

The effect of sonication on the photoluminescence property of carbon quantum dots synthesized by hydrothermal route

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Due to their chemical and physical properties, this study focuses on the effect of sonication over carbon quantum dots synthesized by means of hydrothermal route, having as precursor the sour lemon juice from Michoacán, Mexico. The exfoliation was carried out with a sonotrode in times of 1, 2 and 3 hours to provide an explanation over the effect of it on the photoluminescence, where it was found that with times of 1 hour, the PL emission is improved resulting from 261 a.u. to 448 a.u. Other characterizations were carried out to confirm the results obtained in PL, where the average particle size was analyzed by SEM, particle sizes ranging from 5 to 11 nm were observed, with an average size of 7.5 nm and to confirm the carbonaceous material, UV-Vis was performed showing a resolved UV absorption band around 340 nm.

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1. Introduction

Materials derived from carbon are interesting materials and are currently receiving special attention due to the applications that can be accessed, one of the materials derived from these, are carbon quantum dots (CQD) [1], they are materials that have average sizes of 10 nm[2], due to this they have exceptional structural and electronic properties such as water solubility, photoluminescence, low toxicity, biocompatibility [2], [3], [4], [5], [6]. These characteristics are attractive and result in their use in applications requiring minimal risks, making CQDs good candidates for use in biological imaging [7], photonic devices [8], solar cells [9] and optoelectronic sensors [10]. The optical characteristics of CQDs are very favorable, which facilitates their use for sensors that can detect pollutants, viruses, etc., through photoluminescence [11], [12], [13], for this reason this study focuses on this feature, which is largely provided by the synthesis methods, where mainly we have the hydrothermal treatment, this synthesis is environmentally friendly and contributes to the formation of small particles. The hydrothermal process is one of the most used routes to obtain quantum dots, because it is a method where low temperatures are used, relatively short times and good photoluminescence emission of the particles are obtained [1], [3], [14], [15]. To improve this property, there have been reports where it has been proved that by using sonication, a better PL emission is obtained. This is due to the contact of the sonotrode with the material in aqueous medium, having the effect of fragmentation of large particles to small and therefore more dispersed particles due to mechanical vibrations, which will result in particles that are closer to the blue emission in the electromagnetic spectrum [7], [16], [17]. In this work after the synthesis of CQD, we studied the effects of the use of the sonotrode on the CQD particles during 1, 2 and 3 hours, thus evaluating their particle size and photoluminescence emission by photoluminescence spectrometer (PL), Fourier-Transform Infrared Spectroscopy (FTIR) and Transmission Electron Microscopy (TEM).

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2. Experimental

A modification of the hydrothermal synthesis of carbon quantum dots was developed which has been previously describe [2], [5] where 25 ml of lemon juice was placed inside a stainless-steel reactor coated with Teflon, such synthesis had a hydrothermal treatment at 200 °C for 10 hours. After the hydrothermal synthesis, a filtering process was carried out to remove the larger particles. These initially showed an. Orange color, then turning brown upon filtration. Subsequently, sonication tests were carried out for 1, 2 and 3 hours to determine the changes in photoluminescence. Characterization of quantum dots was performed by PL, as well as analysis of functional groups by FTIR. In addition, the particle sizes were analyzed by TEM.

3. Results and discussion

Figure 1 shows the results obtained upon excitation at 450 nm, where the sample that only underwent a hydrothermal reaction of 10 hours at 200°C (L0), shows a certain degree of photoluminescence, but if subsequently an exfoliation with sonotrode is performed for 1 hour (L1) the photoluminescence emission is significantly increased, from 261 a.u. to 448 a.u. but once the time is increased to 2 (L2) and 3 (L3) with the sonotrode, the photoluminescence decreases. This is due to the conditions of power, frequency, and temperature. As the temperature and reaction time increase, agglomerates begin to form, and in this situation, they will lose their photoluminescence emission because the particles begin to deform and therefore lose their optical properties. In FIGURE 2. it is also observed that when the sample is excited at 468 nm, the sample that continues to show significant PL is the one with 1 hour of sonication.

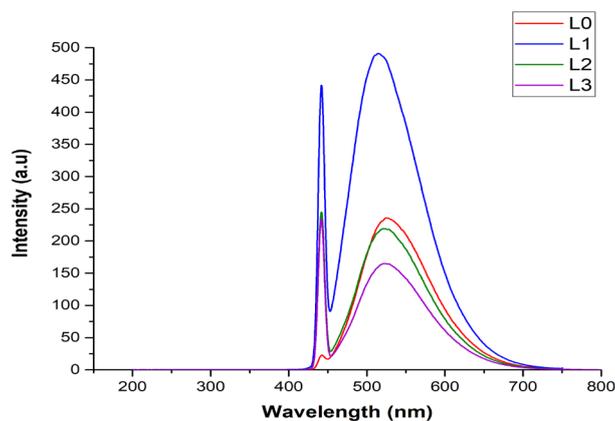


Fig. 1. Photoluminescence with excitation at 450 nm.

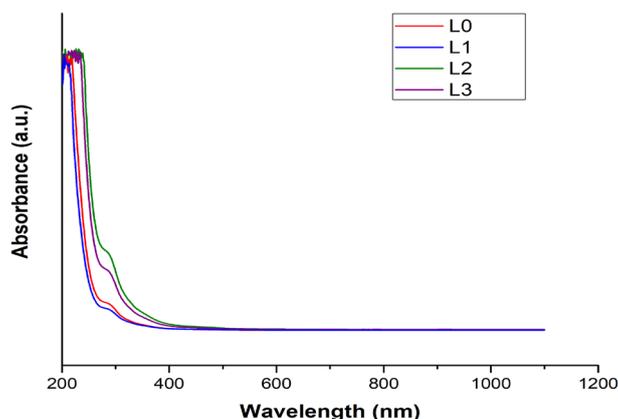


Fig. 2. Photoluminescence with excitation at 468 nm.

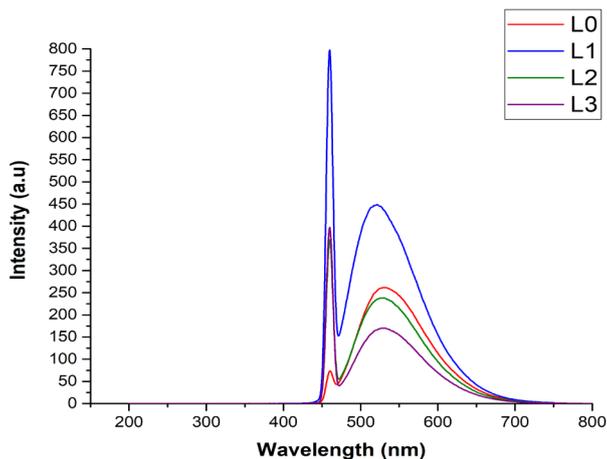


Fig. 3. UV VIS different CQD at sonication times: 0 (L0), 1 (L1), 2 (L2) and 3 (L3) h.

In Figure 3, UV-VIS studies show absorption signals that are typical of these materials, approximately 210 nm and 292 nm are attributed to the $\pi-\pi^*$ transition of the C=C and $n-\pi^*$ transition of the C=O bonds, respectively. In turn in FIGURE 4 the functional groups found in the CQDs can be counted. Where shows mainly the O-H stretching at approximately 3374 cm^{-1} attributed to the water content present in the hydrothermal reaction. Another characteristic bond at 2136 cm^{-1} is the C \equiv C. At 1640 cm^{-1} there is a band belonging to the C=C vibrations of aromatic compounds. However, the combination of absorption phenomena could also occur, which could cause an overlapping of groups, also attributed to the C=O of the amide groups, the non-aromatic double bonds, the hydrogen bonds of the C=O group of the ketones and quinones and the vibrations of the water molecule contributing to the absorption, since the sample is not completely dry. The absorption band at 1235 cm^{-1} is attributed to the carbonoxygen bonds and finally there is a band at 666 cm^{-1} , which represents the deformations of the aromatic C-H rings.

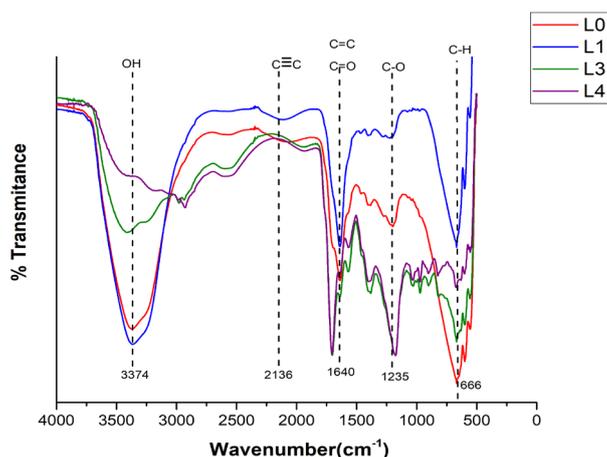


Fig. 4. FTIR CQD at different sonication times: 0 (L0), 1 (L1), 2 (L2) and 3 (L3) h.

Figure 5a, shows the particles obtained in the hydrothermal reaction by SEM, where sizes out of range of the quantum dots were obtained. On the other hand, in FIGURE 5b, which belongs to sample L1, in which ultrasonication was carried out for 1 hour, an improvement was obtained with respect to the size, where the particles range from 5 to 11 nm, with an average size of 7.5 nm this is indicative of obtaining quantum dots. When the sonication time of 2 and 3 hours are authenticated, as shown in FIGURES 5c and 5d, respectively, it is noted that the sonication time affects the particles, considerable changes are observed in the sizes ranging from 17 nm to 31 nm

and even larger, these changes may be due to the effects of sonication, the longer the sonication time, the material will lose its mechanical properties, The reason why the material degrades is related to the amorphous regions that may have the structure and as mentioned by authors [17] [18] the problem is due to the high power with which it works that causes degradation because of the energy absorbed during the cavitation process present in the mechanical methods. This is very useful to separate particles, but it can also deteriorate the material [18]. In addition to these findings, they coincide with the study carried out on the percentages of lemon content, where water can be observed as the main component, followed by citric acid and vitamin C, which we know are the main components that play an important role in the hydrothermal reaction for the formation of carbon quantum dots. It is known with previous studies, the compounds of lemon juice, where they found several acids such as citric, malic, ascorbic, malonic, oxalic and succinic acids, highlighting in higher percentage citric, malic and ascorbic acids [19]. These acids, mainly citric acid and vitamin C, decompose upon heating, in the case studied by hydrothermal synthesis, generating interesting photoluminescent properties. We know that any environmental change with respect to temperature relates to and influences the emission band of a material. High temperature causes a band shift and has been exploited for fluorometric temperature sensing or luminescence thermometry applications [20]. Citric acid (or 2- hydroxy-1,2,3 propane tricarboxylic acid) is a weak triprotic organic acid that is naturally concentrated in a large number of vegetable fruits, especially citrus. Among fruits, citric acid is more concentrated in lime (*Citrus aurantifolia*) and lemon (*Citrus lemon*), so we observed that in lemon, compared to other fruits used to generate quantum dots, it shows a favorable response to the photoluminescence property [20] [21] [22] [23].

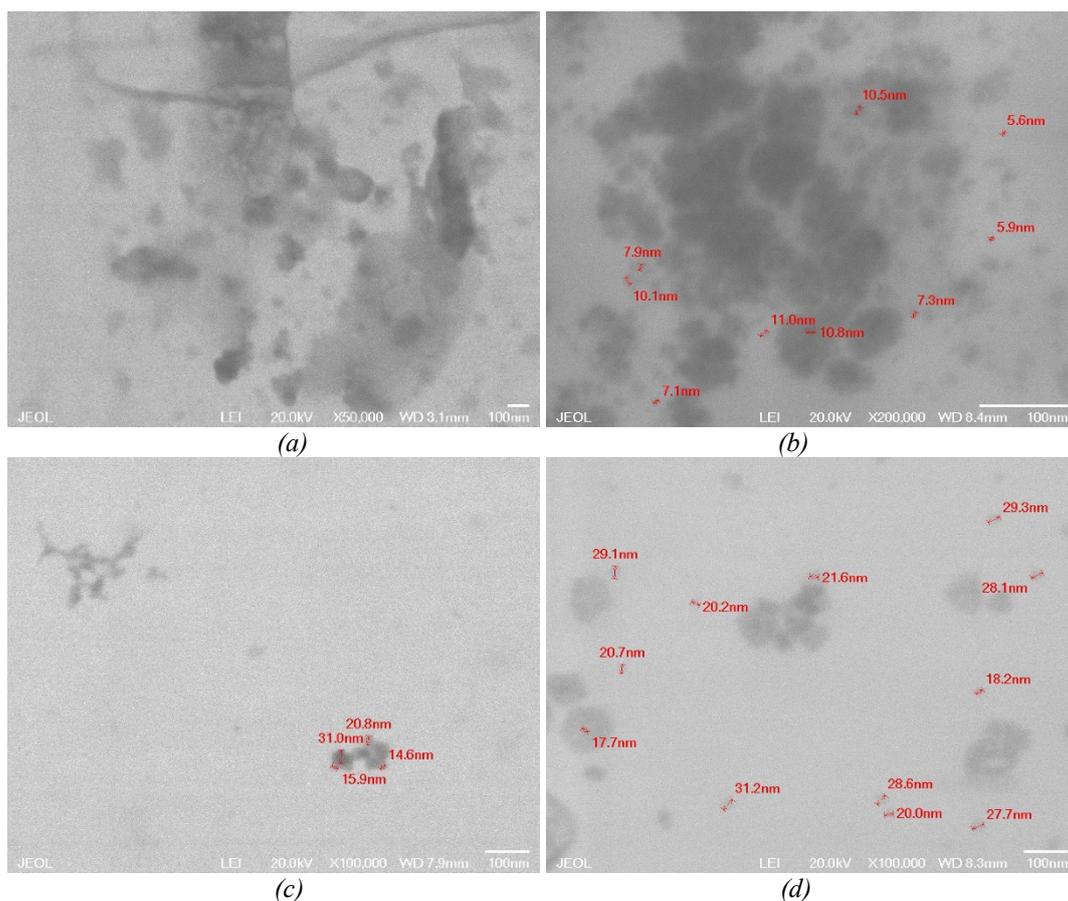


Fig. 5. Shows the particles obtained in the hydrothermal reaction by SEM, where sizes out of range of the quantum dots were obtained.

Table 1. Composition of fresh lemon juice.

ANALYSIS	Result	Reference	METHOD
Total dietary fiber	0.34%	118/002	AOAC 985.29
Vitamin c	35 mg/100ml	118/002	AOAC 967.21
Total sugars	1.28%	117/002	NOM-086-SSA1-1994
Total carbohydrates	7.86%	118/002	By difference
Moisture	91.69%	117/002	NOM-116-SSA1-1994
Total solids	9.31%	117/002	NOM-116-SSA1-1994
Protein	0.19 % N x 6.25	117/002	NMX-F-608-NORMEX-2011
Total titratable acidity (citric acid)	80 mg/100 ml	117/002	AOAC 942.15

4. Conclusions

In summary, it has been possible to significantly improve the photoluminescence property of the carbon quantum dots, prepared by a simple method, where later ultrasonication was performed, this last step is very important because the time in which the sonication will be carried out must be taken into account, This last step is very important because the time in which the sonication will be carried out must be taken into account in order not to degrade the material as in samples L2 and L3, where even in a visible way this change could be noticed, since while the time passed, the sample began to darken, due to the fact that the material is not totally crystalline, the excessive use of sonication is very harmful for the CQDs. In this research it was more feasible to use the 1 hour sonication time (L1), where improvements in the particle sizes and therefore in the optical properties were observed.

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