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Synthesis and spectroscopic study of highly fluorescent carbon dots derived from orange juice using hydrothermal method with stilbene 420 dye

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Abstract

Highly-fluorescent Carbon Quantum Dots (CQDs) are synthesized in a simple step by hydrothermal carbonization method of natural precursor such as orange juice as a carbon source. Hydrothermal method for synthesized CQDs requires simple and inexpensive equipment and raw materials, thus this method is now common synthesis method. The prepared CQDs have been characterized by X-ray, AFM, SEM, FTIR and fluorescence measurements with Stilbene 420 dye. It has found that the synthesized CQDs have amorphous structure and possess ultrafine size up to few nanometers and contains of carbon, oxygen based groups and surface-modified functional groups. Moreover, the prepared CQDs derived from orange juice have extremely good fluorescence. It showed an improvement in the optical properties when mixed with the Stilbene 420 dye.

This work demonstrates the method of preparing highly fluorescent CQDs also briefly introduces the most commonly used techniques for characterizing CQDs and the results obtained and studying their optical properties by adding Stilbene 420 dye in a method that changes the input power of used laser.

Key words

Carbon quantum dots, hydrothermal carbonization, spectroscopic.

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تحضير ودراسة طيفية لنقاط الكربون ذو الانبعاثية العالية من عصير البرتقال باستخدام الطريقة الحرارية المائية مع صبغة الستلبين 420

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الخلاصة

يتم تصنيع نقاط الكربون الكمومية عالية الانبعاثية في خطوة بسيطة بطريقة الكربنة الحرارية المائية من المواد الخام المتوفرة في الطبيعة مثل عصير البرتقال كمصدر للكربون. تتطلب الطريقة الحرارية المائية لتوليف نقاط الكربون معدات ومواد خام بسيطة ورخيصة نسبيا، لذا تعتبر هذه الطريقة شائعة في الوقت الحاضر. تم تشخيص نقاط الكربون المحضرة باستخدام عدة فحوص تشخيصية مثل حيود الاشعة السينية X-ray ومجهر القوة الذرية AFM وماسح المجهر الالكتروني SEM و جهاز "فورييه" لتحويل طيف الأشعة تحت الحمراء FTIR. كما وتمت دراسة طيفية لنقاط الكربون المحضرة لوحدها وكذلك عند مزجها مع صبغة الستلبين 420. لقد اظهر التشخيص أن نقاط الكربون المحضرة ذات هيكل غير بلوري وذات حجم متناهي الصغر يصل إلى بضعة نانومترات ويحتوي على الكربون، والمجموعات القائمة على الأكسجين والمجموعات الوظيفية المعدلة للسطح. علاوة على ذلك ، فإن نقاط الكربون المحضرة من عصير البرتقال لها انبعاثية جيدة للغاية. وقد أظهر تحسنًا في خواصه البصرية عند مزجه بصبغة الستلبين 420.

يوضح هذا العمل طريقة تحضير نقاط الكربون ذو الانبعاثية العالية كما ويقدم بإيجاز التقنيات الأكثر شيوعًا لتوصيف نقاط الكربون المحضرة والنتائج التي تم الحصول عليها ودراسة الخواص البصرية لنقاط الكربون وعند إضافة صبغة الستلبين 420 اليها بطريقة تغيير قدرة إدخال الليزر المستخدم.

Introduction

Carbon Quantum Dots are a new class of carbon nanomaterial's which discovered in the last few years that distinguished as very small by a few nanometers. Self-surface passivation CQDs can be produced in simple step without the need for strong acids or additional passivation agents. CQDs prepared by hydrothermal carbonization of orange juice components such as sucrose, fructose, citric acid, and etc. have important properties including high water solubility and low toxicity and environmentally friendly [1-3].

To make carbon dots fluorescent materials, their size and surface chemical groups should be adjusted carefully. Prepared fluorescent carbon dots are interconnected systems always consist of hybrids sp^2 / sp^3 carbon atoms with a lot of combinations that contain oxygen groups and post-modification chemical groups [4, 5]. CQDs additionally have structural properties such as that are non-crystalline as well as many optical properties, including high optical stability, broad and tuning agitation, excitation-based emission and narrow and tuning fluorescence [6], and have several features such as high solubility in water, low toxicity, high biocompatibility, photo-bleaching resistant, chemical inertness and ease of functionalization [7, 8].

These properties render them ideal for a wide range of functions, e.g. bio-imaging, labelling, waste-water treatment, photo-catalysis electrochemical applications, and biotechnology, as well as chemical sensing, and optoelectronic devices like LEDs [9].

In the present work, CQDs have been prepared by mixing orange juice with ethanol at approximately 120 ° C and 1 atmospheric pressure by a specially designed stainless steel autoclave.

Synthetic method

CQDs are prepared by relatively low temperature hydrothermal carbonization of natural raw material mixed with ethanol. The hydrothermal carbonization method is mainly based on the dehydration, polymerization and carbonization of small non-conjugated molecules such as orange juice components (citric acid, glucose, sucrose, fructose, ascorbic acid, etc.) to form CQDs (Fig. 1).

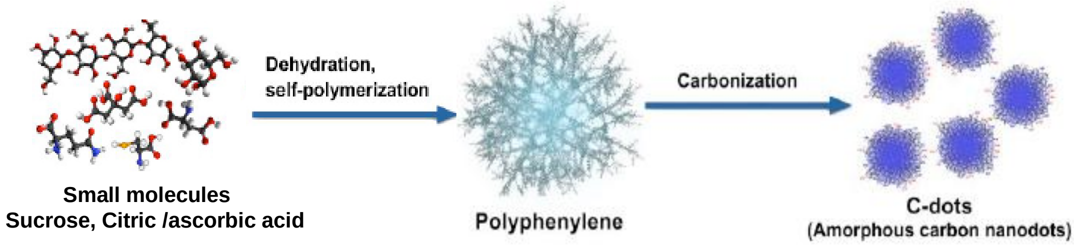

Fig.1: The schematic illustration for CQDs preparation [10].

The amount of pulp-free orange juice is mixed with the appropriate amount of ethanol to obtain a yellow solution. The glass bowl containing the solution is placed in a fully sealed stainless steel autoclave at a temperature of approximately 120 °C and 1 atmosphere for 150 minutes. After the end of the period, the autoclave is extinguished and let to be cooled gradually at room temperature and then the solution, which has a dark brown color and has a volume of approximately 40 ml. Centrifuge of the solution is done and then washed by centrifuge with dichloromethane and then abundant of acetone to obtain liquid and deposit, then separate from each other and the deposit is dried. The dried deposit is CQDs powder. These steps illustrated in Fig.2.

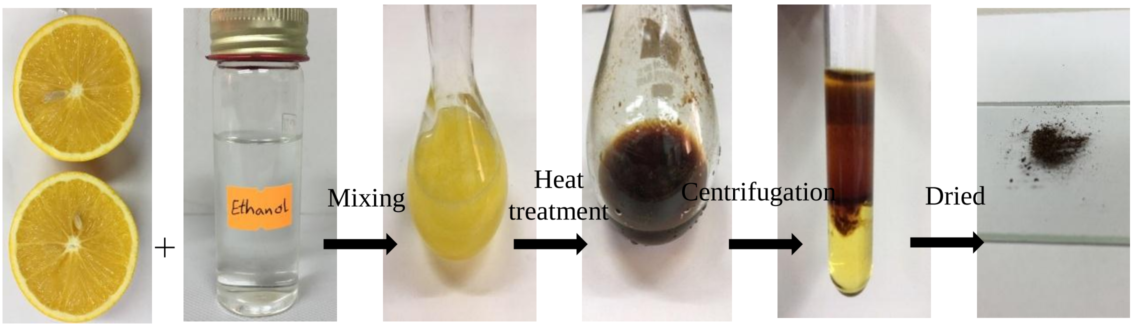

Fig.2: The steps of produced carbon dots (CQDs).

The highly available Stilbene 420 dye has been selected because of its absorption of high energy photons in the UV region and the emission of low energy photons in the visible region. The emission of prepared CQDs is combined with other luminophores for multidimensional applications, so CQDs are mixed with Stilbene 420 dye in distilled water and study the role and effect of CQDs and dye and the interaction between them to obtain the best photo-physical properties [2, 11 and 12].

An amount of prepared CQDs in vitro have been taken and mixed with 10 ml of distilled water to form a solution of 0.2647 [M] concentration.

The solution has been divided into two equal parts. 5 ml of distilled water have been added to the first part and 5 ml of the Stilbene 420 dye solution in distilled water with concentration 10^{-4} [M] added to the second section. The concentration of CQDs in the two sections becomes 0.132 [M] and the concentration of Stilbene 420 dye in distilled water becomes 5×10^{-5} [M].

Results and discussions

The typical x-ray diffraction pattern in Fig.3 illustrates that the CQDs have a broad peak at (002) and is centered at around ($2\Theta\sim23^{\circ}$), and the CQDs have interlayer spacing (*d*) of (~ 0.38 nm) corresponding to the graphite structure (0.34 nm) that is similar to the CQDs prepared in other method. The increase in (*d*) value indicates to the increase in the amorphous nature of the CQDs [1, 2 and 3]. This increase in (*d*) value can be attributed to the introduction of more oxygen-containing groups such as the presence of -OH and -COOH on the surface and edges of CQDs during the hydrothermal reaction to prepare CQDs.

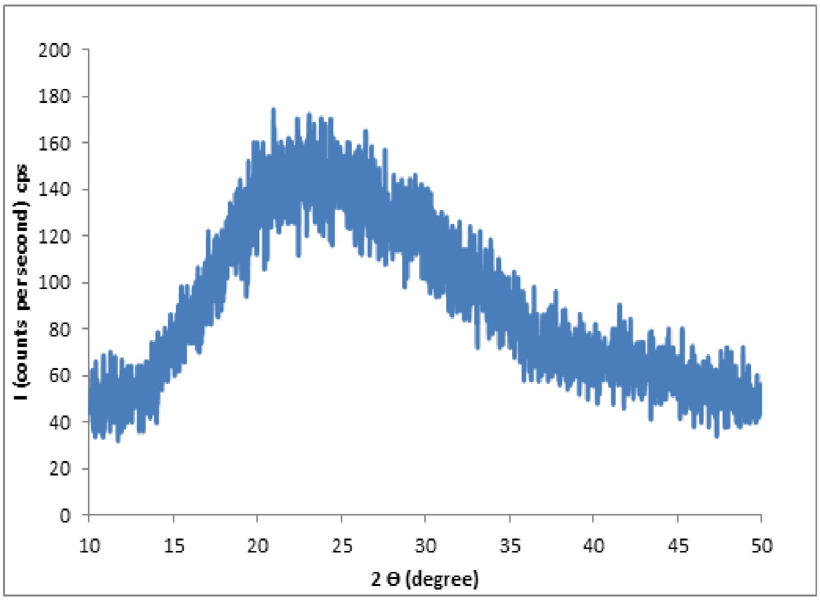

Fig.3: The X-Ray diffraction pattern for synthesized CQDs.

The AFM image and size distribution show that the products consist of small particles of the CQDs with the mean grain size approximately (13 nm). The results of AFM assay for synthesized CQDs can be shown in Fig.4.

The morphology of the synthesized CQDs is characterized by SEM at scale by nanometer to detect about the structure of nanoparticles as presented in Fig.5.

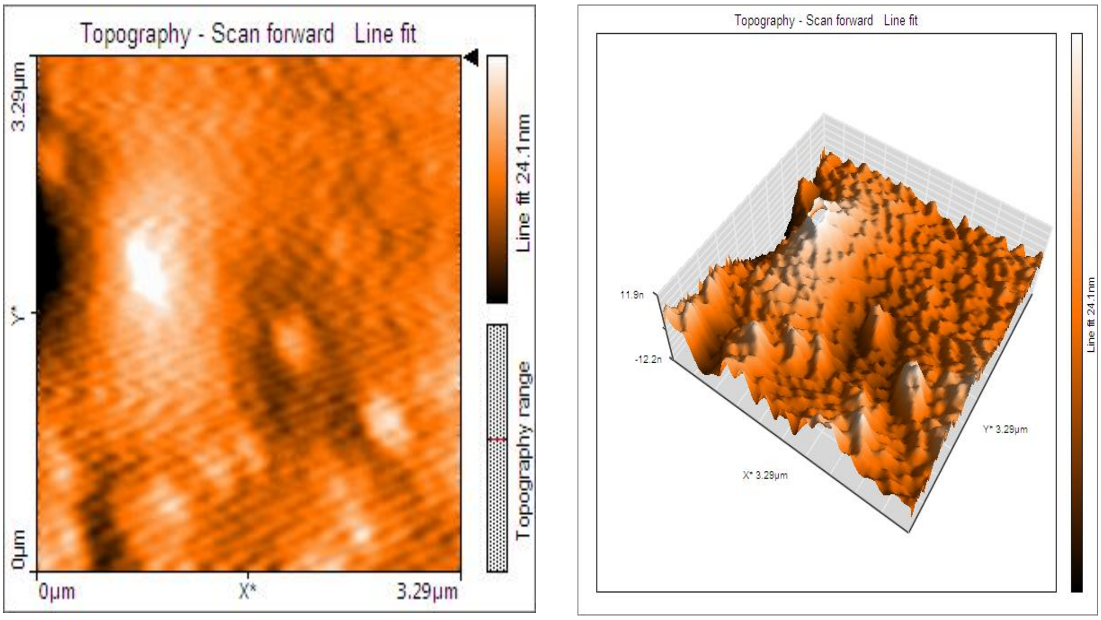

Fig.4: The AFM images of synthesized CQDs.

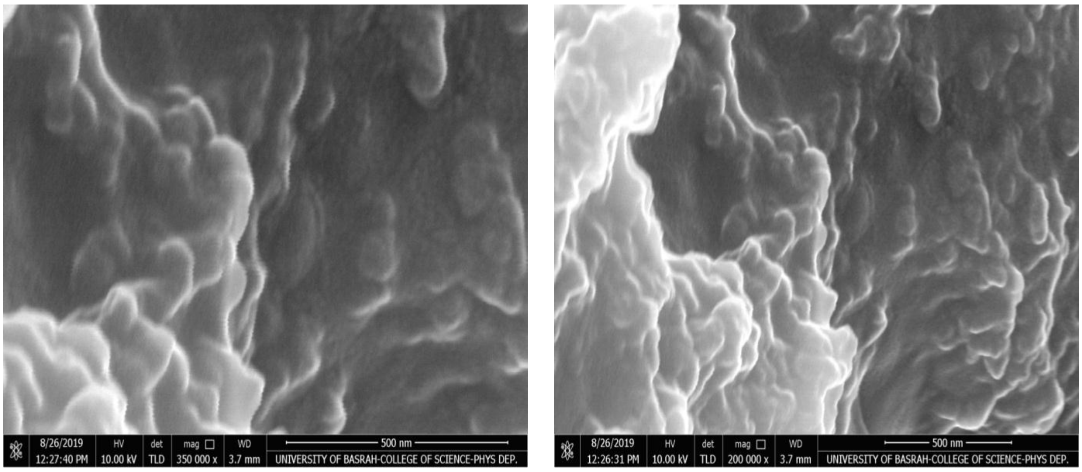

Fig.5: The SEM image for synthesized CQDs with different magnification.

Fig.6 shows the FTIR spectrum of the CQDs. As evident from figure, the prepared CQDs have different types of surface functional groups such as C-O-C/C-O, C=C, C=O, C-H and O-H. The peak at 1062.70 cm^{-1} is due to the C-O-C/C-O stretching vibrations bond. The peak at 1232.43 cm^{-1} is due to the (C-OH) stretching vibrations bond. The peak at 1629.74 cm^{-1} is assigned to the C=C stretching vibrations bond. The peak at 1712.67 cm^{-1} is due to the carbonyl (C=O) stretching vibrations bond. While the peaks at 2925.81 cm^{-1} and 1413.72 cm^{-1} are attributed to the C-H stretching vibrations bond and the peaks at 3398.34 cm^{-1}, 3421.48 cm^{-1} and 3446.56 cm^{-1} are ascribed to hydroxyl (O-H) stretching vibrations bond.

The presence of these functional groups is beneficial to the surface modification and functionalization and contributes to the excellent solubility in water without further chemical modification.

Also, these functional groups on the surface of the CQDs may results in a series of emissive traps between π and π^* states of C=C. These findings are roughly consistent with many of the previously mentioned references such as [1, 2, 3, and 6]. Note that we have adopted an unprecedented new method to prepare CQDs to achieve the result established in this research.

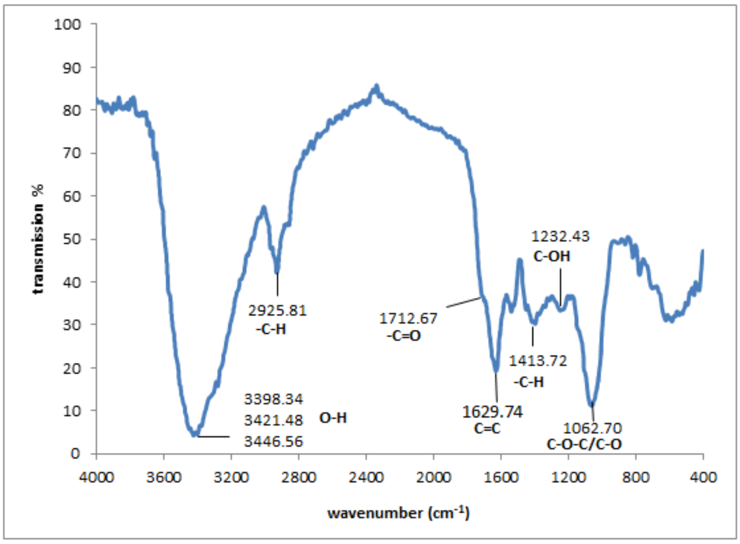

Fig.6: The FTIR spectrum of synthesized CQDs.

The fluorescence spectra of CQDs for concentration 0.132 [M], Stilbene 420 dye for concentration 5×10^{-5} [M] and mixture CQDs with dye for concentration mentioned above have been recorded when excitation by laser source 410 nm with the changing relative input power from 50% to 95.83 %. It was found that the greatest output power (emission intensity) for agitation relative input power 95.83% and less output power (emission intensity) for agitation relative input power 62.5%. A clear output power is not obtained at the relative input power below 62.5%. The emission peak for CQDs has been showed that there are many emission peaks, the highest intensity was at the wavelength about 473 to 477 nm, higher bandwidth at FWHM ~ 122 nm for high output power and lower bandwidth at FWHM ~ 103 nm for low output power as shown in Fig.7(a).

The emission peak for Stilbene 420 dye is about 444 nm, higher bandwidth at FWHM ~ 69 for high output power and lower bandwidth at FWHM ~ 65 nm for low output power as shown in Figs.7(b).

The emission peak for mixture CQDs with Stilbene 420 dye is at 447 nm wavelengths and we can observe that the output of the CQDs with dye is less than the output of the dye alone and more than the CQDs alone as shown in Fig.7(c); this decrease is caused by the presence of CQDs. It can also see that the bandwidth at FWHM exhibits an opposite behavior of intensity; FWHM of the mixture CQDs with Stilbene 420 dye is greater than the FWHM of the dye and smaller than the FWHM of the CQDs as shown in Fig.7(d).

Typical microscopic images of high fluorescence for the (CQDs) derived from orange juice by hydrothermal carbonization can be seen in the Fig.8.

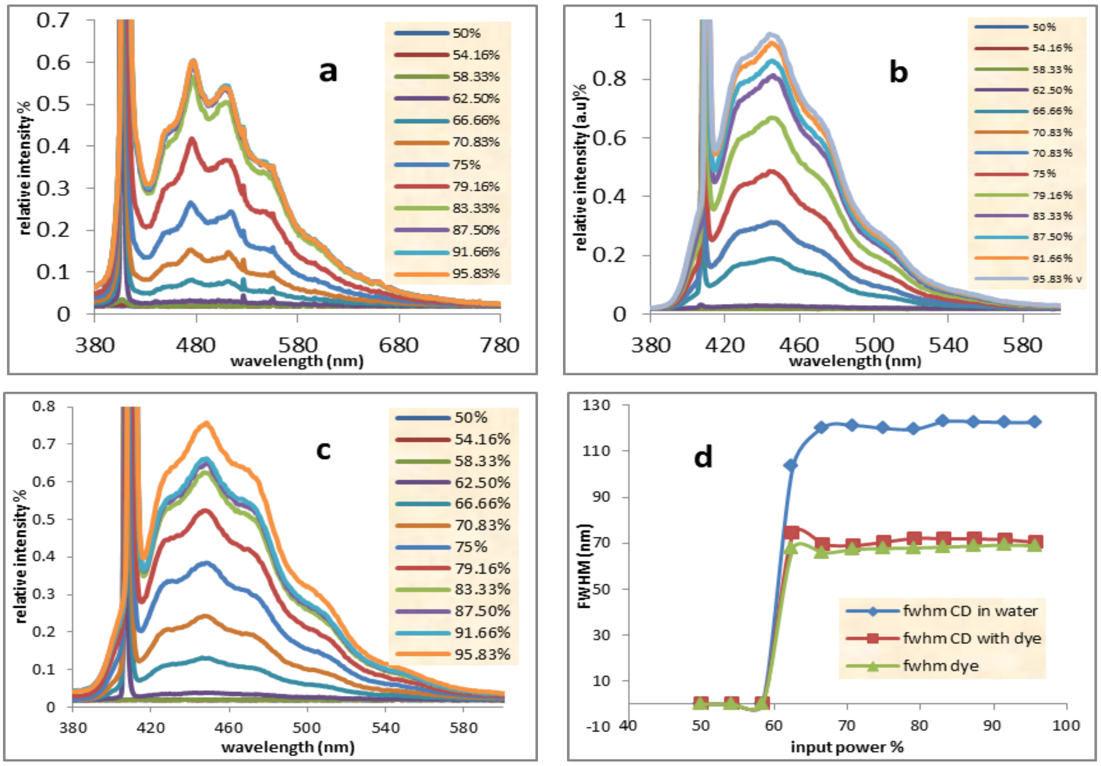

Fig.7: The fluorescence spectra for a- CQDs b- Stilbene 420 dye c- CQDs with Stilbene 420 dye and d- relationship between the input power % to FWHM for all three type in R.T.

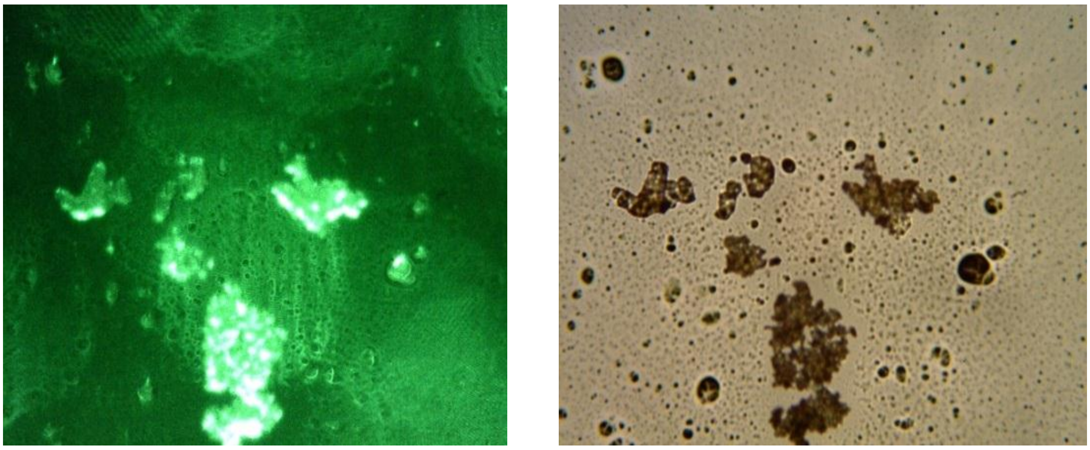

Fig.8: The typical fluorescence microscope images for synthesized CQDs.

Conclusions

The CQDs are synthesized in vitro by low temperature hydrothermal carbonization in simple step, low-cost method using available raw materials and the size of prepared (CQDs) are too small about few nanometers. Synthesized CQDs can be used in many complex optical and medical applications. Furthermore, the behavior of complex material from mixing the CQDs and other organic dyes were found to behave like the laser threshold behaviors.

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