Study of the Photophysical Properties of Carbon Dots Derived from Banana Peels From Different Cities Used to Produce Ink and Film Fluorescence

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In this study, carbon dots (CDs) were synthesized via microwave, using precursor banana peel extract from different cities (Maceió and Aracaju) to evaluate their optical and structural properties. In addition, the volumes of the extract were varied for laboratory scale-up tests. DLS analyses showed that the most significant size frequencies for all CDs were less than 10 nm. UV-Vis and FTIR absorption spectra indicated the presence of aromatic groups and heteroatoms. In addition, the CDs showed excitation wavelength-dependent emission, with maximum intensities at 457 nm. The results indicate the high robustness of the method and its potential application in the production of fluorescent films and inks.
Keywords: Nanoparticle. Carbon Dots. Green Synthesis. Reproducibility.

Introduction

Carbon dots (CDs) are luminescent carbon nanoparticles that exhibit sizes smaller than 10 nm and physicochemical properties, good dispersion in water, biocompatibility, photostability, low toxicity, and vast emission range in the visible region [1].Morphologically, CDs are formed by a core containing functional groups on the surface, composed of sp^2 and sp^3 hybridized carbons, respectively. In turn, the literature suggests that the groups present on the surface of these nanoparticles are responsible for their optical properties, such as excitation wavelength-dependent/independent emission [2]. Therefore, many efforts have been employed to synthesize CDs due to their various applications, which stand out in their use in optoelectronic devices and invisible inks in anti-counterfeiting processes [3]. However, after its accidental discovery by Xu and colleagues in 2004, the methods for obtaining CDs were limited to onerous processes, referred to as laser ablation and electrochemical oxidation, in addition to using expensive materials [4]. However, simpler processes have been adopted since 2010 to reduce environmental impacts and facilitate the synthetic routes of CDs, such as using precursors from renewable sources [5].

In 2020, researchers synthesized carbon dots by hydrothermal method using banana peels and obtained CDs with emissions in the blue, producing fluorescent ink [6]. However, the work has a long synthesis time and needs to present reproducibility tests since the composition of the residue may change due to different species and climatic conditions. In this regard, a study conducted in 2015 by Zhang and colleagues used pollens from different flowers (colza, camellia, and lotus) to analyze the reproducible nature of CDs through their optical and structural properties [7]. Meiling and colleagues (2016) conducted a similar study using different types of starches as precursors [8]. Both works have highlighted the importance of reproducibility testing to ensure that the properties of carbon dots remain similar, even if the same biomass is from different species and/or localities.

In this study, we extracted banana peels from the cities of Maceió and Aracaju to prepare CDs with different volumes via microwave. This process ensured the material's reproducibility and scaling to be evaluated through photophysical properties and applied as inks and fluorescent films.

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Materials and Methods

Materials

The banana peels were obtained from supermarkets in Maceió and Aracaju's cities. The solution of sodium hydroxide (NaOH) 5 mol/L was prepared in the laboratory, and distillate water was used during synthesis, purification, and characterization.

Synthesis and Purification of Carbon Dots (CDs) (Figure 1)

Banana peels from the city of Maceió were triturated in a food processor with 1 L of distilled water to prepare 25 mL, 50 mL, and 100 mL samples. All were filtered using a plastic sieve to remove residues, and every sample was added 1 mL, 2 mL, and 4 mL of sodium hydroxide, respectively. The extracts were then submitted in microwave reaction for 2 mins at 630 W. The resultants supernatants were centrifuged at 13000 rpm for 10 min and filtered on 0.22 µm membranes to remove larger particles. The CDS procured from the 25 mL (CDS-M25), 50 mL (CDS-M50), and 100 mL (CDS-M100) volumes were stored in a refrigerator. The method was reproduced for banana peels from the city of Aracaju, named CDS-A25, CDS-A50, and CDS-A100, for 25 mL, 50 mL, and 100 mL, respectively.

Preparation of Fluorescent Film

150 mg of PVA [Poly(polyvinyl alcohol)] were dissolved in 5 mL of water under stirring at 85º C on the heating plate for 3 min. After cooling, 60 µL of glycerol (plasticizing agent) was added to the solution. Then, 100 µL of the CDs were added to the mixture, which was transferred to the plastic petri dish (35mm x 10mm). Finally, the film solution remained in the oven at 50 °C for 30 h for drying. The method was applied separately for each CD.

Preparation of Fluorescent Ink

The fluorescent inks were prepared using the solutions of the CDs (0.01 g/mL). The solutions were employed in the brush pen for writing on commercial filter paper, which was subjected to UV light under 360 nm radiation to visualize the words.

Characterizations Techniques

The quantity of light absorbed by the samples, diluted at 25µL/2mL, was measured by UV-VIS spectroscopy. In addition, the dynamic light scattering (DLS) technique was used to evaluate the dimensions of the nanoparticles in suspension. Additionally, in order to characterize the functional and bonding groups present in the CDs, 10µL of each solution were dripped separately onto approximately 50 mg of KBr and subjected to heating in the oven (around 90 ºC, for 4h), obtaining the dry samples in which tablets were prepared for the acquisition of Fourier Transform Infrared Spectroscopy (FTIR) observations. Finally, the photostability and fluorescence of the CDs were analyzed using a spectrofluorometer with the samples diluted to 25µL/2mL. For this study, the photostability was analyzed for 60 min, and the emission spectra obtained were excited in the 300 nm to 440 nm wavelength.

Results and Discussion

Figure 2A/B shows the dynamic light scattering (DLS) histograms of CDS-M25 and CDS-A25, in which the nanoparticles of CDS-M25 are mainly distributed in the range of 3.8 – 9.0 nm with an average diameter of 5.33 ± 0.12 nm. The distribution of CDS-A25 is in the same range, but its average diameter is 6.22 ± 0.22 nm. Both sizes are similar to works in the literature that used banana peel as precursor material [6,9].

The chemical compositions of the CDS from the different cities were characterized by FTIR spectra (Figure 3A). Broadbands are visualized around 3450 cm^{-1}, assigned to O-H/N-H stretching vibrations,

Figure 1. Schematic representation of carbon dots synthesis.

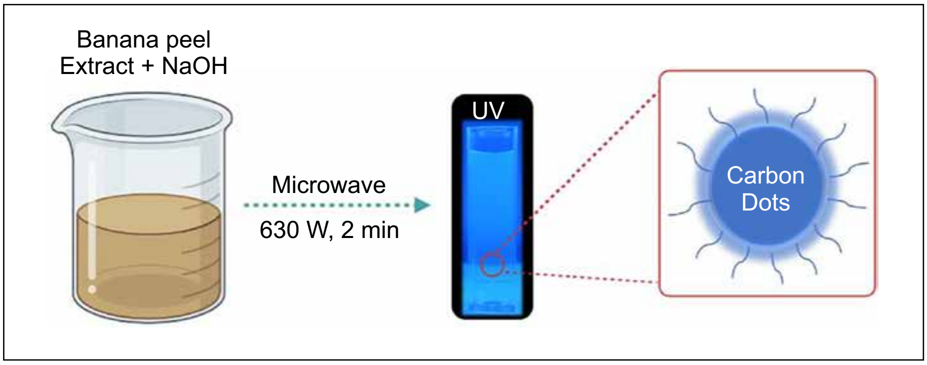
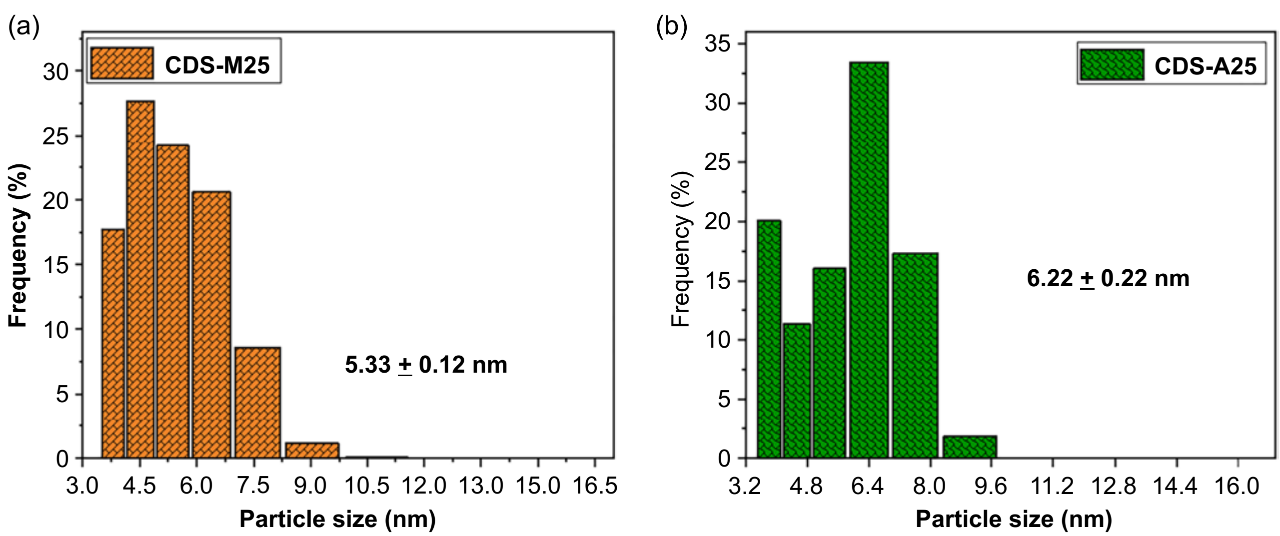


Figure 2. Dynamic light scattering (DLS) histogram of carbon dots.



and C=O and aromatic ring (C=C) groups are identified at 1646 cm^{-1} and 1585 cm^{-1}, respectively, indicating the sp^3 and sp^2 hybridizations of the CDS. C-N, C-O bonds, and S=O vibrations are found at 1340 cm^{-1}, 1085 cm^{-1}, and 1043 cm^{-1}, respectively, revealing the presence of nitrogen, oxygen, and sulfur, which may have been derived from the amino acid tryptophan, vitamin B6 and B2 found in the precursor [6,9,10]. Oxygen on the surface groups favors the hydrophilic behavior of these nanoparticles, facilitating their applications due to high dispersion in water. Figure 3B shows the UV-VIS absorption plots of the CDS obtained from both cities (Maceió and Aracaju), with absorption peaks centered at 266 nm and 327 nm. The highest energy peak, visualized around 266 nm, is characteristic of the $\pi - \pi^*$ bond of C=C associated with the aromatic ring (sp2). The second peak, at around 327 nm, is attributed to the $n - \pi^*$ transition referring to groups present on the surface, convenient of the C=O and C=N of sp^3 carbon [10].

The photoluminescence of CDS-M25 and CDS-A25 was analyzed at different excitation wavelengths ranging from 300 to 440 nm. The fluorescence spectra demonstrate that the carbon dots' emission depends on the excitation wavelength and most of the works reported in the literature [9] (Figure 4A/C). Upon increasing the excitation wavelength, the emission is shifted from blue to green due to the different energy levels on

Figure 3. FTIR (a) and UV-vis (b) spectra of carbon dots.

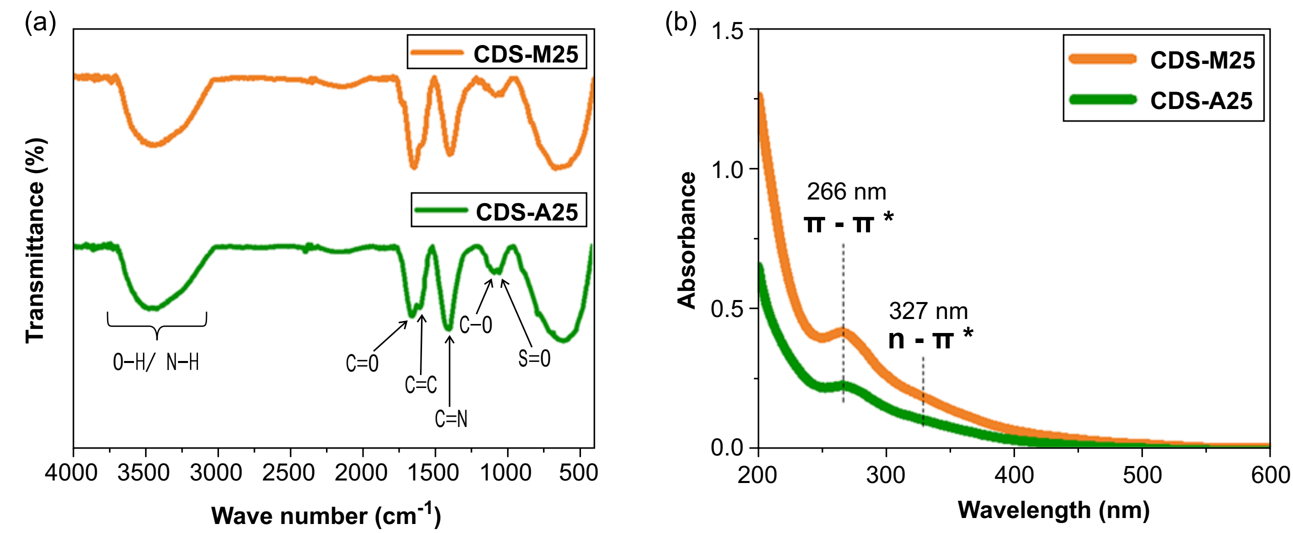
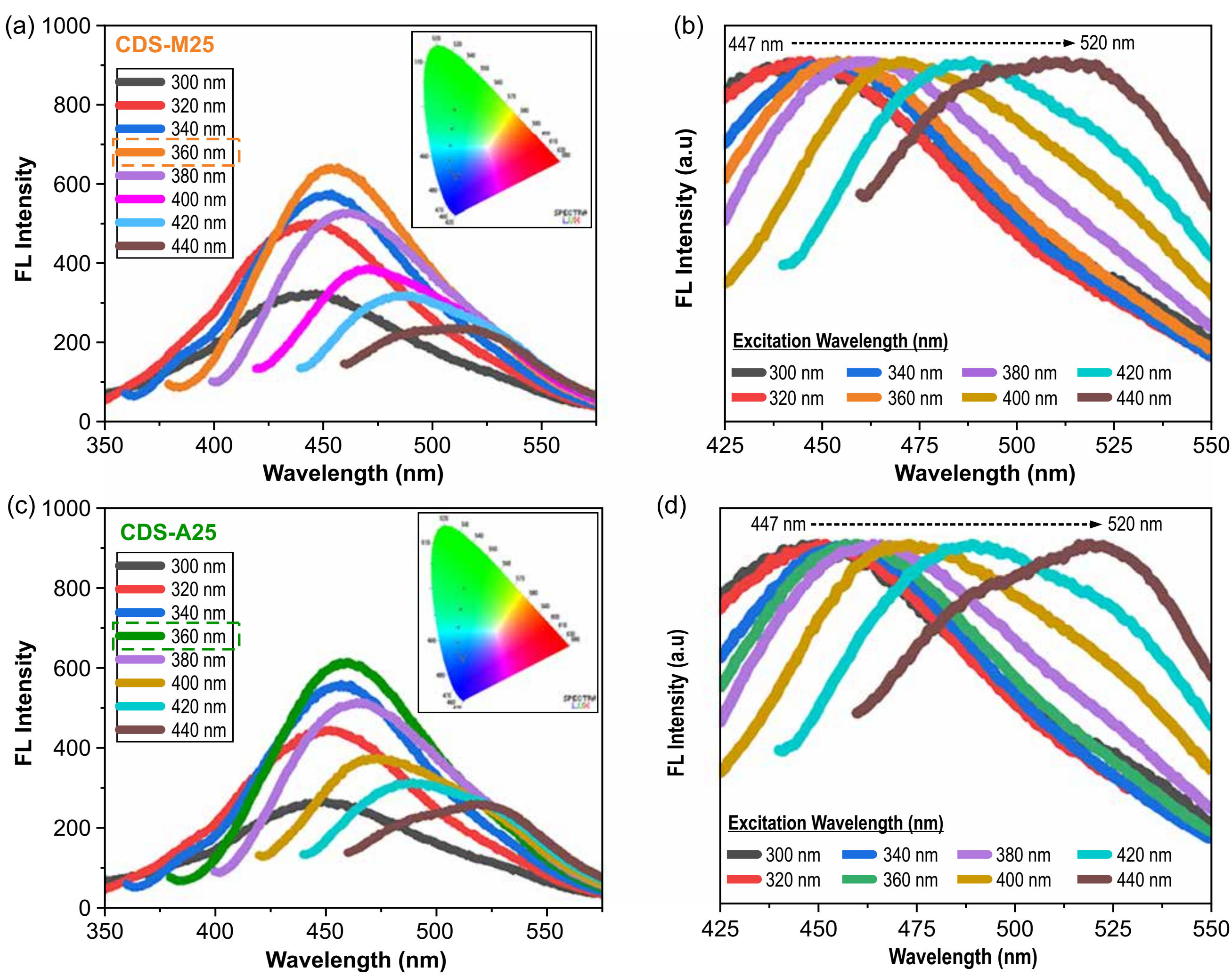


Figure 4. Fluorescence (a,c) and (b,d) emission shift spectra of carbon dots.



the surface of the CDs (Figure 4 B/D). In addition, the CDs showed excellent photostability. Scalable synthesis was an essential and rarely-reported aspect in the literature approached in this study. Using the banana peel extract from different cities as a precursor, we prepared six carbon dots by gradually increasing the reaction volume, de 25, 50, and 100 mL, which were denoted CDS-M25, CDS-M50, and CDS-M100 and CDS-A25, CDS-A50 and CDS-A100 for the cities of Maceió and Aracaju, respectively. Under natural light and 360 nm UV light, it is possible to visualize no difference in the coloration and fluorescence of the nanoparticles, The absorption plots of the CDs exhibited peaks at around 266 nm and 327 nm, independent of the synthesized volume (Figure 5 A/B). Also, they demonstrated emissions with maximum intensities located at 457 nm when excited at 360 nm Figure 5C). These results indicate that obtaining carbon dots from banana peels via microwave promotes a sustainable and reproducible method for CD fabrication. The strong fluorescence of carbon dots in the visible region and their unique properties, such as biocompatibility, photostability, and good dispersion in water, make these nanoparticles excellent candidates for fluorescent ink application [3]. For this study, the aqueous solutions of CDs were employed in sketch pens for writing on commercial filter papers. Under daylight, the inks are colorless and cannot identify the words. However, under UV light with excitation at 360 nm, the words are visualized, and even after months of storage under ambient conditions, the fluorescence on the papers remains constant (Figure 6A). Complementarily, the inks have a good potential to be used in covert and anti-counterfeiting communications since they have clear, long-lasting colorations and do not cause environmental damage. They can be great alternatives to traditional inks. The solid-state carbon dots emission usually suffers self-quenching due to the aggregation of the CDS. The particles close to the CDS are at minimal distances from each other, which causes the energy transfer between them to be excessive, leading to a decrease in the fluorescence of the carbon dots [11]. Some organic matrices are employed to avoid these effects and preserve the optical properties of solid CDS because their chains form obstacles and increase the distance between the particles adjacent to the CDS. In this work, the CDs are incorporated into PVA, which has excellent film-making properties, to maximize its applicability and analyze possible optical similarities between the CDS from the cities of Maceió and Aracaju. Figure 6B presents that the films are highly transparent under natural light, while under UV light, under excitation of 360 nm, they show bright blue fluorescence. All other carbon dots exhibited the same profile as CDs-M25 as luminescent ink and film.

Since this is a study rarely reported in the literature, this work is important because it allows the scale-up of CDs using a unique residue from different localities. Furthermore, it is interesting because it ensures that the optical properties of these nanoparticles derived from biomass will not be significantly modified and can range their localities and applications. In addition, the films produced here can minimize the problems associated with the aggregation effect generally characteristic of these solid-state nanoparticles.

Conclusion

CDs-derived banana peel extract from different cities (Maceió and Aracaju) was successfully synthesized by a simple microwave method, with excellent luminescence in the blue. Finally, all CDs exhibited an expressive similarity of their photophysical properties and promising application as ink and film fluorescent.

Acknowledgments

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Figure 5. UV-vis (A), Photos of the blue-emitting CDs under sunlight (left) and UV irradiation (B) and (C) Fluorescence spectra of the CDS-M25, CDS-M50, CDS-M100, CDS-A25, CDS-A50, and CDS-A100.

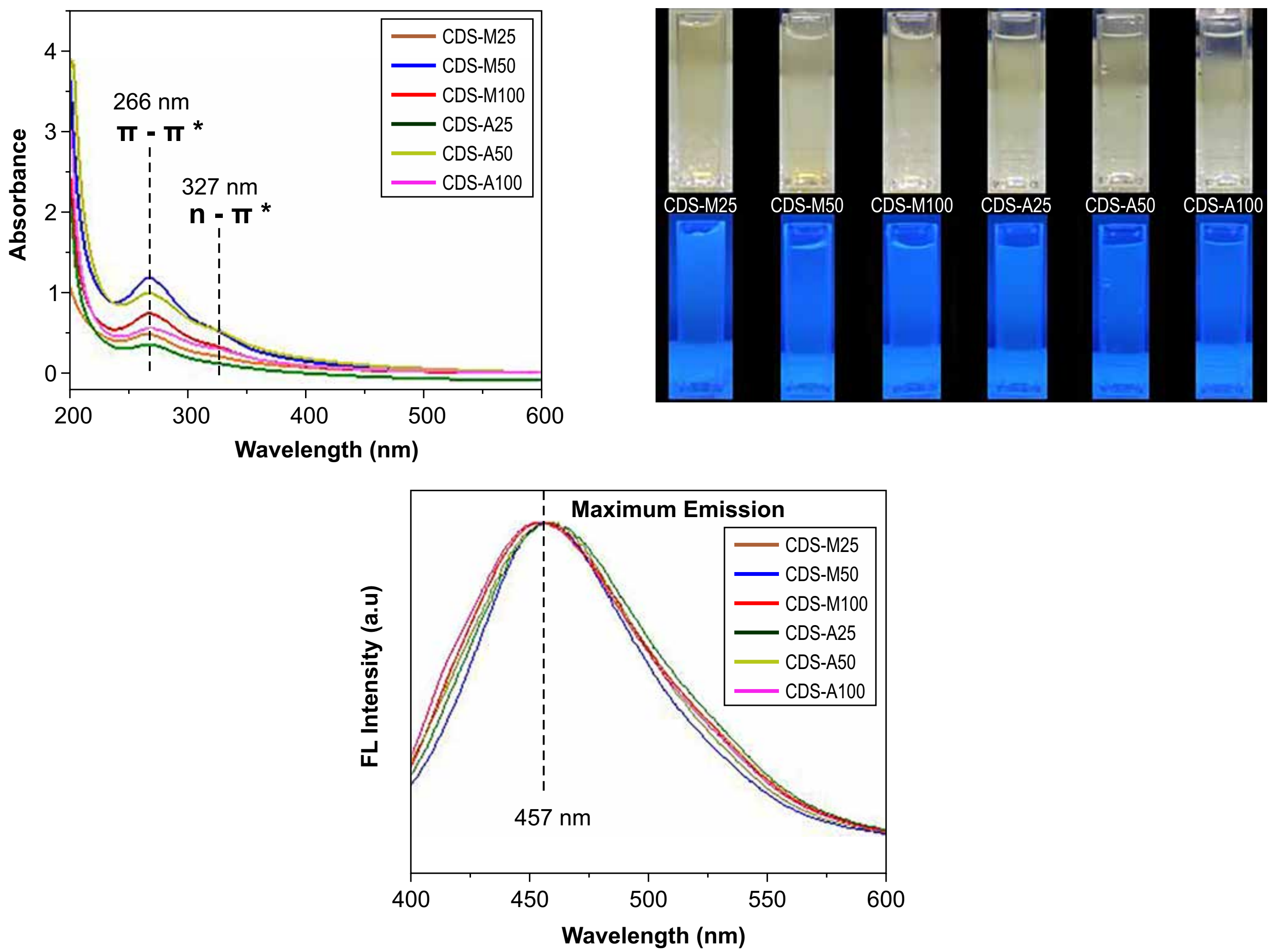
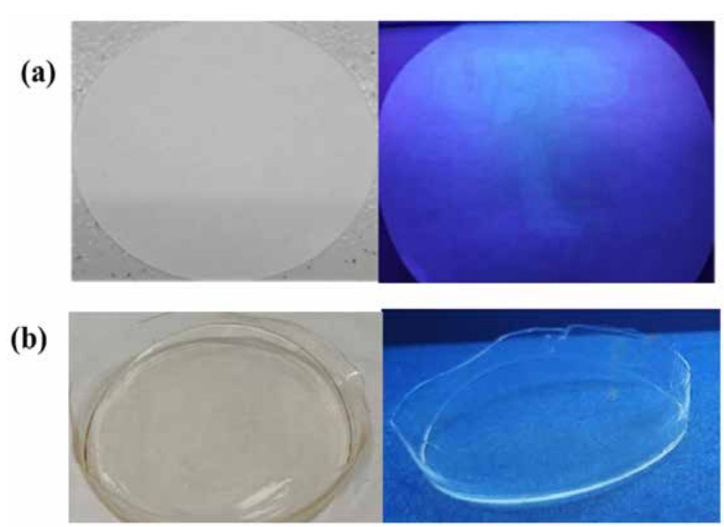


Figure 6. Photos on paper of CDS-M25 under sunlight (left) and UV irradiation (A) and (B) film fluorescent of CDS-M25 under sunlight (left) and UV irradiation.



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