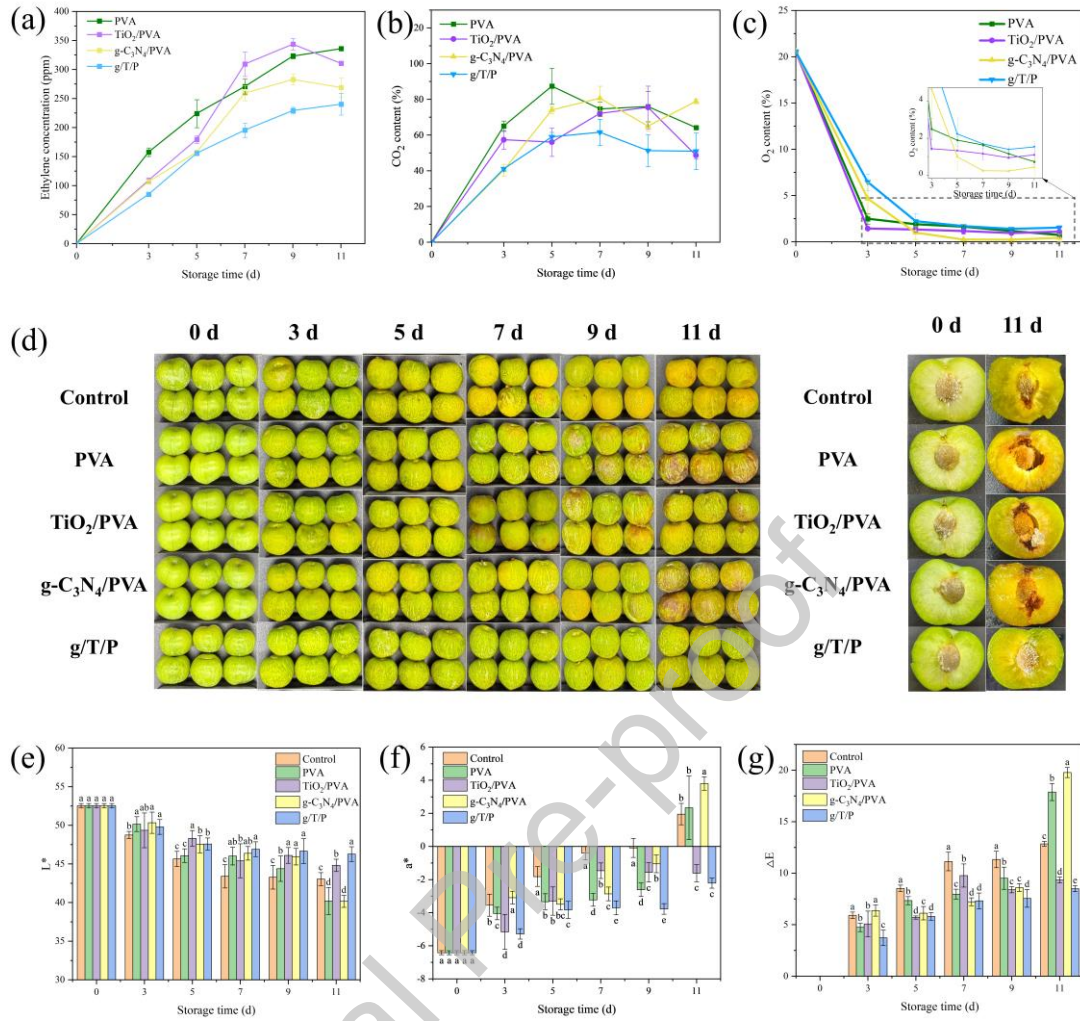


Fig. 7 Ethylene in bags (a), CO₂ in bags (b), O₂ content in bags (c), appearance and cross-section (d), L* (e), a* (f) and ΔE (g) in different treatment groups.

3.5.2. Appearance

Freshly picked plums were initially green, turning yellow with duller skin during storage (Fig. 7(d)). This demonstrated reduction in ethylene, the key plant hormone regulating ripening, directly translated to a visible preservation of fruit quality and delayed senescence. By day 11, fruit in the control group had significantly yellowed, softened, reaching commercial unacceptability (experiment terminated). In the PVA and TiO₂/PVA groups, browning appeared on the fruit surface by the day 7, whereas browning in the g-C₃N₄/PVA group began on the day 9. Elevated packaging CO₂ concentration likely induced membrane stress, causing cellular damage and browning^[37]. Anaerobic stress and ethanol fermentation from high CO₂ worsened

discoloration and deterioration, generating alcoholic odors that reduced plum quality^[38]. In contrast, the g/T/P packaging significantly reduced ethylene levels while maintaining lower CO₂ and higher O₂ concentrations, effectively delaying the ripening and aging process. This significantly reduced browning and preserved plum quality.

Control group became runny by day 11. Fruit in other control groups (PVA, TiO₂/PVA, and g-C₃N₄/PVA) exhibited kernel-pulp separation and browning caused by pathogen infection. In contrast, g/T/P-packaged plums maintained freshness with minimal pathogen infection. The g/T/P packaging's enhanced preservation resulted from lower ethylene concentration and reduced respiration (decreased CO₂). This combination delayed the aging and prevented surface/internal browning in plums.

3.5.3. Color

Plum maturity was assessed using color parameters L*, a* and ΔE during storage. L* (0-100) measures luminosity, with higher values indicating brighter surfaces. The a* value represents the red-green spectrum (positive=red; negative=green), and larger absolute values signify deeper color intensity. ΔE quantifies color change magnitude, with increasing values indicating greater deviation from baseline. The L* values decreased in all groups (Fig. 7(e)), demonstrating reduced plum luminosity during storage. After 11 d of storage, the PVA and g-C₃N₄/PVA groups exhibited maximal browning with minimal L* values. Conversely, the L* values of the other packaging groups were higher than the control, with the g/T/P group having the highest L* values, showing better luminosity retention. All groups showed increasing a* values (Fig. 7(f)), reflecting progressive yellowing during storage. On day 11, the g/T/P group had the lowest a* value (minus), confirming its yellowing suppression efficacy. The ΔE values (Fig. 7(g)) increased over time in all groups, indicating progressive color change. However, the g/T/P group showed minimal ΔE after 11 d, effectively delaying color change.

These quantitative color measurements (Figs. 7(e-g)) correlate directly with the reduced ethylene levels, confirming that the photocatalytic activity of the g/T/P film is

responsible for delaying the chlorophyll degradation and browning pathways that are normally triggered by ethylene.

3.5.4. Firmness

Firmness is a key indicator of quality changes in ‘Wushan plum’ during storage. The preservation of fruit texture, a critical commercial attribute, was quantified by measuring firmness (Fig. 8(a)). While all groups exhibited softening, the g/T/P group consistently maintained the highest firmness, validating the packaging's protective effect. This phenomenon is a direct consequence of the photocatalytic ethylene degradation. By scavenging ethylene, the film inhibits the expression of ethylene-dependent enzymes, such as polygalacturonase and pectinase, which are responsible for cell wall degradation and fruit softening^[39]. The PVA group showed browning and shrinkage of the fruit on the 7th day. The fruit was inedible despite increased firmness from surface dehydration.

3.5.5. Weight loss

Weight loss is a critical indicator of postharvest fruit quality, driven simultaneously by physical transpiration and physiological respiration. Weight loss rates increased across all groups during storage (Fig. 8(b)). The unpackaged control group showed the peak weight loss (26 %) by day 11 due to continuous air exposure. In comparison, the g/T/P group significantly reduced the weight loss rate, maintaining it at around 13 % after 11 d. Although the g/T/P film exhibited a higher water vapor transmission (WVT) than pure PVA (Fig. 6(e)), the packaged plums still achieved the lowest total weight loss. This indicates that the macroscopic weight retention is primarily attributed to the synergistic suppression of fruit respiration. Specifically, the active photocatalytic scavenging of ethylene delays climacteric ripening, while the film's inherent gas barrier properties (e.g., lower OTR) create a modified atmosphere. This combined effect drastically reduces the metabolic consumption of carbon substrates, which effectively offsets the slightly increased physical moisture loss.

3.5.6. Decay rate

As depicted in Fig. 8(c), decay onset varied among the different groups. Rotting started at day 3 in the control, PVA and g-C₃N₄/PVA groups, versus day 5 in the TiO₂/PVA and g/T/P groups. The g/T/P group had the slowest increase in decay rate and significantly lower decay levels than other groups during the 11-day storage. This enhanced preservation is likely due to the production of •O₂⁻ and •OH radicals (Fig. 3(g) and 3(h)) and other antimicrobial agents under LED light irradiation. These reactive species can damage microbial lipids, proteins, and DNA, causing impaired cell function or microbial death^[40]. Furthermore, ethylene degradation in g/T/P packaging delayed the ripening and enhanced the pathogen resistance. The findings highlighted that the functional g/T/P packaging effectively reduced decay (Fig. 8(c)). This is attributed to a dual mechanism: (i) the generation of reactive oxygen species at the film's surface, which can have an antimicrobial effect, and (ii) the primary function of ethylene degradation, which delays senescence and maintains the fruit's natural resistance to pathogens.

It is worth noting that while the generated ROS (•O₂⁻ and •OH) effectively scavenge ethylene, they may also gradually attack the polymer chains of the PVA matrix. Although no macroscopic structural failure or obvious embrittlement was observed during the 11-day storage trial, the potential decline in mechanical properties over extended periods of illumination cannot be ignored. Interestingly, from an environmental perspective, this ROS-mediated slow degradation could serve as an advantageous feature, facilitating the post-use degradation of the active packaging. The quantitative degradation kinetics of the PVA matrix and its evolution during the service period will be systematically investigated in our future studies.

3.5.7. Ascorbic acid and solid-acid ratio

Ascorbic acid is a key to evaluate the quality and nutritional value of plums, while also contributing to the maintenance of the sensory attributes and extended storage life. Ascorbic acid changes were displayed among the groups (Fig. 8(d)). During the storage, the ascorbic acid content fluctuated in all groups, but was more stable in the plums

packaged with the g/T/P film. The g/T/P group maintained higher ascorbic acid levels than controls during late storage. This effect was due to the g/T/P packaging's ability to degrade ethylene, reducing ascorbic acid oxidation. Additionally, inhibiting metabolic activities like respiration after harvest also helped preserve ascorbic acid levels^[41].

The solid-acid ratio is key to assessing fruit maturity. As plums ripen, SS content (mainly sugars) rises while TA content (mainly organic acids) falls, increasing the solid-acid ratio^[42]. The solid-acid ratio exhibited a general upward trend across all treatment groups during the storage (Fig. 8(e)). The g/T/P group maintained lower solid-acid ratios with more gradual changes than controls. This suggested that g/T/P packaging effectively reduced SS and organic acid consumption by suppressing plum metabolic processes during storage, maintaining a stable solid-acid ratio.

The g/T/P packaging preserved the ascorbic acid content and maintained a balanced solid-acid ratio, showing potential to enhance postharvest quality and extend shelf life of plums. By inhibiting ethylene accumulation and slowing the metabolism, the g/T/P packaging preserved the fruit's nutritional and sensory quality over time.

3.5.8. The plum preservation mechanism of the g/T/P packaging

Fig. 8(f) illustrates the mechanism of ethylene degradation during plum storage. Under LED illumination, both g-C₃N₄ and TiO₂ are photoexcited to generate e⁻-h⁺. As analyzed in Section 3.2.2, the composite system followed a Z-scheme charge transfer mechanism: photogenerated electrons in the CB of TiO₂ migrate to the interface and recombine with holes in the VB of g-C₃N₄. Meanwhile, the strongly reductive electrons retain in the CB of g-C₃N₄ (-1.085 eV) reduced O₂ to •O₂⁻, and the strongly oxidative holes retain in the VB of TiO₂ (+2.85 eV) oxidized H₂O/OH⁻ to •OH. Compared with conventional Type-II heterojunctions, the Z-scheme configuration achieves efficient spatial separation of charge carriers while preserving the maximum redox potentials of both components. The generated •O₂⁻ and •OH radicals act synergistically on C₂H₄, leading to its stepwise oxidation and eventual mineralization into CO₂ and H₂O. By continuously scavenging the accumulated ethylene within the packaging

microenvironment, this active photocatalytic process effectively suppresses the respiratory climacteric and delays the senescence of the plums during storage.

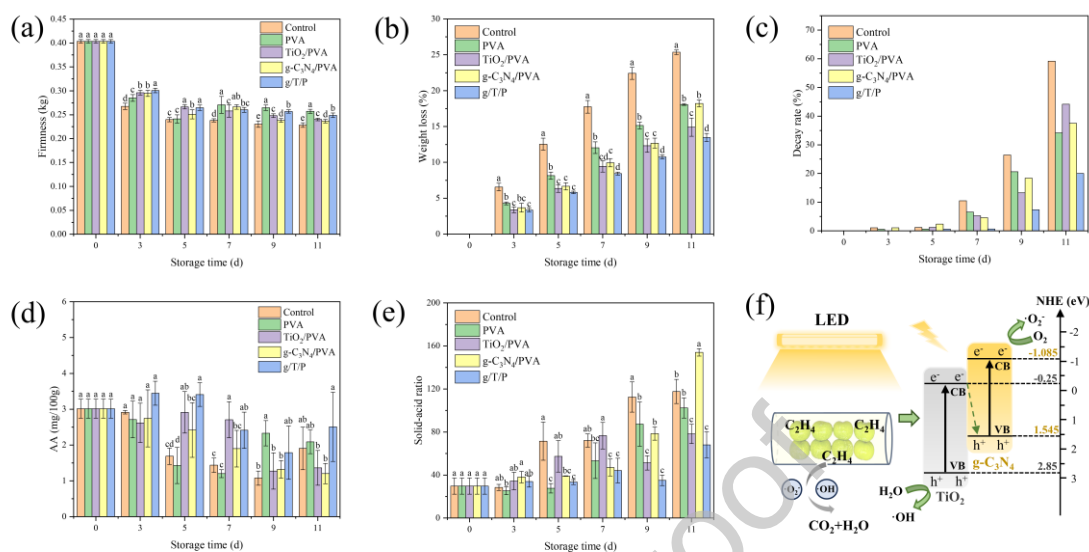


Fig. 8 Firmness (a), weight loss (b), decay rate (c), ascorbic acid (d) and solid-acid ratio (e) in different treatment groups and schematic diagram of the ethylene degradation mechanism (f).

4. Conclusions

In this study, we have successfully demonstrated the viability of a simple and scalable synthesis route—a green aqueous mixing method—for producing an efficient $\text{g-C}_3\text{N}_4/\text{TiO}_2$ photocatalyst for active packaging applications. Through systematic investigation, the optimal synthesis conditions were determined to be a $\text{g-C}_3\text{N}_4$ -to- TiO_2 mass ratio of 1:8 and a precursor calcination temperature of 500 °C. Comprehensive material characterization confirmed that this facile method achieves the formation of a direct Z-scheme heterojunction driven by strong interfacial electronic interactions. This configuration significantly enhances photogenerated charge separation and enables the mass generation of reactive oxygen species ($\cdot\text{O}_2^-$ and $\cdot\text{OH}$) to drive photocatalytic activity under LED light.

The optimized catalyst powder demonstrated a tangible ethylene degradation capacity of ~40 % in 10 h. When incorporated into a PVA film, the resulting composite

packaging retained significant efficiency, degrading ~33 % of ethylene under the same conditions. The proof-of-concept application in postharvest preservation was successful; the g-C₃N₄/TiO₂/PVA packaging effectively reduced ethylene accumulation, suppressed respiration, and delayed quality deterioration in ‘Wushan’ plums, extending their shelf life by 3–5 d. Although the green wet-chemical approach employed in this study may not achieve the photocatalytic efficiency of sophisticated sol-gel methods, this work establishes a crucial baseline and validates an industrially relevant manufacturing approach. These findings contribute valuable knowledge toward the development of cost-effective and scalable active packaging solutions, bridging the gap between laboratory-scale research and practical, commercial implementation in the food supply chain.

CRedit authorship contribution statement

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Data availability

All data generated or analyzed during this study are included in this published article.

References

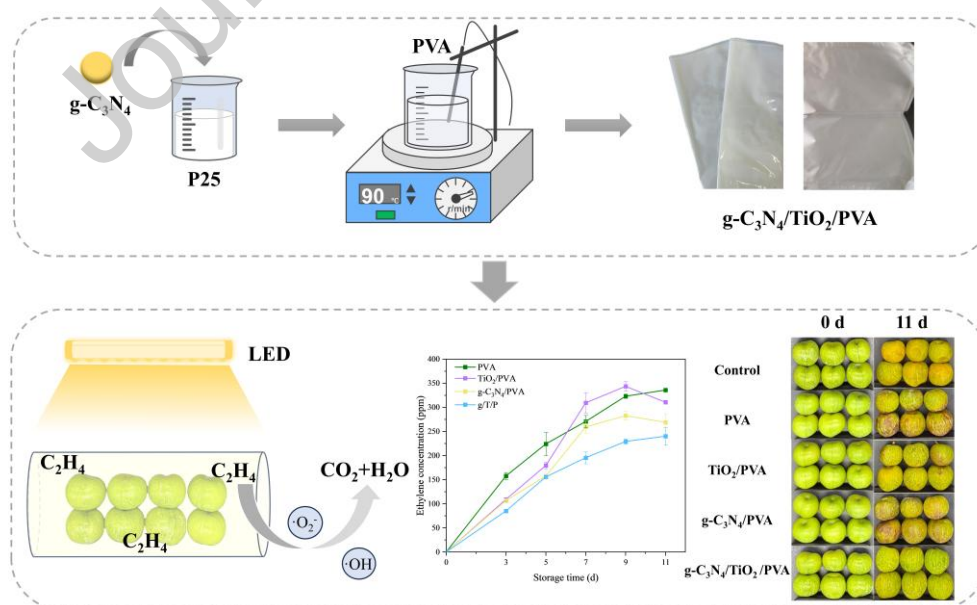
- [1] Y. Cheng, Y. Wang, L. Lou, et al., Transcriptomic analysis reveals the role of abscisic acid and ethylene in regulating starch-source biosynthesis associated with soft nose disorder in 'Keitt' mango fruit during postharvest, *Postharvest Biol. Technol.* 209 (2024) 112698. <https://doi.org/10.1016/j.postharvbio.2023.112698>.
- [2] M. Zakriya, A. Hussain, A.A. Mahdi, et al., Effect of different types of ethylene scavengers used in different combinations, on the post-harvest quality and phytochemicals retention of tomatoes (*Solanum lycopersicum* L.), *Chem. Biol. Technol. Agric.* 10 (2023) 90. <https://doi.org/10.1186/s40538-023-00465-w>.
- [3] R. Alonso-Salinas, S. López-Miranda, A.J. Pérez-López, et al., Strategies to Delay Ethylene-Mediated Ripening in Climacteric Fruits: Implications for Shelf Life Extension and Postharvest Quality, *Horticulturae* 10 (2024) 840. <https://doi.org/10.3390/horticulturae10080840>.
- [4] L. Hua, N. Li, W. Zhang, et al., Photocatalytic ethylene scavenging for fresh produce preservation: A comprehensive review, *Trends Food Sci. Technol.* 150 (2024) 104604. <https://doi.org/10.1016/j.tifs.2024.104604>.
- [5] N. Keller, M.-N. Ducamp, D. Robert, et al., Ethylene removal and fresh product storage: A challenge at the frontiers of chemistry. Toward an approach by photocatalytic oxidation, *Chem. Rev.* 113 (2013) 5029–5070. <https://doi.org/10.1021/cr900398v>.
- [6] W.-J. Ong, L.-L. Tan, Y.H. Ng, et al., Graphitic carbon nitride (g-C₃N₄)-based photocatalysts for artificial photosynthesis and environmental remediation: Are we a step closer to achieving sustainability?, *Chem. Rev.* 116 (2016) 7159–7329. <https://doi.org/10.1021/acs.chemrev.6b00075>.
- [7] J. Wen, J. Xie, X. Chen, et al., A review on g-C₃N₄-based photocatalysts, *Appl. Surf. Sci.* 391 (2017) 72–123. <https://doi.org/10.1016/j.apsusc.2016.07.030>.
- [8] N. Boonprakob, N. Wetchakun, S. Phanichphant, et al., Inceesungvorn, Enhanced visible-light photocatalytic activity of g-C₃N₄/TiO₂ films, *J. Colloid Interface Sci.* 417 (2014) 402–409. <https://doi.org/10.1016/j.jcis.2013.11.072>.
- [9] C.-Q. Ruan, W. Zhang, M. Zhao, et al., Preparation and characterization of g-C₃N₄-TiO₂ based photocatalyst and its effect on the delaying for the ripening of green banana under LED irradiation, *Postharvest Biol. Technol.* 230 (2025) 113774. <https://doi.org/10.1016/j.postharvbio.2025.113774>.
- [10] A. Belet, C. Wolfs, J.G. Mahy, et al., Sol-gel syntheses of photocatalysts for the removal of pharmaceutical products in water, *Nanomaterials* 9 (2019) 126. <https://doi.org/10.3390/nano9010126>.
- [11] M. Fu, J. Pi, F. Dong, et al., A cost-effective solid-state approach to synthesize g-C₃N₄ coated TiO₂ nanocomposites with enhanced visible light photocatalytic activity, *Int. J. Photoenergy.* 2013 (2013) 158496. <https://doi.org/10.1155/2013/158496>.
- [12] D. Navas, S. Fuentes, A. Castro-Alvarez, et al., Review on sol-gel synthesis of perovskite and oxide nanomaterials, *Gels* 7 (2021) 275.

- <https://doi.org/10.3390/gels7040275>.
- [13] W. Zhang, L. Hua, M. Zhao, et al., Engineering a Multifunctional g-C₃N₄/TiO₂ Active Packaging Film With Enhanced Barrier and Photocatalytic Properties for Postharvest Preservation of Plum Fruit, *Future Postharvest Food* (2026) fpf2.70051. <https://doi.org/10.1002/fpf2.70051>.
 - [14] D.R. Paul, R. Sharma, P. Panchal, et al., Silver Doped Graphitic Carbon Nitride for the Enhanced Photocatalytic Activity Towards Organic Dyes, *J. Nanosci. Nanotechnol.* 19 (2019) 5241–5248. <https://doi.org/10.1166/jnn.2019.16838>.
 - [15] A. Sewnet, E. Alemayehu, M. Abebe, et al., Single-Step Synthesis of Graphitic Carbon Nitride Nanomaterials by Directly Calcining the Mixture of Urea and Thiourea: Application for Rhodamine B (RhB) Dye Degradation, *Nanomaterials* (Basel) 13 (2023) 762. <https://doi.org/10.3390/nano13040762>.
 - [16] Z. Liu, J. Zhu, P. Wei, et al., Candidate for Magnetic Doping Agent and High-Temperature Thermoelectric Performance Enhancer: Hard Magnetic M-type BaFe₁₂O₁₉ Nanometer Suspension, *ACS Appl. Mater. Interfaces* 11 (2019) 45875–45884. <https://doi.org/10.1021/acsami.9b16309>.
 - [17] M. Zhang, T. Wang, C. Bian, et al., Designing novel step-scheme heterojunction g-C₃N₄/TMCs/GO with effective charge transfer for photocatalytic degradation of organic pollutant under visible light, *Sep. Purif. Technol.* 306 (2023) 122736. <https://doi.org/10.1016/j.seppur.2022.122736>.
 - [18] H. Xiao, T. Wang, Study on the catalytic activities of g-C₃N₄@TiO₂ hollow microspheres under UV–visible light, *J. Mater. Sci. Mater. Electron.* 32 (2021) 5104–5115. <https://doi.org/10.1007/s10854-021-05244-7>.
 - [19] F. Hu, S. Sun, H. Xu, et al., Investigation on g-C₃N₄/rGO/TiO₂ nanocomposite with enhanced photocatalytic degradation performance, *J. Phys. Chem. Solids* 156 (2021) 110181. <https://doi.org/10.1016/j.jpcs.2021.110181>.
 - [20] W. Tao, M. Wang, R. Ali, et al., Multi-layered porous hierarchical TiO₂/g-C₃N₄ hybrid coating for enhanced visible light photocatalysis, *Appl. Surf. Sci.* 495 (2019) 143435. <https://doi.org/10.1016/j.apsusc.2019.07.177>.
 - [21] D.R. Paul, R. Sharma, S.P. Nehra, et al., Effect of calcination temperature, pH and catalyst loading on photodegradation efficiency of urea derived graphitic carbon nitride towards methylene blue dye solution, *RSC Adv.* 9 (2019) 15381–15391. <https://doi.org/10.1039/C9RA02201E>.
 - [22] M. Li, B. Dong, Z. Chang, et al., Synthesis of TiO₂/g-C₃N₄ Photocatalyst with Recovered TiO₂ from Spent SCR Catalyst for Photodegrading Rhodamine B, *Waste Biomass Valorization* 14 (2023) 687–701. <https://doi.org/10.1007/s12649-022-01917-4>.
 - [23] R. Hao, G. Wang, C. Jiang, et al., In situ hydrothermal synthesis of g-C₃N₄/TiO₂ heterojunction photocatalysts with high specific surface area for Rhodamine B degradation, *Appl. Surf. Sci.* 411 (2017) 400–410. <https://doi.org/10.1016/j.apsusc.2017.03.197>.
 - [24] X. Du, X. Bai, L. Xu, et al., Visible-light activation of persulfate by TiO₂/g-C₃N₄

- photocatalyst toward efficient degradation of micropollutants, *Chem. Eng. J.* 384 (2020) 123245. <https://doi.org/10.1016/j.cej.2019.123245>.
- [25] C. Zhang, S. Xin, X. Wang, et al., Photoelectrocatalytic degradation of m-chloronitrobenzene through rGO/g-C₃N₄/TiO₂ nanotube arrays photoelectrode under visible light: Performance, DFT calculation and mechanism, *Sep. Purif. Technol.* 302 (2022) 121944. <https://doi.org/10.1016/j.seppur.2022.121944>.
- [26] A.A. Alothman, A. Ayub, S.K. Hachim, et al., Facile synthesis and comparative study of the enhanced photocatalytic degradation of two selected dyes by TiO₂-g-C₃N₄ composite, *Environ. Sci. Pollut. Res.* 30 (2023) 37332–37343. <https://doi.org/10.1007/s11356-022-24839-z>.
- [27] J. Wang, P. Ren, Y. Du, et al., Construction of tubular g-C₃N₄/TiO₂ S-scheme photocatalyst for high-efficiency degradation of organic pollutants under visible light, *J. Alloys Compd.* 947 (2023) 169659. <https://doi.org/10.1016/j.jallcom.2023.169659>.
- [28] J. Xie, W. Situ, R. Wang, et al., The visible light photocatalytic degradation of ethylene using a polyvinyl alcohol film loaded with Ag₂O-TiO₂-Bi₂WO₆ heterojunction microspheres, *Appl. Surf. Sci.* 584 (2022) 152562. <https://doi.org/10.1016/j.apsusc.2022.152562>.
- [29] N.M. Farrage, N.H. Teleb, W.A. Abd El-Ghany, Investigation of the structural and optical properties of Sb₂S₃/PVA/PVP nanocomposites blended sheets for optoelectronic applications, *Opt. Quantum Electron.* 56 (2024) 488. <https://doi.org/10.1007/s11082-023-06117-5>.
- [30] A. Ahmed, M.B.K. Niazi, Z. Jahan, et al., In-vitro and in-vivo study of superabsorbent PVA/Starch/g-C₃N₄/Ag@TiO₂ NPs hydrogel membranes for wound dressing, *Eur. Polym. J.* 130 (2020) 109650. <https://doi.org/10.1016/j.eurpolymj.2020.109650>.
- [31] S. Khimhun, B. Baro, A. Banerjee, et al., Hydrogen bonding mediated modified triboelectric characteristics of g-C₃N₄ nanosheet loaded PVA films for improved sweat sensing application, *Chem. Eng. J.* 532 (2026) 174566. <https://doi.org/10.1016/j.cej.2026.174566>.
- [32] Z. Qian, M. Wang, J. Li, et al., Preparation and Adsorption Photocatalytic Properties of PVA/TiO₂ Colloidal Photonic Crystal Films, *Gels* 10 (2024) 520. <https://doi.org/10.3390/gels10080520>.
- [33] J. Xie, R. Wang, Y. Li, et al., A novel Ag₂O-TiO₂-Bi₂WO₆/polyvinyl alcohol composite film with ethylene photocatalytic degradation performance towards banana preservation, *Food Chem.* 375 (2022) 131708. <https://doi.org/10.1016/j.foodchem.2021.131708>.
- [34] C. Yin, J. Qian, T. Guo, et al., Antibacterial photocatalytic films for effective degradation of organic compounds, *Res. Chem. Intermed.* 51 (2025) 195–215. <https://doi.org/10.1007/s11164-024-05447-7>.
- [35] X. Liu, C. Chen, Y. Cao, et al., Effect and enhancement mechanism of sodium lignosulfonate on the chitosan-based composite film, *Colloids Surf. Physicochem.*

- Eng. Asp. 678 (2023) 132505. <https://doi.org/10.1016/j.colsurfa.2023.132505>.
- [36] D. Qin, H. Liu, J. Yan, et al., Large-scale preparation of UV photo-crosslinked composite membrane with high pervaporation desalination properties and excellent fouling resistance, *J. Membr. Sci.* 691 (2024) 122175. <https://doi.org/10.1016/j.memsci.2023.122175>.
- [37] J. Li, T. Yao, Y. Xu, et al., Elevated CO₂ exposure induces core browning in Yali pears by inhibiting the electron transport chain, *Food Chem.* 378 (2022) 132101. <https://doi.org/10.1016/j.foodchem.2022.132101>.
- [38] X. Cui, Y. Ding, C. Sun, et al., Improving the storage quality and suppressing off-flavor generation of winter jujube by precise micro-perforated MAP, *Front. Plant Sci.* 15 (2024). <https://doi.org/10.3389/fpls.2024.1372638>.
- [39] A. Mditshwa, L.S. Magwaza, S.Z. Tesfay, et al., Postharvest quality and composition of organically and conventionally produced fruits: A review, *Sci. Hortic.* 216 (2017) 148–159. <https://doi.org/10.1016/j.scienta.2016.12.033>.
- [40] Y. Xie, A. Liu, E.R. Bandala, et al., TiO₂-biochar composites as alternative photocatalyst for stormwater disinfection, *J. Water Process Eng.* 48 (2022) 102913. <https://doi.org/10.1016/j.jwpe.2022.102913>.
- [41] M. Mujtaba, Q. Ali, B.A. Yilmaz, et al., Understanding the effects of chitosan, chia mucilage, levan based composite coatings on the shelf life of sweet cherry, *Food Chem.* 416 (2023) 135816. <https://doi.org/10.1016/j.foodchem.2023.135816>.
- [42] J. Zheng, Y. Wang, X. Zhou, et al., Correlation of released gases and quality classification of bananas during storage, *J. Food Meas. Charact.* 18 (2024) 4592–4600. <https://doi.org/10.1007/s11694-024-02516-8>.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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