

Effect of Photoluminescence of Nanomaterials to Verify Corrosion in Carbon Steel

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Received: January 30, 2024; Revised: April 04, 2024; Accepted: April 09, 2024

The use of fluorescent nanomaterials in various fields of study has become increasingly common. In this work, the use of carbon quantum dots as a corrosion marker in carbon steel is proposed. To produce the sensor, carbon quantum dots based on ethylenediamine and citric acid were used, dissolved in a polymeric matrix. The quantum dot used showed a quantum yield of 42.34%. The nanomodified coatings emitted blue light under ultraviolet radiation lamp. However, it was observed that there is a loss of photoluminescence in the coating on the carbon steel substrate compared to the coating on the polymeric substrate, which maintained photoluminescence activity after natural exposure. Thus, it is inferred that the loss of photoluminescence may be associated with the corrosion process.

Keywords: *Nanomaterials, carbon quantum dots, corrosion, carbon steel, photoluminescence.*

1. Introduction

Corrosion has a far-reaching impact on society and the associated degradation of materials, not only metallic materials but also ceramics, polymers, and composites. Detection techniques using light sensors are useful for determining corrosion or other types of flaws that arise during material degradation¹. Chemosensors based on aggregation-induced emission luminogen, applied to epoxy coatings, of the turn-on fluorescence type, and a visual chemosensor for detecting metallic corrosion have been reported².

Carbon quantum dots (CQDs), Photoluminescent material under ultraviolet light action, which due to its optical properties, low cost, non-toxicity, and biocompatibility has been studied for potential applications in sensing, information security, biomedicine, and light-emitting diode³. In the field of corrosion, CQDs have been studied as a material for inhibiting the corrosion of carbon steel in the presence of CQDs and HCl acidic solution⁴, as well as a corrosion sensor using photoluminescent images obtained by confocal microscopy of the coatings in contact with carbon steel and under ultraviolet (UV) radiation⁵. Additionally, the use of photoluminescence extinction intensity graphs of NaCl and CQDs solutions in the presence of iron ions is reported in

the study of the effect of corrosion products on steel⁶. In this study, the sodium chloride (NaCl) solution is the medium chosen to accelerate the corrosion of the carbon steel sample immersed in the solution. The solution was exposed to ultraviolet radiation, and the turn-off of the iron ions in the solution originating from the corrosion of the sample on the CQDs is evaluated.

Carbon quantum dots (CQDs) are materials developed from structures containing mostly carbon atoms. Under ultraviolet radiation, CQDs emit visible light via photoluminescence and have been used for the detection of metallic ions^{7,8}.

The use of CQDs as sensors is mainly based on changes in the luminescent response of the nanoparticle when in contact with the analyte. Contact between the carbon quantum dot and the analyte can lead to changes in the fluorescent response, which may result in suppression or reinforcement of luminescence, however it is worth highlighting that suppression is the most observed phenomenon⁹.

Currently, the literature reports some studies in which CQDs were used as sensors to identify different analytes, such as nitric oxide¹⁰, ascorbic acid¹¹, and fungicides¹². However, CQDs are also excellent metal ion sensors, having been used to identify copper ions¹³ and, mainly, iron ions^{5,6,9}. Iron ions are capable of suppressing CQD fluorescence due

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to the strong interactions between Fe^{3+} ions and hydroxyl groups present on the nanoparticle surface.

Alongside the study on the effect of iron ions on the extinction of CQDs photoluminescence^{5,6,9,14}, there is also research on the efficient production of solid-state photoluminescent CQDs¹⁵. Additionally, in the field of mineralogy, to detect solid photoluminescent materials present in rocks, a technique adopted is illuminating minerals with a ultraviolet light emission lamp and using photoluminescent images^{16,17}. Under ultraviolet radiation, only the photoluminescent minerals emit visible light, and the color is recorded through photographic images. A similar procedure can be adopted in the study of metal corrosion using CQDs as a photoluminescent sensor, where the dark regions of the photoluminescent images can be associated with the turn-off effect due to corrosion products. It is from this idea that the work is developed.

The objective of this work is use CQDs as a visual chemosensor in the detection of carbon steel corrosion via a sensitive turn-off photoluminescence response through photoluminescent images. For the characterization of CQDs in aqueous media, analyses by Fourier transform infrared (FTIR) vibrational spectroscopy, fluorescence microscopy (in the range of 300 nm to 400 nm), and UV-visible absorption microscopy are adopted. In the solid state, polymer coatings with CQDs were analyzed based on color, brightness, and the use of photoluminescent images, based on the principle of the technique for detecting photoluminescent minerals and rocks. The method is simple, fast, and has potential for use in detecting the corrosion of metallic structures that may use CQDs or other photoluminescent materials as corrosion sensors.

2. Experimental

2.1. Synthesis of carbon quantum dots

The carbon quantum dot was synthesized through hydrothermal synthesis (bottom-up method)¹⁸. To carry out the synthesis, citric acid was used as a carbon source and ethylenediamine as a source of the amine groups responsible for functionalizing the surface of the carbon dot. Initially, 2.6 mmol of citric acid and 33 mmol of ethylenediamine were weighed and dissolved in 7.5 mL of distilled water until complete dissolution. Then, the mixture was transferred to a 50 mL Teflon-lined autoclave and heated to 180°C for a period of 5 hours. After this period, the autoclave was cooled to room temperature (+ 25°C). Subsequently, the sample was dialyzed in two 12-hour cycles and the obtained suspension was freeze-dried. The solid content (%) was determined as 0.26 mg g⁻¹, that is, 0.26 mg of solid material for each gram of suspension. The quantum yield (QY) of the material was also calculated using the procedure described by Li and his collaborators¹⁹, in which quinine sulfate in H₂SO₄ 0.1 mol L⁻¹ was used as reference.

2.2. Preparation of test specimens

The carbon steel specimens were initially painted with acrylic primer-based paint. After 12 h, a volumetric mixture of 60% CQD and 40% aqueous solution containing

chitosan and acetic acid was applied on substrates. Also, volumetric mixtures containing 60% CQD and 40% water-based acrylic resin were prepared on carbon steel and polymeric substrates, and their photoluminescence was analyzed after 72 hours.

2.3. Characterizations

Absorption spectra were recorded on a Shimadzu UV-2600 UV-vis spectrophotometer. Fluorescence spectra were obtained on the Shimadzu RF-6000 spectrum fluorophotometer. Fourier transform infrared (FTIR) vibrational spectroscopy analyzes were performed on a Shimadzu FTIR 8300 device and recorded using a scanning range of 400-4000 cm⁻¹.

The samples were exposed to UV light lamp and photos were taken. The methodology is based on the procedure adopted in the characterization of photoluminescent minerals and rocks^{16,17}. Photoluminescence images were obtained using a commercial camera and a commercial lamp with UV-vis polychromatic radiation with wavelengths shorter than 400nm. Color and gloss analyze of the coatings were carried out on samples before and after being exposed to UV light. The coatings were analyzed using CIELAB color spaces with an X-Rite spectrophotometer and a 60° Zehntner gloss meter.

3. Results and Discussion

3.1. Characterization of carbon quantum dots

Initially, the quantum yield was calculated, and the value obtained was 42.34%. This value is considered high since carbon quantum dots have quantum yield values lower than the yields of organic dyes and semiconductor quantum dots²⁰. The optical properties of the synthesized CQDs were investigated using UV-vis absorption and photoluminescence spectroscopy. Figure 1 presents the UV-vis, excitation and emission spectra obtained for CQDs. The optical properties of the synthesized CQDs were investigated using UV-vis absorption and photoluminescence spectroscopy. Figure 1 presents the UV-vis absorption, excitation and emission spectra obtained for CQDs.

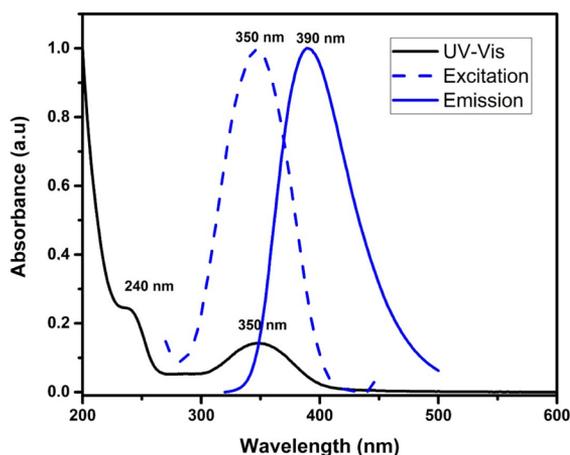


Figure 1. UV-vis absorption spectrum, excitation, and emission of CQDs.

Analyzing the obtained UV-vis absorption spectrum, it is possible to observe that the CQDs analyzed presented two characteristic bands. The first one is located at 240 nm and is attributed to $\pi \rightarrow \pi^*$ transitions of aromatic groups with sp^2 carbons. The second band was found in the 350 nm is

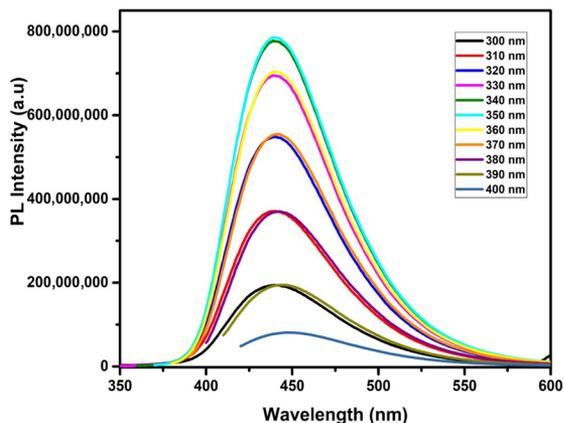


Figure 2. Photoluminescence spectra with different excitation wavelengths (300 to 400 nm).

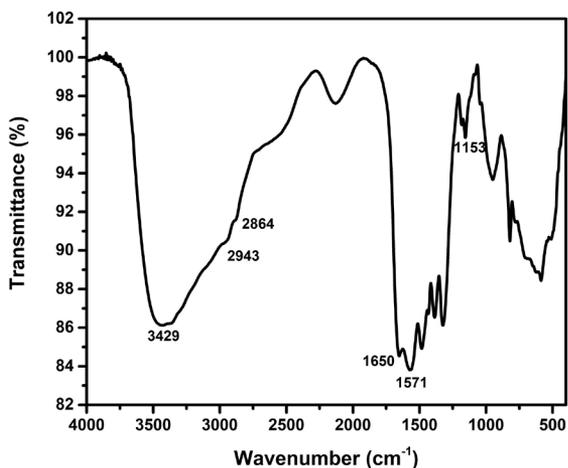


Figure 3. FTIR spectrum of CQDs.

assigned to $n \rightarrow \pi^*$ type transitions arising from the functional groups present on the CQDs surface²¹.

Another very interesting study carried out was the monitoring of photoluminescence emitted at different excitation wavelengths (300 to 400 nm), shown in Figure 2.

Analyzing the spectra shown in Figure 2, it is possible to observe that there was no shift in the emission band, even with the excitation at different wavelengths. This observation indicates that the CQDs has excitation-independent behavior, with a maximum excitation wavelength at 350 nm. The observed behavior suggests that the particles have similar sizes and few defects on their surface²².

FTIR analyzes were performed to obtain information about the functional groups present on the CQDs surface. Figure 3 presents the FTIR spectrum obtained for the sample under study.

It is possible to observe the presence of a very broad band located at 3429 cm^{-1} , indicating the stretching vibration of the OH group²³. It was also observed the presence of two bands located at 2943 cm^{-1} and 2864 cm^{-1} that can be attributed to the asymmetric and symmetric stretching of CH_2 groups²⁴. The band in the region of 1650 cm^{-1} can be attributed to the stretching vibration of the C = O group²³. The band at 1571 cm^{-1} is associated with the bending vibration of the NH_2 group²⁴. The band at 1153 cm^{-1} can be attributed to the stretching of the C – OH bond²³. The presence of these groups indicates that the reaction between citric acid and ethylenediamine occurred satisfactorily.

3.2. Color

For the samples with coating made using a volumetric mixture of 60% CQD and 40% aqueous solution containing chitosan and acetic acid. The presence of the acidic chitosan solution contributes to accelerating the corrosion of the metal, making it possible to find more details about the corrosion of metals by chemicals in other sources^{4,6}. The results of the characterizations of the samples can be seen in Table 1, as well as in Figures 4 and 5.

In the CIELAB color space, it is assumed that two colors cannot be yellow and blue or green and red at the same time. In the system, parameters a^* and b^* are the chromatic coordinates and take on positive or negative values. If $+a$ indicates red and $-a$ indicates green, while $+b$ indicates yellow and $-b$ indicates blue. The L^* parameter indicates the

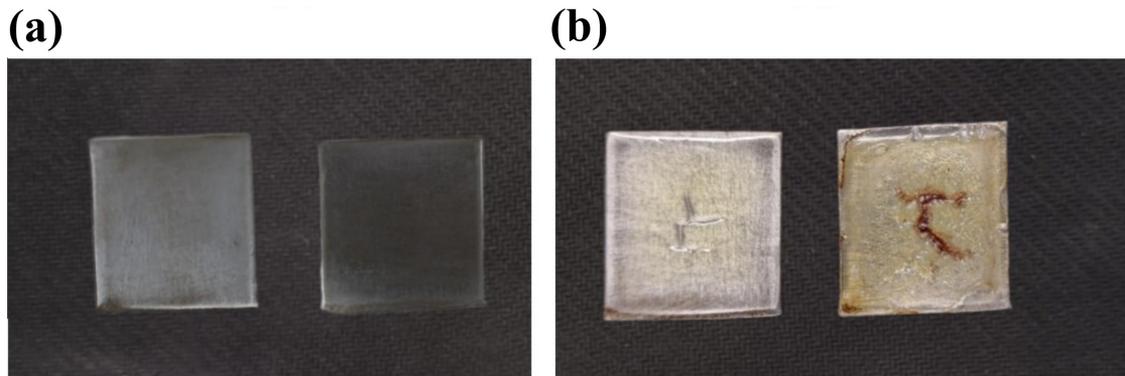


Figure 4. Test specimens with acrylic coating: (a) initial $t = 0\text{ h}$ and (b) $t = 72\text{ h}$. Left side (without CQDs) and right side (with CQDs).

luminosity. The presence of corrosion products influenced the reduction of the L^* , a^* and b^* parameters, Table 1. In addition to color, corrosion products affect gloss, where without corrosion it is 39.1 gloss units and with etching to 8.5 gloss units.

The use of ultraviolet radiation on ores, assisted by a camera to capture photoluminescent images, allows for the detection of photoluminescent minerals, as these minerals emit visible light when irradiated with ultraviolet radiation¹⁷. Yiqian and collaborators applied a qualitative analysis using photos obtained by confocal microscopy to generate maps with the aim of evaluating the loss of photoluminescence of the composite coating of epoxy resin/g- C_3N_4 /CQDs due to the iron ions from the carbon steel⁵. The use of a microscope

to generate photoluminescent images, while suitable for laboratory analysis, may be impractical for field detection of corrosion using photoluminescent sensors. On the other hand, the use of UV lamp and a camera may be more appropriate. This method is simple and has the potential for field analysis. In this context, obtaining photoluminescent images of polymer coatings with CQDs through a camera and UV lamp constitutes a qualitative analysis. Furthermore, based on the literature, regions of polymer coatings with CQDs on carbon steel that do not emit photoluminescence may be indicative of corrosion.

Figure 4 shows images of the specimens painted with acrylic primer, at the beginning of $t = 0$ h (24 hours after application) and $t = 72$ h (72 hours after application), without and with CQD in the coating. CQD nanomodified coatings emit blue light under ultraviolet radiation on non-oxidized substrates. After $t = 72$ h, there is a loss of photoluminescence at locations in the coating over the carbon steel substrate, Figure 5.

The loss of photoluminescence is observed in the region where there is the presence of corrosion product, illustrated in Figure 4a. Possibly, the presence of the corrosion product was accelerated due to the presence of the chitosan acidic solution (Figure 4b, left side).

In Figure 6, the liquid CQD solution (Figure 6a), is illustrated when exposed to ultraviolet radiation (Figure 6b),

Table 1. CIELAB color space of specimens with acrylic coating without and with CQDs.

CIELAB Color	Without CQDs (t=0)	With CQDs (t=72h)
L^*	58.92	50.85
a^*	- 0.83	+ 0.38
b^*	+ 10.37	+ 15.70

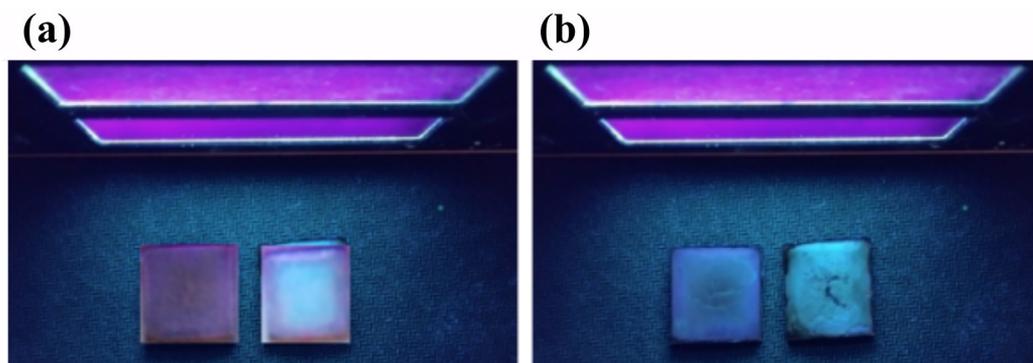


Figure 5. Test specimens with acrylic coating under UV radiation: (a) initial $t = 0$ h and (b) $t = 72$ h. Left side (without CQDs) and right side (with CQDs).

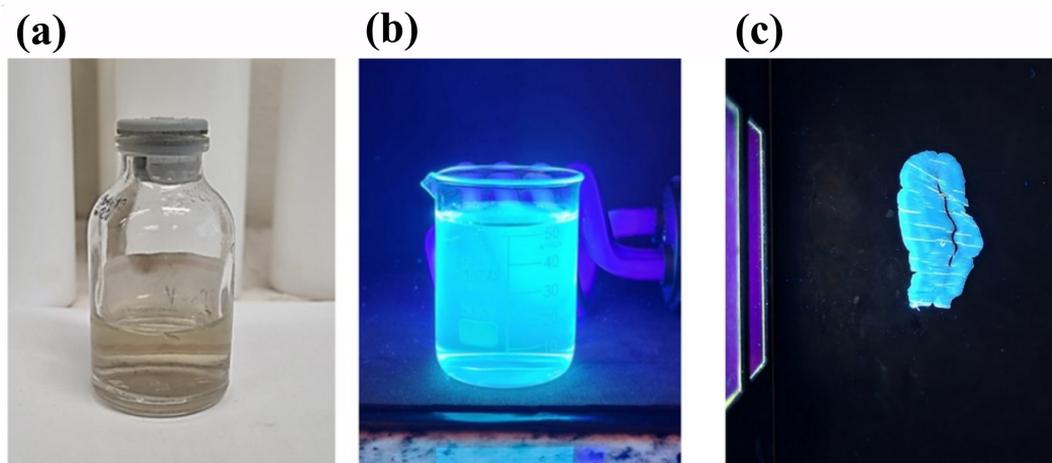


Figure 6. CQDs without exposure to UV light (a) and with exposure to UV light (b) and (c).



Figure 7. Test specimens without and with acrylic resina and CQDs coating under UV radiation.

and the solid solution made from a volumetric mixture containing 60% CQD and 40% water-based acrylic resin (Figure 6c). The solid film was obtained using a polymeric substrate, allowing the mixture to rest on the substrate for 24 hours. After 72 hours, following the application of the mixture, the film remains photoluminescent (Figure 6c).

After 72 hours of application, in Figure 7, the photoluminescence is illustrated when carbon dots deposited on a carbon steel surface come into contact with corrosion product. Similar to what is illustrated in Figure 5, in the region where corrosion occurs, there is no photoluminescence (Figure 7, central plate). In Figure 7, the non-photoluminescent layer (far left) consists solely of acrylic resin.

The coating on a polymeric substrate maintains photoluminescent activity after exposure to ultraviolet radiation. However, there is a loss of photoluminescence when carbon dots are deposited on a carbon steel surface (Figures 5b and 7). This result indicates that the loss of photoluminescence may be associated with the carbon steel corrosion process. Since, CQD photoluminescence is based on the injection of electrons into the conduction band of CQDs, and subsequently, the electron in the conduction band when returning to the valence band produces luminescence⁷. The loss of luminescence is associated with the interaction of suppressors (e.g., Fe^{3+} and Fe^{2+}) with CQDs, forming a non-fluorescent complex that is formed before ground-state excitation occurs⁸.

4. Conclusion

In this work, the use of a simple and widely used technique in the detection of photoluminescent minerals

and rocks is reported, but directed towards the analysis of carbon steel corrosion. From the qualitative analysis with photoluminescent images and the use of color and gloss characterizations of the coatings, as well as optical absorption, photoluminescence, and FTIR characterizations of the CQDs, it is inferred that the water-based polymeric coatings with CQDs emitting blue light under UV radiation when on the substrate is not oxidized and there is a loss of photoluminescence when there is oxidation in carbon steel. Like this, this work aims to be another contribution to the study focused to generate a new tool for visual inspection of metallic structures through a technique that uses UV radiation to identify corrosive processes in steel substrates painted with coatings containing CQD.

5. Acknowledgments

The research received financial support from the following research support agencies: Fundação Cearense de Apoio ao Desenvolvimento Científico e Tecnológico (Cearense Foundation to Support Scientific and Technological Development) - FUNCAP, and Fundação de Desenvolvimento Científico e Tecnológico (Foundation for Scientific and Technological Development) - FUNDETEC. The authors would like to express their gratitude to the Núcleo de Tecnologia e Qualidade Industrial do Ceará - NUTEC, and the Universidade Federal do Ceará - UFC, which provided the necessary facilities to complete this work.

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