Progressive Physics Journal
Volume 6, Nomor 1, Juni 2025
ISSN 2722-7707 (online)
http://jurnal.fmipa.unmul.ac.id/index.php/ppj

Preliminary Investigation of pH-Dependent Optical Properties of Curcumin-Derived Carbon Dots

Arum Sinda Santika[1*], Fitri Aulia Permatasari[2,3*], Ferry Iskandar[2,3]

[1)] *Department of Physics, Universitas Pembangunan Nasional "Veteran" Jawa Timur, Surabaya, Indonesia, 60294*
[2)] *Department of Physics, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, Jalan Ganesha 10, Bandung, West Java, Indonesia, 40132*
[3)] *Research Center for Nanoscience and Nanotechnology, Institut Teknologi Bandung, Jalan Ganesha 10 Bandung, West Java, Indonesia, 40132*

*E-mail korespondensi: arum.sinda.ft@upnjatim.ac.id; fauliap@itb.ac.id

Article Info:
Received: 01-06-2025
Revised: 26-06-2025
Accepted: 26-06-2025

Keywords:
Biomedical Applications
Carbon Dots
Photoluminescence
Curcumin
pH

Abstract

Carbon dots (CDs) are photoluminescent nanoparticles smaller than 10 nm with excellent optical properties, including high photostability, UV and visible light absorption, water solubility, low toxicity, and good biocompatibility. These features make them attractive for biomedical, optoelectronic, and catalytic applications. Curcumin, a polyphenol from turmeric, possesses anti-inflammatory, antibacterial, anticancer, and antiviral properties, but its poor water solubility limits its biomedical use. In this study, CDs were synthesized from curcumin and urea via a solvothermal method at 140 °C for 180 minutes to improve curcumin's solubility. The effect of pH on the optical properties of CDs was investigated by adjusting acidity with citric acid and alkalinity with NaOH. UV-Vis and photoluminescence (PL) spectroscopy revealed that the optical properties of CDs are strongly influenced by pH, likely due to the presence of keto-enol tautomerism in curcumin. The pH sensitivity of these curcumin-derived CDs highlights their potential for biomedical applications such as photothermal therapy, bioimaging, drug delivery, and antiviral agents.

Introduction

Carbon dots (CDs) are carbon-based quantum dots with diameters below 10 nm. These nanomaterials possess superior optical and chemical properties, including high photostability, low toxicity, tunable optical characteristics, good water solubility, and excellent biocompatibility.[1]–[3] These attributes make CDs highly attractive for a wide range of applications, including sensors, bioimaging, photocatalysis, supercapacitors, and biomedical fields. In particular, the development of CDs for biomedical applications has drawn increasing attention, owing to their potential roles in bio-labeling, photothermal therapy, drug delivery, and anticancer treatments.[4]–[6]

Curcumin, the principal component of turmeric (Curcuma longa), exhibits various therapeutic effects including anticancer, antioxidant, anti-inflammatory, antitumor, and antimicrobial properties. Its chemical structure ($C_{10}H_{21}O_6$), however, results in poor water solubility, limiting its physiological absorption and bioavailability—factors critical for its antiviral efficacy.[7], [8] To overcome this limitation, curcumin can be converted into hydrated

carbon dots through self-assembly in aqueous conditions, thereby enhancing its water solubility and biocompatibility.

Du et al. (2018) synthesized curcumin-derived CDs via a hydrothermal method to enhance its antiviral properties. The resulting CDs exhibited blue photoluminescence, with absorption peaks at 225 and 282 nm and emission wavelengths ranging from 460 to 501 nm depending on excitation from 310 to 400 nm.[9] Similarly, Lin et al. (2019) synthesized CDs via pyrolysis of curcumin at various temperatures to improve its water solubility and antiviral activity. However, although the resulting CDs showed good antiviral activity, their photoluminescence decreased significantly compared to the original curcumin.[10] These studies have not investigated and explained the dependence of curcumin-derived carbon dots under acidic and alkaline conditions. CDs are often functionalized with pH-responsive groups to optimize their performance in the acidic TME. For instance, CDs doped with gadolinium (Gd^{3+}) exhibit pH-dependent optical and magnetic properties, with enhanced relaxivity at acidic pH (5.5) compared to physiological pH (7.4).[11] Similarly, TiO2-immobilized CDs demonstrate pH-triggered fluorescence "on/off" behavior, enabling selective targeting of acidic tumor environments.[12] The pH dependence of carbon dots significantly influences their efficacy in photothermal cancer therapy. By leveraging the acidic tumor microenvironment, pH-responsive CDs achieve selective drug release, enhanced heat generation, and targeted tumor ablation. Their integration with chemotherapy and imaging capabilities further amplifies their therapeutic potential. As research progresses, the optimization of these systems will pave the way for their clinical application in cancer treatment.

Curcumin is a natural polyphenol responsible for turmeric's yellow color and possesses a keto-enol tautomeric structure.[13] This tautomerism is pH-sensitive and strongly influences the photophysical properties of curcumin in aqueous media. In water, the keto form dominates, producing yellow fluorescence, whereas the enol form, more prevalent in organic solvents, appears reddish and exhibits reduced fluorescence with increasing pH. Under basic conditions, the acidic phenolic groups deprotonate to form phenolate ions, increasing both solubility and biocompatibility. Therefore, studying the effect of pH on curcumin-derived CDs is essential for evaluating their antiviral potential and solubility in aqueous environments.[14], [15]

In this study, curcumin-derived carbon dots were synthesized to enhance the biomedical properties and water solubility of curcumin by pH dependence. Because the pH dependence of CDs related to cancer therapy, which cancer cells has acider than normal cells. CDs also was evaluated the acid–base response of curcumin-derived CDs, which in turn is influenced by the keto-enol tautomeric structure. Their optical properties—absorbance and photoluminescence—were compared to those of pristine curcumin under varying pH conditions to understand their responsiveness and potential biomedical applications.

Method

1. Materials and Sample Preparation

This study involved two samples: (1) curcumin (5 mg/mL), dissolved in ethanol, and (2) curcumin-derived carbon dots (CDs), synthesized using curcumin and urea ($CO(NH_2)_2$) as the primary precursors. Citric acid ($C_6H_8O_7$) and sodium hydroxide (NaOH) were used to adjust the acidic and basic conditions, respectively, while ethanol was employed as the solvent throughout the experiments. The synthesized curcumin CDs were later subjected to pH variation using citric acid (for acidic conditions) and sodium hydroxide (for basic conditions), followed by optical characterization to evaluate their pH-dependent behavior.

2. Synthesis Carbon dots

Curcumin (0.2 g) and urea (1.5 g) were dissolved in 40 mL of ethanol at room temperature and stirred using a magnetic stirrer at 500 rpm for 15 minutes until a homogeneous solution was obtained. Care was taken to ensure complete dissolution of both curcumin and urea, with no visible precipitate. The resulting solution was then transferred into a Teflon-lined stainless steel autoclave and subjected to a solvothermal treatment at 140 °C for 3 hours.

In addition, a reference sample of pristine curcumin was prepared by dissolving curcumin in ethanol at a concentration of 5 mg/mL without any solvothermal processing. This sample was used as a control for comparative analysis in the pH-dependent optical property studies.

3. pH Characterization

Citric acid (CA) and sodium hydroxide (NaOH) were used to evaluate the pH sensitivity of the curcumin-derived carbon dots (CDs). Various molar concentrations of CA and NaOH were added to create acidic and basic environments for both the synthesized curcumin CDs and pristine curcumin. After the solvothermal synthesis, the resulting dark red curcumin CDs solution was diluted 100-fold with ethanol. A 30 mL aliquot of the diluted solution was then mixed with 400 µL of either CA or NaOH solution.

The same treatment was applied to the pristine curcumin solution, which initially had a pH of 8.77. After adjustment, the pH values of the pristine curcumin samples were 4.87 and 10.48. In comparison, the as-synthesized curcumin CDs had an initial pH of 10.46. After the addition of citric acid, the pH was reduced to 5.77. Each sample thus represented both acidic and basic conditions, and was subsequently subjected to photoluminescence and UV-Vis absorbance analysis.

4. Photoluminescence and Absorbance Characterization

Photoluminescence (PL) measurements were performed at room temperature using an excitation wavelength of 500 nm. This analysis aimed to evaluate the emission behavior of both pristine curcumin and curcumin-derived CDs under different pH conditions. In addition to PL measurements, UV-Visible absorbance spectroscopy was conducted to determine the wavelength regions absorbed by the samples.

Prior to measurement, all pH-adjusted samples were further diluted 30-fold to ensure optimal optical density for spectral analysis. These characterizations were used to investigate how the optical properties of curcumin and its carbon dot derivatives respond to variations in acidity and alkalinity

Result and Discussion

Curcumin, with the IUPAC name [(1E,6E)-1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione], exists in two tautomeric forms: diketone and keto-enol. As a natural polyphenol responsible for the yellow color of turmeric, curcumin is highly sensitive to pH due to keto-enol tautomerism (Figure 1).[16] At room temperature, the keto form tends to predominate; however, the enol form is energetically more stable in the solid phase and may constitute up to 95% of the structure depending on the solvent.[17]

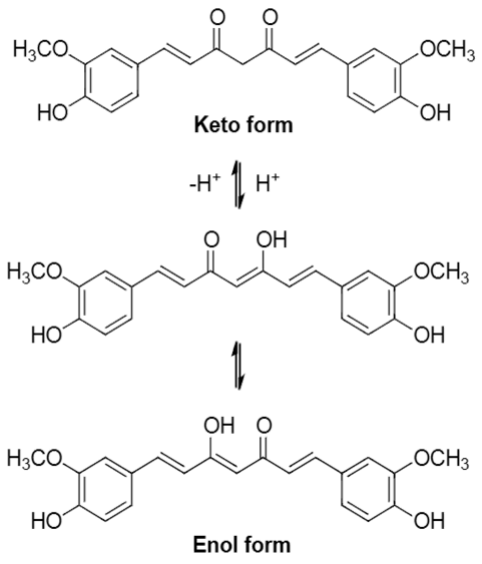

Figure 1. Reversible keto-enol form of curcumin.[16]

Curcumin contains three key reactive functional groups: one diketone group and two phenolic groups, which are primarily responsible for its biological activity. In particular, the anticancer activity of curcumin is strongly influenced by the hydroxyl groups (-OH) on the phenolic rings.[18] These phenolic rings are present in both tautomeric forms but are more stable in the enol form due to aromatic stabilization.[14]

When curcumin is treated with a base, the keto form is converted to the enol form, resulting in a significant increase in fluorescence intensity and a dramatic color change from bright yellow to orange-red. This transformation underscores the critical role of pH in modulating the optical properties of curcumin and its derivatives.[14]

The visible color and photoluminescence responses of pristine curcumin under different pH conditions were evaluated. Figures 2 illustrate In acidic (pH 4.8), curcumin retained its bright yellow color under visible light, indicating the dominance of the keto form, which is associated with high fluorescence emission, as pristine curcumin with pH neutral condition as showed in Figure S1. At a basic pH of 10.5, curcumin exhibited a deep red color in visible light and showed no fluorescence under UV light, suggesting a shift toward the enol form and a corresponding quenching of fluorescence.

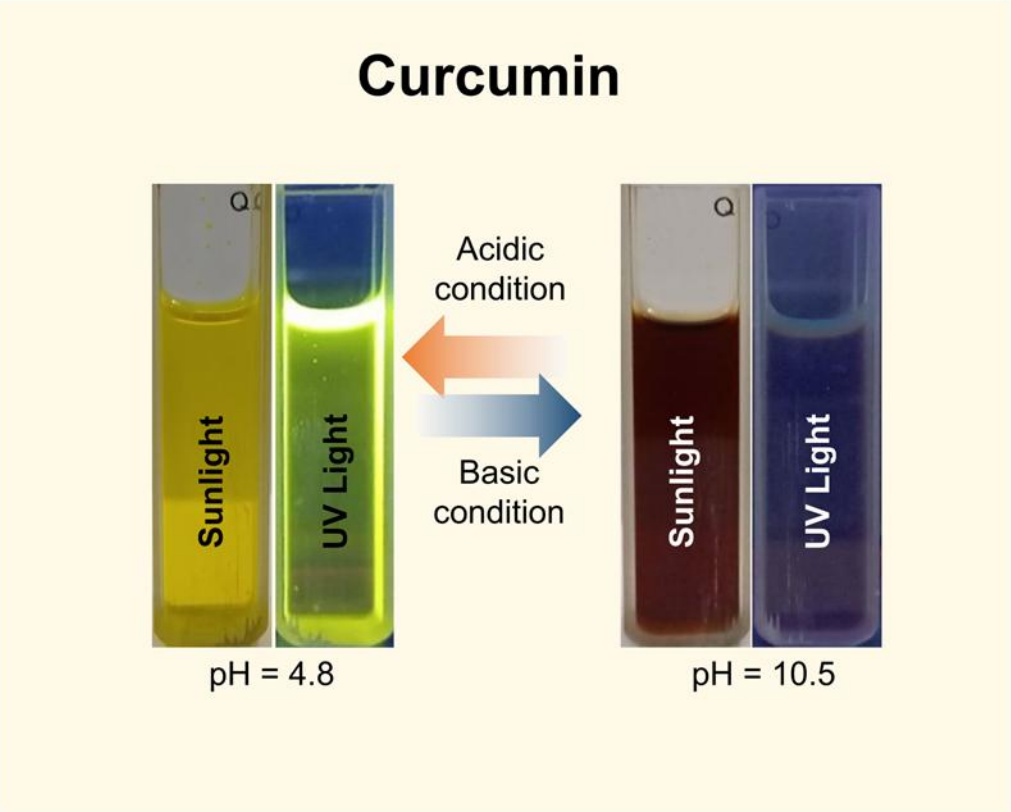

Figure 2. Curcumin in visible light and UV light under pH condition.

Figures 3 present similar behavior for curcumin-derived CDs. Under visible light, the CDs appeared bright yellow in acidic conditions (pH 5.7) and deep red under basic conditions (pH 10.4). Under UV light, the acidic curcumin CDs exhibited intense fluorescence, while the basic samples showed significantly reduced emission. These findings are consistent with previous reports, where acidification promotes the keto form, leading to bright yellow coloration and enhanced fluorescence, while alkalization shifts the equilibrium toward the enol form, resulting in red coloration and diminished emission intensity.

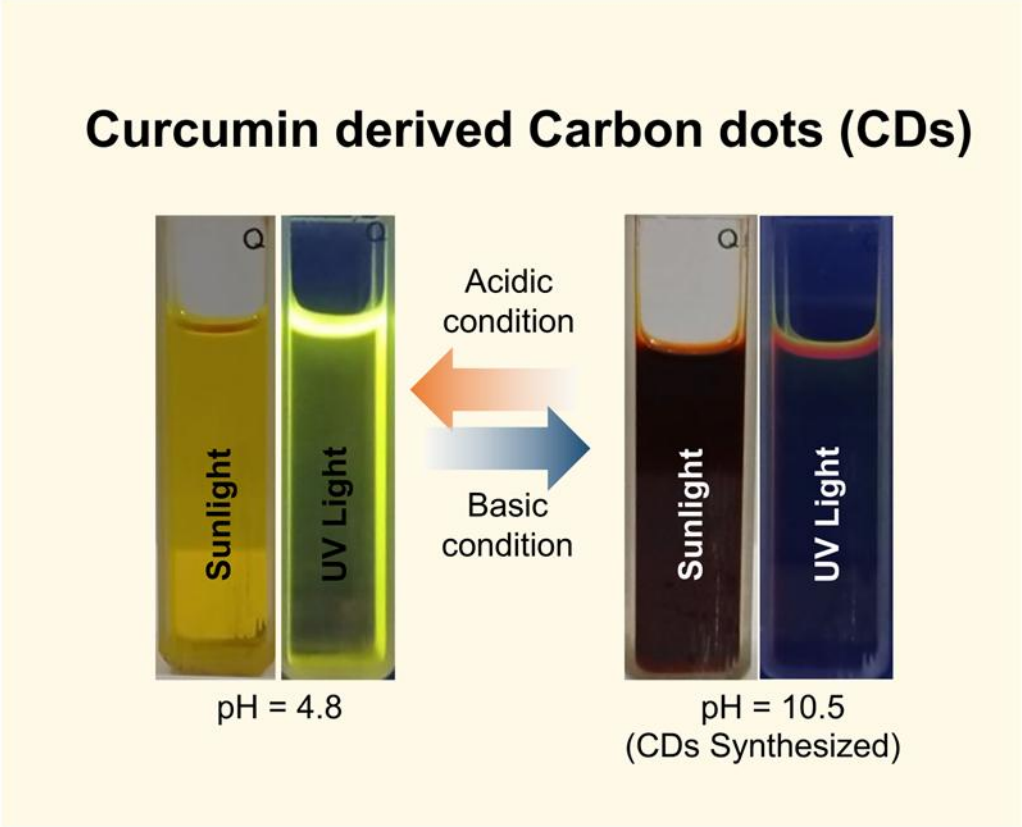

Figure 3. Curcumin-derived CDs in visible light and UV light under pH condition.

Figure 4 shows the UV-Vis absorbance spectra of pristine curcumin dissolved in ethanol under acidic and basic conditions. At its native pH of 8.7, pristine curcumin exhibited a maximum at 423 nm and a shoulder near 261 nm, in figure denotes as intial. The overall features of the spectrum are found to be similar to those reported in previous studies.[13]–[15] These peaks correspond to the π–π* transitions of the dominant keto-enol tautomeric form.[15] Upon acidification using citric acid (adjusted to pH 4.8), the intensity of the 261 nm peak decreased slightly and shifted to 264 nm, while the 423 nm peak remained relatively stable, indicating that the enol form (responsible for the 423 nm band) is more resistant to proton-induced disruption and remains energetically favored.[14] In contrast, the addition of NaOH resulted in a substantial hypsochromic (blue) shift and intensity reduction of the 423 nm peak, which moved to approximately 352 nm. This ~71 nm shift suggests a significant tautomeric transformation from the enol to the diketone form, consistent with deprotonation and rearrangement of the electronic structure in a basic environment.[17]

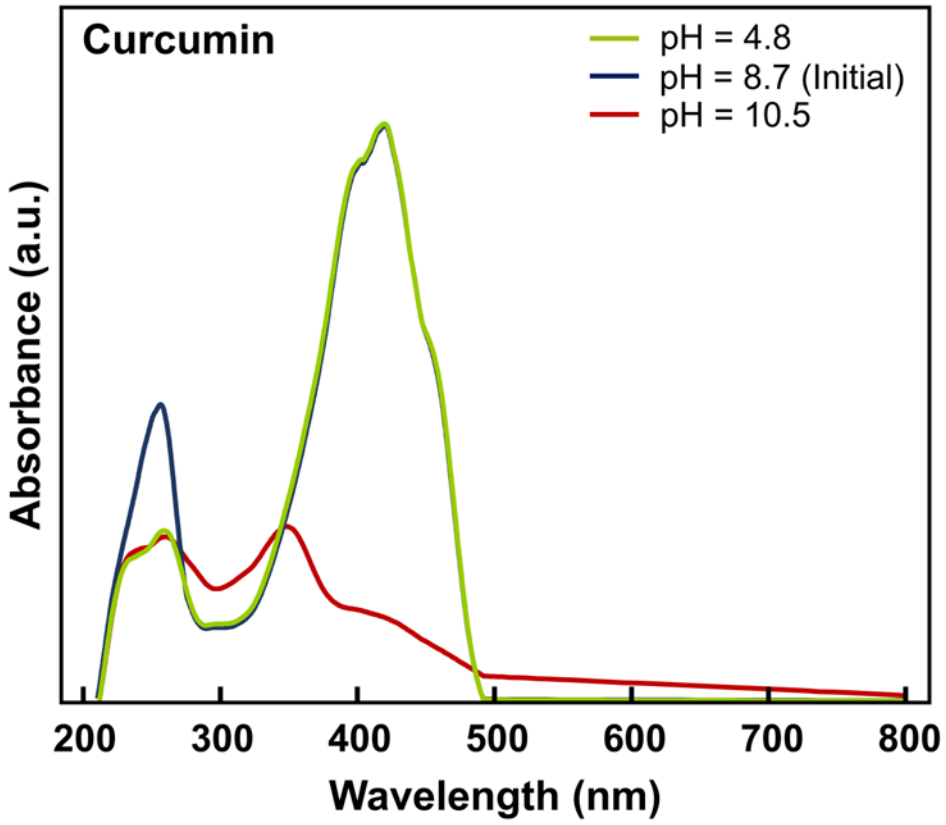

Figure 4. the UV-Vis absorbance spectra of pristine curcumin dissolved in ethanol under acidic and basic conditions.

Figure 5 presents the UV-Vis spectra of curcumin-derived CDs synthesized via a solvothermal method. The CDs in their native basic condition (pH 10.4) exhibited a strong absorbance peak at 422 nm—similar in position to the enol peak of pristine curcumin but without the suppression observed in the base-treated curcumin sample. This suggests that the CDs retain a stable enol-like structure even in basic conditions, potentially due to stabilization from surface passivation or nitrogen functionalities derived from urea. UV-Vis characterization revealed absorbance features at specific wavelengths corresponding to curcumin's tautomeric structures. In general, the dominant form in solid and solution phases is the planar keto-enol tautomer stabilized by intramolecular hydrogen bonding, with an absorption band typically in the range of 408–434 nm due to π–π* transitions.[15] Variations in temperature, solvent polarity, and pH can promote the stabilization of the non-planar diketone form, resulting in a broadened absorption shoulder around 355 nm. Previous studies have shown that the equilibrium between diketone and keto-enol forms in curcumin can evolve over time, as indicated by spectral changes—specifically, a decrease in the absorbance peak at 428 nm (enol form) and an increase in the shoulder around 351 nm (diketone form).

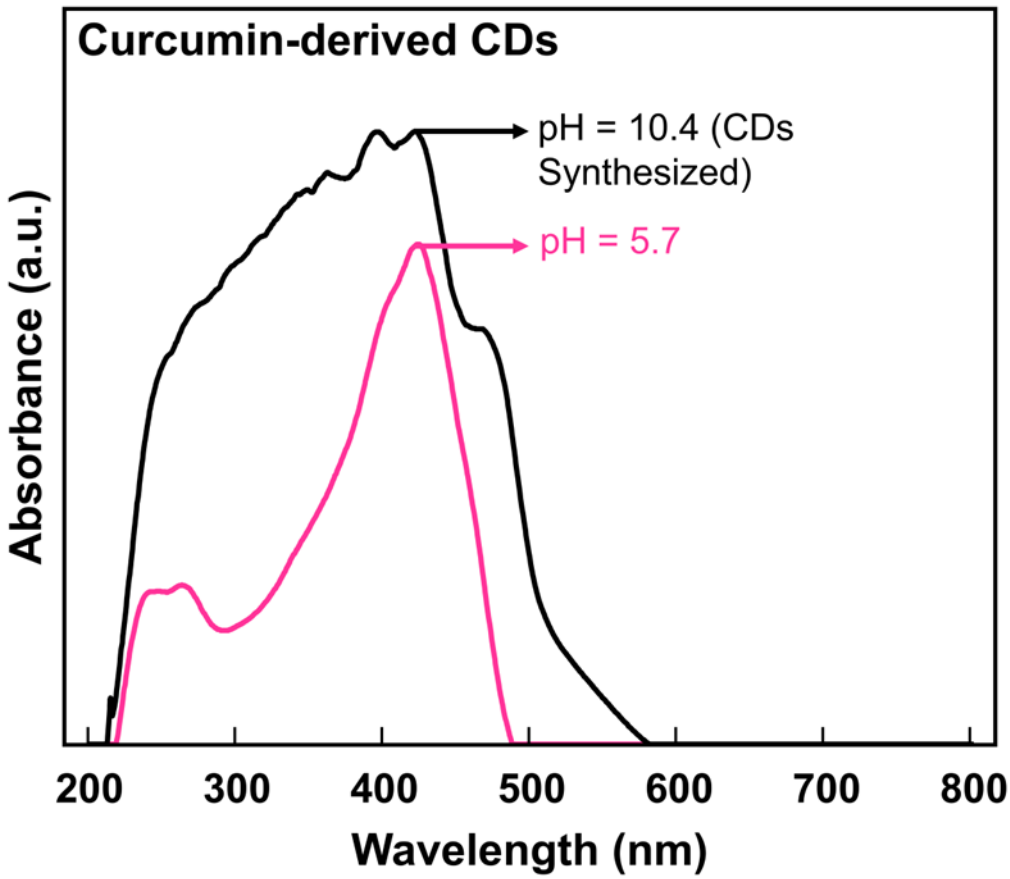

Figure 5. the UV-Vis absorbance spectra of curcumin-derived CDs dissolved under acidic and basic conditions.

When citric acid was added to adjust the pH to 5.7, the absorbance intensity at 422 nm decreased without a noticeable shift in wavelength. Additionally, a new peak emerged at 245 nm, indicating possible structural rearrangements or new electronic transitions due to the protonation of functional groups on the CD surface.[17] This behavior suggests that under acidic conditions, curcumin CDs undergo partial conversion from enol to keto forms, resulting in decreased absorbance in the visible region and new absorption features in the UV region. These spectral changes indicates that both pristine curcumin and curcumin-derived CDs exhibit pH-sensitive optical responses, with the CDs demonstrating more stable absorbance profiles under basic conditions and distinct structural transitions under acidification.

Fluorescence spectra of both pristine curcumin and curcumin-derived carbon dots (CDs) were analyzed under varying pH conditions. As shown in Figure 6(a), the fluorescence intensity of pristine curcumin at its native pH of 8.7 (mildly basic) was relatively low when excited at 500 nm. Interestingly, a marked increase in fluorescence intensity occurred when the pH was adjusted to 4.8, indicating enhanced emission. This suggests that at pH 4.8, curcumin predominantly adopts the keto tautomeric form, which is associated with its bright yellow appearance and strong fluorescence emission. Conversely, the addition of NaOH to increase the pH caused a significant decrease in fluorescence intensity, along with a red-shift of approximately 113 nm. This spectral shift is attributed to the transformation from the fluorescent keto form to the non-emissive enol form, which is characterized by a dark red color and weak fluorescence.

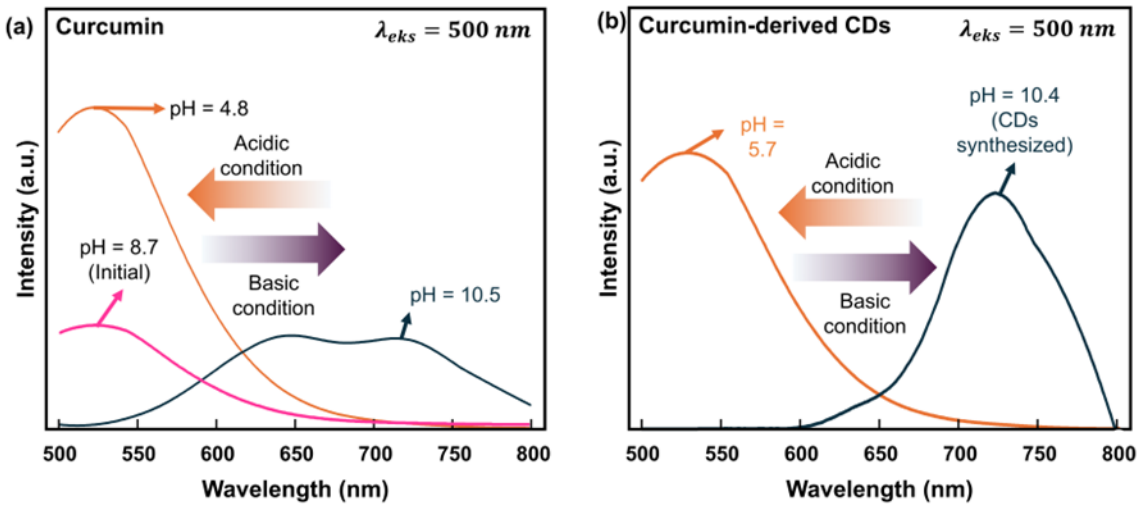

Figure 6. Fluorescence spectra of (a) curcumin and (b) curcumin-derived CDs dissolved under acidic and basic conditions, with excitation wavelength 500 nm.

In Figure 6(b), the normalized fluorescence spectra of curcumin-derived CDs show a different pH response. At basic pH (10.4), the CDs displayed low fluorescence intensity, suggesting dominance of the enol form. Upon acidification to pH 5.7, a significant increase in fluorescence intensity was observed, accompanied by a red-shift of approximately 180 nm. This behavior implies that the acidic environment promotes conversion from the enol to the more emissive keto form in the CDs, enhancing fluorescence emission.

Similar with curcumin, curcumin-derived CDs displayed a blue-shift upon acidification. This trend highlights the structural similar between curcumin and its carbon dot derivative. In the CDs, the dominant enol structure at basic pH leads to reduced fluorescence. Upon acid addition, structural rearrangement toward the keto form enhances emission intensity.These results indicates that both curcumin and curcumin-derived CDs exhibit pH-dependent fluorescence behavior, with the CDs showing greater sensitivity and tunability, making them promising candidates for pH-responsive fluorescence applications.

Conclussion

The study of the optical properties of curcumin and curcumin-derived carbon dots (CDs) under varying pH conditions demonstrates that curcumin exhibits keto-enol tautomerism, which plays a critical role in its optical behavior. In acidic environments, the keto form predominates, resulting in a bright yellow color under visible light and strong fluorescence emission. Under basic conditions, the keto form is converted into the enol form, producing a dark red color and significantly reduced fluorescence intensity.

This keto-enol equilibrium also influences curcumin's antiviral properties. The enol form provides greater stability to the phenolic ring, which is believed to enhance antiviral activity. Consequently, the formation of curcumin-derived CDs not only improves the water solubility and optical tunability of curcumin but also potentially enhances its biocompatibility. These findings suggest that curcumin CDs hold significant promise for biomedical applications, particularly in cancer therapy.

Acknowledgment

Recognize those who helped in the research, especially funding supporters of your research. Include individuals who have assisted you in your study: Advisors, Financial

supporters, or many other supporters, i.e., Proofreaders, Typists, and Suppliers who may have given materials.

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