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Original Article

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Modulating Selectivity of Avocado Seed-Derived Carbon Dots Toward Pesticides: Role of Synthesis Temperature on Paraquat Detection

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Abstract: *The widespread use of pesticides in agriculture has boosted productivity but raised environmental and health concerns due to their persistence and toxicity. In this study, carbon dots (CDs) were synthesized from avocado seed, a sustainable biomass precursor, via carbonization at 250, 400, and 600 °C. The influence of synthesis temperature on structural, surface, and optical properties was systematically examined along with the sensing performance towards pesticides. All the proposed nanoprobes were tested against malathion, dimethoate, dichlorvos, diazinon, paraquat, propiconazole, glyphosate, and chlorpyrifos. Results revealed a clear synthesis temperature-dependent selectivity toward paraquat, attributed to variations in surface functionality and electronic structure that modulate CDs interaction with the analytes and charge-transfer processes. Paraquat was detected with a limit of detection (LOD) of ~2.5µM. These findings highlight the critical role of synthesis conditions in tuning specificity and provide insight into the relationships among structure, optical properties, and selectivity of biomass-derived CDs for pesticide sensing.*

Keywords: *Carbon Dots, Paraquat, Temperature-dependent, Selectivity, Optical Sensor, Pesticides.*

INTRODUCTION

Extensive pesticide use in modern agriculture has significantly enhanced crop productivity; however, their persistence and toxicity pose serious environmental and health concerns [1]. Frequently used pesticides such as malathion, dimethoate, dichlorvos, diazinon, paraquat, propiconazole, glyphosate, and chlorpyrifos are often detected in soil and aquatic systems due to excessive usage and improper disposal. Regulatory agencies, including the World Health Organization (WHO), have established permissible limits for pesticide residues in water and food; however, their continuous input and accumulation often exceed these thresholds, leading

to bioaccumulation and associated ecological and health risks [2]. These concerns highlight the need for sensitive, selective, and reliable detection strategies for effective environmental monitoring.

A variety of analytical techniques have been developed for pesticide detection, including high-performance liquid chromatography (HPLC) [3], liquid chromatography–tandem mass spectrometry (LC–MS/MS) [4], gas chromatography (GC) [5], capillary electrophoresis (CE) [6], and electrochemical sensing methods. Although these approaches provide high sensitivity and selectivity, they are often constrained by complex sample preparation, high operational costs, significant solvent consumption, and limited portability. Moreover, the need for sophisticated instrumentation and skilled operation limits their applicability to rapid, on-site environmental monitoring. These limitations motivate the development of alternative sensing platforms that are simple, cost-effective, and environmentally sustainable.

Similarly, conventional remediation strategies for pesticide-contaminated environments often rely on adsorption using activated carbon, polymeric materials, or other engineered sorbents. Although effective, these approaches may suffer from limited selectivity, regeneration challenges, and the risk of secondary pollution. In this context, biomass-derived materials have emerged as promising alternatives due to their low cost, environmental compatibility, and abundant availability. Carbon dots (CDs), a class of quasi-spherical carbon-based nanomaterials typically smaller than 10 nm, have emerged as promising candidates for sensing applications due to their unique electronic structure and surface chemistry [7]. CDs exhibit tunable photoluminescence arising from a combination of quantum confinement effects and surface-state emissions, which are strongly influenced by surface functional groups such as hydroxyl, carboxyl, and amino moieties [8-10]. These functional groups not only impart excellent aqueous dispersibility but also serve as active sites for interaction with target analytes through electrostatic attraction, coordination, and π–π interactions. The ease of synthesis, chemical stability, low toxicity, and structural tunability further enhance their applicability in environmental sensing.

Among the investigated pesticides, paraquat (1,1′-dimethyl-4,4′-bipyridinium dichloride) is a widely used non-selective contact herbicide. Since its introduction in the 1960s, it has been extensively applied in agriculture for rapid weed control due to its ability to disrupt photosynthetic processes and induce rapid plant tissue damage upon contact. Despite its effectiveness, paraquat is recognized as one of the most toxic herbicides to humans and animals, posing serious health and environmental risks. Acute exposure can lead to severe multi-organ damage, particularly affecting the lungs, kidneys, and liver, with progressive pulmonary fibrosis being the most critical and often fatal outcome [11][12]. In addition to these considerations, carbon dots are particularly attractive for fluorescence-modulation-based sensing applications. In this work, pesticide detection is achieved via a fluorescence-quenching mechanism, in which the emission intensity of CDs is reduced upon interaction with analyte molecules [13][14]. The magnitude of fluorescence reduction correlates with analyte concentration, enabling quantitative analysis. Notably, a significantly enhanced quenching response was observed for paraquat compared to other tested pesticides, indicating a preferential interaction. This behavior is attributed to the electron-deficient nature of paraquat and its strong affinity toward the electron-rich functional groups on the CD surface, facilitating charge-transfer interactions that modulate the emissive states. Recent efforts have increasingly focused on synthesizing CDs from renewable biomass and biowaste precursors [15], which inherently contain heteroatoms such as nitrogen, sulfur, and oxygen. These heteroatoms can be

incorporated into the carbon framework during synthesis, thereby modifying electronic structures and enhancing surface reactivity without the need for post-synthetic functionalization. Such intrinsic doping not only improves photoluminescence properties but also strengthens analyte–surface interactions, which are critical for sensing performance.

In this study, carbon dots (CDs) were synthesized from avocado seed, an abundant biomass precursor, via carbonization at three different temperatures (250, 400, and 600 °C). The study systematically investigated how synthesis temperature influences the structural, surface, and optical properties of the CDs, as well as their corresponding sensing performance. The CDs were evaluated for their ability to detect multiple pesticides, including malathion, dimethoate, dichlorvos, diazinon, paraquat, propiconazole, glyphosate, and chlorpyrifos. A clear temperature-dependent selectivity toward paraquat was observed, highlighting the critical role of synthesis conditions in tuning analyte specificity. This behavior is attributed to variations in surface functionality and electronic structure, which govern analyte–surface interactions and charge-transfer processes. These findings provide insight into the structure–property–selectivity relationships of biomass-derived CDs for selective pesticide sensing.

METHODOLOGY

Synthesis and characterization of CDs

CDs were synthesized by direct carbonization of avocado seed biowaste. Finely ground avocado seed powder was dried and subjected to thermal treatment in a muffle furnace at three distinct temperatures (250, 400, and 600 °C) for 2 h each. Thermal carbonization resulted in dark black materials at 250 °C (CDs-250) and 400 °C (CDs-400), while processing at 600 °C produced a distinctly dark gray product (CDs-600). The resulting material was further ground and dispersed in deionized water (10 mg/mL), followed by sonication for 4 h. The suspension was centrifuged at 13,000 rpm, 30 min and then filtered through 2.5 µm filter paper. The resulting solution (effective concentration of 2.5mg/ml, measured gravimetrically) was stored in a refrigerator for subsequent analysis. The absorbance spectra were obtained using a Perkin-Elmer Lambda 950 spectrophotometer, while fluorescence measurements were carried out with a Varian Cary Eclipse Fluorescence Spectrometer. FTIR spectra were recorded using a Varian 660-IR spectrophotometer, and X-ray photoelectron spectroscopy (XPS) analyses were performed with a Thermo Scientific Escalab 250Xi instrument. All pesticides used in this study were commercial formulations.

Evaluation of the selectivity of CDs towards pesticides

In addition to visual monitoring of the samples under UV and daylight illumination, the selectivity of CDs toward various pesticides (malathion, dimethoate, dichlorvos, diazinon, paraquat, propiconazole, glyphosate, and chlorpyrifos) was evaluated using a 1:1 (CDs: pesticide) volumetric ratio at a pesticide concentration of 2 mM and the stock solution of CDs. To evaluate the relative sensitivity of CDs to paraquat (volumetric proportion 1:1), the fluorescence intensity was measured at varying concentrations of the pesticide solution (5-1000 µM) in the presence of a fixed concentration of CDs.

RESULTS AND DISCUSSION

Basic characterization of carbon dots

Structural and optical characteristics of the synthesized CDs were comprehensively examined through FTIR, XPS, UV-Vis absorption, and photoluminescence (PL) analyses. FTIR provided

insights into the surface functional groups, while XPS revealed elemental composition and chemical states. UV-Vis absorption characterized electronic transition features, and PL analysis elucidated emission behavior and defect-related states. Together, these complementary techniques established a detailed understanding of the synthesis-temperature-dependent structure-property relationships of avocado seed-derived CDs.

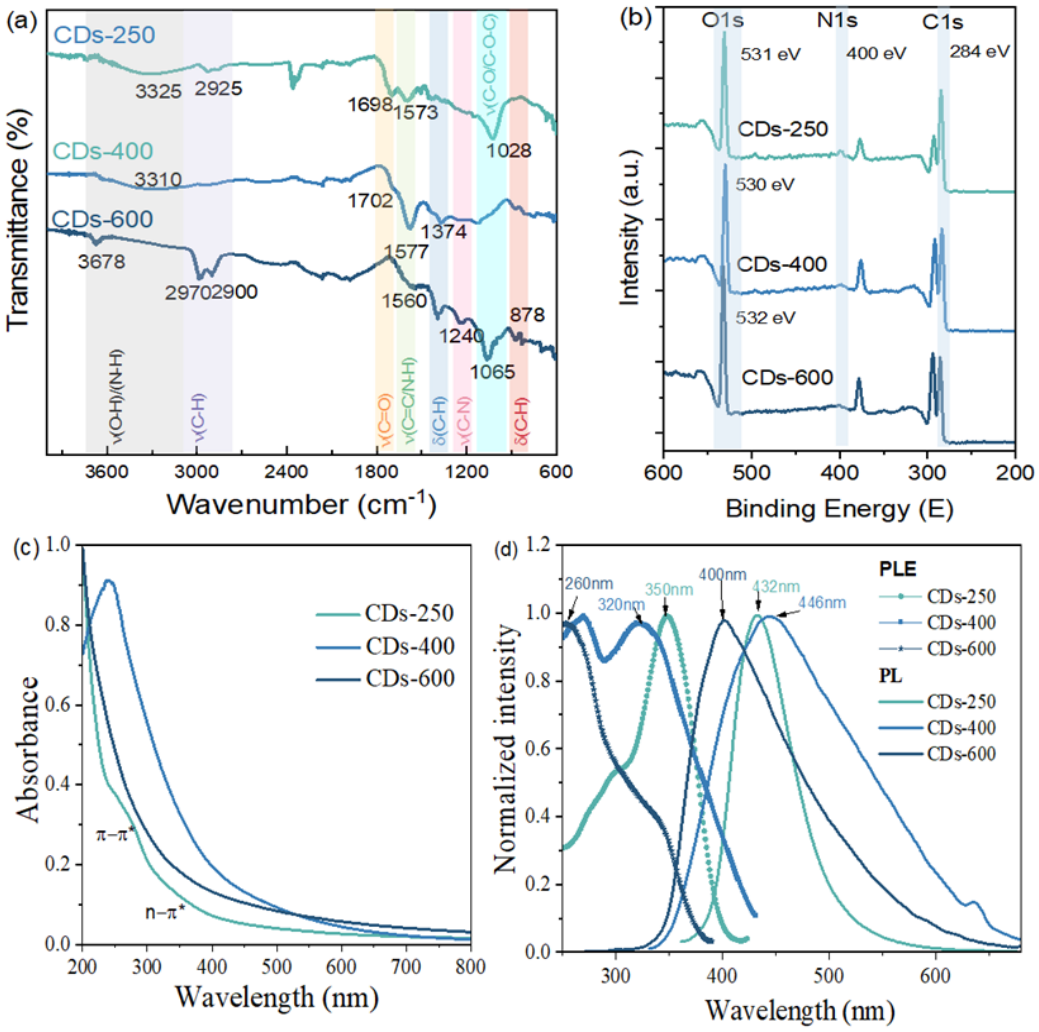

Figure 1: (a) FTIR spectra, (b) XPS survey scan, (c) UV-vis absorbance spectroscopy, and (d) Photoluminescence emission and excitation (PLE) corresponding to CDs-250, CDs-400 and CDs-600.

Figure 1(a) displays the comparative FTIR spectra of CDs-250, CDs-400, and CDs-600. The absorption bands observed around 3300–3325 cm^{-1} are characteristic of the stretching vibrations of hydroxyl (–OH) and/or amino (–NH/–NH_2) functional groups, whereas this signal is found to decrease with an increase in synthesis temperature (almost flat in CDs-600). The signals with a peak at approximately 2970-2900 cm^{-1} correspond to the C-H stretching vibration, typically associated with aliphatic C-H bonds. The spectra show for CDs-250, a pronounced absorption peak around 1702 cm^{-1}, which confirms the stretching vibrations of carbonyl (C=O) functionalities. The intensity of this band diminishes significantly for CDs-400 and disappears entirely for CDs-600. The band at 1570 cm^{-1} could indicate the C=C stretching or N–H bending/deformation in nitrogen-doped CDs. As the synthesis temperature rises, the band becomes wider and more pronounced, likely due to enhanced formation of

aromatic graphitic domains. Peak at 1240 cm^{-1} is attributed to C–N stretching vibrations, 1065 cm^{-1} is ascribed to the stretching vibration of C–O or C–O–C functionalities and 878 cm^{-1} is associated with out-of-plane aromatic C-H bending [16-18].

The XPS survey scan reveals two pronounced peaks corresponding to C1s (284eV) and O1s (531eV), along with a very weak signal attributed to N1s (400eV), indicating the presence of carbon and oxygen-containing functional groups with minor nitrogen incorporation in the three avocado seeds derived CDs as shown in Figure 1(b) [17]. Figure 1(c) displays the absorbance bands, with a prominent feature at 240nm corresponding to the transition of C=C bonds in the carbon core. A weaker band at ~340 nm, is attributed to the transitions of C=O and C=N groups, indicating the presence of oxygen and nitrogen-containing functional moieties on the surface of the CDs [19]. The maximum emission spectra of CDs-250, CDs-400, and CDs-600, together with their corresponding photoluminescence excitation (PLE) spectra, are presented in Figure 1(d). CDs-250 exhibit a sharp PL peak maximum centered at 432 nm when excited at 350 nm, reflecting the relatively well-defined electronic states of the lower-temperature product. Upon increasing the synthesis temperature to 400 °C, the resulting CDs display a broader emission profile, with the maximum band shifted to 446 nm under 320 nm excitation. This broadening and red shift suggest enhanced structural complexity and surface state contributions. In contrast, CDs-600 show a distinct maximum emission in the ultraviolet region at 400 nm (excitation at 320 nm), indicating significant modification of the electronic structure at higher synthesis temperatures, likely due to increased graphitization and altered surface functionalities.

As an additional result, the relative quantum yield (QY), measured with respect to Rhodamine 6G, is found to decrease with increasing synthesis temperature: 9% for CDs-250, dropping to 2-3% for CDs-400 and CDs-600.

Optical response of CDs-250 towards pesticides

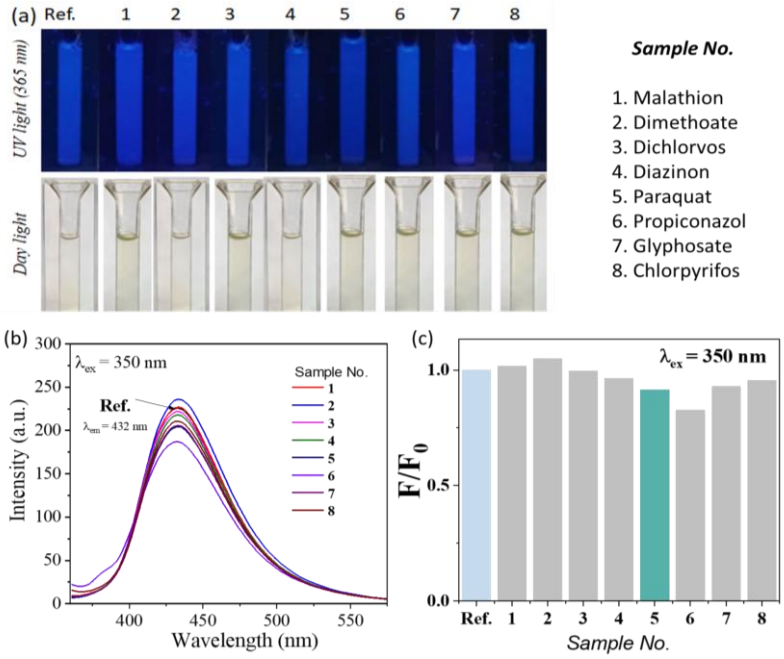

Figure 2: (a) Photographic images under UV-light (365nm) and daylight, (b) PL spectra recorded at 350 nm excitation, and (c) relative fluorescence intensity (F/F_0) of CDs-250 (PL response of pure CDs-250, F_0, was used as reference), showing minimal variations upon exposure to eight toxic pesticides.

In order to test the selectivity of CDs-250 towards pesticides, the optical response of avocado seed-derived CDs (at 250 °C) was assessed by monitoring variations in PL spectra. Figure 2(a) shows photographic images of the reference sample (CDs-250) and CDs in the presence of 1 mM paraquat, appearing as a semitransparent solution under daylight and exhibiting blue emission under 365 nm UV excitation. Figure 2(b) and 2(c) present the PL spectra and relative fluorescence intensity (F/F_0), respectively, which indicate no significant specificity toward several of the eight toxic pesticides tested.

Optical response of CDs-400 towards pesticides

Increasing the synthesis temperature of avocado seed–derived CDs from 250 °C to 400 °C clearly modified their PL response toward pesticides. As shown in Figure 3(a), the CDs-400 (reference and with pesticides) solutions appear brown under daylight and exhibit a bright green emission under UV excitation, except in the case of paraquat, where the emission is weaker and shifts toward a blue-green color. According to Figures 3(b) and (c), the PL spectrum of CDs-400 is blue-shifted by 16 nm and quenched by approximately 50% in the presence of paraquat.

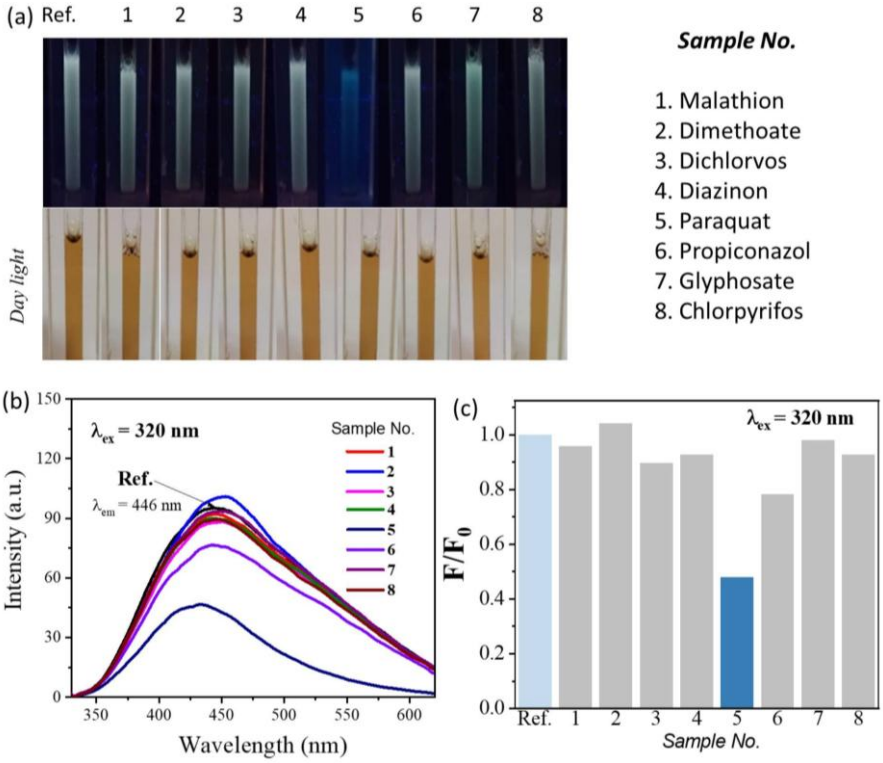

Figure 3: (a) Photographic images under UV-light (365nm) and daylight, (b) PL spectra recorded at 350 nm excitation, and (c) relative fluorescence intensity (F/F_0) of CDs-400 used as reference, showing variations upon exposure to eight toxic pesticides.

Selectivity of CDs-600 towards pesticides

The CDs-600 nanoprobes demonstrated high specificity toward paraquat. As shown in Figure 4(a), both the reference and CDs/paraquat solutions exhibit a slight brown coloration under daylight; however, upon excitation at 365 nm, apart from some changes in the presence dimethoate and glyphosate, CDs-600 become non-emissive with paraquat. The PL spectral changes in Figure 4(b) reveal a shift in the maximum emission from 400 nm (reference) to 396 nm (blue-shift) for CDs-600 exposed to paraquat, accompanied by complete fluorescence quenching (exceeding 85%) as shown in Figure 4(c).

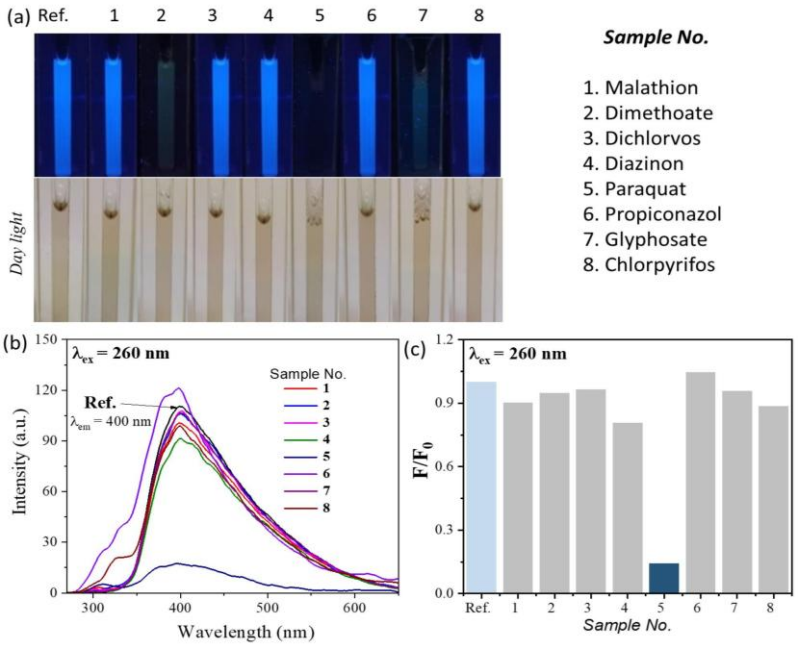

Figure 4: (a) Photographic images under UV-light (365nm) and day light, (b) PL spectra recorded at 350 nm excitation and (c) relative fluorescence intensity (F/F_0) of CDs-600 used as reference, showing variations upon exposure to eight toxic pesticides.

Comparison of the responses of three different CDs towards paraquat and possible interaction mechanism

Figure 5(a) presents a comparison of the photoluminescence response of the three CDs synthesized at 250, 400, and 600 °C toward paraquat, showing a progressive decrease in PL intensity. This trend is further evidenced in Figure 5(b), where the relative fluorescence diminishes as the synthesis temperature increases.

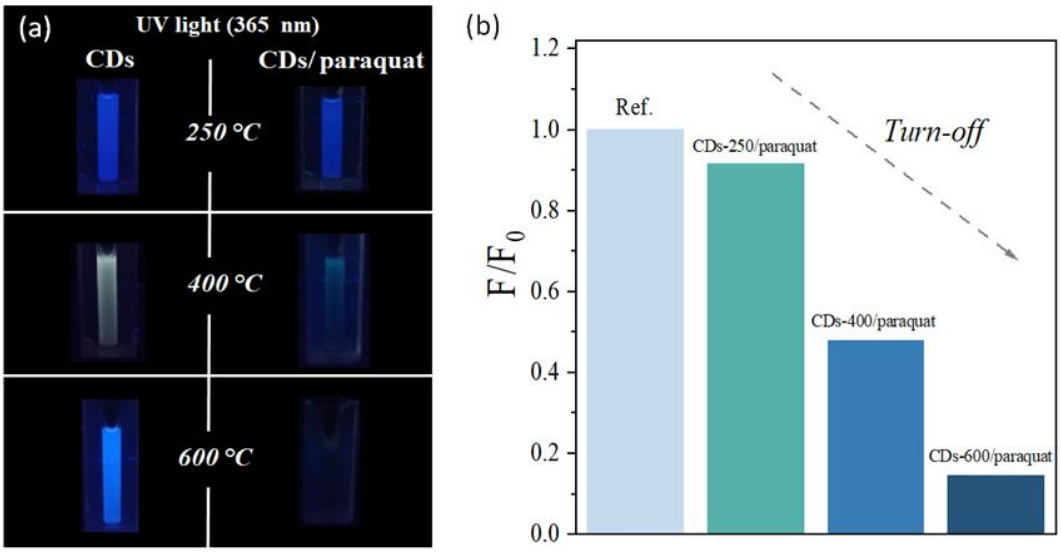

Figure 5: (a) Photographic images of CDs and CDs/paraquat under UV-light (365nm) and day light, and (b) relative fluorescence intensity (F/F_0) of reference compared with CDs-250, CDs-400 and CDs-600 in the presence of the toxic paraquat.

Graphitization alters both the electronic structure and the surface chemistry of the CDs [20]. Paraquat was quenched more efficiently by CDs synthesized at higher temperatures, owing to

their increased degree of graphitization. Greater graphitization enhances the formation of extended sp^2 domains, which provide delocalized -electron systems capable of stronger stacking interactions with the planar paraquat molecules [21-23]. In addition, the improved electronic conductivity and reduced band gap of graphitized CDs facilitate more efficient electron transfer to paraquat, an electron acceptor, thereby promoting non-radiative relaxation pathways. The reduced abundance of oxygen-rich functional groups at higher synthesis temperatures also shifts the balance toward charge transfer processes rather than radiative recombination. Together, these structural and electronic modifications could explain how paraquat exhibits stronger fluorescence quenching with CDs of higher graphitic character [24].

Sensitivity of CDs-600 towards paraquat

To evaluate the sensitivity of CDs-600 towards paraquat, Figure 6(a) presents the photoluminescence (PL) spectra of the reference CDs-600 along with its response to paraquat concentrations ranging from 5 to 1000 µM. Figure 6(b) shows the Stern–Volmer plot fitting of the fluorescence quenching data, yielding a determination coefficient (R^2) of 0.99. The limit of detection (LOD) was calculated to be 2.5 using the 3σ/K method, where σ represents the standard deviation of the blank and K is the slope of the calibration curve.

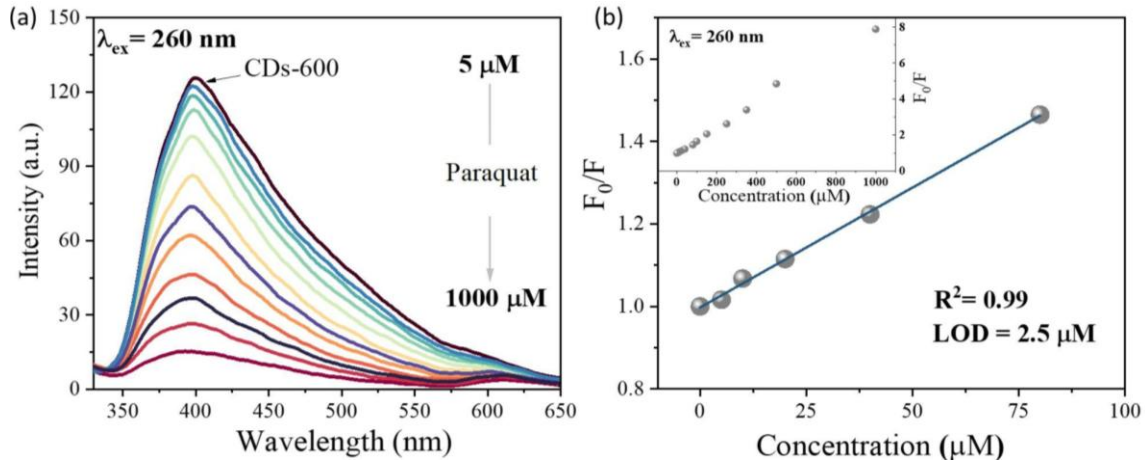

Figure 6: (a) PL spectra of CDs-600 nanoprobes for paraquat detection across the concentration range of 5-1000, and (b) Stern–Volmer plot fitting of the fluorescence response.

CONCLUSION

This study demonstrates avocado seed derived CDs can serve as sustainable nanomaterials for pesticide sensing, with synthesis temperature playing a decisive role in tuning their structural and optical properties. Increasing carbonization temperature leads to reduced quantum yield and altered surface functionalities, directly impacting analyte interactions. Among the eight tested pesticides, paraquat exhibited clear synthesis-temperature dependent selectivity, with CDs achieving a detection limit of 2.5 µ M. These findings highlight the importance of synthesis conditions in controlling structure-property-selectivity relationships and underscore the potential of biowaste derived CDs as ecofriendly sensors for monitoring toxic agrochemicals.

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